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Review

Current Progress on the Surface Chemical Modification of Carbonaceous Materials

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Abstract: Carbon-based materials is considered one of the oldest and extensively studied research areas related to gas adsorption, energy storage and wastewater treatment for removing organic and inorganic contaminants. Efficient adsorption on activated carbon relies heavily upon the surface chemistry and textural features of the main framework. The activation techniques and the nature of the precursor have strong impacts on surface functionalities. Consequently, the main emphasis for scientists is to innovate or improve the activation methods in an optimal way by selecting suitable precursors for desired adsorption. Various approaches, including acid treatment, base treatment and impregnation methods, have been used to design activated carbons with chemically modified surfaces. The present review article intends to deliver precise knowledge on efforts devoted by researchers to surface modification of activated carbons. Chemical modification approaches used to design modified activated carbons for gas adsorption, energy storage and water treatment are discussed here.

Keywords: activated carbon; surface modification; energy storage; clean environment

1. Introduction

Activated carbon (AC) generally refers to carbonaceous materials fabricated from various carbon-rich sources, such as wood, lignite, coal and coconut shells [1]. Activated carbons can be produced from these materials by carbonization process. During carbonization, moisture and volatile compounds are removed, leaving behind char. This char can be further activated via physical or chemical activation methods to generate highly porous activated carbons. These carbonaceous materials are widely studied as effective adsorbents owing to their porous structure, high surface area, enriched surface chemistry with the highly reactive surface functionalities. By virtue of these interesting features activated carbon is considered as a class of versatile materials with the practical applications in the fields of adsorption, catalysis, energy storage and pollutant removal from gaseous and liquid phases [2–5]. The performance of AC can be improved by tuning the textural features along with the generation of a wide range of surface functional moieties. Heteroatom doping of AC as surface functional groups is a common practice nowadays. These heteroatoms include oxygen, hydrogen, sulfur and nitrogen. By considering the surface of adsorbent, the primary functional groups which, when considered together, are essential for removal of organic and inorganic pollutants like carboxyl, carbonyl, phenols, lactones and quinones. Tailoring the surface of activated carbons produces the exceptionally high adsorption performance of these materials [6–8].

With the growing population and industrial revolution, pollutants have accumulated in air and water. Researchers are left with the challenge of developing the most efficient adsorbents with particular chemical characteristics in order to alleviate rising pollution. Nowadays, enormous research effort is devoted to modification of activated carbons, specifically their surfaces and textural features in order to meet the demands for cleaner water and air [9–12]. Many approaches have been adopted in the literature for effectively modifying surface of carbon-based materials by considering the surface chemistry and reaction mechanism, permitting higher uptake of particular contaminants by these adsorbents [13–19]. It is widely accepted that functional groups can bond directly to fused aromatic rings in hydrocarbons. Therefore, one would expect that their chemical properties resemble those of aromatic hydrocarbons. Consequently, similar chemical reactions that involve aromatic rings and functional groups can be performed, thus adsorbents with the desired specifications can be designed through thermal or chemical methods. For example, a group of researchers successfully generated weakly acidic surface functionalities on activated carbons using oxidation reactions [20–24]. Such carbons were exploited as metal adsorbents with exceptionally high affinity for metals compared to pristine carbon. Heteroatom doping and nitrogen-doping specifically, has also been well-explored and such carbons have shown enhanced catalytic activity during oxidation [25–29]. Despite the fact that activated carbon is an emerging field of interest for wastewater treatment, the exact adsorption mechanisms for organic and inorganic solutes are still vague. Recently, a π–π dispersion interaction mechanism was proposed for adsorption of organic compounds [30–32]. This mechanism suggests that aromatic species and the basal planes in carbon interact with π electrons in each system. In contrast, some experimental data claim the electron donor–acceptor mechanism governs adsorption of organic species, considering the complex formation among the adsorbed species and the surface carbonyl group in the sorbent.

Recent research has placed emphasis on modifying these physical and chemical attributes and the success achieved in the last few years regarding synthesis of surface-modified activated carbons and various modification techniques and their effects on energy storage, adsorption of pollutants from gaseous and liquid phases, is summarized in this review. Generally, carbon-based materials are activated, generating a well-defined porous structure followed by surface modification. Considering the modifying agents, the synthetic method can be classified into three main categories: (i) physical modification, (ii) chemical modification and (iii) biological modification. Herein, we have primarily reviewed surface chemical modification methods, characterization and their merits from the perspective of adsorption behavior. The characterization techniques used to analyze modified surfaces of activated carbons are acid/base titration, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). For information related to detailed experimental procedures and conditions, readers are referred to full articles from the references.

2. Surface Chemical Characteristics

The surface chemistry of carbon-based materials fundamentally relies upon heterogeneity of the chemical surface, which is associated with the placement of heteroatoms on the surface [33]. Heteroatoms are generally referred to as a group of atoms other than the carbon that are present in parent matrix, for example, oxygen, nitrogen, hydrogen, sulfur and phosphorus. The nature and measure of these elements depends upon the nature of the precursors or inoculation methods used in the activation process [34–36]. By observing the nature of these heteroatoms, it was proposed that surface functionalities comprising of heteroatoms along with delocalized electrons in aromatic carbon can generate activated carbon with acidic or basic surfaces.

2.1. Acidic Surfaces

Activated carbons with acidic surfaces mainly include oxygen-containing functional groups [37–39]. Such groups are generally located on the outer surfaces or edges of the basal plane and play a major role in controlling the chemical nature of carbon. These specific outer positions are mainly considered as adsorption sites, hence the concentration of oxygen at these particular points has a great influence on the adsorption capabilities of carbon. Extensive research effort and results suggest that few groups containing oxygen atoms, including carboxylic, chromene, lactone, phenol, quinone, pyrone, carbonyl and ethers, are usually located on the carbon surfaces (Figure 1). Functional groups with carboxylic moieties are generally responsible for surface acidity [40–43]. Other surface acidic groups include carboxylic anhydrides, lactones and phenolic hydroxyls.

