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Developments in activated functionalized carbons and their applications in water decontamination: a review

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ABSTRACT

Extremely high surface area, porosity, and other surface properties make activated carbons (ACs) a versatile and universally acclaimed adsorbent. High production costs limit the use of ACs as adsorbents, and this is a major driver for worldwide research targeting cheap precursors to reduce the production cost and to enhance the adsorption efficiency. This review highlights the preparation of ACs from various precursors, their functionalization, characterization, and their applications in water decontamination. A list of cost-effective precursors derived from agricultural waste materials along with the pollutants removed is presented. ACs can be functionally modified to develop highly efficient and adsorbate selective materials. Enhancement of the adsorption efficiency of ACs for inorganic pollutants and metal ions can be achieved by chemical modification, while physical modification of ACs via thermal treatment can enhance the pore size and surface area. A summary of the various chemical, physical, and biological processes that are utilized for these modifications is presented.

Keywords: Activated carbon; Preparation; Functionalization; Characterization; Water decontamination

1. Introduction

Contamination of surface and groundwater resources has long been recognized as a major environmental problem. Rapid industrialization is chiefly responsible for this contamination. The awareness of the impact of surface or ground water toxicity has increased, due to episodes of contamination of the aquatic environment; examples include the outbreak of Minamata and Itai–itai diseases in Japan. The discovery of conversion of inorganic mercury into methyl mercury and its accumulation in human body through the food chain, particularly through fish, and the carcinogenic nature of certain inorganics and metals have led to a refocusing of the attention of environmental scientists on this issue.

Some of the most widely used methods for water decontamination include ion-exchange, chemical

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precipitation, reverse osmosis, evaporation, and membrane filtration. Most of these methods suffer from a variety of drawbacks, such as high capital and operational costs, or the disposal of the residual contaminated sludge. Besides high capital and operational costs these conventional methods have inadequate efficiencies at low concentrations, particularly in the range of 1–100 mg/L [1].

Adsorption is one of the most promising processes for the removal of inorganic and organic pollutants from water even at concentrations as low as 1 mg/L [2]. Many non-conventional adsorbents have been reported for water decontamination, including inorganic adsorbents, organic adsorbents, and biomass.

Activated carbons (ACs) have proven to be particularly suitable for water and wastewater treatment due to their high surface area, well-developed pore structure, and surface properties. However, the high cost of ACs limits their use as an adsorbent. Much research on water decontamination has focused on the identification of cheaper sources for preparation of ACs and methods for their modification by chemical and physical activation. A variety of agricultural wastes and forestry products have been investigated for the preparation of ACs, including palm oil waste [3], babool seed [4], tamarind kernel powder [5], orange waste [6], palm shell [7], rice husk [8], saw dust [9], corncob [10], eucalyptus bark [11], pine saw dust [12], pistachio shells [13], and sawdust of Algarroba wood [14].

The adsorption efficiency of an AC depends on many parameters, including surface area and pore size distribution (PSD), its ash content, and surface properties. The PSD has been shown to be one of the parameters that influence the adsorption process the most. The PSD determines the fraction of the total pore volume that can be accessed by an adsorbate of a given size [15]. The nature of the adsorbate has also been shown to be very important, including parameters such as the functional groups present, polarity, hydrophobicity, molecular weight and size, solubility, and pK_a or pK_b, for weak electrolytes. The solution conditions (e.g. pH, temperature, adsorbate concentration, presence of competitive solutes, and polarity of solvent) also have an influence [16].

The focus of this review is to collate the latest developments in the functionalization of ACs to improve their potential applicability in drinking and wastewater treatment. Functional groups play a critical role in the adsorption capacity of ACs, with targeted functionalization allowing the enhancement of adsorption selectivity for specific applications. Some of the methods used for the functionalization of ACs include liquid phase oxidation with HNO_3 and H_2O_2 and gas phase oxidation with O_2 or N_2O, as well as thermal treatment at high temperatures [17]. Studies have shown that the introduction of oxygen-based functional groups on the surface of ACs can enhance the adsorption efficiency of nitrogenous compounds [18] and metal cationic species [19,20]. Oxygen functional groups are involved in the formation of surface complexes with metallic species in aqueous medium and ion-exchange with the displacement of protons [19]. There are many functional groups typically present on the carbon surface (Fig. 1) [21]. It is widely known that carboxyl, anhydride, lactone, phenol, carbonyl, and quinone groups are the major types of oxygen functional groups present on the AC surface, although the presence of more complex functional groups on the surface is possible [22]. Among them, carboxyl, anhydride, lactone, and phenol groups typically contribute to the acidity of the AC surface, whereas the carbonyl-, quinone-, and pyrone-like groups contribute to the basicity [23]. Among the basic functionalities contributing to carbon basicity, pyrone-like groups are so far the best characterized both energetically and structurally. The intrinsic basicity of pyrones ranging over a large pK_a interval (0–12), their relative thermodynamic stability and potential redox activity, as well as the relative abundance of oxygen in basic carbons strongly suggest that pyrones can be the most important basic functionalities at the edges of carbon surfaces [23].

2. Activated carbon (AC)

AC is a carbonaceous material produced by heating cellulose-based substances or bituminous coal at 600–1,200°C in the absence of air [24]. It is widely used

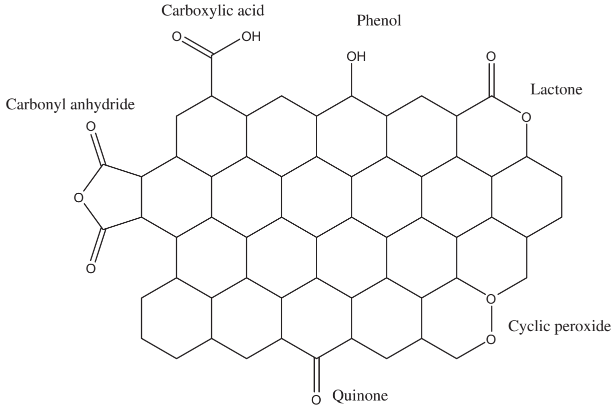

Fig. 1. Functional groups present on AC surface [21].

as an adsorbent in water and wastewater treatment for the removal of relatively lower levels of organic and inorganic contaminants via transfer from the dissolved phase (i.e. liquid phase) to the solid carbon surface (i.e. solid phase). High surface area, porous structure, and surface reactivity are some of the important characteristics of ACs [25]. Besides these properties AC is highly inert and thermally stable, and can be used over a broad pH range [26]. In spite of the huge application of ACs in water and wastewater treatment, the mechanism of the adsorption process is yet to be fully understood. Much confusion exists in the literature regarding these mechanisms [27]. Better understanding is required to study the surface characteristics of AC as it may help us to functionalize/modify the precursors in a better way to come up with more selective and efficient end products. Research on the surface chemistry of ACs started as far back as the 1950s and 1960s [28]. Hassler first raised the significance of the carbon surface chemistry in the adsorption process [29]. ACs are known to have a heterogeneous physical and chemical structure. The former arises from the existence of micro-, meso-, and macropores of different sizes [30]. The latter arises from the variety of functional groups (mainly in the form of carbon oxygen) that exist on the surface. A wide variety of oxides may be produced during the manufacture of ACs. These are the resultants of oxygen present in the precursors of ACs [21]. ACs like soot and carbon black consist of a mixture of sp^2- and sp^3-hybridized materials [31].

According to the International Union of Pure and Applied Chemistry (IUPAC) the classification of pore diameter is as follows: macropores (>500 Å), mesopores (20–500 Å), secondary micropores (8–20 Å), and primary micropores (<8 Å). Micropores constitute the largest part of the internal surface area of AC, constituting at least 90% of the total surface area [32]. The adsorption of organic compounds usually takes place within the micropores [33].

The structure of AC is highly complex and depends on the raw material used to produce it, the method of production, and pretreatment procedure. AC is sometimes described as having a "crumpled" layered surface, in which flat sheets are broken and curved back upon themselves. It generally consists of small graphite crystallites with highly disordered, irregular, rough, and heterogeneous surfaces [34]. The surface area of ACs can range from 500 to 1,400 m^2/g, with values as high as 2,500 m^2/g [35], and they have been shown to contain carbon nanotube (CNT) like porous structures [36]. The porosity of AC can be increased by pretreatment with acids or bases that causes reorganization of their surface [37] and pores [36]. The porous structural characteristics of AC are clearly shown by SEM images of cellulosic jute and coconut fibers ACs (Fig. 2) [38]. There was no obvious mesoporosity in the carbonized precursors (Fig. 2(a) and (c)). The macropores were developed by activation with CO_2 (Fig. 2(b)) and H_3PO_4 (Fig. 2(d)). Contrary to these results, Brasquet et al. [39] observed only micropores and mesopores, but no macropores on activated rayon fibers, which is also a cellulosic material. To get an insight into the effect of temperature on the porosity, AC honeycomb monolith (ACH) was prepared from bituminous coal [40], as shown in Fig. 3. The carbonization temperature and activation time were varied, with a higher carbonization temperature resulting in chars more resistant to steam activation, and yielding ACH with less total-pore volume, higher percentage of micropore volume, and higher mechanical strength. A longer steam activation time resulted in the conversion of a higher proportion of micropores to mesopores.

The surface chemistry of ACs shows the involvement of both hydrophobic graphene layers (Cπ electrons) responsible for the adsorption of organic compounds and hydrophilic functional groups responsible for the adsorption of polar species. Generally, AC is non-polar in nature. Graphene is an atom with a thick layer of covalently bonded carbon atoms tightly packed into a two-dimensional honeycomb lattice. The adsorption of Hg(II), Cr(III), Cd(II), and Pb (II) on graphene layers has been reported in the literature [41–43]. Oxidation of AC has been an effective option to improve the efficiency of heavy metals adsorption, though the adsorption of organic substances is greatly reduced by oxidation [44]. Oxidation increased the concentration of acidic oxygen groups on the AC surface, thereby increasing the polarity and decreasing the point of zero charge. Almazan-Almazan et al. [45] studied the role of AC porosity along with oxygen groups on adsorption using inverse gas-solid chromatography. Benzene, n-alkanes, trichloroethylene (TCE), and 1,2-dichloroethane (DCE) were chosen as model compounds. It was found that the adsorbate–adsorbent interactions were governed mainly by dispersive interactions between the π electrons of the aromatic ring of the adsorbate and those of the graphene layers of the carbon surface. Introduction of electron-withdrawing oxygen groups of AC surface leads to the removal of electrons from the graphene layers of carbon, and thereby weakens the dispersive interactions and prevents aromatic compounds' adsorption to some extent. The dispersive interaction dominates even in cases of adsorbates with strong dipolar moment (TCE and DCE) which are capable of specific interactions. Although the

