Review

Activated carbon modifications to enhance its water treatment applications. An overview

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ABSTRACT

The main objective of this study was to list and compare the advantages and disadvantages of different methodologies to modify the surface of activated carbons (ACs) for their application as adsorbents to remove organic and inorganic pollutants from aqueous phase. These methodologies have been categorized into four broad groups: oxidation, sulfuration, ammonification, and coordinated ligand anchorage. Numerous investigations into the removal of metals from water have modified carbon surfaces to increase their content of acidic surface functional groups by using H_2O_2, O_3 and HNO_3. Because these treatments can reduce the AC surface area, researchers are seeking alternative methods to modify and/or create surface functional groups without the undesirable effect of pore blockage. The nitrogenation or sulfuration of the AC surface can increase its basicity favoring the adsorption of organic compounds. The introduction of nitrogen or sulfur complexes on the carbon surface increases the surface polarity and, therefore, the specific interaction with polar pollutants. Different coordinated ligands have also been used to modify ACs, showing that coordinated ligand anchorage on the AC surface modifies its textural and chemical properties, but research to date has largely focused on the use of these modified materials to remove heavy metals from water by complexes formation.

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Contents

1. Introduction

Activated carbon (AC) has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants from aqueous or gaseous media. It is widely used due to its exceptionally high surface area (ranges from 500 to 1500 m^2 g^{-1}), well-developed internal microporosity, and wide spectrum of surface functional groups. While the effectiveness of ACs to act as adsorbents for a wide range of contaminants is well documented, research on AC modification is gaining prominence due to the need to develop the affinity of AC for certain contaminants to facilitate their removal from water. It is essential to understand the factors that influence the adsorption of ACs prior to their modification in order to tailor their specific physical and chemical properties and enhance their affinity for metals and inorganic and/or organic species present in waters. These properties include their specific surface area, pore-size distribution, pore volume, and the presence of different types of surface functional groups.

The use of oxidizing agents is the most common methodology to modify AC surface [1–68], however, in general this treatment reduces the AC surface area; therefore, researchers are investigating alternative methods like (i) sulfuration [69–83] (ii) ammonification [84–116] and/or (iii) coordinated ligand anchorage to increase activated carbon adsorption capacity [117–125,112,126–129].

The main objective of this study was to list and compare the advantages and disadvantages of existing AC surface modification techniques in relation to the application of the resulting AC as an adsorbent to remove organic and inorganic pollutants from aqueous phase. Based on the extensive literature on this topic, we have categorized the techniques into four broad groups: oxidation, sulfuration, ammonification, and coordinated ligand anchorage.

Table 1
Hydrogen peroxide oxidation treatments.