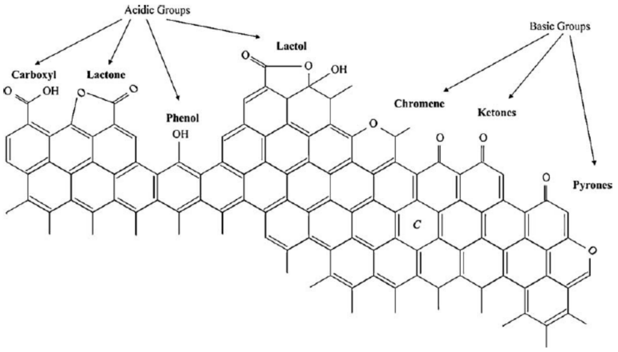

Figure 1. Acidic and basic surface functionalities on a carbon basal plane. Reprinted with permission from [44]. Copyright 2004 Elsevier Ltd.

2.2. Basic Surfaces

Two major features responsible for the basic surfaces of activated carbon are: (i) delocalized π-electrons of fused aromatic structures and (ii) basic surface functional groups (e.g., nitrogen-enriched functionalities) that can bind protons [45–47]. Previous studies explored certain functional groups containing oxygen including chromene, ketone and pyrone can also contribute to the basicity of carbon (Figure 1). On the other hand, extensive studies reveal that the basicity of activated carbons originates from resonating π-electrons in the carbon matrix. To elaborate, π-electrons in carbon layers can act as Lewis basic sites. Leon y Leon et al. [48] examined the basic surface character of two series of carbons and proved that oxygen-free carbon surfaces can efficiently adsorb protons from aqueous media. The excellent adsorption abilities are accredited to sites situated in the π-electron rich areas on the basal plane of carbon crystallites. Consequently, these regions possess Lewis basic character [49]. Similarly, chemical modification via the introduction of nitrogen-enriched functionalities on the carbon surface can facilitate adsorption of CO_2 from the atmosphere. Nitrogen moieties usually induce basic character, which can improve the interaction between the carbon surface and acidic species via dipole–dipole interactions, hydrogen bonding and covalent bonding [50,51].

3. Surface Chemical Modification of Activated Carbons

Activated carbons possess three distinct types of chemical surfaces (acidic, basic and neutral) depending on the chemical nature of surface functionalities [52,53]. These chemical characteristics can be modified by varying the functional groups on the surfaces; this will be explained in this section. Table 1 summarizes recent experiments aimed at modifying carbon surfaces to generate the desired functional groups for improved adsorption of chemical species.

Table 1. Recent research studies on modification of carbon surfaces to generate specific surface functionalities for enhanced removal of metal species.

Techniques Used	Nature of Functional Groups Induced	Applications	References
Oxidation by nitric acid	weakly acidic and non-acidic	Cr(III) and Cr(IV) removal	[54]
Oxidation by nitric and hydrofluoric acid	weakly acidic	Cu^{2+} removal	[55]
Oxidation by ammonium persulfate and sulfuric acid solution	weakly acidic	Zn^{2+} removal	[56]
Treatment using Na_2S	weakly acidic	Pb^{2+} removal	[57]
Heat treatment in H_2S	sulfur-based	Mercury (as $HgCl_2$) removal	[58]
Oxidization using nitric acid, ammonium persulphate	weakly acidic	Cu^{2+} removal	[59]
Oxidization using nitric acid	weakly acidic	Cd^{2+} removal	[60]
Treatment at ambient temperature and 900 °C in SO_2 and/or H_2S	sulfur surface complexes	Cd^{2+} removal	[61]
Treatment using hydrochloric acid	weakly acidic	Cr(VI) removal	[62]

3.1. Acid Treatment

To acidify the surface of activated carbon, the surface is generally oxidized as it enhances the acidic character and hydrophilic nature of the carbon surface by reducing the mineral content [63]. Nitric acid (HNO_3), sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) are widely used for this purpose [64–67]. During oxidation, oxygen-enriched functionalities are generated on the carbon surface including carboxylic, lactone and phenolic hydroxyl groups. The most frequently used activation procedures for producing oxygen-derived acidic groups are oxidation by gases and aqueous oxidants. Carbon dioxide, oxygen, steam and air are used as oxidants in gas phase oxidation. Oxidation at a low temperature leads to the generation of strong acidic functionalities (e.g., carboxylic groups), whereas an elevated temperature is responsible for the formation of weak acidic groups (e.g., phenolic). Liquid phase oxidation uses less energy as oxidation at a low temperature can introduce a higher oxygen content at surfaces compared to gas phase oxidation. Furthermore, gas phase oxidation can enhance the hydroxyl and carbonyl content on the surface of activated carbon, while liquid-phase oxidation primarily increases the concentration of carboxylic and phenolic hydroxyl groups.

From the perspective of applications, these acidic groups (i.e., oxygen-containing functional groups as proton donors) on carbon surfaces can be exploited as adsorbents of heavy metals from aqueous media via formation of metal-complexes between metal ions and negatively charged acidic groups. Numerous experimental efforts are focused on carbon surface modification by introducing acidic groups to enhance the removal of metal ions and organic species from aqueous solutions (Table 2). Some of these acidic surface functional moieties include carboxyl, quinone, carbonyl, lactone, hydroxyl and carboxylic anhydride. These specific functional groups are inclined with respect to the metal-complex formation with alkaline-earth metals and chelation with heavy metal ions. Complex formation with main group metals can be expressed as follows:

$$\mathrm{M}^{n+} + (-\mathrm{COOH}) \leftrightarrow (-\mathrm{COO})_n\mathrm{M} + n\mathrm{H}^{+} \tag{1}$$

Table 2. Acid treated carbons as biosorbents.

