



Review

Porous carbon spheres: Recent developments and applications

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Abstract: Activated or porous carbon is a carbonaceous material which has excellent adsorption capacity. Activated carbon has many applications including heavy metal and toxic gas removal as well as air and water filter applications. Microporous activated carbon in spherical shape (activated or porous carbon spheres) is a variant of activated carbon which has high compressive strength and low ash content. Pitch, polymeric (phenolic and sulfonated polystyrene resins) and other precursor materials (carbohydrate and seeds) have been generally used for production of activated carbon spheres employing carbonization and activation processes. Various parameters viz. carbonization temperature, heating rate, activation time and temperature, and activation media affected the performance and quality of end product. Generally activation by physical and chemical means is used for activated carbon spheres preparation. The use of polymeric precursors yielded better compressive strength and minimal ash content in comparison to other precursors. Activated carbon spheres produced using these processes has been successfully utilized as adsorbent materials for removal of heavy metals, organic dye, carbon dioxide, volatile organic chemicals, support for catalyst, gas and energy storage and also in chemical protective clothings. In present review, we discuss latest developments in activated carbon spheres and its use as adsorbent materials for removal of toxicants and various other applications.

Keywords: activated carbon spheres; carbonization; activation; adsorption; heavy metal removal; energy storage; gas storage; volatile organic compound removal; catalyst

1. Introduction

Activated or porous carbon (AC) adsorbents material like granular activated carbon (GAC), powdered activated carbon (PAC), spherical activated carbon or activated carbon spheres (ACS) and

activated carbon fabric (ACF) are widely used for removal of toxic gases and heavy metals from gaseous mixtures and liquid solutions respectively, and in protective clothing for protection from chemical warfare agents (CWA). These materials were also used in gas and energy storage, biomedical application and catalysis [1–5]. Activated carbon based adsorbents have broad pore size in comparison with Zeolites. This property makes activated carbons, a versatile adsorbent.

ACS or porous carbon spheres, an interesting adsorbent materials have excellent properties such as porous structure, large surface area, high micropore volume, controllable pore size distribution, high mechanical strength, high purity, smooth surface, high wear resistance, excellent durability, good fluidity, low ash content and low moisture content [6–8]. Due to above mentioned qualities, ACS are commonly used in many applications like catalyst supports, purification of blood, supercapacitors, protective suits against chemical warfare agents and adsorptive removal of gaseous and liquid toxicants [9]. Using polymeric and carbohydrate based precursors, specific surface area of greater than $2000 \text{ m}^2/\text{g}$ alongwith total pore volume of more than $1.0 \text{ cm}^3/\text{g}$ have been obtained and successfully used for removal of various types of toxicants [7,10–12]. The application of activated carbon as adsorbents relies on the pore size and its distribution as micropores ($<2 \text{ nm}$) and mesopores (2 to 50 nm) that are mostly utilized for the gas phase and liquid phase [3,4].

Production of ACS is also challenging because perfect spherical shape without any cracks with good compressive strength (for some specific applications) is needed to avoid any damage and dust formation. ACS is most widely produced using tubular reactor, rotary kilns or fluidized bed furnaces. The raw materials or precursors used for ACS preparation are pitch, polymeric resins, lignocellulosic materials and carbohydrate [8]. The most commonly used polymeric resins include phenol formaldehyde (PF) and sulfonated polystyrene divinylbenzene (PSDVB). These precursors have high carbon content and low ash content that resulted in better compressive strength as compared to other raw material. The different steps for manufacturing of ACS include stabilization ($200\text{--}300 \text{ }^\circ\text{C}$ in air), carbonization, and physical or chemical activation. Carbonization is mostly carried out at about $800\text{--}900 \text{ }^\circ\text{C}$ for most of the polymeric precursors in presence of nitrogen or any other inert gases. In physical activation of ACS, steam or CO_2 is used where as in chemical activation alkalis or acids are most widely used [6]. The produced ACS is characterized to ensure physical and chemical surface properties before use as adsorbents for heavy metals and toxic gases removal, various other uses as well as in chemical protective clothings. These properties include pH, surface functional groups or impregnation, Brunauer Emmett Teller (BET) surface area, pore size distribution, pore volumes (Total, micropore and mesopore) and Iodine number.

Mostly, industrial effluents are treated by adsorption process using activated or porous carbon produced from various sources such as wood and coconut shells. The adsorption capacity of activated carbon depends on its porous structure, chemical nature of surface, nature of adsorbate and its substituent groups, and pH of the aqueous solution. Various other factors such as adsorbent dose, contaminant concentration and temperature may also affect the adsorption process. Protective clothing for protection against chemical warfare agents plays a very important role in case of chemical warfare scenario. Chemical protective clothing based on PAC, ACS or ACF are available globally [4,13]. ACS based protective clothing can be used even after multiple laundries as compared to PAC based clothing [4,14]. The present work summarizes recent developements in ACS and its application as adsorbent material for toxicants and other uses.

2. Precursors or raw materials for ACS production

ACS or porous carbon sphere is a carbon-based material having a high surface area and developed internal pores (broad size distribution). A wide variety of precursors with their physicochemical characteristics are responsible for adsorbent properties with structure and textural features. To achieve the desired quality of ACS, selection of suitable precursor is necessary. ACS is prepared from precursor materials such as pitch, polystyrene resin, phenol formaldehyde resin, lignocellulosic materials and carbohydrate. Choice of the precursors used for preparation of ACS depends upon many parameters which include availability, cost and non-toxic for nature.

Raw pitch is generally obtained during refining operations in petroleum industries. This is a high molecular weight distillation residue with thermoplastic properties and have high carbon yield [15]. Pitch has already been utilized for production of ACS and ACF. Mesophase pitch (an anisotropic material) is prepared using raw pitch (isotropic material) by polymerization and condensation processes. Thermal treatment of pitch at 400–500 °C under inert environment or under vacuum resulted in aromatic hydrocarbon spheres [16].

Polystyrene divinylbenzene (PSDVB) resin is also used as precursor for ACS preparation. Styrene-divinylbenzene copolymer resins were prepared by aqueous suspension co-polymerization of styrene and divinylbenzene. The produced beads were further treated with sulfuric acid for functionalization. The elemental analysis of this resin resulted in carbon, oxygen, sulfur, hydrogen, nitrogen in decreasing order (Table 1). Due to the rich carbon content of this polymeric resin with spherical form, it is a choice of precursor used in the production of ACS with high compressive strength. The physical characteristics of this resin can be simply modified by addition of co-monomers or altering various crosslinking strategies.

Table 1. Elemental analysis of phenolic, sulphonated polystyrene beads resins and enzymatic hydrolysis lignin used for ACS preparation.

Precursor	Carbon (C) %	Nitrogen (N) %	Hydrogen (H) %	Oxygen (O) %	Sulfur (S) %	Refs.
Sulphonated polystyrene resins	40.6	1.5	6.1	39.6	12.2	[8]
Phenolic resins	68.9	1.5	6.3	23.3	-	[10]
Enzymatic hydrolysis lignin	77.5	0.25	1.6	20.6	-	[17]

Phenolic based polymeric resins are also used as precursors for the preparation of activated carbons [18]. It can be made by combining phenols and aldehydes in different compositions which ultimately resulted in either thermosetting or thermoplastic type resins. A thermosetting resin, resole obtained using the base catalyst where thermoplastic resin, novolak formed in the presence of acid catalyst. The structure and mechanical properties rely on the catalyst concentration, process temperature and time as well as ratio of the concentrations of phenol and formaldehyde. Upon carbonization and subsequent steam activation, unique pore structures are developed due to presence of phenol and/or low molecular weight substance [10,18]. The effects of stabilizer (polyvinyl alcohol) concentration, mechanical agitation and ratio of monomer to water on size (0.2–1.8 mm diameter) and yield of crosslinked phenolic beads (PB) in spherical form were studied. The PBs size decreased with increase in stabilizer concentration (2.5–12.5%) and agitation

rate, and increased with increase in monomer concentration (22–28%). The conversion percentage of spherical beads increased when agitation rate was increased to 400–700 rpm [19]. In another study, effect of formaldehyde (F) to phenol (P) ratio, initiator (triethylamine), cross linking agent (hexamethylenetetraamine) concentration and temperature on particle size (0.2–2.0 mm) as well as its formation was also investigated. The average particle size increased with increased F/P ratio whereas it decreased when concentration of TEA was increased. Reactions performed at and above 90 °C resulted in cured PB [20]. The main features of this resin include low cost, heat and flame resistance, strength, low level of inorganic impurities and negligible ash content.

Lignocellulosic materials are also used as precursors for ACS preparation due to low cost and environmental safety. These are sugar cane, corn stover, rice straw, lettuce, or algae. Carbohydrates (cellulose, glucose, fructose, saccharose, starch or cyclodextrins) are also selected as precursors because these help in understanding the mechanism of carbon spheres formation [7]. For these precursors, hydrothermal treatment (hydrothermal carbonization) has been used for spherical carbon preparation. The influence of different experimental parameters such as temperature, time, carbohydrate type and its concentration was studied and has provided deep insights into the mechanism of spherical carbons formation [7,21]. The CHNS analysis of sulphonated PSDVB resin, phenolic resin and lignocellulosic material is given in Table 1.

3. Process for production of ACS

The process used for preparation of ACS includes thermal treatment of precursors through carbonization and activation step. Before starting carbonization steps, precursors such as polystyrene resins are subjected to thermal treatment upto 200 °C in presence of air to remove moisture content of resins. Some studies also reported that the mixture of air and nitrogen have been used at 200–300 °C to achieve better quality of the ACS. Due to exothermic nature of reaction in presence of air, controlled heating is necessary during these steps to prevent excessive burning of precursor and yield enhanced compressive strength [2,8].

For nanoporous carbon spheres, synthesis techniques (including the Stöber method and those based on templating, self-assembly, emulsion and hydrothermal carbonization) were discussed earlier [22]. Hollow carbon spheres also gain enormous importance due to their applicability in various fields. In a review, a comprehensive overview of the preparation and applications was discussed [23]. Various synthetic techniques for preparation of porous carbon spheres, including hydrothermal carbonization (HTC) and templating from sustainable biomass and their applications as Li-ion battery anode material was also discussed in a review [24]. Synthesis of carbon nanospheres using various approaches was also discussed in a earlier study with a special focus on sustainable carbon precursors, control of particle size and monodispersity, and mesopores [25]. A typical flow chart for production of ACS from sulphonated polystyrene divinyl benzene resin using physical activation is shown in Figure 1 [8].

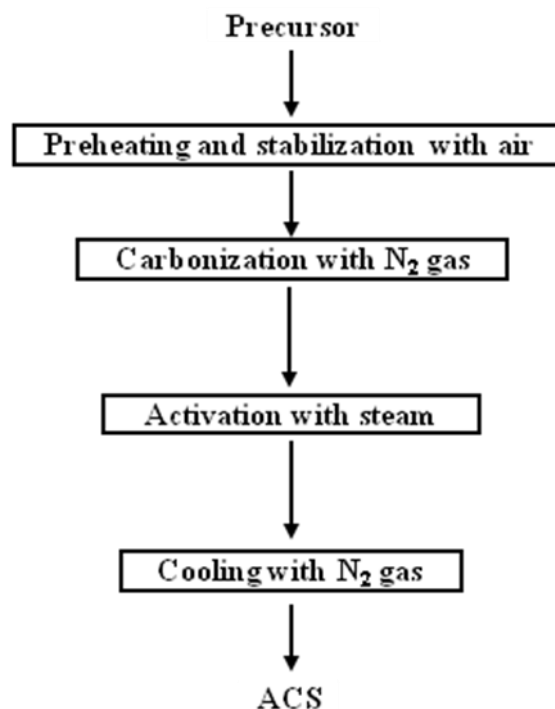


Figure 1. Steps involved in ACS production using physical activation.