Raw material	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
(Commercial) Activated charcoal cloth (FM250) from Charcoal Cloth Ltd; Activated granular charcoal (ACG 80) by Active Carbon Ltd.	Preparation of original materials. Demineralization: HCl 6N, HF 22N, and HCl 12N; Drying: air oven at 110 °C overnight, nitrogen gas for 5 h at the same temperature in horizontal furnace. Oxidation of original materials. Contact with 30% H$_2$O$_2$ (1 g of AC: 10 mL solution) for 48 h. Washing. Hot double-distilled water. Drying overnight at 110 °C under nitrogen flow.	Surface area decreased. Microporosity persisted after oxidation.	Oxygen content increased due to the formation of surface oxygen complexes.	Oxidized samples have almost the same or slightly higher acidity *versus* original materials; Minimum decrease in adsorption capacity (according to N$_2$ adsorption isotherms) Adsorption capacity of granular ACs was increased in comparison to activated charcoal cloth.	[8]
(Commercial) GAC from CECA; previously demineralised by treatment with HF and HCl solutions.	Treatment with an H$_2$O$_2$ solution.	Surface area increased; Mesopore volume markedly increased; Textural parameters were similar.	Surface oxygen chemical groups increased in number after treatment.	Chemical groups were introduced on both external and internal surfaces.	[7]
Almond shells	Raw material preparation. Pyrolysis: at 900 °C in nitrogen flow for 1 h; Activation: steam flow at 850 °C for different periods of time (final particle size range between 0.15 and 0.25 mm). Oxidation. 1 g of carbon: 10 mL of concentrated H$_2$O$_2$ (9.8 M) at 25 °C in shaking bath for 48 h.	Surface area and pore texture were similar after treatment.	Carboxyl, ketone, and ether groups and probable carboxyl-carbonate structures were detected.	Oxygen surface complexes were fixed at the entrance of the micropores in some samples, causing restricted diffusion of N$_2$ at 77 K.	[93]
(Commercial) Coconut shell	Oxidation. Immersion in H$_2$O$_2$ 10–30%, ratio of H$_2$O$_2$ to carbon of 2.5–10 mL/g at room temperature. Drying 95 °C for 12 h.	Porous structural parameters and surface area not affected.	Oxygen content increased after oxidation; CO$_2$ evolving groups might be largely induced on the surface with oxidation at <100 °C.	H$_2$O$_2$ oxidation is very practical, since it is performed at <100 °C; Simple drying is required as post-treatment; No harmful gas is evolved during the process.	[1]
(Commercial) Norit ROX 0.8; pellets (0.8 mm diameter, 5 mm length), neutral pH, 3 wt.%. ash content	Mixing. 1 g: 25 cm^3 of H$_2$O$_2$ 1 M at room temperature until complete degradation of H$_2$O$_2$. Washing. Distilled water until neutral pH. Drying at 110 °C for 24 h.	Minimal changes in micropore volume and mesopore surface area.	No significant differences compared to the original sample (according to temperature-programmed desorption spectra).	No major effect on surface chemistry.	[6]
(Commercial) Waterlink Sutcliffe Carbons; Grade: 207 A; Mesh: 12 × 20.	Oxidation. 10 g of carbon: 100 mL of H$_2$O$_2$ (15% and 30%, v/v) stirred at room temperature for 3 h. Washing and Filtration. Drying 110 °C overnight.	No marked changes.	CO$_2$-evolving groups slightly increased and CO-groups slightly decreased with increases in oxidant concentration.	The modified material showed similar porosity and surface chemistry.	[5]
(Commercial) Coal particles carbonized and steam activated at 850 °C, BET surface area 770.4 m^2/g.	Heat treatment. 500 °C in nitrogen. Oxidation. Concentration of oxidizing agent 3–15%, 100 °C, 1 h. Washing Distilled water until neutral pH.	Not evaluated.	Carboxylic groups on the surface decreased.	Oxidation with 15% H$_2$O$_2$ introduced a large number of lactone and phenol groups on the surface.	[11]

Table 2
Nitric acid oxidation treatments.