Samples	Acid Used	Species Biosorbed	References
Aquatic weeds	H_2SO_4	Cr(III), Cr(VI)	[68]
Agricultural waste	H_3PO_4, H_2O_2	Cd	[69]
Olive mill solid residue	HCl	Phenol	[70]
Activated coconut shell carbon	H_3PO_4	Zn(II)	[71]
Rice bran	HNO_3	Cd(II0, Cu(II), Pb(II), Zn(II)	[72]
Olive stone	H_2SO_4, HNO_3	Pb(II)	[73]

The reaction proceeds by cation exchange between the metal cation and the hydrogen ion attached to the carboxylic group [74]. Apart from using strong acids as oxidizing agents, such as nitric acid and sulfuric acid, other chemical oxidants such as hydrogen peroxide, acetic acid and oxygen can also generate acidic functional groups [75–77]. These conventional chemical oxidation methods can provide beneficial effects on adsorption of metal ions but they destroy the desired physical attribute of the adsorbents. The textural parameters including BET surface area pore diameter and pore volume can also be modified and the pores subsequently lose their desired original features. Many studies in the literature, including the experiment performed by Maroto-Valer et al. [78] demonstrate that nitric acid treatment reduces the specific surface area and total pore volume by 9.2% and 8.8%, respectively, where pores are blocked by newly generated oxygen groups. Similar results were also presented by Rios et al. [79] Aburub and Wurster [80] where the specific surface area of activated carbon decreased by 33.7% and 6.5%, while treating with pure nitric acid for 38 h and with an equimolar ratio mixture of nitric/sulfuric acid for 24 h. They proposed that this unprecedented reduction can be attributed to annihilation of the porous matrix within the activated carbon caused by harsh nitric acid oxidation. As these conventional methods can reduce the physical characteristics, researchers are continuously searching for alternative methods to generate acidic surface functionalities without unwanted pore blockage. One favorable technique involves the use of oxygen plasma, originally studied by Garcia et al. [81]. Their conclusions show that the technique could be used to modify the external surfaces and produced acidic groups, whereas the internal surface was nearly unaffected. The general assumption regarding plasma treatment is that the oxidizing species do not penetrate the interior of the carbon. Highly reactive mono-oxygen radicals etch the carbon surface without destroying the microporosity. Moreover, this assumption was considered true by an experimental study performed by Domingo-Garcia et al. [82] they declare that the chemical surface groups induced by oxygen plasma are located on the external surface, while those generated by treatments in aqueous media of $(NH_4)_2S_2O_8$ and H_2O_2 are located on the external and internal surfaces. Contrary to this, Lee et al. [83] used a helium–oxygen plasma produced in a reactor with dielectric-barrier discharge. During oxidation of activated carbon by this plasma, it was demonstrated that Fe^{2+} adsorption improved by a factor 3.8 after treatment. However, the specific surface area decreased by as much as 22.5% due to demolition of pore walls via gasification of carbon and pore blockage. These two isolated plasma oxidation methods reveal that not all plasma treatments can offer favorable outcomes with respect to textural specifications. Therefore, a more rigorous focus on eliminating this drawback is required in future studies. While acid treatment is a promising method for enhancing adsorption of metal ions, it weakens adsorption of organic compounds (especially phenol) from an aqueous environment. This can be attributed to the fact that acid treatment can result in the destruction of prevailing basic functionalities on the surface of activated carbon, which decreases the phenolic adsorption. This suggestion was considered in a study directed by Santiago et al. [84] where nitric acid treatment destroyed basic sites of activated carbon, resulting in a considerable decrease in phenol uptake. Furthermore, it was suggested that damaging the basic sites ultimately leads to decreased catalytic activity by phenol in the dilute phenol solutions. Nevertheless, at high phenolic concentrations, Terzyk et al. [85] found that phenol uptake improved after nitric acid treatment. This effect was explained via generation of adsorbate–adsorbate interactions at high phenolic concentration.

3.2. Base Treatment

Activated carbon with a base treatment induces a positive charge on the surface that enhances adsorption of negatively charged moieties. The most convenient way for generating porous carbons with basic surface characteristics is treatment with hydrogen or ammonia at high temperature. High temperature treatment (400–900 °C) of activated carbons with ammonia causes formation of basic nitrogen groups on the carbon surface. Nitrogen functionalities can be doped via reaction with precursors containing nitrogen (such as ammonia, nitric acid and various amines) or activation in the nitrogen-enriched environment [86–88]. Possible existing forms of the nitrogen include the following groups: amide, imide, lactame, pyrrolic and pyridinic groups. The chief role of ammonia treatment is to enhance the basicity of the activated carbon surface. Apart from the introduction of basic nitrogen atoms at high temperature, the exclusion of oxygen-based groups can significantly increase the basicity of activated carbons. These nitrogen functional groups usually induce basic character, which can boost the interaction between adsorbents and acidic species through dipole-dipole interactions, hydrogen bonding and covalent bonding.