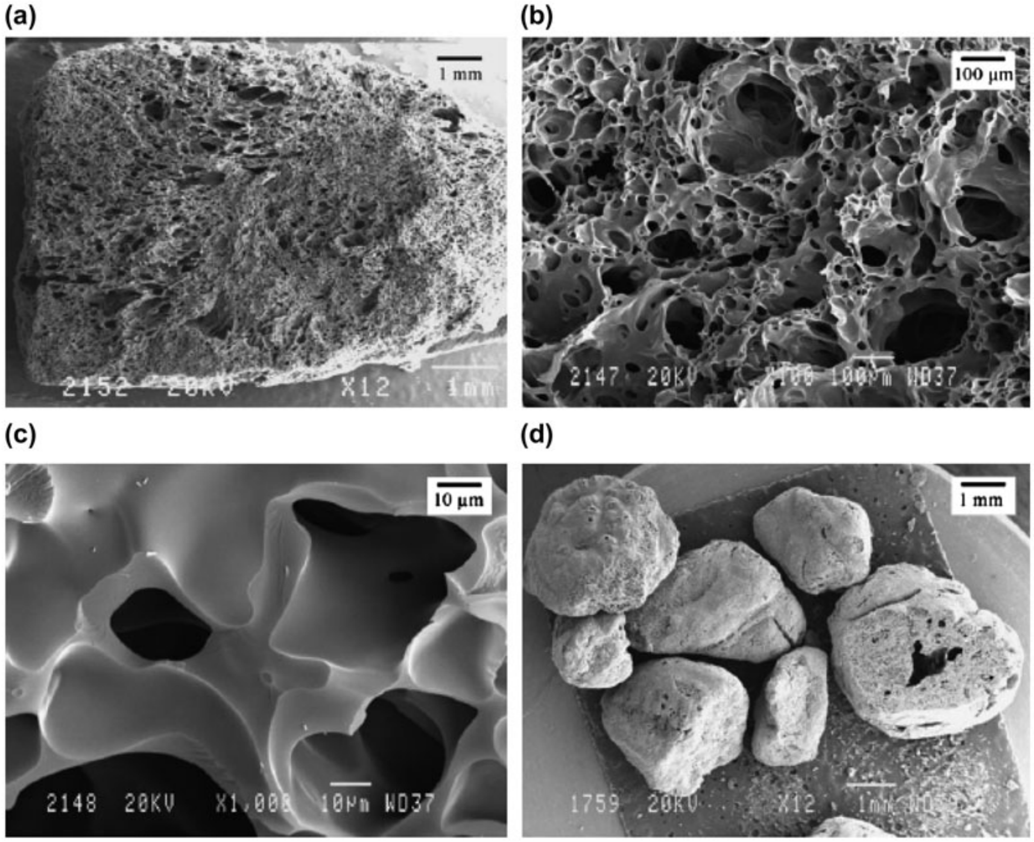

Fig. 2. SEM images of (a) carbonized jute fibers, (b) CO_2-activated jute fibers, (c) carbonized coconut fibers, and (d) H_3PO_4 activated coconut fibers [46].

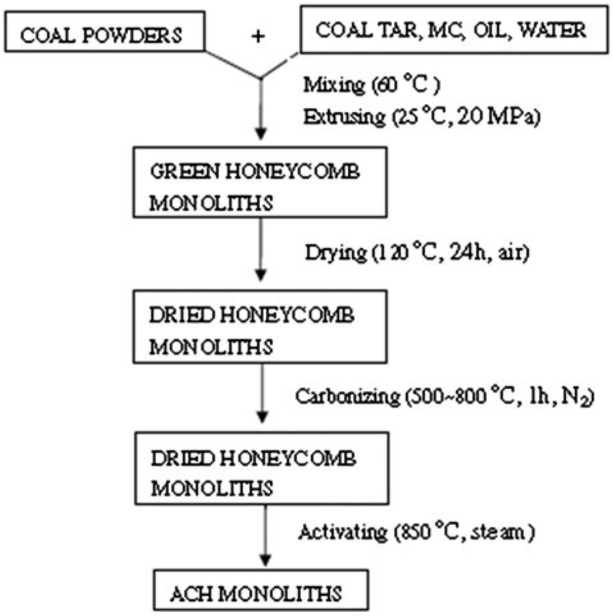

Fig. 3. Scheme for the preparation of activated carbon honeycomb (ACM) monolith [40].

introduction of large amounts of oxygen groups on the surface of the AC increases the specific component of the adsorption, the dispersive component is still clearly dominant. In addition, the introduction of oxygen groups corresponds to a decrease in the adsorption capacity. Nevertheless, it was shown that the presence of pores with appropriate sizes has a more important effect on the retention of the adsorbates than on the chemical surface groups. These results on oxygen functionality are in good agreement with the adsorption of VOCs (benzene and toluene) on AC where narrow micropores dominate for adsorption, especially for benzene [46]. Therefore, the limiting parameter for optimum adsorption of these molecules is the availability of accessible pores of appropriate size, rather than functional oxygen groups.

2.1. *Preparation of ACs*

The two most common forms of AC are powdered (PAC) (<0.177 mm) and granular (GAC) (>0.177 mm)

[24]. Powdered activated carbon (PAC) is used extensively in dedicated adsorber vessels (e.g. biological sewage treatment systems) owing to its high contact surface but with potential head loss. Granular activated carbon (GAC) is widely used for the removal of a wide range of toxic organic compounds and heavy metals from water and vapor-phase waste streams due to its high fluid conductivity and ease of recovery. There are two main preparation methods for GACs, reagglomeration (manufactured by thermally activating crushed briquettes of agglomerated raw material powder) and direct activation (carbon prepared directly from raw material granules). The reagglomerated GACs demonstrate a higher adsorption capacity and a longer application life than those manufactured by direct activation, but the extra pulverizing, binding, and agglomerating steps in reagglomeration involve additional costs [47].

Any cost-effective raw material with high carbon and low ash content could potentially be utilized as the precursor material for the preparation of AC. Carbonaceous precursors such as coal, wood, and peat are commercially used for synthesis [48]. Various techniques involving both chemical and physical activations of the raw materials are also used for the preparation of ACs. ACs can be prepared by a chemical activation technique, which involves impregnating the precursor with strong dehydrating agents such as H_3PO_4 and $ZnCl_2$ at 400–600°C to simultaneously form and activate the carbon matrix producing an L-type AC. Physically activating the raw materials (prepared without any chemical activation) produces an H-type AC. The differences in L-type and H-type ACs are listed in Table 1. Due to the growing need for cheap ACs in our society, researchers have attempted to utilize various wastes such as agricultural, industrial, and municipal wastes for the production of AC. This section gives a brief overview of some of the waste materials that have been utilized, and the preparation methods used.

2.1.1. Agricultural wastes

Table 2 lists a variety of ACs derived from a range of agricultural wastes, along with the pollutants removed. Agricultural wastes have been shown to be effective precursors for a range of ACs. For example, ACs derived from agricultural byproducts such as bean husk waste, rice husk, and sugar cane bagasse have been utilized for the removal of heavy metals [74,75], while a highly porous AC was developed from *Prosopis ruscifolia* wood sawdust by impregnation of H_3PO_4 followed by activation with self-generated atmosphere [72]. The BET surface area analysis showed a total volume of 1.7 cm^3/g and surface area of 2,281 m^2/g. Foo and Hameed [76] reported the utilization of oil palm waste [biodiesel waste] as an AC for wastewater treatment.

The preparation of a variety of types of ACs is possible from the same precursor material depending on the method of preparation. As an example, olive stones have been used to prepare modified powdered AC [52] and carbon foam [77]. Powdered olive stones were treated with 5% aqueous HCl solution, followed by washing several times by distilled water, and drying at 125°C. They were then subjected to

Table 1
Difference between L-type and H-type AC [49,50]

L-type activated carbon	H-type activated carbon
• Low activation temperature (450–600°C) with appropriate impregnating chemical agents such as H_3PO_4 or $ZnCl_2$ • Surface oxygen groups present, originating from the precursor materials • Wider micropores present due to the formation of smaller polyhexagon sheets but with higher aliphatic and hydrogen content • Pore size distribution obtained by N_2 adsorption indicates that L-type carbons have large micropores but narrow mesopores • Lower particle size reduction and higher yields in chemically activated carbons	• High activation temperature (800–1,000°C) with appropriate activation with vapor/gas such as CO_2 and H_2O • Surface oxygen groups resulting from partial oxidation mechanism by the activation atmosphere • Smaller micropores present due to the different polyhexagon sizes being linked by oxygen bridging in the intersheet spacings • Pore size distribution obtained by N_2 adsorption indicates that H-type carbons have narrow micropores and wider mesopores • Higher particle size reduction and lower yields in physically activated carbons

Table 2
ACs derived from agricultural wastes

Agricultural waste	Pollutants removed	References
Euphorbia antiquorum L. wood	Acid blue 92	[51]
Olive stones	Pb(II)	[52]
Nut shell	Cu(II)	[53]
Corncob	Phenols and dyes	[54]
Pine bark	Malachite green	[55]
Oil palm shell	2,4,6-trichlorophenol	[56]
Coconut shell	Phenol	[57]
Bamboo waste	Dyes and COD	[58]
Oil palm fronds	Bentazon	[59]
Bamboo waste	Reactive black 5	[60]
Rattan sawdust	4-chlorophenol	[61]
Rattan sawdust	Methylene blue	[62]
Hevea brasiliensis seed coat	Basic dyes	[63]
Coconut husk	Basic dyes	[64]
Coconut husk	2,4,6-trichlorophenol	[65]
Rattan sawdust	Phenol	[66]
Oil palm empty fruit bunch	2,4,6-trichlorophenol	[67]
Date stones	2,4-D pesticide	[68]
Bamboo waste	Methylene blue	[69]
Oil palm fibers	Methylene blue	[70]
Eucalyptus grandis sawdust	Cr(III)	[71]
Prosopis ruscifolia sawdust	Cu(II) and Cd(II)	[72]
Coconut shell	Cu(II)	[73]
Coconut and jute fibers	Phenol, acid red 27 dye and Cu(II)	[38]

destructive distillation for 5 h at 600˚C under nitrogen atmosphere. The resulting material was subsequently activated by gasification with steam at 900˚C. The modified AC sample was prepared by treatment with ammonium peroxisulfate. The suspension was shaken for 48 h at room temperature, after which the modified AC sample was removed by filtration, washed with distilled water, and dried in an air oven for 24 h at 125˚C. While hot, the treated carbon sample was then quickly transferred into a desiccator and subjected to low-pressure evacuation [52]. Rio et al. [77] used olive stones as a precursor for the preparation of carbon foam. The uniformly grounded olive stones of particle size 3.5 mm were loaded in a glass tube with internal diameter of 65 mm. This glass tube was introduced into a 1,000 mL stainless steel reactor placed inside a sand-bath furnace previously heated to 500˚C. A thermocouple inserted in the center of the bed of the precursor registers the solid temperature during pyrolysis, and another thermocouple placed near the outlet of the reactor (5 cm below) detects the temperature of the gases evolved during pyrolysis. The carbon obtained with initial atmosphere (N_2 and H_2O), pressure (1 MPa), and temperature (500˚C) showed 73% of carbon foam and 23% of granular char. The SEM images of foam or granular sections are shown in Fig. 4. Fig. 4(a) shows a transverse cut of the foam block, showing a continuous mass with a different appearance to the precursor forming with no detectable grain boundaries. A higher magnification image (Fig. 4(b)) shows the existence of voids/pores with size in the range of several tens of microns and even up to 100 μm. Observing the surface with more detail (Fig. 4(c)), a smooth texture is visible in contrast to that of a char prepared in a conventional pyrolysis, which is rough, and reflects the cellular structure of the precursor. A group of fissures and blisters can be observed on the surface of the granular fraction (Fig. 4(d)), the aspect of which suggests that they have been generated by the release of gases throughout a liquid of high viscosity. In the same way, a labyrinth of holes has formed in the fractured grain, some of them exhibiting an unusual large size.