3.1. Carbonization for preparation of ACS

Carbonization is a process where the precursors are subjected to a thermal treatment (pyrolysis) to enhance the carbon percentage in the precursors in presence of inert gases such as N_2 . During this process, low molecular weight volatiles such as sulphur containing compounds, light aromatics and hydrogen gas are removed and resulted in fixed carbonaceous material. During carbonization, pores are filled with tarry residues. Proper optimization of carbonization parameters is very crucial because the quality of final ACS rely on this aspect. These important parameters include carbonization temperature, heating rate, presence of inert gases and its flow rate as well as carbonization time. Generally, 700 °C or more temperature resulted in reduced yield with better quality of final product [26].

Hydrothermal carbonization (HTC) is also utilized for carbon spheres preparation with controlled size, oxygenated functional groups on the surface, high surface area and high thermal stability. It is carried out under mild operating conditions in a sub-critical water medium. During the HTC procedure, the solution of carbohydrate precursors is usually heated to 130–250 °C under self-generated pressures. HTC process used for carbon spheres preparation and influence of process parameters on it were well described in a review [21]. Micro-carbon spheres preparation by carbonization of polymer spheres from low-temperature polymerization reactions (as below 250 °C), various polymerization process, morphology and surface characteristics of the CSs obtained by different synthetic approaches was also described in a review [27].

A novel and facile template-free method referred to as “secondary-crosslinking pyrolysis” to fabricate discrete and dispersible hollow carbon spheres (HCSs) has been successfully developed by using the deformed poly(styrene-co-divinylbenzene) capsules as precursors. This method resulted in

a perfect spherical shape (surface area, 432 m²/g; total pore volume, 0.39 cm³/g and micropore volume, 0.15 cm³/g) and used for energy storage with a high specific capacitance up to 192 F/g at 5 mV/s [28]. Paramagnetic mesoporous carbon spheres (diameters of 1–3 μm) were synthesized through the HTC of carboxymethylcellulose with nickel acetate, followed by high-temperature carbonization in a N₂ atmosphere and this CSs (surface area, 586 m²/g and total pore volume, 0.53 cm³/g) was successfully used for vitamin B12 adsorption [29]. Carbonization followed by etching with NaOH solution processes were used to prepare a series of mesoporous carbon microspheres (MCMs; average diameter, 500 nm and mesopore size, 3.2–14 nm) with surface area of 659–672 m²/g using resorcinol/formaldehyde polymer microspheres by controlling the size of SiO₂ nanoparticles templates and successfully used in electrochemical application [30]. A microfluidic approach to generate porous carbon particles using sucrose/silica precursor was also used and showed that the size of the particle and pores can be tuned by adjusting the deionized water content in droplets and preheating temperature [31]. Synthesis of monodisperse, polyaniline (PANI)-derived mesoporous spherical carbon nanoparticles were done by polymerization of aniline with the aid of (NH₄)₂S₂O₈ as oxidant and colloidal silica nanoparticles as templates. Carbonization of the resulting PANI/silica composite material was done at different high temperatures, and finally removal of the silica templates from the carbonized products was carried out. These materials (surface area, 652 m²/g and total pore volume, 1.21 cm³/g) were showed much better catalytic activity in fuel cells reaction. This method was also used for polypyrrole to produce monodisperse, mesoporous carbon nanoparticles [32].

A spherical meso-perforated carbon (SSMPC) was produced from resorcinol-formaldehyde/silica precursor, prepared using colloidal silica-mediated spray drying method followed by carbonization and silica removal. High surface areas and pore volumes were achieved for SSMPC (1050 m²/g and 2.1 cm³/g). This material was then successfully evaluated the charge storage properties in organic media from supercapacitor as well as Li-ion battery (LIB) perspectives [33]. Colloidal, spherical polymer resins synthesized by enhanced copolymerization and polycondensation of resorcinol-formaldehyde resins were further carbonized at 600 and 900 °C which resulted in surface areas of 592.4 m²/g and 952.5 m²/g for capacitor applications [34]. Nitrogen-containing carbon microspheres (NCMs) were prepared via directed carbonization of poly(1,5-diaminonaphthalene) at different temperatures which was synthesized from 1,5-diaminonaphthalene with ammonium persulfate as oxidizing agent for electrochemical application. A sample carbonized at 700 °C (NCM-700) showed a surface area of 403 m²/g (total pore volume, 0.35 cm³/g) with regular spherical geometry (0.2–0.5 μm in diameter) [35]. Nitrogen-containing ultramicroporous carbon nanospheres (N-UCNs) were prepared using carbonization. Hexamethylenetetramine was utilized to substitute ammonia and formaldehyde to polymerize with resorcinol on the surfaces of the polymer colloids for the preparation of SCs under the Stöber condition. The introduction of phloroglucinol/terephthalaldehyde brings regular ultramicroporous (0.58 nm) to the typical N-UCNs. The N-UCNs has high surface area (1439 m²/g) with total pore volume of 2.12 cm³/g (micropore volume, 0.52 cm³/g) and showed excellent electrochemical performance [36].

Direct pyrolysis was used to prepare microporous carbon spheres using linecaps nanospheres (synthesized by the reaction of the kleptose linecap with the pyromellitic dianhydride) as precursor. This process resulted in surface area of 684 m²/g with 5–17 Å pore size and micropore volume of 0.16 cm³/g [37].

Porous polymer resins and carbon spheres have also been successfully prepared by an extended Stöber method using phenol derivatives of different functionality. The preparation of phenolic resin spheres from a series of hetero-atoms containing phenol derivatives (such as nitrophenol, aminophenol and halide-substituted phenols), which upon carbonization are converted to heteroatom-doped carbon spheres with surface area of 482 m²/g. These resultant carbon spheres were successfully examined as potential CO₂ adsorbents and electrode materials for supercapacitors [38].

3.2. Activation for preparation of ACS

There are two types of methods used to activate carbonized materials that are chemical and physical activation. Apart from this, combination of both (chemical and physical) activation is also used as an alternative to improve the performance of the ACS [39,40].

In physical activation, carbonized materials are subjected to the heat treatment at about 700–900 °C in presence of oxidizing gases namely, air, steam or carbon dioxide or combination of two (Table 2). During carbonization process, the resulting materials have less surface area with very small adsorption capacity due to presence of tarry products in pores. These oxidizing gases remove tarry products, creates new pores and increases the diameter of pores at high temperatures where weight loss occurs. This activation process resulted in a well-developed pore structure with higher BET surface area. The weight loss is proportional to increase in activation temperature and time. Activation of carbonized materials with air or oxygen causes excessive burning due to the exothermic reactions and loss of strength. The endothermic reactions taking place during physical activation with steam or CO₂. It is also reported earlier that the H₂O molecules diffuse faster into the pores of the carbon due to small size in comparison to the CO₂ molecule and the reaction between carbon and steam is faster than that with CO₂. Pretreatment of precursor, pyrolysis parameters (temperature and time), selection of activating agents, steam and gas flow rate, activation temperature and activation time have important effects on the surface area, pore volume, strength and porosity of ACS. The following reactions are involved in steam activation process:



where C is a carbon-free active site, C(O) is the oxygen surface complex and C(H₂) is the adsorbed hydrogen. The C(O) complexes are energetically more difficult to remove from the surface [26].

The preparation of spherical activated carbons (SACs) has been studied with *Rhamnus alaternus* (RA), *Osyris lanceolate* (OL), and *Canna indica* (CI) seeds. Carbonization followed by CO₂ activation procedures resulted in spherical shapes and integrity with reduction in diameter around 48% and 25%, for RA and CI seeds respectively. About 1600 m²/g surface area and similar mechanical strength with commercial activated carbons were achieved using these precursors [9]. The influences of the gasification time, gasification temperature, and flow rate on ACS preparation from resole phenolic beads using CO₂ gasification has been studied and resulted in 3101 m²/g of BET surface area and 2.08 cm³/g of pore volume at 950 °C. The porosity decreased with increasing gas flow rate from 0.25 to 1.0 L/min. The mechanical strength of the ACS varied from 120

to 3 N/mm² when the extent of burn-off varied from 32 to 88% [10]. They have also studied preparation of ACS from sulphonated polystyrene beads using combination of activation and concluded that the ACS produced from steam and CO₂ activation have shown 1266 m²/g BET surface area and 1.13 cm³/g pore volume in comparison to ACS from steam activation with 949 m²/g (BET surface area) and 0.98 cm³/g (pore volume) [2]. In a study of producing iron-containing pitch spheres by adding ferrocene, higher temperature resulted in higher pore (10.0–80.0 nm) volume and the ratio of mesopore. Further, the loading method of iron controlled the catalytic reaction in a wider range [16]. Polymeric based spherical activated carbon (PBSAC) was prepared using single step (steam) as well as two step (steam followed by CO₂) activation. Surface area of 1432 to 1996 m²/g with total pore volume of 0.7 to 1.3 cm³/g (micropore volume, 0.52–0.70 cm³/g) was resulted in using one step activation. However, surface area of 1503 m²/g with total pore volume of 0.9 to 1.2 cm³/g (micropore volume, 0.51–0.53 cm³/g) was resulted in using two step activation [39].

Table 2. Characteristics of some physically activated ACS produced from different precursors.

Precursor	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Refs.
Polystyrene beads	CO ₂	1266	1.13	[2]
Polystyrene beads	Steam	949	0.98	[2]
Polystyrene beads	Steam	1009	0.89	[8]
CI seed	CO ₂	1616	0.64*	[9]
RA seed	CO ₂	889	0.40*	[9]
Phenolic beads	CO ₂	3101	2.08	[10]
Phenolic beads	CO ₂	2284	0.89	[11]
Polystyrene beads	Steam	1160	0.478*	[14]
Pitch	Steam	-	0.65	[16]
Phenolic beads	Steam	1280	0.91/0.43	[40]
Resorcinol-formaldehyde	CO ₂	2905	1.6	[41]
Phenol-formaldehyde	Steam	840	0.40*	[42]
Phenol-formaldehyde beads from bamboo tar	CO ₂	189	0.10	[43]
3-methylphenol-formaldehyde	Steam	1501	0.72	[44]
Alkylphenol-formaldehyde	Steam	1585.13	0.69/0.45	[45]
Alkylphenol-formaldehyde	Steam	1066	0.52/0.47	[46]
Sucrose	Steam	824	0.37/0.36	[47]
Phenolic beads	CO ₂	1065	0.53*	[48]
Phenolic beads	Steam	1128	0.45/0.43	[49]
Polystyrene beads	Steam	1555	1.29/0.56	[50]
Pitch	Steam	1573	0.68/0.50	[50]
Polystyrene beads	Steam	979	0.84/0.31	[51]
Phenolic beads	Steam	1663	20.77	[52]

* Micropore volume.