Przepiorski [89] demonstrated the effect of heating conditions on the adsorbent during ammonia treatment. It was found that the uptake capacity towards phenol improved by as much as 29% at an optimum temperature of 700 °C. In another study, Chen et al. [90] inspected the modification of activated carbon surfaces during thermal treatment in the presence of ammonia, yielding increased perchlorate adsorption capacities from aqueous conditions without damaging the porous structure, which is beneficial for perchlorate adsorption. They demonstrated that the most promising results were obtained for samples prepared at temperatures between 650 and 700 °C with a four-fold rise in perchlorate adsorption. Economy et al. [91] used ammonia with activated carbon fibers (ACF) at higher temperatures to acquire a material with basic properties. They also claimed that such fibers were highly effective for adsorbing acidic gases like SO_2 and CO_2. Similarly, Stöhr et al. [92] evidently proved that the high performance of nitrogen-doped activated carbons prepared at high temperatures (600–900 °C). Free radicals (e.g., NH_2, NH, hydrogen and nitrogen) will start to form when carbon-based materials are kept in an atmosphere containing ammonia at elevated temperatures. These free radicals then attack the carbon surface and generate nitrogen-based functional groups [93,94]. Ammonia reactions at particular carboxylic acid groups located on the carbon surface can produce ammonium salts that generate amides and nitriles upon dehydration:

$$-\mathrm{COO}-\mathrm{NH_4}^+ \rightarrow -\mathrm{CO}-\mathrm{NH_2} \rightarrow \mathrm{C}\equiv\mathrm{N} \quad (2)$$

Substitution of OH groups with ammonia can result in the formation of amines:

$$-\mathrm{OH}+\mathrm{NH_3} \rightarrow -\mathrm{NH_2} + \mathrm{H_2O} \quad (3)$$

During the reaction with ammonia at high temperatures, ether-like oxygen surface functionalities are substituted for –NH– on the carbon surface, resulting in generation of imine and pyridine moieties upon dehydrogenation [95–97]. It was found that amides, imides, imines, amines and nitriles are the predominant species at low temperature (<600 °C), while thermally stable aromatic structures such as pyrrole and pyridinic-like groups dominated at higher temperatures (>600 °C). In conclusion, basic treatment with ammonia does not require any preliminary oxidation stages, hence basicity can be induced in a facile manner. A summary of research into the modification of activated carbon with gaseous ammonia is shown in Table 3.

Table 3. Recent research studies conducted on the modification of activated carbon with gaseous ammonia.

Materials	Amination Temperature	Applications	References
Carbon adsorbents from biomass residue (almond shells)	800 °C	CO_2 adsorption	[98]
Commercial activated carbon	1000 °C	CO_2 adsorption	[99]
Commercial granular activated carbons	385 °C	Adsorption of model aromatic compounds (aniline and nitrobenzene)	[100]
Carbon materials (biomass residues, sewage sludge, pet coke)	400 °C	CO_2 adsorption	[101]
Activated carbon from peat	900 °C	Enhancement of catalytic activity of AC in oxidation reaction	[92]
Activated carbon from sulfonated styrene–divinyl-benzene copolymer	600 °C	Enhancement of molybdenum adsorption	[102]

3.3. Chemical Impregnation

It is widely accepted that the adsorption capacities of activated carbon for eliminating hazardous toxins can be significantly enhanced by impregnation with the appropriate chemicals [103]. Henning and Schafer [104] explained impregnation as a uniform distribution of chemicals in the internal surface of activated carbon. However, some researchers [105,106] associate the introduction of surface functional groups as impregnation techniques. In this context, we refer to impregnation with substances that do not affect the pH of the activated carbon surface. These impregnating materials can be metals or polymeric substances, which generally induce no significant pH changes. Henning and Schafer [84] indicated that impregnating an activated carbon surfaces should enhance the prevailing properties of the materials by improving its built-in catalytic oxidation capabilities, promote synergy among the activated carbon and impregnating agent in order to boost adsorption and augment the capacity of the material as an inert porous carrier. General industrial processing methods for producing impregnated activated carbon involve spraying virgin carbon with impregnating agents using a rotary kiln or fluidized bed. Generally, impregnating materials include hydroxides, carbonates, chromates or nitrates.

Two famous researchers (Monser and Adhoum) [107] are actively working on impregnating activated carbon with foreign compounds. In 2002, they conducted an experiment involving adsorption of copper(II), zinc(II), chromium(VI) and cyanide (CN^-) ions by activated carbons. These activated carbons were modified with tetrabutyl ammonium (TBA) and sodium diethyldithiocarbamate (SDDC). From the experimental data, it was found that TBA-modified carbons exhibit a factor 5 greater removal performance compared to pristine carbons. Similarly SDDC-modified activated carbon exhibited higher adsorption of copper (II) and zinc(II) (a factor 4 greater), as well as chromium(VI) (a factor 2 greater) than the parent activated carbon. It was concluded that the high adsorption performance is due to virgin activated carbon and the ion exchange mechanism exhibited by chemical species impregnated on the surface of activated carbon. In another study, silver and nickel-doped activated carbons were used as effective adsorbents of cyanide from an aqueous environment. From the results it was concluded that silver-doped adsorbents exhibit doubles the efficiency of nickel-doped carbons. The possible uptake mechanisms include adsorption, ion exchange with groups bearing positive charge located on the carbon surface or complex formation (e.g., $Ag(CN)^{2-}$ and $Ni(CN)_4{}^{2-}$). A few years later, they modified activated carbons with tetrabutyl ammonium (TBA) and copper to be exploited for efficient phthalate adsorption from industrial wastewater. Their results show that metal modification on the carbon surface exhibits a factor 2 higher adsorption compared to the parent activated carbon, while TBA-loaded AC improved phthalate uptake by a factor 1.7 compared to pristine carbon.