2.1.2. Industrial wastes

Industrial wastes such as tires [78] and resins [79] have been used as raw materials for the production of ACs. The potential for ACs derived from waste tires for the removal of organic pollutants, heavy metals, and dyes have been reported [80–83]. Mendez and coworkers [55] pyrolyzed paper industry waste to

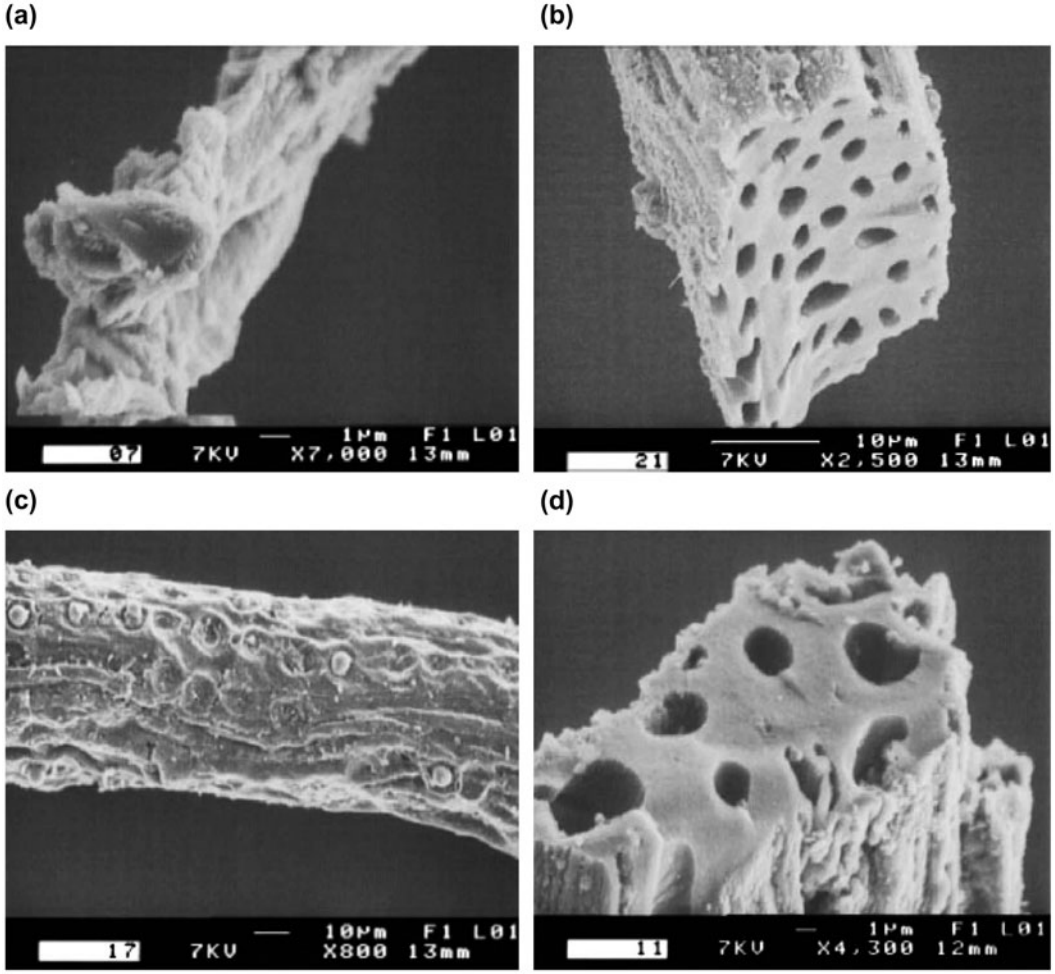

Fig. 4. SEM images of a carbon: (a–c) foam shape, (d) granular shape [77].

prepare AC, reporting a promising removal rate (99%) for malachite green dye. Bagasse pith, a sugar industry waste, was utilized for the removal of Cd(II) [84], Cu(II) [85], Cd(II), and Pb(II) [86]. Petroleum pitch was chemically activated with KOH to obtain an AC for successfully removing VOCs (ethanol and benzene) [87]. Surface characterization of the petroleum pitch AC showed an apparently large surface area (S_{BET}: 3,000 m^2/g) together with well-developed narrow micropore size distribution. Dynamic column adsorption experiments showed that mesophase pitch exhibits a superior saturation capacity compared to conventional carbon (18 g/100 g AC and 40 g/100 g AC, for ethanol and benzene, respectively). The regeneration studies showed that ethanol can be easily desorbed at room temperature by flowing clean air through the adsorbent, whereas benzene requires further heating for complete desorption/regeneration.

Fly ash from a thermoelectric power plant has been utilized for the preparation of GACs (Fig. 5(a)) [88]. Granular samples were formed by pressing the mixture in a die with the 30 wt.% coal tar and 20 wt.% water as the binder under 30 MPa. Samples were subjected to carbonization and steam activation. For physical activation, the activation temperature varied from 750 to 850℃; For chemical–physical activation, the carbon powder was pretreated with either a KOH or an ammonium-salt solution first [NH_4SO_4 6.6 wt.% + $(NH_4)_3PO_4$ 3.4% + H_2O 90 wt.%], with the content of KOH varying from 0.75 wt.%, 1 wt.%, 1.5 wt.%, 2 wt.% separately or the ammonium-salt solution ratio (mL g) varying from 1.1 to 4.1 (activation temperature 850℃). Results showed that pretreatment with ammonium-salt solution proved to be a good method for preparing an AC with better adsorption efficiency than the KOH, while the KOH treatment inferred an

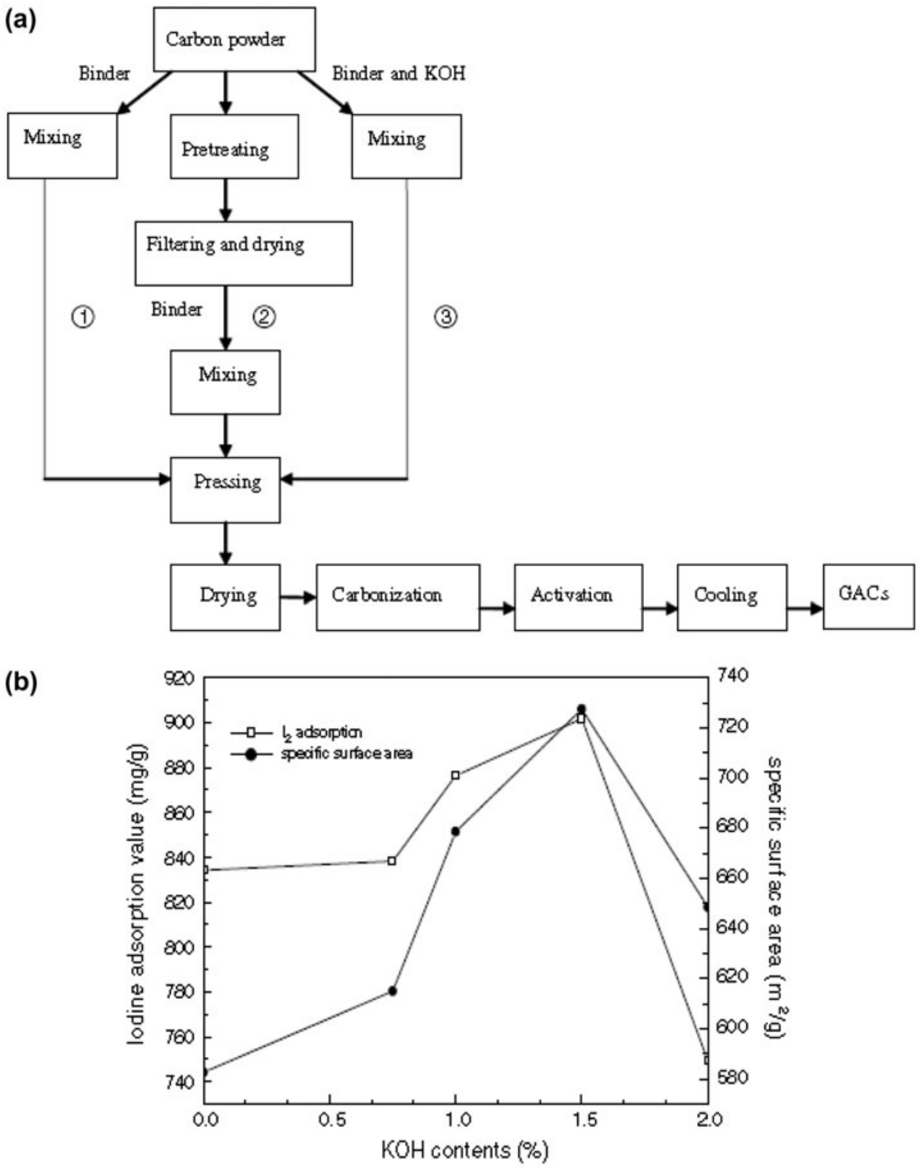

Fig. 5. (a) Different processes for the preparation of GACs from fly ash [88], (b) plot for specific surface area and iodine value vs. KOH content [88].

increase in specific surface area (Fig. 5(b)) but reduced the yield rate of the GACs.

2.1.3. Domestic and municipal wastes

Activated sludge is the waste generated from a municipal waste treatment plant. AC derived from dried sewage sludge was utilized for the removal of Hg(II) from wastewater [89,90]. Wet activated sludge (WAS) was chemically activated by $ZnCl_2$, KOH, and KCl [91]. The effect of varying concentration, time of impregnation, activation temperature, and time were studied to determine and to optimize the control parameters for the process. The maximum iodine value (mass of iodine adsorbed/100 g adsorbent) was observed at 0.5 M KOH concentration. An increase in impregnation time from 10 to 20 h resulted in a 20% increase in iodine value. The highest iodine value was obtained at 600˚C activation temperature with 1-h hour holding time. The sludge water content had a negligible effect on the iodine value of the prepared ACs. Raw WAS with a water content of 93.2% can be converted to an AC with a high specific surface area (737.6 m^2/g) and iodine value (864.8 mg/g) under optimum experimental conditions [91]. Mestre et al. [92] reported AC prepared from municipal waste (plastic) and cork powder for the removal of ibuprofen (a drug) from water. The waste-derived AC outperformed commercial ACs in terms of adsorption capacity for the removal of ibuprofen.

A method termed "express-activation method" was proposed by Kartel et al. [93] for the preparation of AC from Polyethyleneterephthalate (PET), a major post-consumer plastic waste material. The precursor (PET sample) was soaked in concentrated H_2SO_4 and heated to 65–70˚C. After heat treatment, the sample was washed with distilled water and dried at 110˚C for about an hour. The dried sample was then activated with steam. Activation was carried out in a quartz reactor at 500, 600, 700, and 800˚C with 100 mL/h steam flow rate. The BET surface area of the derived AC was 1,030 m^2/g and effective pore size of 1.8 nm. The derived AC showed significantly high adsorption capacity for both methylene blue and iodine in aqueous solution.

In recent years, many researchers have successfully utilized microwave heating for the production of ACs. Higher and more selective heating rates with greater control, reduced equipment size, no direct contact between the heating source and heated materials, and shorter time span for preparation are some of the merits of microwave heating technique [94]. Highly mesoporous AC was prepared within 600 s by microwave irradiation [95]. AC with BET surface area as high as 3,000 m^2/g was produced from mesocarbon microbeads with KOH by microwave heating [96]. Microwave-induced CO_2 reaction was successfully used to convert oil-palm-stone char into AC within 600 s [97]. White pine wood powder as a precursor material was utilized to prepare AC by microwave-induced $ZnCl_2$ treatment [98]. A TEM image of the modified AC shows interconnected nanoporous channels (Fig. 6(a) and (b)). The pores were largest in the sample with a $ZnCl_2$, with a wood ratio of 2.5.1 (Fig. 6(b)) and a BET surface area of 1,459 m^2/g. This was greater than the BET surface area of 1,321 m^2/g obtained by the preparation of an AC from the same sample by a conventional method with similar $ZnCl_2$ wood ratio.