Raw material	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
(Commercial) Merck	Oxidation. 50 mL of concentrated nitric acid added to 5 g of AC. Heating 353 K until dry. Washing. Distilled water until no nitrates were present. Drying. 383 K in oven overnight.	Meso- and macro-porosity decreased; Pore constrictions by fixation of oxygen groups at the entrance of the pores.	Considerable amounts of oxygen were fixed, largely in the form of carboxylic acid groups and nitro and nitrate aromatic compounds.	Chemical and textural properties changed; meso and macropores partially destroyed by loss of pore walls.	[13]
Spanish Lignite	Preparation of original materials. Demineralization with HCl and HF; Pyrolysis: at 840 °C in N_2 flow; Elemental analysis (wt.%, dry basis): C-80.2; H-1.5; N-1.0; S-2.6; O-12.6, ash content-2.1. Activation: in CO_2 flow at 800 °C up to 18% burn-off. Oxidation 1 g of carbon treated for 48 h with 10 cm^3 of concentrated H_2O_2 at 25 °C (final analysis, O (wt.%)-18.2) Heat treatment. He flow at different temperatures up to 1000 °C. After-treatment procedure exposure to ambient air for two years.	Not evaluated.	Basic group regeneration (evolved as CO) less sensitive to the outgassing temperature in comparison to acid groups.	Ageing for two years in ambient air of a previously outgassed oxidized AC restored the pre-outgassing surface oxygen complexes of the carbon; The higher the previous outgassing temperature, the greater was the regeneration. There was a memory effect in addition to oxygen migration to and across the surface during the outgassing process.	[15]
(Commercial) Merck-9631, 18–35 mesh ASTM	Oxidation. 200 cm^3 of concentrated nitric acid heated (25, 60 and 90 °C) and 20 g of AC added and mixed for 3 h. Washing. Distilled water until neutral pH. Drying. Left under nitrogen atmosphere at 283 K overnight.	Not evaluated.	Carbonyl, lactone, ether and hydroxyl groups were formed.	The quantity of the evolved gases increased with higher treatment temperature.	[4]
(Commercial) Coconut shell based carbon (activation in steam at around 900 °C)	Extraction. Soxhlet extraction with water to remove soluble materials. Oxidation. Carbon refluxed in 7.5 M HNO_3 solution for 4 and 48 h; soxhlet extraction with water until constant pH to remove residual HNO_3; vacuum-drying at 75 °C. Heat treatment At 10 °C min-1 under helium flow to the desired temperature, holding for 1 h at the maximum temperature (300 or 800 °C).	Micropore volume (CO_2) and total pore volume (N_2) decreased; Pore volumes showed greater reduction with longer oxidation times; Surface area and both micropore and total pore volumes were gradually increased by heat treatment.	Oxygen, nitrogen, and hydrogen content increased and carbon content decreased; Oxygen largely introduced into the carbon.	Increasing oxidation time increased oxygen functional groups; Small amounts of nitrogen were also incorporated into the carbon; The structural changes not completely reversed by heat treatment at 800 °C.	[16]
(Commercial) Activated charcoal cloth (FM250) by Charcoal Cloth Ltd; Activated granular charcoal (ACG 80) by Active Carbon Ltd.	Preparation of original materials Demineralization: HCl 6N, HF 22N, and HCl 12N; Drying: in air oven at 110 °C overnight; Nitrogen gas for 5 h at the same temperature in horizontal furnace. Oxidation of original materials Boiling in 1N HNO_3 (1 g of AC:10 mL of solution) for 24 h with reflux condenser. Washing. Double distilled water until free of nitrate ions then further reflux with distilled water for 3–4 h. Drying 110 °C overnight under nitrogen flow. Heat treatment. Oxidized samples under N_2 for 5 h at 600 °C in horizontal furnace.	Surface area decreased; ACs retained their predominantly microporous nature.	Oxygen content markedly increased due to the formation of surface oxygen complexes.	Total acidity increased three-fold due to the presence of stronger acidic groups; N_2 adsorption isotherms showed marked decrease in adsorption capacity, which was more marked for granular ACs than for activated charcoal cloth.	[8]
(Commercial) Norit ROX; Hydraffin (Degussa).	Preparation of the raw material ACs ground and sieved to 200–300 μm prior to their use. Oxidation HNO_3 5N solution at boiling temperature for 3 h. Washing Boiling distilled water till pH 5.5. Drying. 110 °C overnight.	Micropore volume significantly decreased; Mesopore surface area increased 10%.	CO and CO_2 markedly increased, releasing groups on both Hydraffin and Norit samples; Acidity increased.	The decrease in micropore volume was explained by the collapse of pore walls due to the attack of highly concentrated nitric acid.	[17]

Table 2 (*Continued*)