Highly porous CSs were synthesized through the emulsion polymerization of resorcinol-formaldehyde followed by carbonization and CO₂ activation. Using carbonization (400, 600 and 800 °C) and subsequent activation temperatures (900 and 950 °C) tuning, monodispersed CSs were prepared with high surface area (1500–2900 m²/g) and narrow pore size distribution (<3 nm) and used for electrochemical capacitors and capacitive flowable suspension electrodes [41]. A facile, aqueous, self-catalyzed polymerization method prepared phenolic resin was used to produce monodisperse carbon microspheres followed by treating the phenolic resin with steam. The resultant carbon spheres with surface area of 840 m²/g and micropore volume of 0.40 cm³/g provided a new avenue for the mass production of monodisperse carbon microsphere [42]. Bamboo tar was mixed with formalin under a weak alkaline condition to form cured phenol-formaldehyde (PF) beads (9–16 mesh) through suspension polymerization and used for ACS preparation followed by carbonization and physical activation using CO₂ at 900 °C for 2 h. This ACS was successfully used for adsorption and recovery of toluene [43]. Activated carbon spheres (ACSs) from 3-methylphenol-formaldehyde was prepared by suspension polymerization and steam activation. The effects of additives [ethylene glycol and poly(ethylene glycol)], to the textural structure and adsorptive dibenzothiophene (DBT) of ACSs were also investigated. The prepared ACS have surface area of 1501 m²/g and a total pore volume of 0.72 cm³/g [44]. Alkyl phenol and formaldehyde were used to prepare spherical carbon by suspension polymerization and steam activation. The prepared ACS were subjected to oxidation modification by dry air at various temperatures to improve the pore framework and the introduction of oxygen containing functional groups for better element mercury capture that resulted in surface area of 1585.13 m²/g [45]. Further, they have prepared ACS and some metallic oxides were doped to enhance the elemental mercury removal ability. The experimental results indicated that prepared activated carbon spheres (PAC-surface area, 1066 m²/g) and PAC-Cu (surface area, 954 m²/g) presented almost identical with a smooth surface without cracks and showed well-developed pore structure [46].

The sucrose derived spherical carbon prepared by HTC and physical (800 °C) or chemical activation method was used as adsorbents for pharmaceutical active compounds (PhACs). Carbons prepared with steam as activating agent retain the spherical shape of the hydrochar and resulted in 814 m²/g surface area [47].

In chemical activation, both carbonization and activation occurred simultaneously in a single stage for the activated carbon preparation process [26]. This activation is carried out using chemical agents such as ZnCl₂, H₂SO₄, KOH, NH₃ and H₃PO₄ at low temperatures (500–700 °C) as compared to physical activation. These chemicals are generally dehydrating agents and inhibit the tar formation and also other undesired products in the course of the carbonization process. The highly alkaline chemical agents support to develop the pores structure by dehydration and polymeric structure degradation. The advantages of chemical activation include less energy costs and minimum activation time. The characteristic of ACS produced by chemical activation is given in Table 3. In a study, ACS by chemical activation resulted in surface areas of more than 3000 m²/g with pore volume of greater than 1.0 cm³/g [7]. Some studies also reported the use of mixed (both chemical and physical activation) to improve the surface area of the ACS where single step is not efficient to penetrate inside the material and generate abundant pores. A two-stage process, in which first the precursor is carbonized and then chemically activated, is also used for preparation of ACS. The important parameters which affect the chemical activation include, type of activating agent, ratio of precursor and chemicals, activation temperature, activation time, heating rate. All these parameters

should be controlled to achieve better quality of ACS with desired adsorbent potential. The surface area and pore size distribution are influenced by the ratio of the precursor and chemical activating agent. The characteristics of chemical activating agents include water generation instead of carbon oxides (CO_x) and hydrocarbons from hydrogen and oxygen present in carbonized material. Further, the loss of tars and volatile matter is also inhibited by chemical agents and resulted in more fixed carbon and carbon yield. The surface area of activated carbons prepared using chemical activation is more but also associated with problems of corrosion. Further, washing of activated carbons is also necessary to recover residual chemicals [53].

Table 3. Characteristics of some chemically/Physico-chemically activated ACS produced from different precursors.

Precursor	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Refs.
Polystyrene beads	H ₂ SO ₄	976	0.68/0.47	[6]
Saccharose	H ₃ PO ₄	2120	1.0*	[7]
Glucose	KOH	3152	1.18*	[7]
Enzymatic hydrolysis lignin	KOH	1240	0.62	[17]
Sucrose	K ₂ CO ₃	1375	0.63/0.62	[47]
Phenolic beads (PR4_800 ACS)	KOH	1171	0.50/0.47	[49]
Polystyrene beads	KOH	1566	1.05/0.62	[50]
Sucrose	KOH	2217	1.006/0.776	[54]
Glucose	KOH	3003	-	[55]
Pectin	KOH	2440	1.28/0.65	[56]
Jute	KOH and CO ₂	856.89	0.889/0.689	[57]
Corncob	KOH	1652	0.948/0.416	[59]
F108/resorcinol-formaldehyde	KOH	703	0.645/0.317	[60]
Resorcinol-formaldehyde	KOH	1096	0.97/0.14	[61]
m-phenylenediamine and hexamethylenetetramine	ZnCl ₂	1237	0.58/0.35	[62]
Resorcinol-formaldehyde	KOH	1227	0.90/0.81	[63]
2-keto-l-gulonic acid mother liquor	KOH	2478	1.24/0.99	[64]
PAN	KOH	2134	1.41/0.82	[65]
Glucose	ZnCl ₂	2902.5	1.49/0.34	[66]
Resorcinol-formaldehyde	ZnCl ₂	2437	1.37	[67]
Polystyrene beads	KOH	844.9	0.48/0.33	[68]
Polystyrene beads	KOH	1526	0.72/0.61	[69]
Polystyrene beads (NSCS-4-700)	KOH	1757	0.81/0.73	[70]

* Micropore volume.

Spherical carbons were also produced from three carbohydrates (glucose, saccharose and cellulose) using hydrothermal treatment and activated by means of chemical activation using H₃PO₄,

NaOH and KOH (Table 3) or physical activation with CO₂ (Table 2). Surface area upto 3100 m²/g was obtained by chemical activation with textural properties. The activation using H₃PO₄ yielded ACS with higher developed surface areas as compared to others [7]. In another study fast KOH activation via microwave heating using enzymatic hydrolysis of lignin as the precursor for carbon sphere preparation via environmental friendly hydrothermal carbonization was carried out. Carbonization temperature (270 °C) and time (7 h) resulted in large particle sizes, high sphericity, uniform size, and high dispersity of the carbon spheres. Fast KOH and microwave heating (2450 MHz, 700 W) developed the BET surface area of ACSs upto 1278 m²/g, which occurred more efficiently (10 min) than the increase to 1276 m²/g for hemicellulose-based ACS with a KOH/ratio of 1.0 at 800 °C for 3.5 h [17]. The sucrose derived spherical carbon prepared by HTC and chemical activation method was also used for use as adsorbents of PhACs. Carbons prepared with K₂CO₃ as activating agent resulted in 1375 m²/g surface area [46].

ACS prepared from sucrose using HTC and subsequent KOH activation [C-4(char and KOH ratio of 1:2)] resulted in high surface area of 2217 m²/g was also used for adsorptive desulfurization [54]. A simple way to convert glucose to nitrogen-doped carbons by HTC with NH₄Cl, followed by KOH activation at 800 °C resulted in surface area of more than 3000 m²/g. The extra pores and/or defects generated in this activated N-doped carbon can be ascribed to the chemical etching of nitrogenous groups. This material showed high rate performance and high cycling stability [55]. Porous carbon spheres (PCSs) were prepared via a facile HTC and chemical activation route with pectin as the biomass precursor. The resulted PCSs revealed a large surface area (2440 m²/g), well-balanced micro/mesoporosity with narrow pore size distribution and high content of oxygen-containing functional groups [56].

Activated carbon produced by physico-chemical activation of hydrothermally carbonized material derived from the dried stem of *Corchorus olitorius* commonly known as jute (JS), using KOH as an activation agent. This study resulted in ACS of 856.89 m²/g surface area and further used for adsorption of Cu(II) [57].

Microporous and mesoporous carbon spheres (CSs) were fabricated using resorcinol and formaldehyde as precursors in the presence of Pluronic F127 (for generating mesopores) as porogen and KOH (brought abundant micropores) as the activating agent. This study resulted in surface area of 735.4 m²/g with pore volume of 0.622 cm³/g and used for electrochemical performance [58]. The hierarchical porous carbon microspheres (HPCS) were obtained using corncob as precursor and showed that the pore size and surface area affected by the amount of KOH during the activation process [59]. Carbon nanospheres with distinguishable microstructure were prepared by carbonization and subsequent KOH activation of F108/resorcinol-formaldehyde composites. With addition of F108, the polydisperse carbon nanospheres (PCNS) with microporous structure, monodisperse carbon nanospheres (MCNS) with hierarchical porous structure, and agglomerated carbon nanospheres (ACNS) were obtained. The MCNS sample (surface area, 703 m²/g) showed improved electrochemical performance [60].

A nickel-doped activated mesoporous carbon microsphere (Ni-AMCM) was synthesized by an emulsion-assisted hydrothermal method, followed by a KOH activation process and nickel-doping strategy for high performance electrode material. The Ni-AMCMs has high surface area (~1096 m²/g), uniform mesopore size (4.0 nm), regular microspherical shape (0.5–1.0 μm in diameter), and partially graphitic structure [61].

Nitrogen-enriched carbon spheres (NECS) were obtained after ZnCl_2 activation of high nitrogen content polymer spheres prepared by one-pot hydrothermal synthesis using *m*-phenylenediamine and hexamethylenetetramine as raw materials. This spherical carbon resulted in diameters of about 0.6–1.2 μm and a high surface area (1237 m^2/g) and successfully used for removal of Cr(VI) [62]. Hollow and hierarchical porous carbon has been synthesized by a simple one-step KOH chemical activation process for enhanced pollutant adsorption and energy storage. Porous carbon spheres has exhibited a high surface area of 1227 m^2/g and revealed superior VOCs adsorption as compared to non-activated carbon spheres. Furthermore, supercapacitance measurements has also shown high capacitive performance of 353 F/g. TiO_2 nanosheets has also been grown on the above mentioned carbon leading to improved photocatalytic degradation [63].

2-keto-l-gulonic acid mother liquor (GAML) as the precursor was used for the preparation of PCS by HTC, carbonization and KOH activation, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used as an oxidizing agent during carbonization. This material showed excellent porosity and high surface area of 2478 m^2/g and was successfully used as carbon-based electrode materials for electric double-layer capacitor [64]. Polyacrylonitrile (PAN) carbon nanostructure microspheres (CNM) with the average particle size of 200 nm were prepared in the range of 500 to 800 $^\circ\text{C}$ using KOH. The results revealed that the CNM has surface area of 2134 m^2/g and showed usability as electrode material [65].

4. Characterization of ACS

Till date, full description of the microstructure and the adsorption characteristics of activated carbon are not determined by X-ray diffraction or high-resolution transmission electron microscopy (HRTEM) [26]. First, precursors for ACS may be characterised by surface area analyser (for BET surface area, total pore and micropore volume, and pore size distribution), electron microscopy (for morphology), CHNS analysis (for elemental composition) and thermal analyses [by thermogravimetric analyser (TGA) to evaluate the thermal stability]. All these analysis are also necessary for final product. The adsorption capacity of ACS is determined using iodine number apart from surface area and pore volume [8]. Thermal analysis by TGA of any precursor is necessary when it is used for first time. In TGA graph, first weight loss represent the moisture removal (25 to 150 $^\circ\text{C}$), second represents the elimination of volatile matters and tars (150–400 $^\circ\text{C}$) and third the decomposition of a structure (400–550 $^\circ\text{C}$). Above that the mass loss is less. The ultimate analysis of materials are carried out to analyse the carbon (C), hydrogen (H), nitrogen (N), sulphur (S), ash and oxygen (O) content. X-ray powder diffraction is used to determine the structure of the activated carbon. Raman spectroscopy is utilized for bulk structure of activated carbon. Scanning electron microscopy (SEM) is used to analyse the morphology of the precursors as well as ACS. HRTEM resulted in local nanostructure pictures.