Waste ion-exchange resins were also used as a precursor for the preparation of AC and were compared with AC derived from commercial ion-exchange resin under similar conditions [99]. The porosity (0.4 cm^3/g) and specific surface area (600 m^2/g) of the AC derived from waste ion-exchange resins was relatively higher than that prepared from commercial ion-exchange resins. Kubato et al. [100] utilized phenolic resin as a precursor material for the preparation of AC under microwave irradiation. The prepared AC was chemically activated with KOH. The input microwave power was varied, while weight ratios of KOH to phenolic resin, R, were changed. Phenolic resin was also activated at $R = 4$ using electric furnace heating. The highest surface area ($2{,}208 \times 10^3\ m^2/kg$) and total pore volume ($1.559 \times 10^3\ m^3/kg$) of AC were obtained at $R = 4$ with a microwave power of 0.39 kW, and the AC was characterized by a high mesopore ratio. The development of mesopores under microwave heating was attributed to the rapid temperature rise of the sample in contrast to slow electric furnace heating. Some other precursors reported for the preparation of ACs are coffee grounds [101], acrylic textile fibers [102], textile fibers [103], commercial coal-tar pitch [96], and waste tea [104].

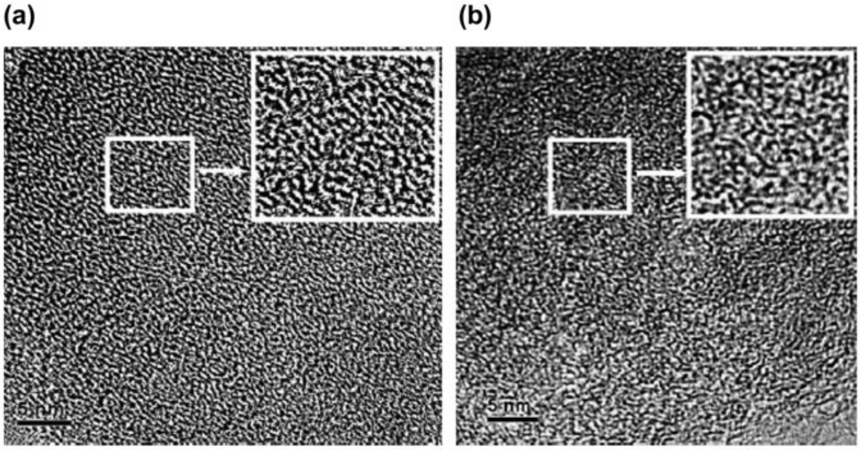

Fig. 6. TEM images of AC prepared from white pine wood powder by microwave-induced $ZnCl_2$ treatment with $ZnCl_2$. Wood ratio (a) 0.75.1, (b) 2.5.1 [98].

The "template technique" was developed for the preparation of a long-range ordered microporous carbon with a structural regularity of zeolite-Y [105]. Results showed that the use of chemical vapor deposition (CVD) gas with a small molecular size (acetylene) and low CVD temperature (600˚C) was the key factor in obtaining ordered microporous carbons. The derived microporous carbon showed high BET specific surface area (>3,000 m^2/g) with pore size distribution in the range of 1–1.5 nm and almost no mesoporosity. Inagaki et al. [106] derived mesoporous carbon from coal tar-pitch using MgO precursors [magnesium acetate $Mg(CH_3COO)_2$ and magnesium citrate $Mg(C_6H_5O_7)_2$] in different mass ratios. Initially, the pitch was pulverized in an agate mortar before mixing. The mixtures thus prepared were heated at 900˚C (heating rate—5˚C/min) for an hour under Ar atmosphere (flow rate—60 mL/min). From the carbon-coated MgO powder thus obtained, the substrate MgO was dissolved out using 2 mol/L H_2SO_4 and carbon powders were isolated. A high yield of mesoporous carbon was obtained by coupling with $Mg(C_6H_5O_7)_2$, as this itself gives carbon. The surface area of the resultant carbons reached up to 1,600 m^2/g, most of which was due to mesopores. A relatively sharp pore size distribution at about 12 and 5 nm was obtained from the mixture of pitch with $Mg(CH_3COO)_2$ and $Mg(C_6H_5O_7)_2$, respectively.

2.2. *Functionalization/Modification of ACs*

As mentioned previously, the performance of ACs is largely governed by their texture and surface modification [107]. In general, modification of ACs can be achieved via chemical, physical, and biological processes depending on the characteristic which needs to be altered. Fig. 7 shows a flow chart of the modification techniques that have been applied. While ACs have proved to be excellent for the removal of organic compounds from aqueous solutions, generally, it has been observed that ACs are less effective in removing inorganic compounds and metals. This is due to the fact that metals often exist in solution either in the form of ions or as hydrous ionic complexes. Research has shown that chemical modifications of ACs can enhance the adsorption potential for removal of inorganic compounds and metals in aqueous solutions [108].

Much ongoing research is directed towards modifying carbon's surfaces to improve its adsorption properties. Physical modifications such as altering the surface area and pore volume of ACs can be achieved by thermal treatment [109]. Chemical modifications of ACs initiated with the introduction of primary functionalities for further introduction of other molecules or a system is known as secondary introduction. The concentration and distribution of primary

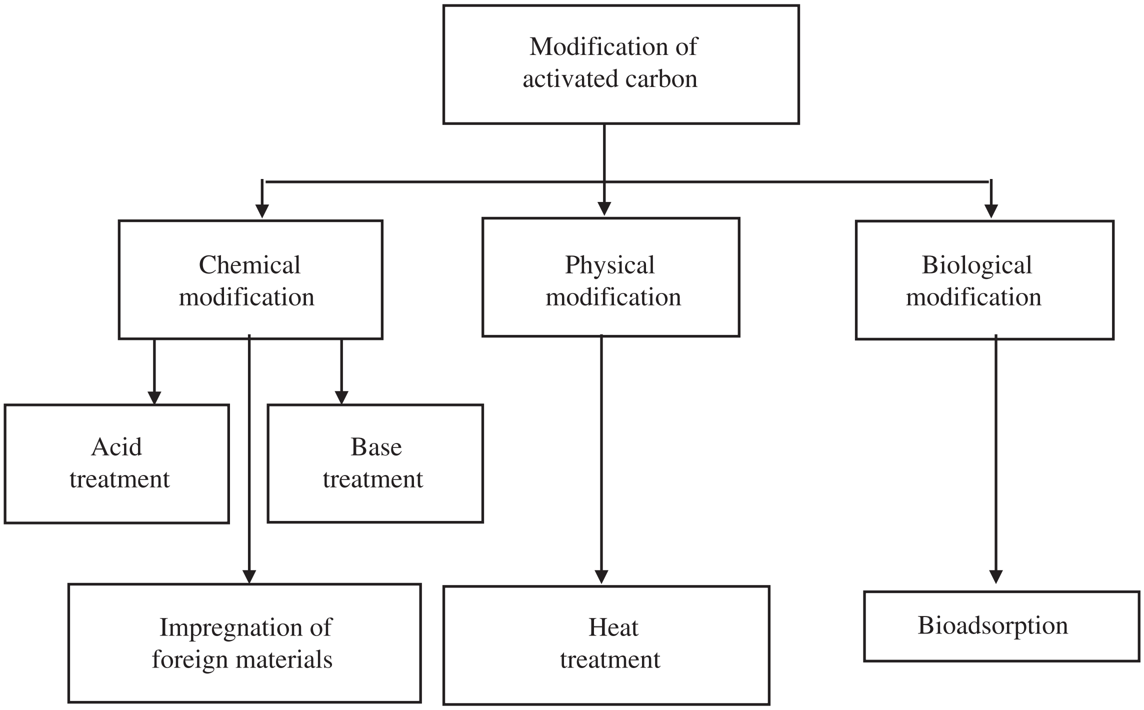

Fig. 7. Modification techniques of activated carbon [109].

functionalities have been shown to have a significant effect on the yield of secondary introductions. As such, the selection of primary functionalities onto the AC surface is a very important step [110]. Secondary functionalization can be carried out in two steps. Firstly, the target AC is obtained in a one-pot process, and the fragment of interest is then introduced directly onto the surface of the functionalized AC. Secondly, the fragment of interest is introduced successively in two or more steps. In this approach, an organic molecule is anchored onto the AC surface, and other fragments are then grafted onto the spacer to afford the target carbon-supporting functions [110].

Some of the precursor materials along with modification processes and the effect of modification on adsorption are reported in Table 3. Usually, a high adsorption activity of AC is attributed to the surface functional groups. An infrared (IR) study [17] indicates that the most common oxygen functionalities on carbon surface are C=O in lactones and carboxylic anhydrides (stretching frequency 1,750 cm^{-1}), quinone and ceto-enol groups (1,600 cm^{-1}), and C–O group in ethers, lactones, phenols, and carboxylic anhydrides (a broad band centered around 1,250 cm^{-1}). Chemically activated AC has partly aromatic and aliphatic structures or a highly cross-linked polymer produced from an almost infinite number of different monomers and containing a relatively large amount of heteroatoms. ACs prepared from steam activation consist of basal planes, which have an aromatic carbon skeleton with some functional groups involving heterogeneous oxygen atoms at their edges. It has been shown that gas-phase oxidation of AC mainly increases the concentration of hydroxyl and carbonyl surface groups, whereas oxidation in the liquid phase especially increases the concentration of carboxylic acids. Due to the presence of a polar –OH group, a phenol molecule is able to form hydrogen bonds with surface functional groups. On the other hand, the aromatic ring of the molecule determines its ability to have hydrophobic interactions. The effect of surface acidity for the adsorption of ammonia on metal-modified ACs was studied [107]. The adsorption of ammonia depends on the nature of metal (Fe, Co, and Cr) deposit and on its acidity. Moreover, moisture and surface functional groups play a significant role in the adsorption. Highly acidic surface functionality favors the adsorption of ammonia, indicating that the removal process is essentially governed by acid–base interactions.

The chemical treatment of powdered AC prepared from olive stone with an aqueous oxidizing agent such as $(NH_4)_2S_2O_8$ leads to the introduction of (COOH) and (OH) groups onto the surface [52]. Moreno-Castilla et al. [122] claimed that modification of ACs with strong acids like HCl, HF, or HNO_3, apart from the removal of the mineral matter, introduced oxygen surface complexes that are responsible for changing the surface chemistry and also altering the surface area and porosity of the original samples. It was reported that the chemical treatment of ACs with HNO_3 [123], ammonia, urea, and melamine suspension dissolved in ethanol followed by thermal treatment [124] leads to the introduction of nitrogenous functionality over the surface of ACs. In addition, treatment with melamine affects the pore size distribution to a large extent [125]. These groups significantly increase the polarity of the carbon surface, and thus its specific interactions with polar species via electrostatic forces [123] or via hydrogen bonding [126]. Nitrogen-containing groups generally provide basic properties enhancing the interaction between porous carbon and acid molecules [127]. The nature of nitrogen-containing surface groups differs depending on the thermal activation. At lower activation temperatures (400–700˚C), amides, aromatic amines, and protonated amides dominate the surface [128]. Pyridine, pyrrol, aromatic amines, quaternary nitrogen, and protonated pyridine dominate at higher temperatures (>700˚C) [129]. At lower temperature, nitrogen tends to appear in functional groups that are external to the aromatic ring structure (with localized charge), whereas at higher temperatures nitrogen is rather localized within the aromatic ring structure with a delocalized charge or no charge [130]. Dai et al. [131] studied the influence of thermal activation of AC on the adsorption of N-nitrosodimethylamine. They concluded that thermal activation promotes the hydrophobicity over the surface which in turn enhances the adsorption (Fig. 8).