Recently, metal impregnation is one emerging field of research. Huang and Vane [108] reported excellent removal efficiency of arsenic from waste water. The effectiveness of iron-loaded activated carbon reveals an improved efficiency by a factor 10 compared to unloaded activated carbon. They further claimed that higher adsorption of arsenic can be attributed to arsenic complex formation involving ferrous ions. In another study, Leyva Ramos et al. [109] reported the effectiveness of aluminum-impregnated activated carbon for eliminating fluoride ions from aqueous media. Aluminum-doped carbons exhibit excellent fluoride uptake at pH 3.5. In a separate experiment, Dastgheib et al. [87] examined removal of dissolved natural organic matter (DOM) from natural water using activated carbon impregnated with iron. They concluded that the DOM uptake efficiency increases up to 120% due to iron impregnation, followed by ammonia treatment at high temperature. Further examples of chemically impregnated species on activated carbon are listed in Table 4.

Table 4. Chemical impregnated activated carbons and their potential applications.

Samples	Species Impregnated	Species Removed	References
Activated carbon	iodine and chlorine	Gas-phase elemental mercury	[110]
Granular activated carbon	sulfur	Gas-phase elemental mercury	[111]
Activated carbon	metallic silver and copper	Arsenic	[112]
Activated carbons	silver and nickel	Cyanide	[107]
Granular activated carbon	copper and silver	Cyanide	[113]

3.4. Surfactant-Modified Activated Carbons

Numerous research efforts are being devoted to surface modification of activated carbons with anionic and cationic surfactants [114–118]. A comprehensive explanation of adsorption of these surfactants on carbon surfaces is still not clear. A general assumption declares that hydrophobic interactions among surfactants and activated carbon were the primary source for surfactant adsorption on the surface of activated carbon. However, the direct implication of these surfactant-modified carbons as adsorbents for removal of pollutants from aqueous solutions is rare. An experiment conducted by Parette and Cannon [119] illustrate a new approach for modification in which granular activated carbons were doped with cationic surfactants in order to improve removal of ppb levels of perchlorate from groundwater in small-scale laboratory tests. They found that activated carbons modified with cetyl trimethyl ammonium chloride (CTAC) surfactant improved the perchlorate breakthrough time in a simulated 20–22 min empty bed by a factor 30 compared to virgin activated carbon. Few examples from the literature, for surfactant-modified carbons as adsorbents, are summarized in Table 5.

Table 5. Surfactant-modified carbons to adsorb contaminants from aqueous media.

Samples	Surfactant Used	Species Adsorbed	References
Surfactant modified activated carbon	HDTMA (hexadecyltrimethylammonium bromide) CPC (cetylpridinium chloride)	Cr(VI)	[120]
Surfactant-modified mesoporous FSM-16	cetyltrimethylammonium bromide (CTAB)	Acid dye (acid yellow and acid blue)	[121]
Activated carbon	CPC (cetylpridinium chloride)	Reactive black 5	[122]
Surfactant-modified carbon	cetyltrimethylammonium bromide (CTAB)	Cd(II)	[123]
Surfactant modified coconut coir pith	HDTMA (hexadecyltrimethylammonium bromide)	Cr(VI)	[124]

3.5. Ligand Functionalization

Recently, an innovative functionalization technique for graphitic layers of activated carbons was established by Garcia-Martin et al. [125] where N-(4-amino-1,6-dihydro-1-methyl-5-nitroso-6-oxo2-pyrimidinyl)-l-lysine (AMNLY) and N-(4-amino-1,6-dihydro-1-methyl-5-nitroso-6-oxopyrimidin-2-yl)-N-[bis(2-aminoethyl)] ethylene diamine (AMNET) were introduced on basic activated carbon with relatively low oxygen and nitrogen contents. This functionalized carbon was then used to eradicate chromate (VI) from aqueous media. They proposed that the inoculation of AMNLY and AMNET would enrich the π-electron density in the graphene layers, thus improving the adsorptive abilities of the receptors via π-dispersive and/or donor–acceptor interactions among the pyrimidine moiety in the receptors and the basic arene centers in the graphene layers. It was found that the adsorption of Cr(VI) on AMNET-supported AC was roughly amplified by a factor 1.7 as compared to virgin AC. They accredited the improved adsorptive ability to strong and selective interactions between chromate anions and NH_3^+ groups in this compound. On the other hand, impregnation of AMNLY decreased the uptake of Cr(VI) by 75%; this was attributed to the suppressed interaction among chromate anion and NH_3^+ groups as a direct consequence of the proximity of a carboxylate center with negative charge. Examples from literature are presented in Table 6.

Table 6. Ligand functionalization of activated carbons and their applications.

Samples	Ligand Functionalized	Species Adsorbed	References
Activated carbon	Benzoylthiourea	U(VI)	[126]
Carbon	5-azacytosine	U(VI)	[127]
Activated carbon	Hybrid ligands (nitric acid, thionyl chloride, ethylenediamine)	Hg(II)	[128]

4. Surface Analyses of Activated Carbons

Characterization of surface functional groups in porous carbon is complex due to the convoluted surface functionalities and inadequate understanding of their nature. The conventional and fundamental method for qualitative and quantitative determination is elemental analysis. As this method is widely used in most experiments due to its convenience, it cannot be used to predict functional groups, hence it cannot be used as an effective tool for analyzing surface chemistry. Different characterization techniques have been used to identify and confirm the presence of surface functionalities on the surfaces of activated carbon [129]. Details of some common methods are as follows.