The nitrogen adsorption-desorption isotherms analysis is commonly used for determination of the BET surface area, the pore volume and the pore size distribution of ACS. Six types of isotherms are used for the study of porous texture of the activated carbon material. The BET theory is the most commonly used for determining the surface area of activated carbon. In BET theory the relative pressure is from 0.05 to 0.25 for specific surface area and 0.99 for total pore volume. As per new IUPAC report, caution is required in applying the BET method for the assessment of surface area and a recommended procedure improves the reproducibility of the method, when micropores are present. It is now recognised that due to nitrogen quadrupole moment, uncertainty in the value

of σ_m (N_2)—possibly ~20% present for some surfaces. For various reasons, argon adsorption at 87 K is considered to be more reliable and is now recommended—particularly for micropore size analysis. It may be impossible to separate the processes of monolayer/multilayer adsorption and micropore filling. With microporous adsorbents, the linear range of the BET plot may be very difficult to locate. A useful procedure allows one to overcome this difficulty and avoid any subjectivity in evaluating the BET monolayer capacity. It must be re-emphasised that this procedure should not be expected to confirm the validity of the BET monolayer capacity. Thus, the BET-area derived from a Type I isotherm must not be treated as a realistic probe accessible surface area. It represents an apparent surface area, which may be regarded as a useful adsorbent “fingerprint” [71].

Kelvin equation based pore size distributions are used for characterization of ACS. The micropore size distribution is determined using the Howath-Kawazoe, Dubinin-Radushkevich and Dubinin-Astakov methods. It is now evident that pore size analysis of narrow mesopores cannot be reliably achieved by the application of procedures based on the Kelvin equation, such as the Barrett Joyner Halenda (BJH) method. Density functional theory (DFT) based computational procedures are included in commercially available software and provide a reasonably reliable assessment of the nanopore size distribution (i.e., for both mesopores and micropores), provided that the given nanopore structure is compatible with the chosen DFT kernel [71]. Generally activated carbons have macropores of greater than 50 nm size, mesopores of 2–5 nm and micropores of less than 2 nm. Adsorption is a process used for removal of solutes (from gaseous or liquid mixtures) on solid surface. It is carried out using two ways either physical adsorption or chemical adsorption. Vander-Waals forces are the driving forces for physical adsorption whereas chemical bonding is responsible for chemical adsorption. Generally, iodine number is used for determination of adsorption capacity of the ACS and defined as the number of mg of iodine adsorbed by 1 g of activated carbon from an aqueous solution when the iodine concentration of the residual filtrate is 0.02 N. Characterization of the surface functionalities is done by infrared (IR) spectroscopy. X-ray photoelectron spectroscopy (XPS) gives about the carbon, oxygen, hydrogen and nitrogen composition of activated carbons for characterization [26].

In a study, the textural structure was determined by SEM and XRD of ACS based on coal which was prepared using phenolic resin (PR) bonding materials. The iodine number was 720–780 mg/g and best spherical shapes resulted in with AC and PR at a ratio of 60:40 [72]. In another study the detailed characterization in terms of porosity was carried out for ACS prepared using phenolic resin by CO_2 activation at 950 °C. The BET surface area, micropore volume and total pore volume increased from 960 m^2/g to 2092 m^2/g , 0.3662 cm^3/g to 0.7221 cm^3/g and 0.4093 cm^3/g to 1.159 cm^3/g respectively on increasing soaking time from 3 h to 12 h. However, the crushing was found to be greater than 2 kg/sphere at the surface area below 738 m^2/g . The crushing was found to be 0.953 kg/sphere at the highest surface area of 2092 m^2/g [73]. Scanning electron microscopic image of ACS prepared from sulphonated PSDVB is shown in Figure 2.

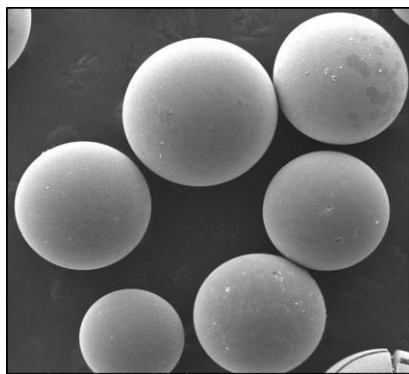


Figure 2. Activated carbon spheres.

5. Applications of ACS

The main applications of ACS include the adsorption of heavy metals ions, adsorption of volatile organic matters, dyes, catalyst support, gas storage, energy storage and adsorbent materials in chemical protective clothings.

5.1. Removal of heavy metals

Heavy metals such as Mercury Hg(II), Chromium Cr(VI), Cadmium Cd(II), Arsenic As(V) and Lead Pb(II) are found in waste generated from industries like textile, mining, tanneries, electroplating and petrochemical industries. These heavy metals have serious effects on human health including animals and crops. Adsorption studies of heavy metals using ACS from different precursors have been carried out by various researchers. Adsorptive removal of heavy metals from aqueous solutions was carried out using ACS prepared from polystyrene (PS) resins by chemical activation. This ACS resulted in 976 m²/g surface area and 0.68 cm³/g pore volume (total surface acidity, 1133 meq/100 g and surface basicity, 275.3 meq/100 g). ACS revealed their utility for the adsorption of CN (50%), and Pb(II), Mn(II), Hg(II), Cu(II), Cd(II), Zn(II), and Ni(II) (50–90%) from their contaminated solution [6]. Pilot scale produced ACS from sulphonated polystyrene resins using steam activation was also evaluated for the adsorptive removal of Cr(VI) from aqueous solutions. The ACS produced using this pilot scale process have BET surface area of 1009 m²/g and total pore volume of 0.89 cm³/g. The carbon content of ACS was 92.32% with 1.1 kg/sphere crushing strength. This ACS resulted in 99.1% Cr(VI) removal from aqueous solution (initial concentration, 50 mg/L; pH, 2; ACS dose, 1 g/L; contact time, 2 h; agitation, 120 rpm and temperature, 30 °C) [8]. Parameters such as acidic pH significantly affect the adsorption of these heavy metals on activated carbons. The oxygenated surface contributed at both pH either less than 7 or greater than 7. The important factors that affecting adsorption of heavy metals include adsorbent dose, solution pH and its temperature, contact time, agitation speed and heavy metal concentration. It was also reported that the use of same adsorbent to remove two heavy metals behave in differet ways in terms of pH, the contact time and and the adsorption behaviour [26]. The mercury removal efficiency of the oxidized ACS samples presented better performance with the increase in the oxidation temperature. The oxidation-modified ACS at 300 °C (ACS-O300) was the optimal sorbent for removal of elemental mercury from simulated flue gas [45]. Further, some metallic oxides were doped to prepare activated

carbon spheres (PAC) to enhance the elemental mercury removal ability and resulted that the PAC-Cu have the highest removal ability among doped metallic oxides. Meanwhile, PAC-Cu has an ability of sulfur resistance [46].

Activated carbon produced by hydrothermal carbonization and physico-chemical activation from jute (JS) resulted in 856.89 m²/g surface area and was further used for adsorption of Cu(II) [57]. Nitrogen-enriched carbon spheres (NECS) with surface area (1237 m²/g) was used for removal of Cr(VI) and resulted in the maximum Cr(VI) removal capacity as high as 279 mg/g at pH 2.0. Further, the NECS adsorbent was shown to maintained over 90% Cr(VI) removal efficiency after six cycles. Finally, the Cr(VI) removal efficiency of NECS reached 99.9% with a dosage of 12 g/L for real acidic electroplating wastewater (the initial concentration, 936.68 mg/g and pH, 1.5), clearly showed the potential of this novel adsorbent for treating Cr-containing wastewater [62].

Carboxyl-rich carbon microspheres (CSp) prepared by HTC from hemicellulose-derived by-products of pulp refining was used for adsorption of Pb(II) and Cd(II) from aqueous solution. This study revealed the adsorption capacities of 380.1 and 100.8 mg/g for Pb(II) and Cd(II), respectively [74]. Mesoporous carbon microspheres were successfully synthesized by a spraying method for adsorption of Cr(VI) from waste water. As the adsorption process was pH dependent, it showed maximum removal efficiency of Cr(VI) at pH 3.0 [75]. Magnetically separated and N,S co-doped mesoporous carbon microspheres (N/S-MCMs/Fe₃O₄) were fabricated by encapsulating SiO₂ nanoparticles within N,S-containing resorcinol/formaldehyde polymer based microspheres and cysteine as the nitrogen and sulfur co-precursors, followed by the carbonization process, silica template removal, and the introduction of Fe₃O₄ into the carbon mesopores. This material exhibits an enhanced Hg²⁺ adsorption capacity of 74.5 mg/g, and the adsorbent can be conveniently and rapidly separated from wastewater using an external magnetic field [76]. A colloidal carbon nanospheres (CNS: 400–500 nm in diameter) synthesized via simple hydrothermal treatment of glucose solution was used for adsorption of Ag(I) ions from aqueous solutions. The surface of nonporous CNS after activated by NaOH was enriched with –OH and –COO– functional groups. Despite the low surface area (<15 m²/g), the maximum adsorption capacity obtained with CNS activated with 0.5 M NaOH was 152 mg/g with the initial Ag(I) concentration lower than 2 ppm and the adsorbent dosage of 1 g/L [77]. Adsorption capacities of some ACS for heavy metals are given in Table 4.

Table 4. Adsorption capacity for some heavy metals using ACS produced from various precursors.

Precursor	Activation agent	BET surface area (m ² /g)	Total pore/ micropore volume (cm ³ /g)	pH/ Temperature	Order of the kinetic model	Adsorption model	Adsorption capacity/ Recovery with heavy metal	Refs.
Polystyrene beads	H ₂ SO ₄	976	0.68/0.47	-	-	-	Pb(II)-96.4%; Hg(II)-96%; Cu(II)-93%	[6]
Polystyrene beads	Steam	1009	0.89	2	-	-	Cr(VI)-99.1%	[8]

Continued on next page

Precursor	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	pH/ Temperature	Order of the kinetic model	Adsorption model	Adsorption capacity/ Recovery with heavy metal	Refs.
Alkylphenol-formaldehyde	Steam	1329.11	0.62/0.41	25 °C	-	-	Elemental Hg-71%	[45]
Alkylphenol-formaldehyde	Steam	954	0.49/0.42	150 °C	-	-	Elemental Hg	[46]
Jute	KOH and CO ₂	856.89	0.889/0.689	30 °C	Pseudo-second order	Langmuir	31.44 mg/g for Cu(II)	[57]
m-phenylenediamine and hexamethylenetetramine (HMT)	ZnCl ₂	1237	0.58/0.35	1.5	Pseudo-second order	Freundlich	279 mg/g for Cr(VI)	[62]
Pentosan	Hydrothermal	13.7	0.026*	30 °C	-	Freundlich and Langmuir	380.1 mg/g for Pb(II) and 100.8 mg/g for Cd(II)	[74]
Resorcinol-formaldehyde/SiO ₂	-	1221	2.7/0.253	3	Pseudo-second order	Freundlich and Langmuir	165.3 mg/g for Cr(VI)	[75]
Resorcinol-formaldehyde	-	542	-	-	Pseudo-second order	-	74.5 mg/g for Hg ²⁺	[76]
Glucose	NaOH	12.7	0.02	RT	Pseudo-second order	Langmuir	144.9 mg/g for Ag(I)	[77]

* Micropore volume.