Raw material	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
(Commercial) Q and CV, commonly used by the pharmaceutical industry.	Oxidation HNO_3 at different concentrations (1, 20 and 60%, v/v); 1 g of carbon: 10 mL of acid solution boiled until dryness. Washing. Distilled water until nitrate elimination.	Micro- and mesoporosity increased at low concentrations of the oxidizing agent; Texture of the carbons significantly destroyed by severe oxidation conditions.	Surface oxygen content increased, being greater at higher concentrations (20 and 60%).	Oxidation alters not only the chemical properties but also the texture of the surfaces	[9]
Almond shells.	Preparation of the raw material Pyrolysis at 900 °C in nitrogen flow for 1 h, activation with steam flow at 850 °C for different times; final particle size range between 0.15 and 0.25 mm. Oxidation. 1 g of carbon treated with 10 mL of concentrated HNO_3 (13.9 M) at 80 °C until dryness. Washing. Residue washed with distilled water until nitrate removal.	Surface area and microporosity decreased; Effects increased with stronger degrees of activation.	Carboxyl groups and probable carboxylcarbonate structures as well as nitro and nitrate groups were detected after treatment.	Stronger acid groups were introduced by treatment with $(NH_4)_2S_2O_8$ *versus* treatment with HNO_3, in spite of the fixation by HNO_3 of more CO_2-evolving oxygen surface complexes.	[93]
(Commercial) Coconut shell.	Oxidation. HNO_3 4 N at room temperature for 10 h. Drying 70 °C in a rotary evaporator. Heat treatment N_2 flow at 400 °C for 1 h.	Surface area markedly reduced.	Oxygen content markedly increased.	Temperature treatment needed to eliminate the remaining oxidants on the surface; The harmful gases involved, such as SO_3, SO_2, NO_2 and NO must be eliminated after treated.	[1]
Corncob.	Raw material preparation. Dried and crushed corncobs at 500 °C with N_2 flow, activation with steam/N_2 at 850 °C; Steam pyrolysis of the raw precursor at 600 and 700 °C; Activation: with 50% H_3PO_4 at 500 °C. Oxidation. HNO_3 (50 cm^3:5 g of prepared carbon), at 60 °C with constant stirring for 1 h. Washing. Distilled water. Drying 110 °C.	Total surface area markedly decreased (from 13 to 25%); Mesopore volume slightly increased and some pores were widened.	Increased density of acidic oxygen groups at carbon surface.	Large amount of oxygen functionalities on the carbon surface, especially when carried out under severe acidic conditions; simultaneous partial destruction or degradation of the porous structure.	[14]
Olive stones.	Preparation of the raw material. Washing with sulfuric acid and again with distilled water up to sulfate ion elimination, carbonization at 1000 °C for 1 h under N_2 flow, activation with stream of carbon dioxide at 840 °C for 16 h (grains of 1–1.4 mm). Oxidation treatment. 80 cm^3 of concentrated HNO_3 solution (15 M): 4 g of material and then left in contact with nitric acid at ambient temperature for 24 h. Washing. Distilled water until neutral pH. Separation Filtration. Drying. Vacuum at 50 °C overnight.	Surface area decreased.	CO_2-evolving oxygen groups strongly increased.	Oxidized samples have smaller surface area; The subsequent partial outgassing increased the surface area but to lower values than before oxidation.	[2]
(Commercial) Bituminous-coal BPL and WPL, from Calgon Carbon Corporation.	Pre-treatment De-ionized water washing and air-drying. Oxidation 6 M HNO_3 solution at room temperature for 5 h. Washing De-ionized water. Drying 110 °C overnight.	Surface areas and pore volumes slightly decreased, possibly as a result of the destruction of some of the thin pore walls and blocking of the pore entrances by oxygen functional groups.	Total oxygen concentrations significantly increased; acidic group formation.	Strong chemical effect produced by treatment, creating oxygen surface functional groups and resulting in low CO/CO_2 ratio; Higher mercury adsorption.	[10]
(Commercial) Norit ROX 0.8; pellets (0.8 mm diameter, 5 mm length), neutral pH, ash content of 3 wt. %.	Soxhlet extraction 5 M HNO_3, 9 g of AC, 3 h reflux. Washing. Distilled water until neutral pH. Drying. 110 °C for 24 h.	Micropore volume decrease was more drastic when degree of oxidation increased.	Large amount of surface oxygen-containing groups.	Textural modifications due to the drastic conditions used, leading to the collapse of some pore walls. Acidic surface was due to the acid character of the majority of the surface oxygen-containing groups.	[6]
(Commercial) Filtrasorb 200 (Calgon Corp.), particles with 20–32 mesh size.	Oxidation. 1 g carbon to 10 mL HNO_3 (10, 30, 50% and concentrated HNO_3). Washing. De-ionized water or treatment with concentrated HCl followed by washing with de-ionized water.	Surface area not affected.	Surface functional groups such as carbonyl, carboxyl and nitrate groups were formed.	Chemical properties of carbon (pH and total acidity capacity) significantly changed.	[12]

Table 2 (*Continued*)