The treatment of AC derived from palm oil shells with HCl was reported to introduce carboxylic and ether groups over the surface [132]. Catalytic decomposition of AC by H_2O_2 involves directly the exchange of a surface hydroxyl group with hydrogen peroxide anion ($^{-}$OOH) to generate peroxide on the surface, which then decomposes another H_2O_2 molecule producing oxygen and regenerating the AC active site [133]. It was also reported in the literature that H_2O_2 introduces hydroxyl free radicals on the AC surface [134,135]. Studies showed that pre-oxidation with peroxide promotes the formation of surface oxygen complexes, and at the same time decreases the alkyl groups over the surface. Lu et al. [136] observed a reduction in the intensity of alkyl groups (2,900 cm^{-1}) and the appearance of C=O stretching vibrations (1,700 cm^{-1}) for H_2O_2 pre-oxidized petroleum coke (PC) further activated by KOH. The conversion of

Table 3
Comparison of adsorption capacity of AC before and after modifications

Precursor	Modification	Pollutant removed	Adsorption Capacity		References
			Before modification	After modification	
Commercial activated carbon fibers	Magnetite doped with chitosan	As(V)	0.51 mg/g	2.53 mg/g	[111]
Commercial granulated AC	Treated by steam at 900°C and treated by concentrated H_2SO_4 at 250°C	Dibenzothiophene	10.9 mg/g	47.1 mg/g	[112]
Peach stone	Impregnated with H_3PO_4 followed by activation under the flow of steam	p-nitrophenol	315 mg/g	435 mg/g	[113]
Peach stone	Impregnated with H_3PO_4, activation under flow of breathing air	Methylene blue	362 mg/g	543 mg/g	[113]
AC	Impregnated with Urea, activation with nitrogen at 450°C	Phenol	0.338 g/g	0.540 g/g	[114]
Cherry stone	Activation in the presence of N_2 at 900°C for 2 h further activation in CO_2 at 850°C for 2 h, followed by O_3/HNO_3 treatment	Cu(II)	4.13 mg/g	22.21/28.12 mg/g	[115]
Commercial AC	SDS impregnate AC	Cd(II)	0.016 mmol/g	0.198 mmol/g	[116]
Commercial AC (carbon WV A1100)	Thermal treatment with N_2	Bisphenol A	375.53 mg/g	430.33 mg/g	[117]
Nut shell AC	SO_2 activated	Cd(II)	19.18 mg/g	32.02 mg/g	[118]
Wood based AC	High temperature activation with moist air	NO_2	63.8 mg/g at 45°C	139.6 mg/g at 45°C	[119]
Cork Waste AC	K_2CO_3 activation followed by steam activation	Ibuprofen	153.2 mg/g at 45°C	416.7 mg/g at 45°C	[120]
Coconut shell AC	Modified by 15% Sodium acetate	Cu(II)	20.45 mg/g	45 mg/g	[73]
Jute and coconut fibers AC	Chemically modified with H_3PO_4	Cu(II)	2.52 and 2.41 mg/g	57.73 and 46.27 mg/g	[38]
Rice husk-based AC	Poly(*N*,*N*-dimethylamino ethyl methacrylate)	Cu(II)	–	31.46 mg/g	[121]

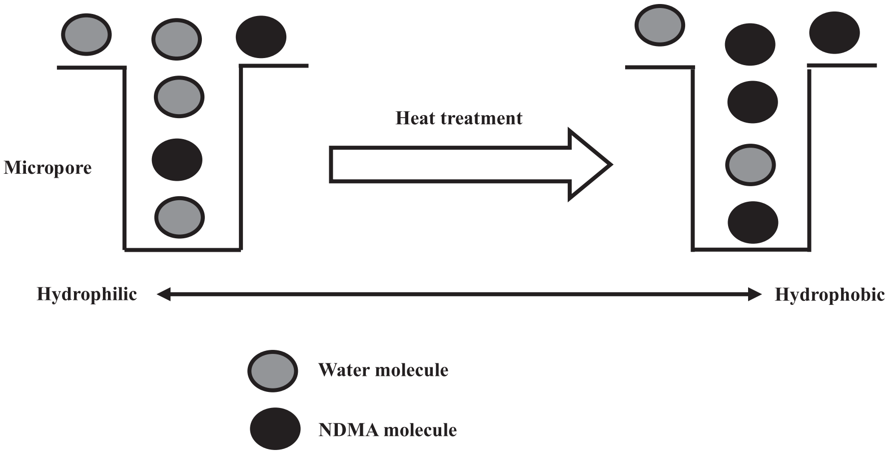

Fig. 8. Mechanism for the adsorption of N-nitrosodimethylamine on thermally treated AC [131].

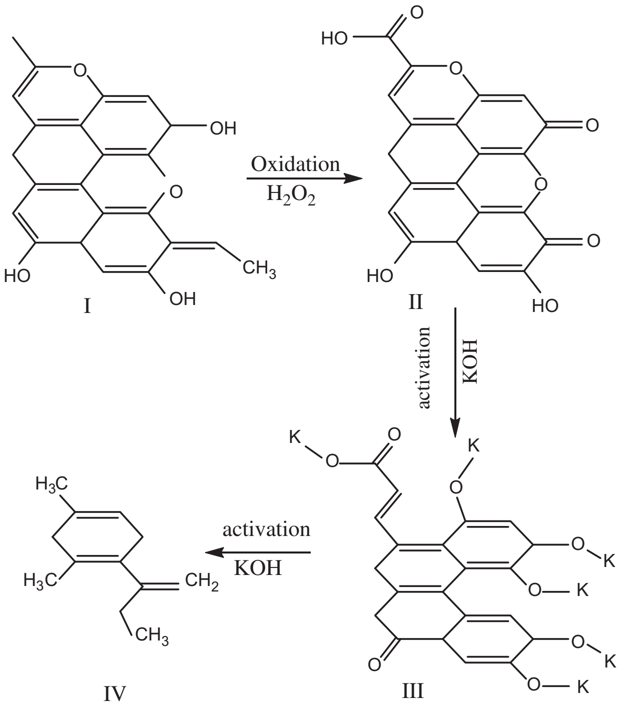

Fig. 9. Schematic mechanism for the chemical activation of petroleum coke [PC] [136].

alkyl groups into oxygen complexes may occur during the oxidization process. The systematic activation scheme is shown in Fig. 9.

Physicochemical activation of pomegranate seeds was carried out by $ZnCl_2$ at 600 and 800°C. Zinc chloride is an effective dehydrating agent that influences pyrolytic decomposition and inhibits the formation of tar [137]. High yield of AC compared to bio-chars was obtained. Impregnation of $ZnCl_2$ initially results in the degradation of cellulosic material and on carbonization produces dehydration that results in charring and aromatization of the carbon skeleton creating a porous structure [138]. Increasing yield of hydrogen can be partly attributed to the decomposition of the phenolic compounds and to the decrease of formation of other gases [139]. Hydrogen is released from the aromatic/phenolic structure of the precursor, leaving behind active sites for the reactions [140]. At this stage, aromatization reactions can take place and restrict the volatilization of molecules at the process temperature. Due to the aromatization processes, the yield of AC increases [141].

In an attempt to functionalize AC, Lukens [142] tried to alkylate nitrogenous groups on the surface of AC to convert the pyridinic sites into cationic alkylpyridinium sites selective for binding perchlorate ions. The effects of alkylation and treatment with reducing gases like ammonia and hydrogen as well as the results of the XPS studies strongly suggest that these chemical modifications mainly change the nature of the oxygen-containing functional groups rather than the nitrogenous groups (Fig. 10).

Chen et al. [143] modified commercially available AC using 1.0 M citric acid for the removal of Cu(II). Four grams of AC was reacted with 25 mL of citric acid solution. It was shaken for 30 min before being dried at 50°C overnight. The BET measurement showed that the specific surface area of the modified AC was reduced by 34% compared to unmodified AC. This could arise from pore blockage by adsorbed citric acid molecules. As the size of the citric acid molecule is small, it can easily access the pore structure of an AC. However, the apparent reduction in the surface area of the carbon does not adversely affect the adsorption of Cu(II) ions. Equilibrium results showed that the adsorption capacity of Cu(II) on citric

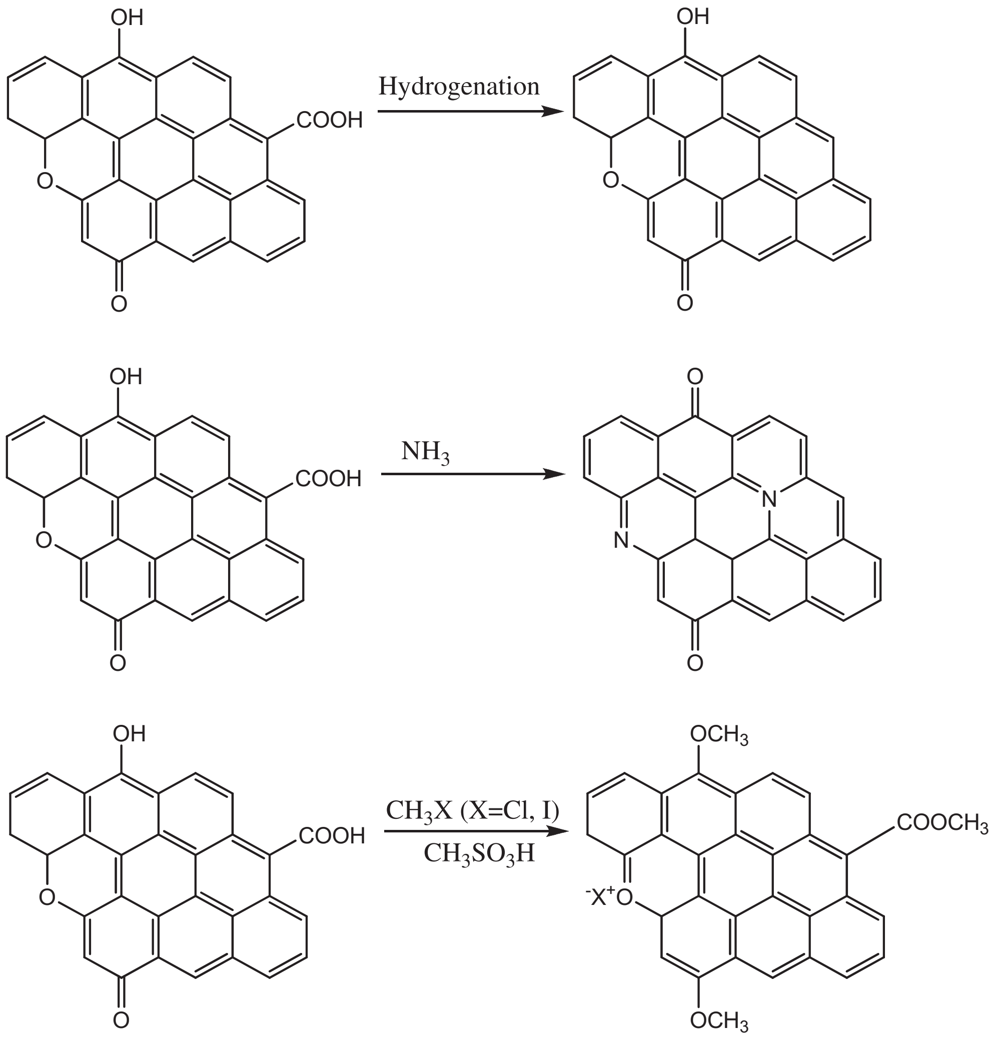

Fig. 10. Changes in the activated carbon surface caused by chemical modifications [142].