5.2. Energy storage

Novel energy storage systems have gained enormous importance and activated carbons are the key materials utilised for this applications due to microporosity, large surface area, electrochemical inertness and relatively high electrical conductivity. It is established that the porous structure and surface area of activated carbon are the most important characteristics that influence the performance of the capacitors. The use of ACS in supercapacitor electrode materials has been studied and found well. The resorcinol-formaldehyde resins carbonized at 600 and 900 °C resulted carbon spheres with surface areas of 592.4 m²/g and 952.5 m²/g with specific capacitances of 17.5, and 33.5 F/g (scan rate of 5 mV/s), respectively [29]. Mesoporous carbon microspheres were used as electrode materials for supercapacitor and resulted in specific capacitance of 268 F/g under a current density of 1.0 A/g [30]. Nitrogen-containing carbon microspheres (NCMs) were prepared via directed carbonization and evaluated for the electrochemical properties of the NCMs electrodes. It showed a

high specific capacitance of 228 F/g at a current density of 1.0 A/g in 6 M KOH aqueous electrolyte, indicating good capacitive behaviour and also retained 86% capacity after 5000 charge/discharge cycles [35]. Nitrogen-containing ultramicroporous carbon nanospheres (N-UCNs) with high surface area (1439 m²/g) have showed excellent electrochemical performance such as high specific capacitance (269 F/g at 1.0 A/g) and long-term cycle stability (90.3% retention after 10000 charge/discharge cycles) in 6 M KOH aqueous electrolyte [36]. Spherical carbons (SCs) prepared using modified stober method upon carbonization were used for capacitor application which resulted in electrochemical capacitance of 127 F/g under basic conditions using SCs of 482 m²/g surface area [38]. A monodisperse carbon microsphere with surface area of 840 m²/g and micropore volume of 0.40 cm³/g exhibited a size-dependent electrical double-layer capacitor performance in which the capacitance increases with decreasing particle size. The nitrogen and oxygen codoped carbon spheres with the smallest size (0.8–0.6 μm) delivered a high specific capacitance (282 F/g at 0.5 A/g) [42].

Porous carbon spheres (PCSs) with narrow pore size distribution and high content of oxygen-containing functional groups were used as electrode material for electrochemical energy storage. For supercapacitors, the PCSs exhibited a high specific capacitance, good rate capacity and cycling stability [56]. KOH activated carbon spheres (CSs) with 0.308 cm³/g of micropore volume and the pore diameter of 3.381 nm endowed good electrochemical performance with a specific capacitance of 182 F/g under a current density of 0.5 A/g, remarkable rate performance, and longterm cycling stability. The excellent electrochemical performance of this ACS was mainly attributed to the micromesoporous structure [58].

The hierarchical porous carbon microspheres (HPCS) derived from corncob and chemically activated using KOH displayed maximum specific capacitance of 384.5 F/g at scan rate of 5 mV/s and ultra-high rate capacitance of 137.3 F/g at the current density of 100 A/g indicated its significant potential application in the field of energy storage [59]. Polydisperse carbon nanospheres (PCNS) with microporous structure, monodisperse carbon nanospheres (MCNS) with hierarchical porous structure, and agglomerated carbon nanospheres (ACNS) were used for electrochemical applications and showed that the MCNS sample has the highest specific capacitance of 224 F/g (0.2 A/g), the best rate capability (73% retention at 20 A/g), and the most excellent capacitance retention of 93% over 10,000 cycles, making it to be the promising electrode material for high-performance supercapacitors [60]. A nickel-doped activated mesoporous carbon microsphere after KOH activation showed a specific capacitance of 361 F/g at 1.0 A/g and also remained an electrochemical capacitance of 301 F/g under a high current density of 20.0 A/g which established as potentially important for supercapacitor applications, where a fast charge/discharge is required [61]. GAML as a kind of waste liquid based PCS prepared by HTC, carbonization and activation was used as carbon-based electrode material for EDLC. It was also established that the Fe(NO₃)₃ · 9H₂O plays an important role in improving the electrochemical property and resulted in high specific capacitance of 303.7 F/g and a high energy density of 8.54 Wh/kg at 40 mA/g with excellent cycle stability even after 8000 cycles [64]. Polyacrylonitrile (PAN) based carbon nanostructure microspheres was also used for supercapacitor and showed its specific capacitance 311 F/g and 179 F/g in 3M KOH and 1 M organic electrolyte, respectively [65].

Mesoporous ACS (MACSs) prepared from resorcinol-formaldehyde (RF) resin by chemical activation using ZnCl₂ resulted in surface area (up to 2437.1 m²/g), and 1.37 cm³/g total pore volume and revealed the excellent capacitive performance and small internal resistance [67]. In another study, highly monodisperse N-doped microporous carbon spheres prepared using carbonization of

polystyrene-based polymer spheres followed by activation resulted in 884.9 m²/g surface area and over 10% N-doping content. Further, the energy storage performance influenced by the micropores and N doping was studied and resulted in a maximum capacitance of 373 F/g at a current density of 0.2 A/g and excellent stability over 10,000 charge/discharge cycles. This study suggested that these CSs prepared from polymeric spheres will be new materials with high electrochemical performance [68]. A hollow spherical carbon (HSC) was prepared from corncob lignin through spray drying and subsequent heat treatment. The HSC produced at 1000 °C (surface area, 1261.7 m²/g), delivered high rate capability when it was directly used as electrode material for supercapacitors [78].

A series of porous carbon spheres (~300 nm particle size) with precisely adjustable mesopores (4–16 nm) and 2000 m²/g surface area was synthesized through a facile co-assembly of diblock polymer micelles with a nontoxic dopamine source for use as electrode material for electrochemical capacitors. The capacitance value was 111 F/g and established that large mesopores and a relatively low ratio of micropores are ideal for realizing high surface area normalized capacitance [79]. A pathway to produce tunable and porous spherical carbon materials was devised from sugar waste streams recovered from biorefineries and used in energy storage application. Emulsion-based synthesis resulted in hollow spheres with abundant microporosity compared to simple hydrothermal synthesis which produces solid beads with micro and mesoporosity. The renewable carbon product has surface area of 872 m²/g with capacitance of up to 109 F/g and the capacitor exhibited nearly ideal capacitive behavior with 90.5% capacitance retention after 5000 cycles [80].

A nitrogen-doped hollow microporous carbon nanosphere was synthesized via the combination of hyper-crosslinking mediated self-assembly and further pyrolysed using polylactide-b-polystyrene (PLA-b-PS) copolymers and aniline monomers as precursor. With surface area of 945 m²/g and at a current density of 1.0 A/g, the resultant specific capacitance was 250 F/g. In addition, it also exhibited high capacitance retention of ~98% after charging-discharging 1500 times at 25 A/g which established that it can be used as promising supercapacitor electrode materials for high performance energy storage devices [81]. A one-pot reductive amination process (an effective route for heteroatom doping of carbon materials) was used to functionalize 2,3-dialdehyde cellulose (DAC) beads with chitosan and L-cysteine to provide single (N)- and dual (N/S)-doped materials. The electrodes of carbonized carbon beads [chitosan-crosslinked DAC (CS-DAC): Surface area, 167.8 ± 1.93 m²/g] had a specific capacitance of up to 242 F/g at a current density of 1 A/g with electrodes maintained capacitance retention of 91.5% after 1000 charge/discharge cycles, suggesting it can be used as electrode active materials for energy storage [82].

Hollow carbon spheres were also used to design carbonaceous nanotubes (CTs) based nanostructures by encapsulating heteroatom-doping into one carbonaceous nanotube (HCSs@CT). The supercapacitor based on HCSs@CT-60 (surface area, 318 m²/g; pore volume, 0.78 cm³/g and micropore volume, 0.09 cm³/g) has exhibited a specific capacitance of 235 F/g at 0.2 A/g. This HCSs@CTs possessed outstanding performances as electrode materials of supercapacitors with excellent cycling life, demonstrating great potential for applications in energy storage [83]. Nitrogen doped mesoporous carbon nanospheres (NMCs), lychee exocarp-like mesoporous carbon spheres (NLEMCS) and core-shell mesoporous carbon spheres (NCSMCs) have abundant mesoporous structure, high N-doped content, high surface area and large pore volume [(1126.11 m²/g and 1.09 cm³/g for NLEMCS), (744.18 m²/g and 0.63 cm³/g for NMCs) and (434.53 m²/g and 0.55 cm³/g for NCSMCs)]. These materials exhibited specific capacitance of 262.4 F/g, 323.2 F/g and 247.06 F/g, respectively, at a current density of 0.2 A/g in 6 M KOH electrolyte solution [84].

A facile encapsulation of NiO nanoparticles in mesoporous carbon nanospheres (NiO/MCNs) is demonstrated and this material has uniform mesopores (5.9 nm) and high surface area (714 m²/g). NiO/MCNs has high specific capacitance of 406 F/g at 1.0 A/g in 6 M KOH electrolyte and it retains ~91.0% of the original capacity at 3.0 A/g after 10000 cycles [85]. Nitrogen-doped hollow mesoporous spherical carbon capsules (N-HMSCCs) was prepared by depositing mesoporous silica on the surface of the polyacrylonitrile nanospheres, followed by a dissolution-capture process occurring in the polyacrylonitrile core and silica shell. After carbonization and etching of silica, N-HMSCCs with uniform mesopore size (surface area, 718 m²/g; total pore volume, 0.87 cm³/g and average pore size, 4.6 nm) were produced which showed a high specific capacitance of 206.0 F/g at a current density of 1 A/g in 6.0 M KOH. In addition, 92.3% of the capacitance of N-HMSCCs still remained after 3000 cycles at 5 A/g [86]. Core/shell-structured SnO₂-ZnO/C microspheres was prepared by a one-pot spray pyrolysis process transformed into yolk-shell Sn@C microspheres by heat-treatment at 1000 °C under a reducing atmosphere using 10% H₂/Ar mixture gas. This microspheres (surface area, 448 m²/g) showed superior cycling and rate performances as anode materials for lithium-ion batteries [87].

Spherical carbon materials were also used for generation of open-ended, worm-like and graphene-like structures and incorporated in organic solar cells and found to give a measurable photovoltaic response [88].

A carbon nanospheres (CNSs) with three heteroatom co-doped (nitrogen, phosphorous and sulfur) were obtained from carbonization of highly-crosslinked organo (phosphazene) nanospheres of 300 nm diameter. It possessed a high surface area of 875 m²/g (total pore volume, 0.43 cm³/g and micropore volume, 0.27 cm³/g) and its anode showed remarkable stability and coulombic efficiency in a long charge-discharge cycling up to 1000 cycles delivering about 130 mA h/g [89]. Hierarchically structured activated carbon (HAC) from pitch and silica activated using chemical activation (simultaneously removed the silica template and increased the pore volume) was prepared. The HAC with a surface area of 1957 m²/g (micropore volume, 3.0 cm³/g), exhibited an extremely high specific capacitance of 157 F/g indicated its superior energy storage capability and was thus suitable for use in advanced ultracapacitors [90]. Spherical nitrogen-doped porous carbons was prepared through a template carbonization method, in which polyacrylamide (PAM) served as carbon and nitrogen sources, and calcium acetate as hard template. The PAM-Ca-650-1:3 sample displayed the best capacitance performance that have surface area of 648 m²/g and total pore volume of 0.59 cm³/g. At a current density of 0.5 A/g, the resultant specific capacitance is 194.7 F/g and it also retained 97.8% after charging-discharging 5000 times [91].