4.1. Acid/Base Titrations

Conventional acid/base titration methods, such as those studied by Boehm [130], were used to analyze the basic and acidic functionalities of the adsorbent surface. The technique is based on neutralization of specific acids/bases by the basic or acidic functionalities on the adsorbent surface and quantification of the amount of acid or base that has reacted with these functional groups. Boehm titration is used to differentiate basic and acidic functional groups based on their neutralization abilities [131]. The number of numerous oxygen-enriched acidic sites on the activated carbon was determined under the supposition that $NaHCO_3$ can only neutralize carboxylic moieties, Na_2CO_3 would neutralize carboxylic and lactone groups and NaOH will neutralize carboxylic, phenolic and lactone groups [132]. The number of surface basic groups can be determined from the quantity of HCl used by carbon during neutralization. The quantity of consumed acid/base due to neutralization of basic/acidic functional groups on the surface of carbon can be determined using back titration with NaOH and HCl, respectively. The primary drawback of this technique is that it can only be used for samples present in large quantity. Furthermore, this method only could be used to measure the quantity of about half of the total oxygen content of activated carbon. Likewise, the total basicity takes a single value because the nature of basic surface functional groups is not well explored.

4.2. Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared (IR) spectroscopy is one widely used tool to examine the surface functionalities on activated carbon. Unfortunately, IR spectra exhibit some limitations that make the spectra difficult to interpret; the measured peaks are generally a sum of interactions from distinct groups [133,134]. In addition, IR does not offer quantitative evidence regarding the existence of individual functional groups on activated carbon. These limitations of IR analyses can be reduced using Fourier transform infrared (FT-IR) spectroscopy. This technique is commonly used for qualitative determination of the chemical structure and for identifying functionalities on the surfaces of carbon materials [135–138]. The intrinsic signal-to-noise (S/N) ratio can be used to enhance the frequency resolution compared to dispersive IR spectroscopy. FT-IR spectra show the transmitted infrared intensity at various wavenumbers. A comparison of the spectra obtained before and after surface modification treatment can be used to identify which functional groups that form or decompose during the treatment [139]. Aside from the methods explained here, other generally-used techniques for illustrating the surface chemistry of carbon materials include NMR spectra [140], inverse gas chromatography (IGC) [141] and electron microscopy, including SEM and TEM [142].

4.3. Temperature Programmed Desorption (TPD)

Surface functional groups can be identified by considering the relative thermal stability of these groups. Temperature programmed desorption (TPD) is a technique for determining the concentration of functional groups that exploits the thermal stability of various groups. This method has become more famous for analyzing oxygen functional groups on the surface of activated carbon [143,144]. The TPD experiment operates on the principle that surface oxygen groups decompose at low temperatures, release CO_2 and CO at higher temperature and release H_2O and H_2 in some cases at other temperatures [145–148]. Studies in the literature show that decomposition of different groups like carboxyl and lactone generates CO_2, while decomposition of carbonyl, quinone, phenol and ether groups leads to CO production. Some other basic functional groups like pyrone and chromene decompose at high temperature to produce a CO peak. During analysis, different functional groups can be identified as the temperature is slowly increased. Functional groups corresponding to CO_2 are nearly completely utilized at high temperatures (above 1000 °C) and only a slight percentage of CO releasing groups remain on the carbon surface, which can be designated as pyrone and chromene-type functionalities. A complete picture of the surface groups can be obtained by observing the decomposition temperature, amount of devolved gases and the mechanism behind the release of a particular gaseous species (e.g., carbonyl groups devolve as CO) [149,150]. Moreover, it is difficult to interpret the TPD spectra due to the overlapping desorbed gases produced from various oxygen-containing structures. However, recognizing each surface group separately requires isolating CO and CO_2 peaks because TPD spectra exhibit high surface mobility and peaks appear as composites of CO and CO_2, particularly at high temperature [151]. Recently, researchers focused on modification methods for deconvoluting the obtained spectra with the intention of determining distinct kinds of surface oxygen structures [152].

4.4. X-Ray Photoelectron Spectroscopy (XPS)

One widely used non-destructive surface analysis technique is X-ray photoelectron spectroscopy (XPS). In this technique, particular electron binding energies of elements located at the surface are used to quantify the elemental composition and identify the chemical states of surface elements [153–155]. This spectroscopic method can identify all elements on the surface of activated carbon. The XPS technique is widely used to study carbon materials. The C1*s* core region can be used to identify significant changes in the nature of the carbon during surface modification, such as oxidation and acidification. From the XPS spectra, four distinct peaks can be seen at different binding energies corresponding to four different functional groups: C–C or C–H, C–O, C=O and O–C=O [156–159]. Apart from its merits, it cannot be used to distinguish functional groups with very close binding energies, such as C–C and C–H or C–O–C and C–OH. It also cannot be used to detect hydrogen atoms. However, it is one of the best tools in analytical chemistry for examining basic nitrogen functionalities. Modification of carbon surfaces with ammonia is widely explored using XPS. Nitrogen (N1*s*) core level studies were performed in order to obtain additional understanding of the chemical nature of surface functionalities [160,161]. Jensen and van Bekkum [162] found that ammonia modification led to the generation of amides (399.9 eV), as well as lactams and imides (399.7 eV). Mangun et al. [163] determined that pyridine (binding energy of 398.4 eV) was the only nitrogen functionality that formed during high temperature ammonia treatment of activated carbon fibers. Stöhr et al. [92] further found two N1s peaks with binding energies of 401–400 eV and 399–398 eV due to chemisorption of nitrogen during ammonia treatment. These peaks were designated as amine and nitrile and/or pyridine-like nitrogen. Some other XPS surface analysis results indicate that two basic nitrogen functional groups in coals were pyrrolic and pyridinic groups with corresponding binding energies of 400.3 and 398.7 eV, respectively [164–166].

5. Practical Applications of Surface-Modified Activated Carbons

To explore the effects induced by chemical surface modifications, researchers have exploited modified carbons in various practical applications (Table 7). Some of them are described in this section.