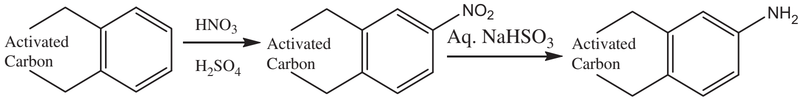

Fig. 11. Reaction scheme for the introduction of amine group on AC [144].

acid-modified AC increased to 14.92 mg/g, which was 140% higher than that on unmodified AC. The result showed that the immobilization of citric acid over the surface of AC introduces more surface adsorptive sites (mainly carboxylic functional groups from the citric acid), which provide excessive binding capacity for Cu(II) ions.

To prepare a Cu(II) selective AC, an electrophilic aromatic substitution reaction was successfully carried out for the introduction of nitro (–NO_2) groups, which were subsequently reduced to amine (–NH_2) groups over the surface of AC (Fig. 11—[144]). Results showed that the functionalized AC was highly selective for the adsorption of Cu(II) even in the presence of competitive ions.

The impact of sulfur (S) and chlorine (Cl) on Hg (II) removal by AC was studied and reported by several researchers [145,146]. They found that the Cl-impregnated carbon exhibited a higher adsorption capacity for Hg(II) than the S-impregnated carbon.

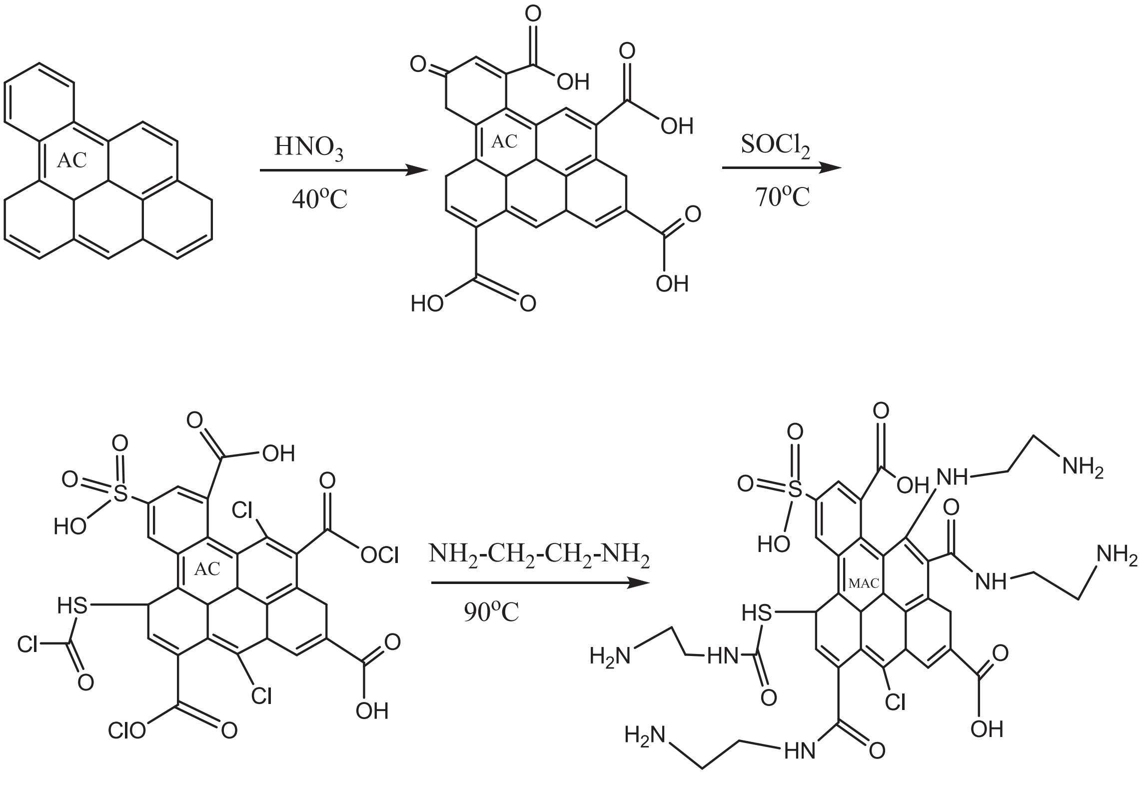

Fig. 12. Systematic scheme of functionalization of AC [148].

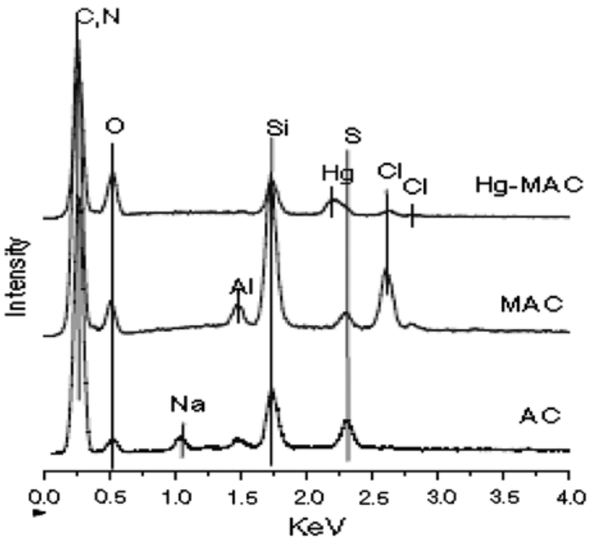

Fig. 13. EDS spectra of AC [148].

Studies showed that sulfurization of AC causes a decrease in surface area and porosity which resulted in significant decrease in the adsorption rate of Pb(II), but markedly enhanced the extent to which it occurred, except at pH 2 [147]. In an attempt to adsorb Hg(II) ions, Zhu et al. [148] modified AC by a combined treatment of nitric acid and thionyl chloride, followed by reaction with ethylenediamine, to introduce N-, S-, and Cl-containing functional groups (Fig. 12). The EDS spectra for virgin AC along with modified (MAC) before and (Hg-MAC) after adsorption of Hg(II) showed that the adsorption of Hg(II) may be associated with S-containing groups, due to the higher affinity of sulfur for Hg(II) ions (Fig. 13). The EDS results also showed that chlorine peaks became weaker after the MAC was exposed to Hg(II) solution, which was probably related to the competition between Cl-active sites and S-active sites (e.g. –HS, –SO$_3$H) over the surface of the AC. The results showed a higher adsorption rate and a larger capacity for Hg(II) ions. It was also reported that AC impregnated with sulfur-containing groups showed higher affinity for Cd(II) species [149–151]. The replacement of oxygen by sulfur over the surface of AC leads to an increase in the adsorption efficiency of the material for heavy metals in the aqueous solutions [150]. A three-step procedure involving oxidation, esterification, and grafting of a hyper-branched polyethylene imine was reported for AC modified with poly-alkyl amine to scavenge Pd(II), a transition metal [152]. The XPS analysis revealed Pd(II) ions loaded on the adsorbent in the form of Pd(II) with chloride as the counter ion.

Electrochemical methods for the surface modification of ACs have also been reported [153–157]. These methods have several merits over other methods [158]: (i) one of the reagents is the electron, which can be easily supplied by a direct current source and does not need any transport or handling; (ii) they can be applied *in situ*; (iii) the treatment can be immediately interrupted and can be run at room temperature and atmospheric pressure; (iv) the reaction conditions can be very precisely reproduced; and (v) oxidation and reduction processes are more selective and easily controlled by means of electrode potential. Berenguer et al. [159] studied the effect of the electrochemical treatment (galvanostatic electrolysis in a filter-press electrochemical cell) on the surface chemistry and porous structure of GAC in the presence of NaOH, H_2SO_4, and NaCl as electrolytes, with applied current between 0.2 and 2.0 A. Observations showed that both anodic and cathodic treatments lead to an increase in the surface oxygen groups without any significant change to the textural properties of the GAC. The anodic treatment in NaCl produces oxidation degrees comparable to those achieved by classical chemical oxidation. In an oxygen-saturated solution, the cathodic treatment develops a porosity, indicating that some carbon gasification occurs.

2.3. *Characteristics of ACs*

AC can be synthesized with a wide range of features characterized by pore size distribution (PSD), specific surface area (SSA), and chemical composition. The characterization of AC requires a considerable amount of effort to better understand specific structural and chemical features that influence their performance [160]. Many experimental techniques have been used to characterize these functional groups, each presenting its own merits and demerits. X-ray diffraction (XRD) studies showed highly amorphous structural characteristics that limit to fully resolve the detailed microstructure of the AC. As a result, a fundamental understanding of how their structural features can give rise to their adsorptive properties remains elusive, and thus the ability to develop ACs with optimal properties for specific applications has not yet been achieved [161]. Potentiometric titrations in combination with a non-linear treatment of the experimental data can be used to study the acid/base properties of carbonaceous materials [162,163]. Among other analytical methods available, temperature-programmed desorption is increasingly utilized. This method is based on the thermal decomposition of the surface groups, and is particularly useful when coupled with mass spectrometric analysis, as this can provide information relevant to the mechanism of thermal decomposition of the surface groups [17]. To understand the surface functionality of AC, Fourier transmittance infrared spectroscopy (FT-IR) is a useful tool, while X-ray photoelectron spectroscopy (XPS) analysis can be used to identify the elemental composition of the ACs.

AC was obtained from *Eucalyptus grandis* sawdust [71], and the XPS analysis before and after the oxidation of the AC in the C(1s), O(1s), N(1s), and Cr(2p) spectral regions was studied. It was observed that the C(1s) XPS spectrum of the CO_2-oxidized carbon shows an asymmetric tailing indicating the contribution of oxygen-containing functional groups. This spectrum has been deconvoluted in four symmetric peaks of the Gaussian type. In addition to a main peak at 284.5 eV due to graphitic carbon, the spectrum can be fitted to three peaks centered at 285.9, 288.3, and 290.7 eV. These peaks could be associated with the C–O bonds of functional groups such as hydroxyl and/or ethers, with a C=O bond as in the carbonyl group, and with a –COO– bond characteristic of carboxylic and/or ester groups, respectively. The O(1s) XPS spectrum for CO_2-oxidized carbon was fitted to three peaks with binding energies 531.7, 533.5, and 535.8 eV that have been assigned to the O=C bond, the C–O and/or HO–C bonds, and to adsorbed water, respectively. Higher thermal treatment of the carbon leads to a significant reduction in the intensity of these three peaks, indicating a substantial loss of surface oxygen.

Canizares et al. [164] modified commercial AC (Calgon F400) by acidic treatment (2 N HCl). The treatment did not significantly affect the surface area of the AC, but had a large impact on the different functional groups. The presence of a stretching vibration at a broad band of 3,400 cm^{-1} in the unmodified carbon spectrum indicates the presence of hydroxyl functional groups over the carbon surface. The spectrum of the modified carbon showed the disappearance of this vibration, indicating that the acid treatment could have transformed this group to carboxylic, carbonyl, or ether groups which are indicated by vibrational peaks appearing as broad bands at 1,200 and 950 cm^{-1}. Fig. 14 shows the FT-IR spectra for the unmodified and modified ACs.