Graphitic porous carbon spheres (GPCS) prepared from spherical resorcinol/formaldehyde resin by Fe-catalysis at 900 °C resulted in surface area of 1100 m²/g with average diameter, 450 nm and pore size, 1–4 nm. Porous carbon spheres (PCS) were also prepared using RF resin spheres as the precursor and by calcining at 900 °C under a N₂ atmosphere. GPCS showed enhanced charge storage capacity, with a specific capacitance of 127.4 F/g in 2 M KOH at a current density of 0.2 A/g that was nearly 3 times larger than that of amorphous porous carbon spheres with 96% retainability after 5000 cycles [92]. Porous silicon/carbon microspheres (GPSCMs) prepared by the ball milling and spray drying methods followed by carbonization and chemical vapor deposition processes resulted in sizes of 8–30 nm with surface areas between 20 and 90 m²/g. As the anode materials for lithium ion batteries, the average charge capacity was 589 mAh/g at a current density of 50 mA/g [93]. Low cost spherical carbon materials with large pore volume (4.0 cm³/g) and surface area (1510 m²/g)

were prepared through a simple in-situ steam etching process, for use in sulfur hosts of lithium/sulfur batteries. The resulted material exhibited good capacity output (about 1300 mAh/g-S) and excellent capacity retention (70% after 600 cycles) [94]. The capacitance values of some ACS used as electrode material for supercapacitors are given in Table 5.

Table 5. Application of some ACS in supercapacitors.

Precursor	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Capacitance (F/g)	Refs.
Resorcinol-formaldehyde	-	1439	2.12/0.52	268	[30]
Resorcinol-formaldehyde	-	687	0.59	269	[36]
Phenolic resin	-	482	-	127	[38]
Phenolic-formaldehyde	Steam	840	0.40*	282	[42]
Glucose	KOH	3003	-	349	[55]
Pectin	KOH	2440	1.28/0.65	231	[56]
Resorcinol-formaldehyde	KOH	735.4	0.622/0.306	182	[58]
F108/resorcinol-formaldehyde	KOH	703	0.645/0.317	224	[60]
Resorcinol-formaldehyde	KOH	1096	0.97/0.14	361	[61]
Resorcinol-formaldehyde	KOH	1227	0.90/0.81	353	[63]
2-keto-l-gulonic acid mother liquor	KOH	2478	1.24/0.99	303.7	[64]
PAN	KOH	2134	1.41/0.82	311	[62]
Resorcinol-formaldehyde	ZnCl ₂	2437	1.37	240	[67]
Polystyrene beads (N-porous CS)	KOH	844.9	0.48/0.33	373	[68]
Polystyrene-block-poly(ethylene oxide)	KOH	2320	1.24/0.64	111	[79]
Sugar	KOH	872	0.511	109	[80]
Poly lactide-b-polystyrene (PLA-b-PS) copolymers and aniline	-	945	-	250	[81]
PAN	-	718	0.87	206	[86]
Pitch	KOH	1957	3.0	157	[90]
Polyacrylamide	-	648	0.59/0.11	194.7	[91]
Resorcinol-formaldehyde	-	1103.4	0.71/0.36	127.4	[92]

* Micropore volume.

5.3. Removal of dyes

Dyes are organic compounds having resistant to light, water and oxidizing agents. Thus the degradation of dyes is difficult after release into aquatic systems. For dyes removal by adsorption process using ACS, the surface chemical properties of adsorbent plays an important role. It was reported that a polymeric ACS was about four times superior in terms of mechanical strength and about 5% smaller in terms of the micropore volume as compared to CAC. The adsorption capacities for methylene blue were 32 and 14 mg/g with PAC and CAC, respectively. These results suggested

that the low mesopore volume was consistent with the values of BJH volume. The Langmuir model fitted better than the Freundlich model. The chemical properties of the activated carbons, solutions pH and the substituents on adsorbates were influenced on removal [14]. Hydrothermally processed and chemically activated porous carbon nanosphere (PCNS), was used for adsorption of methylene blue, malachite green and rhodamine B dyes and resulted in the maximum capacity as 3152, 1455 and 1409 mg/g, respectively. In addition, PCNS exhibited a good reusable property after five consecutive cycles [66]. Chemically activated carbon microspheres (CACMs), prepared by hydrothermal method were synthesized by sulfonation and carbonization of PVA (polyvinyl alcohol) microspheres and used for removal of methylene blue (MB). The adsorption capacity increased from 474.6 to 602.4 mg/g as the initial concentration increases from 20 to 300 mg/L in a wide pH range. The maximum adsorption capacity was 925.9 mg/g at 45 °C and temperature change was found to have a significant effect on the adsorption process [95]. Polydopamine microspheres were used for the removal of a cationic dye (methylene blue, MB) from aqueous solution and also studied the influence of various parameters such as solution pH, temperature, initial concentration, and contact time. This study resulted in adsorption capacity of 90.7 mg/g at 25 °C [96]. Carbon nanospheres were fabricated via the pyrolysis of polyacrylonitrile-poly(methyl methacrylate) (PAN-PMMA) core-shell nanoparticles with a diameter of 35–65 nm and a high surface area of 612.8 m²/g. The carbon nanospheres exhibited a large adsorption capacity of 190.0 mg/g for methylene blue, thus making them excellent adsorbents for the removal of organic pollutants from water [97].

Citrus pectin-derived, tunable carbon microspheres with good reusability toward methylene blue adsorption, were prepared by a facile hydrothermal method and resulted in great potential for the treatment of methylene blue wastewater [98]. ACS obtained by KOH chemical activation of spherical carbon (SC) produced from hydrothermal treatment (HT) of sucrose resulted in average diameter of 2.86 µm with surface area of 1534 m²/g and pore volume of 0.765 cm³/g. The maximum adsorption capacity monolayer was of 704.2 mg/g [99]. The characteristics of ACS used for removal of organic dye are given in Table 6.

Table 6. Application of some ACS for removal of organic dye.

Precursor	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Dye	pH/ Temperature	Order of the kinetic model	Adsorption model	Adsorption capacity/ Efficiency	Refs.
Polystyrene beads ACS (M/s Kureha, Japan)	Steam	1160	0.478*	Methylene blue	3.8–4.4		Langmuir isotherm	32 mg/g	[14]
Glucose	ZnCl ₂	2902.5	1.49/0.34	Methylene blue	-	Pseudo-second-order	Langmuir isotherm	3152 mg/g	[66]
Glucose	ZnCl ₂	2902.5	1.49/0.34	Malachite green	-	Pseudo-second-order	Langmuir isotherm	1455 mg/g	[66]

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Precursor	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Dye	pH/ Temperature	Order of the kinetic model	Adsorption model	Adsorption capacity/ Efficiency	Refs.
Glucose	ZnCl ₂	2902.5	1.49/0.34	Rhodamine B	-	Pseudo-second-order	Langmuir isotherm	1409 mg/g	[66]
Polyvinyl alcohol	H ₂ SO ₄	-	-	Methylene blue	6.5	Pseudo-second-order	Langmuir isotherm	602.4 mg/g	[95]
Polydopamine	-	13.77	-	Methylene blue	25 °C	Pseudo-second-order	Langmuir isotherm	90.7 mg/g	[96]
Citrus-pectin	-	5.22	-	Methylene blue	12	Pseudo-second-order	Langmuir isotherm	979.3 mg/g	[98]
Sucrose	KOH	1534	0.765	Methylene blue	25 °C	Pseudo-second-order	Langmuir isotherm	704.2 mg/g	[99]

* Micropore volume.

5.4. Gas adsorption and storage

Adsorption of gases on ACS is important alternative to storage because ACS is hydrophobic and stable in moisture conditions. Capture of CO₂ from different sources such as thermal power plants has been identified as better means for reduction of the CO₂ present in the atmosphere. The surface properties of ACS influenced the adsorption potential for CO₂ removal. Highly microporous carbon spheres prepared from phenolic resin spheres by CO₂ activation with high surface area (BET surface area, 2930 m²/g; micropore volume, 1.12 cm³/g and diameter, 200 nm) was used for adsorption of CO₂ and resulted in high uptake of 8.05 and 4.55 mmol/g at 0 and 25 °C under 1 bar, respectively. Relatively more CO₂ uptake capacities resulted at low CO₂ pressures as 1.42 mmol/g at 0.2 bar and 25 °C [11]. Spherical carbons (SCs) prepared using modified stober method upon carbonization were used for CO₂ uptake and resulted in 89 cm³ STP/g (at 273 K and 1.0 bar) using SCs of surface area of 482 m²/g [38].

Activated carbon beads (ACS) prepared by phenolic-based resins beads and surface affinity promoted by N₂ incorporation was studied for CO₂ uptake in pre-combustion capture applications. Very high (20–45 wt%) CO₂ uptakes at 40 bar were achieved suggesting the promising potential of these AC beads to be used where the CO₂ pressure is relatively higher such as Integrated Gasification Combined Cycle based power plants [40]. ACS from nitrogen free phenolic resins (0.6–0.8 mm diameter) with high mechanical strength prepared by hydrothermal synthesis and potassium intercalation via a KOH treatment efficacy has been investigated for pulverised fuel post-combustion capture. At 25 °C and 0.15 bar partial pressure of CO₂, the adsorption capacity of this ACS was about twice from 0.79 mmol/g for the untreated carbons to 1.51 mmol/g [49].

Millimeter-sized sulfur-doped microporous ACS was prepared by the sulfonation, oxidation, carbonization, and KOH activation from PSDVB precursor. This ACS was used for CO₂ uptake and

the SCS-700 ACS resulted in the best CO₂ uptake quality at both 25 °C (4.21 mmol/g) and 50 °C (2.54 mmol/g) under ambient pressure. This is due to the presence of abundant ultramicropores and a high proportion of oxidized sulfur functional groups. The ACS have sulfur content of 0.69 wt%, and a surface area of 1526 m²/g with pore volume of 0.726 cm³/g. This ACS with high microporous volume of 0.617 cm³/g, also revealed high CO₂ uptake of 10.66 mmol/g at 8 bar and 25 °C [69]. Further they have also studied CO₂ removal by nitrogen and sulfur co-doped microporous ACS (NSCSs) synthesized from poly (styrene, ST-vinylimidazole, VIM-divinylbenzene) resin spheres. The NSCS-4-700 sample with a molar ratio of ST:VIM = 1:0.75 showed the best CO₂ uptake at various conditions. It is revealed that CO₂ uptake at low pressures resulted from influence of surface chemistry and micropores below 8.04 Å. With moderate pressure (8.0 bar), CO₂ uptake was dominated by the volume of micropores. ACS (NSCS-1-700) resulted in the highest CO₂ uptake of 1.11 mmol/g at 0.15 bar pressure [70].