Table 7. Chemical modification of activated carbons and their applications.

Materials	Modification Methods	Final Outcomes	References
Corn grains	KOH activation	Increased surface area (3199 m^2/g) results in high specific capacitance (257 F/g)	[167]
Porous carbon	Nitrogen-doping with 2 wt.% of hexamine	Modification of porous carbon with nitrogen has increased the capacitance of electrodes for supercapacitor applications.	[168]
Mesoporous carbons	Nitric acid oxidation	An enhanced energy density with a highest value of 5.7 Wh/kg is obtained after oxidation.	[169]
Activated carbon	Activated carbon was prepared from eucalyptus wood with H_3PO_4 and modified by NH_3	Incorporation of nitrogen group in ACs increased their adsorption capacities. The CO_2 adsorption capacity achieved by modified carbon was 3.22 mmol/g at 1 bar.	[170]
Activated carbon	Amino/nitro groups were introduced onto the surface of the activated carbon (AC) with nitration followed by reduction.	Results showed that the contents of nitrogen on the treated samples' surface increased from 0% to 1.38 after modification. The maximum CO_2 adsorption capacity of the modified samples can reach 19.07 mmol/g at 298 K and 36.0 bar.	[171]
Activated carbon	Impregnation of carbon with diethanolamine, methyl diethanolamine and tetraethylene pentaamine.	Materials impregnated with diethanolamine performed best for CO_2 capture; the highest adsorption capacity achieved was 5.63 mmol CO_2/g.	[172]
Activated carbon	Highly polar carbon surfaces were generated by acid and base treatment	Two common drinking water contaminants, relatively polar methyl tertiary-butyl ether (MTBE) and relatively nonpolar trichloroethene (TCE) were successfully adsorbed by activated carbon.	[12]
Activated carbon	Acid treatment with HNO_3 and HCl	Acid treatment produces more active acidic surface groups such as carboxyl and lactone, resulting in a reduction in the adsorption of basic dyes.	[173]
Activated carbon	chemical treatments using HNO_3, H_2O_2, NH_3	Excellent dye adsorption performance as a result of chemical modification of activated carbon.	[174]

5.1. Surface Modified Carbons as Supercapacitors

Activated carbon with surface modified chemically are widely used as energy-storage devices [175]. Ismanto et al. [176] used cassava peel waste to produce activated carbons using simultaneous chemical (KOH) and physical (CO_2) activation methods. The obtained carbon-based materials were then subjected to surface oxidation using hydrogen peroxide (H_2O_2), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) solutions. As a result of modification, no noticeable change in the textural features of the final samples was observed but the chemical characteristics of surfaces exhibit clear changes. New functionalities are introduced on the surface of activated carbon, resulting in enhanced specific capacitance in HNO_3-treated carbons. The results show that the specific capacitance increased to 264.08 $F \cdot g^{-1}$ compared to 153.00 $F \cdot g^{-1}$ for pristine carbon samples. In another experiment, Elmou Wahidi et al. [177] used activated carbons derived from KOH activation of argan seed shells. The modified activated carbons induced oxygen and nitrogen groups on the surface. The experimental findings show that nitrogen-enriched activated carbons exhibited the highest capacitance and retention of 355 $F \cdot g^{-1}$ at 125 $mA \cdot g^{-1}$ and 93% at 1 $A \cdot g^{-1}$, respectively, compared to oxygen-doped activated carbons. These results show that surface carboxyl functionalities in oxygen-enriched activated carbons prevent electrolyte diffusion into the porous network, while the existence of nitrogen groups can produce micro-mesoporosity and excellent pseudo capacitance properties. Furthermore, Liu et al. [178] showed that HNO_3-modified porous wood carbon monolith (m-WCM) could be used in a super capacitor. The results demonstrate a significant enhancement in the electrochemical capacitive performance compared to virgin carbon materials.

5.2. Surface Modified Carbons as Efficient CO_2 Adsorbents

The literature reviewed here reveals the rapid innovation of ammonia-modified activated carbons as an alternative approach for increasing their CO_2 capture capacity. The primary attribute of surface-modified activated carbon is the introduction of nitrogen functionality, which exhibits strong basicity and can induce Lewis acid-base interactions with acidic CO_2 molecules [179–182]. This enhances the adsorption performance. However, very strong chemical interactions between CO_2 molecules and the adsorbent surface can lead to poor adsorbent regeneration and are economically unfavorable. Hence, moderate physisorption is the desired interaction for adsorbing gas molecules efficiently and releasing them when required.

5.3. Surface Modified Carbons as Organic Pollutant Adsorbents

Studies in the literature show that activated carbons are widely being used for adsorption of organic molecules compared to metals. The predominant factors contributing to the high adsorption performance of activated carbons include their excellent textural features and the generation of suitable surface functional groups. It is commonly known that oxygen-enriched acidic surfaces can reduce the adsorption of organic species from aqueous media, whereas their absence boosts the adsorption performance of AC. Weakly acidic functionalities introduced on the surface of carbons can augment the metal adsorption capacity while decreasing the adsorption of phenolic compounds in an aqueous environment. This was experimentally demonstrated by Leng and Pinto [183]. They show that phenol physisorption decreased at high concentrations of surface acidic groups, possibly due to decreased dispersive forces with the carbon basal plane. Such outcomes are consistent with the findings of Mahajan et al. [184] which showed that phenol adsorption was augmented with increased availability of π-electrons on the basal plane of carbon surfaces and decreased oxygen content at adsorption sites. Some other research groups [185,186] explained the decreased adsorption of phenol by the fact that water is preferably adsorbed on activated carbon surfaces via hydrogen bonds with oxygen moieties. This results in the formation of large clusters that hinder the movement of phenol molecules into the microporous structures. These oxygen clusters subsequently decrease the adsorptive performance by localizing free electrons in carbon. Other mechanisms [187,188] suggest the generation of two kinds of interactions among adsorbent electrons and aromatic structure of adsorbate, namely π-dispersion and electrostatic interactions. To date, nearly all experimental studies involving removal of organics from aqueous solutions used phenol and benzene-derived compounds as model studies. This can be attributed to the fact that these aromatics are frequently used in pharmaceuticals, oil refineries and pesticide manufacturing. Apart from surface chemistry, other factors such as pH of solution, temperature of solution, type of adsorbent, oxygen availability and mineral contents should be considered for efficient removal of organic contaminants from waste water.