Raw material	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
(Commercial) Waterlink Sutcliffe Carbons; Grade: 207.	Oxidation. 10 g carbon to 100 mL HNO_3 (2, 10, 30 and 60% v/v) for 3 h stirred at room temperature. Washing, Filtration, and Drying 110 °C overnight.	Porosity increased at higher concentrations (>30% v/v).	CO and CO_2-evolving oxygen groups were promoted, producing important changes in the surface chemistry.	Similar porosity but major differences in surface chemistry.	[5]
(Commercial) Coal particles carbonized and steam activated at 850 °C, BET surface area 770.4 m^2/g.	Heat treatment. 300 °C in air. Oxidation 3.2–13.2 mol/L HNO_3, 100 °C, 1 h. Washing Distilled water until pH near 7. Drying 120 °C for ≈2 h.	Not evaluated.	Surface carboxylic groups increased, especially at high concentrations of HNO_3.	Very strong oxidation effect.	[11]
(Commercial) Merck, Ref. 102514, granular, particle size ranged from 0.5 to 1 mm.	Oxidation 1 g carbon to 10 mL 6 M HNO_3 at boiling temperature up to complete evaporation. Washing Distilled water until neutral pH. Drying At 100 °C overnight.	Texture markedly changed at acid concentrations >20%; Strong oxidation practically destroyed the porous structure of the original material due to erosion of the pore walls	Surface oxygen groups significantly increased.	All types of oxygen groups were significantly increased, but more specially phenol, carbonyl/quinone and lactone groups; The lactone groups could have been formed through condensation of close carboxylic groups formed during treatment.	[18]

Table 3
Ozone oxidation treatments.

Raw material	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
Coal and coffee grounds-based ACs	Oxidation conditions: Pyrex glass tube reactor loaded with 100 mg of AC Gaseous ozone flow: 0.23 mg O_3/min Exposure time: 1 h Room temperature	The volume of micropore decreased to some extent while the surface fractal dimension slightly increased because of AC ozonation.	Not evaluated	The effect of ozonation of ACs on their water vapor isotherms was studied. No major impact was observed.	[60]
Microporous steam-activated coconut-based AC (total pore volume of 0.81 cm^3/g)	Oxidation conditions: Fluidized bed reactor loaded with 0.5 g of AC Gaseous ozone flow: 20 mL /min of a 3% wt/vol ozone-oxygen mixture. Temperature and reaction time: 150 °C for 1 h and 250 °C for 1 and 3 h.	No appreciable changes in micropore and mesopore volumes.	Increase in the content of oxygen from 3.1% (raw AC) to 8.4%	No surface OH groups detected on ozonated samples by FTIR analysis. Oxidation of AC reduced the amount of 2-methylisoborneol adsorbed from aqueous solution.	[61]
Commercial PAC KBB-type, Norit Corp. (1500 m^2/g surface area)	Sample pre-treatment: AC samples were supported onto KBr pellets and degassed at 373 K for 16 h. Oxidation conditions: Ozonation of the sample was carried out in situ inside the vacuum cell of a FTIR spectrometer. Temperature: 300 K Ozone exposure: up to 6 h (26 mg O_3)	Not evaluated	Formation of hydroxyl, carbonyl and, especially, carboxylic surface groups. Removal of aromatic and aliphatic structures	A reaction mechanism for direct formation of –COOH is proposed.	[66]
Filtrasorb 400 (Calgon carbon Corp) Commercial GAC of bituminous origin with BET surface of about 1000 m^2/g	Oxidation conditions: Fixed bed reactor loaded with 2 g of AC. Gaseous ozone flow: 76 mg O_3/min. Exposure time: ranged from 10 to 120 min. Temperature: 25 °C. Post-treatment: Thermal treatment in oven, consisting of four stages: 1 h at 60 °C, 1 h at 100 °C, 1 h at 150 °C, and 24 h at 170 °C.	In general, decrease in BET surface area and volume of micropores but increase in external surface area and volume of mesopore were observed on ozonation. However, at a low ozone dose (10-min exposure), a slight increase of BET surface area was found.	Increase in oxygen content from 1.8% to 24.9%, as deduced from the amount of CO and CO_2 released during TPD experiments. Increase in concentration of acidic surface groups (lactone, carbonyl and carboxyl). Decrease in basic surface groups. Ozone treatment also significantly reduced the pH_{PZC} and ionization constant of the AC	Linear relationships were observed among the formation of acidic groups, the removal of basic groups and the amount of ozone consumed. 1 mmol of ozone consumed gave rise to the removal of ≈3.2 μeq/g of basic sites and the fixation of ≈16 μeq/g of acidic sites. Methylene blue adsorption decreased due to oxidation of the AC with ozone.	[28]
Coconut shell-based AC provided by Kowa Cosmos Company (795 m^2/g surface area; 14.7 nm average pore diameter)	AC pre-treatment: A 500 mg AC sample was immersed in a NaOH aqueous solution (from 1N to 5N) for 24 h. It was then dried in an oven at 105 °C for 48 h. Oxidation conditions: Gaseous ozone flow: 100 mg/min. Ozone exposure: 30 min. Room temperature. Post-treatment Samples were washed with distilled water and then dried in an oven at 105 °C for 48 h	Not evaluated	Increase in surface oxygen functional groups, especially in the phenolic and carboxylic categories	Reaction pathways were proposed for the ozone reaction with AC *via* the formation of hydrotrioxide intermediates.	[65]