The activated mesocarbon microbeads (a-MCMBs) with high surface area of 3180 m²/g were prepared And resulted in methane absorption (14.73 wt% at 298 K and 0.99 MPa) and hydrogen adsorption (7.8 wt% at 77 K and 0.95 MPa) [100]. Styrene divinylbenzene based ACS was prepared using KOH activation with surface area of 730–3870 m²/g and total pore volume of 0.44–2.07 cm³/g (micropore volume, 0.30–1.59 cm³/g). The adsorption of methane was 1.68 mmol/g at 20 °C [101]. A series of microporous carbons prepared through carbonization and KOH activation from sulfonated styrene divinylbenzene resin resulted in surface areas from 725 m²/g to 3870 m²/g and total pore volumes from 0.44 cm³/g to 2.07 cm³/g (micropore volume, 0.2 cm³/g to 1.16 cm³/g with less than 0.75 nm). Physisorption measurements showed very high uptakes of CO₂ and H₂ reaching 356 mg/g of CO₂ (0 °C and 800 mm Hg), 209 mg/g of CO₂ (25 °C and 850 mm Hg), and 39 mg/g of H₂ (196 °C and 850 mm Hg) [102]. The nitrogen-doped mesoporous carbon spheres have been synthesized via soft-template and hydrothermal synthetic strategies using phenol/formaldehyde resins as carbon sources and melamine as a nitrogen source. This carbon spheres showed high performance for hydrogen storage, and the hydrogen adsorption capacities were in the range of 140–185 cm³/g. The incorporation of nitrogen into carbons was favored for hydrogen uptake in low pressure [103]. Surface modification of hydrothermally prepared activated carbon beads via HNO₃ oxidation and subsequent amination at elevated temperatures was investigated for pre-combustion capture CO₂. The highest working capacity of 4.9 mmol/g was resulted in with modified sample having surface area of 1106 m²/g [104]. Characteristics of ACS used for gas storage is given in Table 7.

Table 7. Application of ACS for gas storage.

Precursor	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Gas	Storage capacity/uptake	Refs.
Phenolic beads (CS-6-CD-4)	CO ₂	2284	0.89	CO ₂	4.55 mmol/g	[11]
Phenolic resin spheres	-	482	-	CO ₂	89 cm ³ /g	[38]
Phenolic beads	Steam	1280	0.91/0.43	CO ₂	9.31%	[40]
Phenolic beads	Steam and NH ₃	978	0.41/0.37	CO ₂	10.33%	[40]
Phenolic beads (ACS)	Steam	1128	0.45/0.43	CO ₂	0.79 mmol/g	[49]

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Precursor	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Gas	Storage capacity/uptake	Refs.
Phenolic beads (PR4_8000 ACS)	KOH	1171	0.50/0.47	CO ₂	1.25 mmol/g	[49]
Polystyrene beads (SCS-700)	KOH	1526	0.72/0.61	CO ₂	4.21 mmol/g	[69]
Polystyrene beads (NSCS-4-700)	KOH	1757	0.81/0.73	CO ₂		[70]
Polystyrene beads (NSCS-1-700)	KOH	1269	0.58/0.53	CO ₂	1.11 mmol/g	[70]
Pitch	KOH	3180	1.9	CH ₄	14.73%	[100]
Pitch	KOH	3180	1.9	H ₂	7.8%	[100]
Polystyrene beads	KOH	3870	2.07/1.59	CH ₄	1.68 mmol/g	[101]
Polystyrene beads	KOH	3870	2.07	CO ₂	356 mg/g	[102]
Polystyrene beads	KOH	3870	2.07	H ₂	39 mg/g	[102]
Phenol-formaldehyde	KOH	1200	1.51	H ₂	185 cm ³ /g	[103]
Phenolic resin (novolac)	-	1106	0.49/0.41	CO ₂	4.9 mmol/g	[104]

5.5. Removal of volatile organic compounds (VOCs)

VOCs such as benzene, toluene, and o-xylene are recognized as a source of air pollutants. Adsorption of VOCs using AC has been carried out by various investigators to remove them from the environment. Activated carbon spheres (ACSs) derived from 3-methylphenol-formaldehyde and using poly(ethylene glycol) additives was used for removal of dibenzothiophene from model diesel fuel and proposed that the adsorptive capacity of samples had a good linear correlation with the volume of specific micropores (0.6–1.2 nm) [44]. In toluene adsorption, the importance of the narrow micropores and large bed density at low pressure has been studied and resulted in better adsorption capacity with ACS as 38 g toluene/100 g for GE31C and 46 g toluene/100 g for GE60C [48]. PS based ACS (PACSK up to 2022 m²/g surface area and more than 0.78 cm³/g total pore volume) were produced using KOH activation and studied the adsorption of dibenzothiophene (DBT). The prepared PACSK resulted in better mechanical strength and 153 mg/g adsorption capacity. ACS after using as adsorbent for DBT was washed in shaker bath or ultrasonic bath with toluene for regeneration at 80 °C [50]. Further they have also studied adsorption performance of a sulfur-containing dibenzothiophene (DBT) using steam activated PACS with BET surface areas up to 979–1672 m²/g. The maximum adsorption capacity of PACS to DBT was 109.36 mg/g [51]. ACS prepared from sucrose with 1430 m²/g surface area [C-2(char and KOH ratio of 1:2)-total pore volume, 0.618 cm³/g and micropore volume, 0.516 cm³/g] was also used for the adsorption of thiophenic compounds. It possessed high adsorption capacity (41.5 mgS/g for 300 ppmwS model oil), fast adsorption rate (97% saturated within 5 min) as well as relatively good selectivity for the adsorption of benzothiophene, dibenzothiophene or 4,6-dimethyldibenzothiophene due to the abundant small micropores, suitable mesopore fraction and various oxygen functionalities present in the carbon [54].

Hollow and hierarchical porous carbon prepared through the KOH activation was used for adsorption of ethanol, methanol and isopropyl alcohol. This study revealed superior VOCs

adsorption as compared to non-activated carbon spheres [63]. The influence of surface oxygen groups of adsorbent on the irreversible adsorption of a mixture of OCs was studied using treated beaded activated carbon and established these groups on adsorbate-adsorbent interactions [105]. The high adsorption capacity and high mesopore fraction of beaded activated carbon were also required for organic vapor use requiring extended adsorption/regeneration cycling [105]. Styrene divinylbenzene ion-exchange based ACS was also used for the uptake of benzene apart from methane. The adsorption of benzene was 19.6 mmol/g at 20 °C [101].

Adsorption studies of ethanol using ACS was carried out at relative pressure range from 0.001 to 1. Oxidation (in HNO₃ solution or air) and/or by thermal treatment in N₂ was used to modify oxygen surface contents of the activated carbons. At 225 ppmv ethanol concentration, oxidized samples resulted in good adsorption. With increase in relative pressure of ethanol the role of microporosity was most important [106]. The role of surface oxygen groups to irreversible adsorption (aka heel formation) during cyclic adsorption/regeneration (5 cycles) of organic vapors (a mixture of nine organic compounds) has been studied with three chemically modified ACS, including two oxygen-deficient (hydrogen-treated and heat-treated) and one oxygen-rich sample (nitric acid-treated). This study suggested that the pore size distribution played role in heel formation such as narrow micropores (<7 Å) in the oxygen-deficient samples and midsize micropores (7–12 Å) in the oxygen-rich sample [107]. Porous carbon beads (PCBs) of about 1.5 mm were prepared by phase inversion and subsequent carbonization from PVDF solution containing phenolic resins. PCBs-2 obtained after moderate phase inversion resulted in highest surface area (1166 m²/g) with 0.249 cm³/g mesoporous pore volume and 2.87 nm pore size. PCBs-2 resulted in adsorption capacities for benzene (1.467 g/g), toluene (1.229 g/g), n-hexane (0.600 g/g) and acetone (0.770 g/g) under static adsorption and higher adsorption kinetics for benzene vapour on dynamic adsorption [108]. The characteristic of some ACS used for removal of VOCs is given in Table 8.

Table 8. Application of ACS for removal of volatile organic compounds.

Precursor/Product	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Volatile	Temperature	Adsorption model	Adsorption capacity (mg/g)	Refs.
Phenol-formaldehyde beads from bamboo tar	CO ₂	189	0.10	Toluene	50 °C	Langmuir	29 mg/g	[43]
3-methylphenol and formaldehyde	Steam	1501	0.72/0.25	Dibenzothiophene	25 °C	Langmuir-Freundlich	21.83 mg/g	[44]
Polystyrene beads	KOH	1566	1.05/0.62	Dibenzothiophene	25 °C	Freundlich	153 mg/g	[50]
Polystyrene beads	Steam	1555	1.29/0.56	Dibenzothiophene	25 °C	Freundlich	102 mg/g	[50]
Pitch	Steam	1573	0.68/0.50	Dibenzothiophene	25 °C	Freundlich	93 mg/g	[50]
Polystyrene beads	Steam	979	0.84/0.31	Dibenzothiophene	-	Freundlich	109.36 mg/g	[51]
Phenolic beads	CO ₂	1065	0.53*	Toluene	25 °C	-	236 mg/L	[48]
BAC from pitch (M/s Kureha, Japan)	-	1291	0.55*	Ethanol	25 °C	-	0.51 cm ³ /g	[106]

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Precursor/Product	Activation agent	BET surface area (m ² /g)	Total pore/micropore volume (cm ³ /g)	Volatile	Temperature	Adsorption model	Adsorption capacity (mg/g)	Refs.
BAC4 oxidized with HNO ₃	-	1212	0.53*	Ethanol	25 °C	-	0.49 cm ₃ /g	[106]
BAC-O from Pitch (M/s Kureha, Japan)	-	1189 ± 11	0.50 ± 0.01/ 0.43 ± 0.01	Organic vapours	25 °C	-	-	[105]
BAC-O-400	-	1360 ± 5	0.56 ± 0.01/ 0.50 ± 0.01	Organic vapours	25 °C	-	-	[105]
BAC-H-400	-	1335 ± 24	0.56 ± 0.01/ 0.49 ± 0.01	Organic vapours	25 °C	-	-	[105]
BAC-400	-	1315 ± 15	0.55 ± 0.01/ 0.49 ± 0.01	Organic vapours	25 °C	-	-	[105]

* Micropore volume.

5.6. Catalyst support

The importance of carbon spheres as support materials is well known in catalysis community. In a review carbon nanospheres as support was also described earlier [109]. In catalytic applications, PBSAC was used as catalyst support for platinum and ruthenium in direct methanol fuel cells, in ethylbenzene dehydrogenation, ionic liquid phase (SILP) catalysts using homogeneous Rhodium, catalysts for the hydroaminomethylation of ethylene and decomposition of 2-chloroethylethylsulfide using copper as supported active material or in photocatalysis as support for titanium dioxide nanoparticles. PBSAC are used as catalyst support because it is dust free and has excellent fluid dynamic characteristics. It also takes less post processing times and facilitated catalyst recycling. The Palladium-PBSAC catalysts having ACS of 50, 200 and 500 μm size with surface area of 1159–2350 m²/g (total pore volume, 0.61–1.67 cm³/g and micropore volume, 0.37–0.92 cm³/g) were used in the hydrogenation of cinnamic acid and resulted in full conversion at 0.122 m³ · kg/Pd s of an optimum effective rate constant [12]. Monodisperse, mesoporous carbon nanoparticles (PAMCs) prepared from polymer/colloidal silica self-aggregates using a facile synthetic route have been demonstrated to serve as effective electrocatalysts for the hydrogen peroxide reduction reaction (HPRR) and the oxygen reduction reaction (ORR), both in acidic and alkaline solutions. These findings encouraged further investigation of other carbon-based, metal-free materials for electrocatalysis of HPRR, a reaction that is relatively underexplored [32]. Pt nanowires (PtNWs) grown on the porous carbon spheres (PCSs) interconnected with each other to form a porous nanowires network structure was used as a catalyst. The three-dimensional (3D) hybrid catalyst material consisting of PtNWs network supported on PCSs exhibited superior catalytic activity and stability towards both methanol and ethanol electro-oxidation in acidic media [56]. In another study PBSAC of surface area of 1755 m²/g (total pore volume, 1.07 cm³/g and micropore volume, 0.78 cm³/g), 1714 m²/g (total pore volume, 1.03 cm³/g and micropore volume, 0.76 cm³/g) and 1717 m²/g (total pore volume, 1.04 cm³/g and micropore volume, 0.77 cm³/g) of 500 μm diameter has been used to prepare many Pd/PBSAC (1 wt%) catalysts and utilized in the hydrodechlorination (HDC) of 4-chlorophenol (4-CP) in aqueous phase. The catalyst resulted in a high stability for long use (100 h on stream) continuous application [110].