5.4. Surface Modified Carbons as Dye Adsorbents

Over the last few decades, the textile and dye industries are making significant progress. However, removing excess dyes from waste water is still a challenging task for researchers. Various researchers, including Faria et al. [18] examined surface-modified activated carbons with 6M and 10M nitric acid and hydrogen peroxide, respectively, along with the heating at 700 °C in H_2 or N_2 atmosphere. The results show that samples prepared with H_2 treatment at high temperature exhibit excellent capacity to adsorb anionic and cationic dyes. In another interesting experiment, Orfao et al. [189] used two textile dyes (commonly known as Rifafix Red 3BN and C.I. reactive red 241) for adsorption on acid-modified activated carbon surface and basic carbon surfaces. The adsorption capabilities show that basic surfaces play a beneficial role in dye uptake due to dispersive forces between localized π-electrons in the carbon basal plane and free electrons in the dye molecules. On the other hand, acid-treated samples exhibit reduced adsorption due to the presence of repulsive forces between the oxygenated functionalities of the carbon surface and dye molecules. Conversely, these results cannot be applied to all the textile dyes. Some dyes exhibit reduced adsorption with increased basic character, such as those studied by Attia et al. [190] Here, Acid Red 73 and Acid Yellow 23 show improved uptake but Acid Blue 74 exhibits reduced uptake. However, these dyes predominantly consist of organic structures. Hence, a general hypothesis can be formulated; increasing the acidic functionalities on the surface of activated carbon should result in decreased dye uptake. This concept is strengthened by the experimental evidence obtained by Valdes et al. [40]. They found that continued exposure of activated carbon to ozone gas as an oxidizing agent transformed the basic surface sites to acidic surface sites. Consequently, the uptake of methylene blue was reduced. They further elaborated this by the fact that oxidation can release electrons from activated carbon bands, which decreases the dispersion interactions among the π-electron system in the ring structures of the dye and the graphitic planes on the carbon surface.

In another experiment, 2M nitric and hydrochloric acids were used to modify carbon surfaces. Later on, these carbons were used by Wang et al. [191] to study the uptake capacity of methylene blue. HCl and HNO_3 treatment reduced the adsorption capacity by up to 10.6% and 13.5%, respectively. They concluded a similar mechanism was responsible for these results, where acid functionalities formed on the surface of activated carbon and electrons were extracted, thus reducing the uptake of methylene blue. They further explain the activity differences resulting from the use of both acids. According to the authors, carbons treated with HCl exhibit greater uptake than carbons treated with HNO_3. This can be attributed to the fact that negative ions (Cl^-) can adsorb on positive sites on the carbon surface and can induce negative charge on the carbon surface, thus facilitating adsorption of positively charged dye molecules. However, contrary to these experiments, Jiang et al. [17] claimed that high temperature oxidation by concentrated H_2SO_4 can lead to increased methylene blue adsorption. This can be justified by the increased mesopore volumes after high temperature modification, which can result in enhanced dye adsorption.

6. Concluding Remarks and Future Outlook

In this review, an extensive study based on activated carbon modification methods, in order to improve the adsorption capacity for diverse contaminants in water and air, is presented. Different activating agents are used to induce the formation of different surface functional groups. Generally, uptake of metal ions from an aqueous environment requires an acidic treatment, while inducing basicity is highly recommended for removal of anionic pollutants, organic moieties and CO_2 from air. After examining all the possible modification methods, one finds that an acidic treatment is generally the most studied and used technique, perhaps due to its simplicity, ease of applicability, the availability of many oxidizing agents and the well-understood oxidation mechanism that has been used from many years. Currently, the main focus of researchers is to design activated carbons with modified surfaces and excellent textural parameters. In this context, many experiments were performed in order to develop economically cheap activated carbon electrodes capable of storing large amounts of energy with minimum resistance. Similarly, carbon-based materials with basic surfaces to enhance CO_2 adsorption in order to mitigate global warming, is highly needed. On the other hand, activated carbons with surfactant modification that are tailored to eliminate pollutants from aqueous media require further investigation in order to yield excellent performance as experimental findings in this area are limited. Furthermore, considering the effects of enhanced and decreased uptake of particular pollutants, selective adsorption can be induced, which provides a new pathway in the field of clean energy and environmental science. Apart from these research findings, the most important drawbacks are the cost of the modification process and treatment of the leftover hazardous chemicals used during modification. While recovering adsorbents, one should notice that chemicals used for modification should not enter the atmosphere and must be recovered. Adsorbents should be used in cyclic measurements and easy to regenerate. Keeping all these points in mind, the field requires facile, novel, simple and greener techniques for modification of activated carbons. One example of such a technique is the use of plasma treatment to generate a desired charge on the surface of carbon, making it effective for elimination of contaminants. Thus, the authors find that new, efficient modification methods should be explored as these methods improve the chemical surfaces of activated carbons while simultaneously preventing destruction of the textural characteristics.

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