The effect of the crystallinity of lignocellulosic materials on the porosity of H_3PO_4-activated AC was studied by Zuo et al. [165]. China fir (*Cunninghamia lanceolata*) wood (FW), cotton (*Gossypium* sp.) stalks (CS), and corn (*Zea mays*) cobs (CB) were selected as precursor materials for AC. It was concluded that crystallinity opposes porosity. AC derived from CB showed the least crystallinity (29.7%). The BET surface area analysis of AC derived from CB showed the

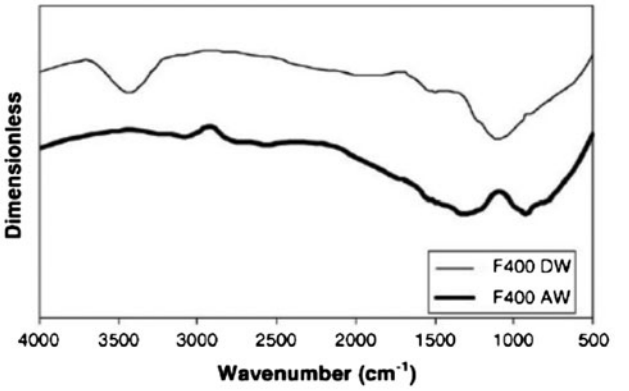

Fig. 14. FT-IR spectrums for unmodified Calgon F400 [F400 DW] and modified Calgon F400 [F400 AW] [164].

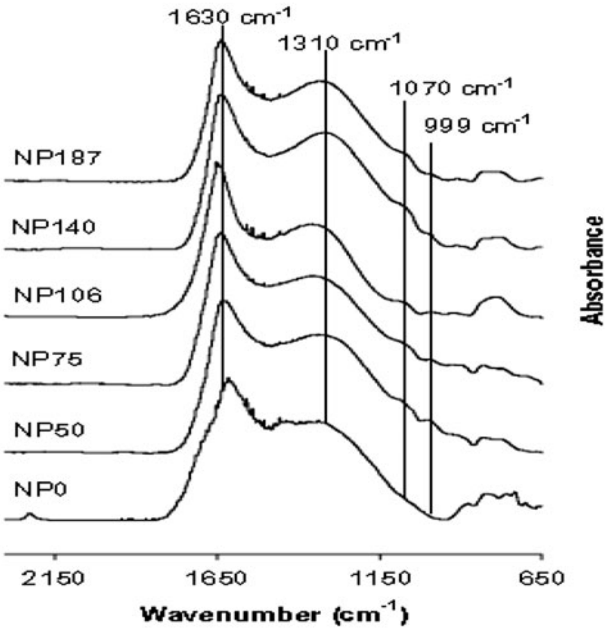

Fig. 15. RIFTS spectra of a Nomex impregnated with phosphoric acid [NP] with different impregnation ratios [167].

highest surface area (2,233 cm^2/g) and total surface volume (2.683 cm^3/g). It was concluded that lesser crystallinity allows H_3PO_4 to penetrate rapidly into the interior of lignocellulosic particles, and thus to be dispersed highly across cells in the composites. Among the precursor materials, the hemicellulose content of CB is the highest (39%), which also favors the development of mesopores due to the higher reactivity of hemicellulose with H_3PO_4 compared to cellulose and lignin [166]. A composite with a high degree of H_3PO_4 dispersal may be formed by ensuring a low impregnation temperature and/or impregnation for a time short enough to ensure that H_3PO_4 penetrates fully into the interior of the particles [165]. A similar effect of crystallinity was observed on AC obtained from highly crystalline fibrous commercial polymer precursors such as Kevlar [poly(p-phenylene terephthalamide)] and Nomex [poly(m-phenylene isophthalamide)] [167]. Diffuse reflectance infrared Fourier transform (DRIFTS) spectra of Nomex impregnated with different ratios of H_3PO_4 (NP) are shown in Fig. 15. An aryl nitriles band (2,231 cm^{-1}) was observed in NP0 (Nomex carbonized alone). The bands at 1,070 and 999 cm^{-1} attributed to phosphorous and phosphocarbonaceous compounds are present in the spectra of samples impregnated with H_3PO_4. A band at 1,070 cm^{-1} can be specifically assigned to the P–O symmetrical vibration in a chain of P–O–P (polyphosphate). A band at 999 cm^{-1} can be assigned to P–O–C asymmetric stretching, interaction between aromatic ring vibration and P–C (aromatic) stretching, and/or symmetrical stretching of PO_2 and PO_3 in phosphate–carbon complexes. Therefore, P-containing carbonaceous structures like acid phosphates and polyphosphates are formed in samples carbonized in the presence of H_3PO_4 (NP50—NP187). The surface analysis showed the highest surface area (1,688 m^2/g) and total pore volume (0.79 cm^3/g) for the AC with the highest impregnation ratio (NP187).

The chemical state of phosphorous on the surface of ACs introduced by impregnation of H_3PO_4 is an issue of controversy. Some researchers had proposed that C–O–P bonding is more stable [168,169], while others argued that this bond would not be strong enough to survive at high temperatures. They proposed the alternative structure C–P–O bonding [170,171]. Red phosphorous was observed in carbon fibers obtained by carbonization of phosphorous containing phenol-formaldehyde resin at 1,000–2,000 °C [172]. A separate phase of phosphorus was observed in carbon obtained by carbonizing a mixture of phenol-formaldehyde resin with P_2O_5 [173]. To shed light on the chemical structure of phosphorus species and the way they are bound to the carbon matrix, Puziy et al. [174] examined two series of H_3PO_4 ACs obtained at different temperatures from polymer and lignocellulose precursors by XPS and solid-state NMR methods. The XPS spectra of polymer-based H_3PO_4 ACs obtained at various temperatures showed the presence of carbon, oxygen, phosphorus, sulfur, and silicon in the samples. The comparison between surface and bulk concentrations showed that the surface of the samples was enriched with oxygen for carbons obtained at 400–600 °C and with phosphorus for carbons obtained above this temperature. The enrichment of the AC surface with oxygen for the samples prepared at lower temperatures as compared to the bulk suggests that H_3PO_4 acts as an oxidizing agent resulting in the formation of oxygen–carbon structures. The surface concentration of phosphorus is higher than in the bulk, signifying that chemical reaction of both precursors with H_3PO_4 occurs superficially. The difference between surface and bulk concentration of oxygen progressively decreases as carbonization temperature increases, implying progressive involvement of deeper layers of carbon in the oxidation process. The NMR analysis revealed a small contribution of phosphonates at 500–700˚C, which implies that phosphate-like structures may only be partly bonded by C–P bonding. The presence of phosphonates at higher temperatures was not observed, showing higher thermal stability of C–O–P over C–P–O bonding. The resolution of XPS and NMR methods did not allow the researchers to clearly distinguish between phosphates and polyphosphates. Another chemical reaction that could be expected to take part during H_3PO_4 activation is the reduction of pentavalent phosphorus by carbon. However, the study did not reveal reduced forms of phosphorus at temperatures up to 900˚C. The elemental phosphorus was observed in the matrix of polymer-based carbon obtained at 1,000˚C. Taking into account the volatility of elemental phosphorus at this temperature, its location should be in closed pores, between carbon crystallites or at least in very fine pores that hinder evaporation.

To study the influence of surface chemistry on the adsorption characteristics, AC was developed with similar textural characteristics but different surface characteristics. Phenanthrene (Phe), a polycyclic aromatic hydrocarbon, was studied as a model compound [175]. The results suggest that, in addition to the non-specific dispersion forces and due to the polyaromatic structure of the adsorbate, the Phe molecules can specifically interact with the carbon surface. The interaction of the electron-rich regions located in the graphene layers with π electrons of the aromatic compounds was the proposed mechanism for Phe adsorption. A similar mechanism for the adsorption of phenols and substituted phenols on AC in liquid phase was proposed by other researchers [176,177] An increase in the number of oxygen groups during the oxidation of AC results in electron withdrawal from the graphene layers (π–π argument), and consequently decreases the specific interaction between Phe and the carbon surface.

The adsorption mechanism of Pb(II) on modified AC was studied [178]. Commercial AC (ROW 0.8 Supra—Norit, the Netherlands) was used as the precursor material. It was washed (demineralized) with concentrated HF and HCl acids, and subsequently modified by different methods. A part of this carbon (indicated by AW—parent sample) was used without any additional processes. The remainder was divided into several portions and thermally and/or chemically modified in different ways. (i) heating at 1,173 K under vacuum 10^{-2} Pa (HTV), (ii) heating in a stream of ammonia at 1,173 K (HTA), (iii) heating in a stream of 1.1 oxygen–ammonia mixture at 673 K (OPA), (iv) oxidation with moist air at 673 K (OWA), and (v) oxidation with concentrated HNO_3 at 353 K (ONA). The results from spectroscopic and electrochemical analyses showed that the adsorption of Pb(II) on ACs with a Lewis base-type surface takes place partially with the participation of a OH^- intermediate (Fig. 16, reaction 1). For amphoteric carbons (AW, OPA) and basic carbons (HTV, HTA) (besides those in Eq. (1)), interaction between carbon π electrons and Pb(II) ions occurs (Fig. 16, reaction 2). Additionally, for basic carbons (HTV, HTA), the adsorption of Pb(II) was supported by reaction Eqs. (3)–(5). For acid-oxidized carbon (ONA, OWA) reactions 6, 7, and 8 dominate. The proposed reaction schemes present the differences in the adsorption capability and indicate a variation in the mechanism of interaction between the carbon surface and ionic metal species present in aqueous solution and/or formed in the solution penetrating the internal pore structure of AC granules. The spectral studies suggest that not only ion-exchange adsorption (dominant for acidic carbon) but also surface complexes formation (with π electrons and

$$\succeq C : H_3O^+ + PbOH^+ \rightarrow \succeq C : PbOH^+ + H_3O^+ \qquad (1)$$

$$\succeq C : + Pb^{2+} \rightarrow \succeq C : Pb^{2+} \qquad (2)$$

$$\succ C{-}OH + Pb^{2+} + 3H_2O \rightarrow \succ COPbOH + 2H_3O^+ \qquad (3)$$

$$\succ C{-}O^{-*} + Pb^{2+} + 2H_2O \rightarrow \succ C{-}O{-}PbOH + H_3O^+ \qquad (4)$$

$$\succ N : + Pb^{2+} + 2H_2O \rightarrow \succ N{-}Pb(OH)^+ + H_3O^+ \qquad (5)$$

$$\succ C{-}COOH + Pb^{2+} + H_2O \rightarrow \succ C{-}COOPb^+ + H_3O^+ \qquad (6)$$

$$(\succ C{-}COOH)_2 + Pb^{2+} + 2H_2O \rightarrow (\succ C{-}COO)_2Pb + 2H_3O^+ \qquad (7)$$

$$\succ C{-}OH + Pb^{2+} + H_2O \rightarrow \succ C{-}OPb^+ + H_3O^+ \qquad (8)$$

Fig. 16. Systematic scheme for the adsorption of Pb(II) on modified ACs [178].

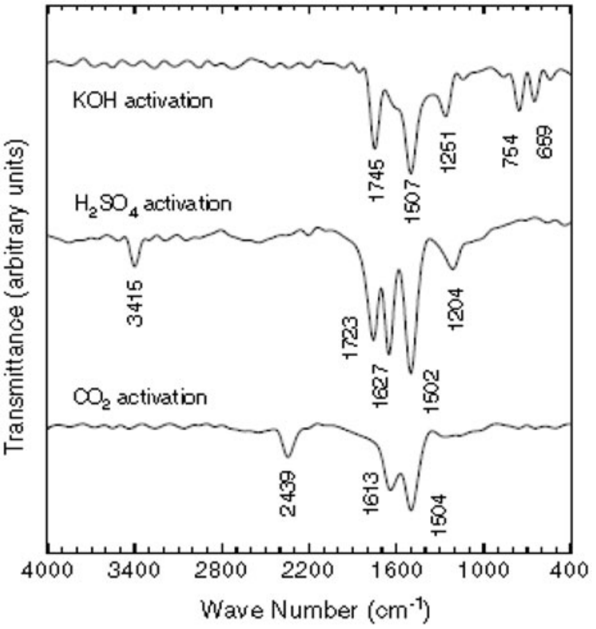

Fig. 17. FT-IR spectra of ACs prepared from palm shell by different activation methods [179].

heteroatoms—O, N) and sedimentation of lead oxide and hydroxide may occur during adsorption.