The catalytic activity of the hollow mesoporous carbon spheres (surface area, 187 m²/g and the pore volume, 0.2 cm³/g) derived from cellulose nanocrystals (CNCs) and prepared by templating CNCs onto sacrificial silica spheres followed by heat treatment was successfully used for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by sodium borohydride (NaBH₄) with superior performance compared to that of metal nanoparticle and metal nanoparticle-carbon hybrid based catalysts [111]. Nitrogen, phosphorus, and sulfur co-doped hierarchical porous carbon spheres (NPS-HPCs) were synthesized by combining the polymerization of hexachlorocyclophosphazene and 4,4'-sulfonyldiphenol with co-assembly of colloidal SiO₂ NPs, followed by a pyrolysis and etching process. The NPS-HPCs with high surface area (960 m²/g) and pore volume (1.86 cm³/g) showed that the palladium nanoparticles (Pd NPs) loaded NPS-HPCs using methanol as a reductant exhibit high activity, excellent stability and recyclability for hydrogenation of nitroarenes [112]. The Pd NPs immobilized on m-aminophenol/formaldehyde resin (APF)-derived porous carbon spheres (Pd@PCS) was used as heterogeneous catalysts for organic dye reduction reactions. The Pd NPs with an average particle size of ca. 12 ± 0.8 nm were highly dispersed on the surface of PCSs possessed surface area and pore volume as high as 896.3 m²/g and 0.934 cm³/g, respectively. The prepared catalysts exhibited the high catalytic activity towards crystal violet (CV), eosin yellow (SY) and sunset yellow (SY) with reusability [113]. A nitrogen-doped hollow carbon spheres (NHCS) was synthesized by nanocasting using nonporous core/mesoporous shell silica spheres as exotemplate followed by carbonization of PAN at 850 °C consist of hollow spheres with a diameter of about 200 nm and a shell thickness of about 30 nm with 1761 m²/g surface area and 1.3 cm³/g total pore volume. This material was studied as a support for platinum-based electrocatalysts. The electrochemical activity in the ORR and stability was studied for two Pt@NHCS materials, one Pt@NHCS with a Pt particle (<2 nm) and other after thermal treatment at 850 °C (Pt@NHCSΔT) with a Pt particle size (2–3 nm). The results showed that nitrogen doping of the carbon supports can offer benefits for achieving high initial mass activities due to improved high platinum dispersion [114].

Catalysts consisting of microporous titanium silicalite-1 (TS-1) as reactive and polymer-based spherical activated carbon (PBSAC: Surface area, 1748 m²/g; total pore volume, 2.0 cm³/g and diameter of particle, 0.45–0.50 mm, Blucher, Germany) as sorptive component were used for epoxidation of commercially available biodiesel with aqueous H₂O₂ as an oxidant. In this catalyst, the active titanium sites were utilized four times more efficiently than in the commercial TS-1 [115]. Synthesis of spherical activated carbon with mesoporous structure using a soluble low molecular weight phenolic resol precursor through an ammonium alginate assisted sol-gel method was carried out. Introducing CaCO₃ during the preparation process promoted the formation of a mesoporous structure of carbon spheres and evidently increased the surface area and oxygen content. The conversion of isobutane reached up to 28% for this spherical activated carbon, and the selectivity of isobutene reached up to 96% [116].

5.7. Biomedical applications

ACS also has potential for use in biomedical applications [117]. Paramagnetic mesoporous carbon spheres (surface area, 586 m²/g and total pore volume, 0.53 cm³/g) were successfully used for vitamib B12 adsorption and showed highest vitamin B12 adsorption capacity of 103 mg/g [29]. Sucrose derived ACS prepared using physical and chemical activation was used for removal of

pharmaceutical compounds, paracetamol and iopamidol. The maximum adsorption capacity was 472 and 151 mg/g with K_2CO_3 activated carbon for paracetamol and iopamidol respectively [47].

ACS with mesopores (3 and 5 nm) prepared from phenolic resin using steam activation at 800 °C have good properties for adsorption of creatinine. Moreover, ACS (surface area, 1663 m²/g) with mesopores and macropores with 3–5 to 10–90 nm resulted in adsorption properties of VB12, that is larger molecule than creatinine [52].

The antibacterial activity of ZnO containing ACS was studied and reported that the antibacterial activity for *Staphylococcus aureus* was greater than that for *Escherichia coli*. This activity was due to the result of H₂O₂ formation from ZnO dispersed in ACS [118]. AST-120 (Kremezin; Kureha Chemical, Tokyo, Japan) is an oral ACS adsorbent used to remove indole and avoids indoxyl sulfate production in intestines. The treatment effect of AST-120 in chronic kidney disease (CKD) still remains a controversy, and physicians are required to carry out an individualized treatment plan for each CKD patient, in order to provide an optimal treatment to retard the progression of CKD and uremia-related complications, including cardiovascular disease [119]. The adsorptive removal of 5-Hydroxymethylfurfural (HMF) and fructose from aqueous solutions using PBSAC (surface area, 1770–1920 m²/g; Blucher, Germany) as adsorbents was studied and showed a high capacity (450–603 mg/g at 20 °C) and selectivity for the adsorption of HMF from aqueous solutions. The adsorption capacity for fructose was 280 mg/g. This study on biogenic platform chemicals with polarity differences utilizing commercial ACS may give basis for process development in future [120].

Polyethyleneimine-grafted oxidized mesoporous carbon nanospheres (OP) were also developed for combined photothermal combined gene therapy *in vitro* and *in vivo*. This work also revealed that it cannot only deliver the therapeutic gene (pING4) to tumors for gene therapy, but also can eliminate the tumors by photothermal ablation that suggested the OP's potential for cancer therapy [121]. Uniform mesoporous carbon spheres (UMCS) were also used as a carrier to improve the bioavailability of the model drug, celecoxib (CEL) and further investigated the mechanism responsible for the improved bioavailability of CEL. UMCS (surface area, 1069 m²/g and total pore volume, 1.49 cm³/g) significantly reduced the rate of drug efflux and improve CEL permeability [122].

5.8. ACS in chemical protective clothing, air and water filters

Chemical threat is a major challenge in present day war scenario. In order to protect personnel against chemical threat, personnel protection suit/clothing is most important. Some manufactures around the world have developed chemical protective clothing using ACS. These clothing/ensembles include NBC suit and socks. ACS based chemical protective clothings provide good comfort due to less weight, better air permeability and less water vapor resistance alongwith protection capability against chemical warfare agents. For fabrication of ACS based chemical protective clothing, ACS is coated/adhered on a fabric (knitted or woven base fabric of cotton or aramid) with the help of a polyurethane based adhesive to get strength along with good air permeability and low water vapour resistance. Further, non-woven fabric is laminated over ACS coated fabric either using same adhesive or by hot melt techniques. Finally, fabrication of complete suit or clothing is carried out in combination with this fabric and outer layer fabric [4,13]. Saratoga™ is composite filter fabric containing ACS adhered onto textile carrier fabrics. The ACS density varied from 180 to 220 g/m² that give 24 h protection against chemical warfare agent and at least 45 days of wear under

battlefield conditions alongwith multiple field washings. ACS outer surface of more than 85% is available to toxic gases that resulted in fast adsorption [123]. ACS based filter fabric covered with a polyamide fabric was used to protect against acetic acid, acetone, ethanol, ethylenediamine (1,2-diaminoethane), and toluene (methylbenzene), n-hexane, methanol, and styrene (phenylethene) and cyclohexylamine (cyclohexanamine) [124].

The usage of PBSAC-based agglomerates in AX canisters resulted in low pressure drops compared to the standard reference. The activation with steam can be terminated during PBSAC production at any time to define the micropore volume. The CO₂ activation generates substantial amount of meso- and macropore volume. PBSAC was used in air purification for adsorption of organic gases (cyclohexane, isobutene and di-methyl ether) with respiratory canister. Furthermore, PBSAC are also suitable for the removal of trace amounts of pharmaceuticals (diatrizoic acid, carbamazepine, bisoprolol and diclofenac) with fast adsorption kinetics and more capacity from waste water [39]. PBSAC with copper oxides (Cu₂O and CuO) was produced on a 1 kg scale using cross-linked polystyrene of 0.3–0.7 mm size and utilized for decomposition of 2-chloroethylethylsulfide. A batch process using a rotary kiln reactor using steam and CO₂ activation (two steps) was utilized. This copper modified PBSAC can be a potential hybrid material for self-detoxification used for individual protection from chemical warfare agents. In future, this self-decontamination potential needs validation with real CW agents [125].

5.9. Miscellaneous application

ACS derived from polymeric precursor was studied for adsorption of steroid micropollutants and resulted in better performance as compared to conventional GAC, and comparable to PAC at realistic concentrations (10 ng/L to 1 mg/L). This performance of ACS may be attributed to its enhanced hydrophobic characteristics alongwith 2125 m²/g of surface area formed by 98% of small mesopores (<5 nm, average 1–2 nm) [126].

6. Conclusions and future perspectives

The use of activated carbon is increasing due to the various types of novel applications. Preparation of the better quality of ACS with low-cost, high specific surface area, defined pore size distribution and compressive strength are the important parameters for this increased use. Proper choice of precursors, carbonization conditions, activation types (physical, chemical or combination of both), activation temperature and time, and the burn off percentage are the the most important parameters to achieve high adsorption capacity. The precursors used for ACS preparation include pitch, phenolic and polystyrene resins, lignin, carbohydrates and some other materials. ACS are used for adsorptive removal of toxicants from gases and liquid, separation of gases from mixture, energy storage, chemical catalysis, purifying water and many other applications. Chemical protective clothing has also been developed for personnel protection against chemical warfare agents using ACS. Significant efforts have been made to optimize the carbonization and activation conditions to achieve desired surface area and compressive strength of ACS used in chemical protective clothing. In chemical protective clothing, compressive strength is very important characteristics. It is essential to fully characterize both precursor and ACS to know all the features. For use as an adsorbent material (adsorption of heavy metals, volatile organic contents, dyes, catalysis, gas storage and

energy storage), the surface chemistry plays an important role. Process optimization could lead to get excellent characteristics of ACS for many novel applications. Still, it is needed to use alternative precursors or develop a novel approach or methodology to make low cost ACS with greater strength, well pores size distribution, good surface properties and high specific BET surface area.

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Conflict of interest

The author declares that there has no conflict of interest.

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