The adsorption of hydrogen sulfide (H_2S) onto ACs derived from oil palm shell by thermal or chemical activation methods were investigated [179]. The FT-IR spectrum (Fig. 17) of AC prepared by 30% KOH impregnation displayed the following bands: 1,754 cm^{-1}, C=O stretching in ketones; 1,507 cm^{-1}, C=C stretching in aromatic rings; 1,251 cm^{-1}, C–O stretching; and 754 cm^{-1}, C–H out-of-plane bending in benzene derivatives. Alkaline groups were presumed to be the dominating surface functional groups present on the KOH-impregnated AC. The spectra of the AC prepared by 40% H_2SO_4 impregnation displayed the following bands: 3,415 cm^{-1}, H–O stretching in hydroxyl groups; 1,723 cm^{-1}, C=O stretching in carboxylic acids or isolated carbonyl groups; 1,627 cm^{-1}, C=O stretching in quinines or carboxylic anhydrides; 1,502 cm^{-1}, C=C stretching in aromatic rings; and 1,204 cm^{-1}, C–O–C stretching in ethers or ether bridges between rings. For AC prepared by thermal activation with CO_2, the band at 2,439 cm^{-1} is attributed to C–H stretching vibrations in aliphatic structures. The AC prepared by KOH impregnation showed lactone (0.355 meq/g) and carbonyl (1.167 meq/g) groups (Fig. 18(a)). Carboxyl (0.089 meq/g), phenol (0.208 meq/g), lactone (0.416 meq/g), and carbonyl (0.604 meq/g) groups were detected on the surface of the AC prepared by H_2SO_4 impregnation (Fig. 18(b)), while phenol (0.120 meq/g) and carbonyl (0.285 meq/g) groups were detected on thermally activated AC (Fig. 18(c)).

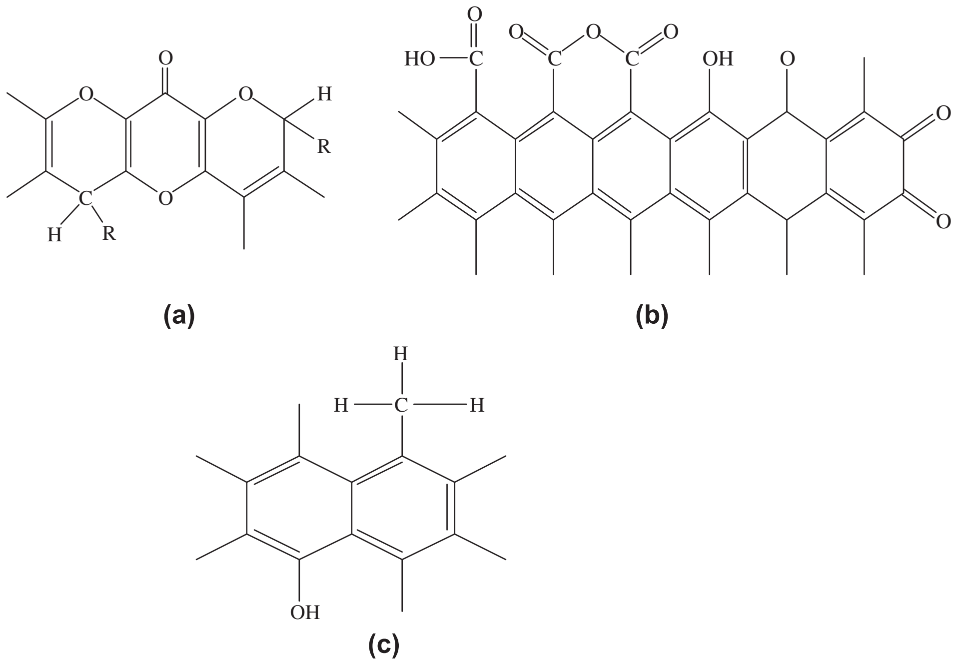

Fig. 18. Surface structures of oil palm shell ACs (a) KOH impregnated, (b) H_2SO_4 impregnated, and (c) thermally activated by CO_2 [179].

Table 4
Modification/Functionalization of ACs

Precursor	Modification/functionalization	Results/conditions	Reference
AC	Chemically impregnated by sulfur	Impact of flue gases was observed. Excellent adsorption of mercury under nitrogenous conditions	[183]
AC	Chemically modified with H_2SO_4	Introduces acidic surface oxides on the carbon surface. Adsorption of mercury, lead, and cadmium increases	[184]
Nut shell AC	Air oxidation in the presence of H_3PO_4	Copper adsorption showed good correlation with surface functional groups	[53]
AC	Chemically modified by $(NH_4)_2S_2O_8$ as oxidizing agent	Modification leads to the development of sulfur active sites over the surface favoring the adsorption of lead	[52]
Nanoporous AC	Oxygen and nitrogen functionalized	Follows Langmuir isotherm for all metal ion/AC system. The amount of Cd(II), Pb(II), and Hg(II) adsorbed decreases with decreasing surface oxygen functional group concentration	[185]
AC	Oxygen functional groups incorporated	Cd(II) adsorption enhanced dramatically with functionalization. Significantly decreased after heat treatment to progressively eliminate the oxygen functional groups	[20]
Euphorbia antiquorum L. wood	Chemically modified by H_3PO_4	Adsorption of acid blue 92 increased	[51]
Corncob waste	Chemically modified by $ZnCl_2$	AC was microporous with higher surface area	[186]
Bagasse pith	Steam activated and sulfurized	Cadmium uptake was much higher on the modified AC	[181]
AC	Ozonation coupled with biological process	Removal of TOC content increased	[187]
Bamboo waste	Chemically modified by H_3PO_4	Promising for the treatment of textile industry wastewater	[58]
Bamboo waste	Chemical activation by K_2CO_3 and subsequent gasification with CO_2	The adsorption for malachite green dye was 263.58 mg/g at 30˚C	[188]
Oil palm fibers	Chemically treated with KOH and gasified with CO_2	Obeyed Langmuir model, giving maximum monolayer adsorption capacity as high as 400 mg/g at 30˚C	[189]
Coffee used grounds	Iron dispersed	Intense removal of methylene blue	[190]
Wool waste	Phosphoric acid activation by muffle furnace and microwave heating	Ni(II) adsorption was 17.87 mg/g on muffle furnace and 6.09 m/g on microwave heating-modified AC	[191]
Sour cherry stones	Zinc chloride	Optimum conditions resulted in AC with carbon content 80.78%, surface area 1,704 m^2/g, and total pore volume 1.566 cm^3/g	[192]
Chinese fir wood	Phosphoric acid	Heat pretreatment can be regarded as an excellent method for manufacturing H_3PO_4 AC with high micropore volume	[193]
Commercial-grade Carbon black	Mixture of nitric and sulfuric acid	The suspension pH and pH_{pzc} were found to decrease substantially demonstrating the creation of surface acidic functional groups during modification	[194]
Polyethyleneterephthalate (PET)	Chemical activation, which comprises heat treatment of PET impregnated with sulfuric acid, washing, and steam activation.	The methylene blue and iodine tests have shown high adsorption capacity of the AC towards organic and inorganic compounds in aqueous solution	[93]

3. Application of Functionalized ACs

AC is a material of major industrial importance due to its well-developed pore structure and excellent adsorption properties. ACs have been extensively studied and produced on a commercial scale. Conventional ACs have poor adsorption capacities [116,180], and therefore various product modifications such as sulfurization, phosphoric acid activation, and surfactant impregnation were attempted to increase uptake capacities [116,181,182]. For example, coal, biomass, and synthetic polymers can be precursors of ACs either through carbonization followed by activation, or through a direct activation. During these processes, porosity and surface area are created, as well as surface chemical functions over the carbon matrix. Table 4 shows the precursor materials used with the modification and functionalization material along with the impact of the surface modifications.

4. Major challenges and future development

"AC, an ideal adsorbent for water and wastewater treatment." To what extent is this statement true? No one can deny the merits of AC as an adsorbent, as it is the most reliable technology for the treatment of dissolved organic and inorganic contaminants in wastewater. However, despite the numerous merits there are several demerits. One issue association with the use of AC beds for adsorption is the generation of hydrogen sulfide due to bacterial growth resulting in odor and corrosion problems. This is a particular problem on GAC beds. The wet form of GAC is highly corrosive and abrasive. Pretreatment of suspended solids is essential. Costs associated with regeneration of ACs may be prohibitive, and if not regenerated the use of ACs may present a land disposal problem.

The worldwide demand for ACs was 650,000 metric tons in 2007 and it is projected to increase annually at 5% through 2015 [195]. In 2008, 220,000 metric tons of AC was consumed in the USA [196]. The two most common materials used for producing AC are bituminous coal and coconut shell. Due to the rapidly increasing price of coal and the limited availability of coconut shell, the search for alternative resources for manufacturing affordable AC is a major challenge.

Waste derived from cork processing plants could be an economically appealing precursor for AC. Portugal currently produces about 185,000 tons of cork annually, which is more than 50% of the world production [197]. The most important byproduct of cork processing is cork powder, comprising on an average 25–30% of the cork processed [198]. Calculations based on the forest production, industrial yields, and quantities of different cork products indicate that in Portugal 32,000–37,000 tons of cork powder is produced annually [199]. This residue is usually used as fuel at cork processing plants, ending up as a low-value heat source with little practical use.

Use of residual plastic materials, particularly PET bottles, as a precursor for AC may potentially be a good alternative. Worldwide annual consumption of plastic materials has increased sharply from around 5 million tons in the 1950s to nearly 100 million tones today. PET consumption has recorded the fastest growth rate in the global plastic market due to the ongoing expansion of the PET bottle market [200]. The current PET consumption rate constitutes a relevant environmentally unsustainable problem, due to the huge amount of solid waste produced and due to its low bio- and photodegradability.

5. Conclusions

The versatility of ACs for water decontamination applications is well established. AC surface chemistry and its applications, specifically targeting water decontamination, has been a topic for research since the 1950s. High production cost is the biggest hurdle for its large-scale use in water decontamination. Research targeting agricultural, industrial, and domestic waste as precursor for ACs is ongoing in order to overcome this hurdle. High production cost is a major drawback for the production of ACs. Research is ongoing to develop efficient and inexpensive techniques to prepare ACs. Microwave energy could be a better alternative in comparison to conventional heating techniques, as the heating rate is very high and selective with greater control of the heating process. There is no direct contact between the heating source and heated materials, reduction in the equipment size and waste produced, and a highly mesoporous form of AC has been prepared within a time frame as short as 600 s.

Various physicochemical processes have been investigated for the preparation of functionally modified ACs to enhance the adsorption potential and also to make the AC adsorbate selective. Electrochemical methods for surface modification of ACs have been shown to have greater potential over other methods. In the electrochemical method, oxidation and reduction processes are more selective and easily controlled by electrode potential, the reaction conditions can be precisely reproduced, and one of the reagents is the electron supplied by direct current source and does not need any transport or handling.

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