Table 3 (*Continued*)

Raw material	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
Coconut shell-based AC provided by Kowa Cosmos Company (795 m^2/g surface area; 14.7 average pore diameter)	Oxidation conditions: Gaseous ozone flow: 100 mg/min. Ozone exposure: 30 min. Room temperature. Post-treatment: Samples were washed with distilled water and then dried in an oven at 105 °C for 48 h	The specific surface area of the treated AC increased by 8.7% *versus* the non-treated AC. A 7.5% increase in micropore volume was also observed.	Increase in surface oxygen functional groups, especially in the phenolic and carboxylic categories	Ozone treatment enhanced the adsorption capacity of the AC for VOCs (methylethylketone and benzene).	[63]
Filtrasorb 400 and AQ40, both from Chemviron Carbon. Commercial GACs of bituminous origin with BET surface areas of about 850 m^2/g	Pre-treatment of AC: Washing with boiling water and drying overnight at 110 °C. Oxidation conditions: Fixed bed reactor loaded with 0.25 g of AC Gaseous ozone flow: 16.6 mg O_3/min Exposure time: 15 min. Temperature: 25 °C and 100 °C	No major textural changes: Moderate BET surface area loss (<8%) and decrease in microporosity (<20%). Moderate increase in external surface area (<15%) and mesoporosity (<12%)	Strong fixation of acidic surface oxygen groups as deduced by FTIR analysis and titration methods. Removal of basic surface groups and decrease in pH_{PZC}.	Carboxylic groups accounted for >50% of acidic sites on AC ozonated at 25 °C. Ozonation at 100 °C allowed more even distribution of acidic sites of different strength. Exposure of GACs to ozone at room temperature decreased their ability to adsorb phenolic solutes from aqueous solution.	[64]
Coconut shell-based granular AC (Nacalai Tesque)	Oxidation conditions: Glass flask reactor loaded with 1 g of AC. Gaseous ozone flow: 5 L/min of 3–7% wt/vol ozone-oxygen mixture. Ozone exposure: 2 h Room temperature	Morphological changes were observed upon ozonation. The microstructure of the ozone-treated sample was more porous *versus* the untreated sample (SEM observations).	Increase in O/C ratio from 0.18 to 1.27 as a result of the oxidation treatment		[31]
(Commercial AC from Dong-Yang Carbon Co, Korea)	Oxidation conditions: Fixed bed reactor loaded with 2 g of AC. Gaseous ozone flow: 6 g O_3/h. Exposure time: ranged from 1 to 4 h. Room temperature. Post-treatment: Thermal treatment in oven consisting of four stages: 1 h at 60 °C, 1 h at 100 °C, 1 h at 150 °C and 24 h at 170 °C.	Specific surface area, total pore volume, and micropore volume decreased with longer ozone treatment time.	Some oxygen-containing functional groups increased with longer ozone treatment time, especially carbonyl (C=O) and ether (C–O) groups, as deduced from XPS analysis.	Ozone treatment led to an increase in ammonia removal efficiency of the AC	[62]
Twenty granular ACs of different textural and chemical properties	Oxidation conditions: Two reactors were used: a packed bed reactor (PBR) and an expanded bed reactor (EBR) loaded with varying amounts of AC between 0.25 and 1.5 g. Gaseous ozone flow: 25 L/h of an air-ozone mixture with an ozone concentration of 20–50 g/m^3. Exposure time: 15 min Temperature: ranged from 298 and 473 K.	Not evaluated	Ozonation resulted in an increase in acidic surface oxygen groups, especially carboxylic groups, and a decrease in basic groups.	The ozone-AC reaction followed first-order kinetics, with deactivation due to the formation of acidic oxygen functional groups on the surface of the AC.	[24]
Commercial coal-based AC received from CarboTechAC GmbH (surface area > 1000 m^2/g)	AC pre-treatment: A 200 mg AC sample was dried at 100 °C for 30 min. Oxidation conditions: Fixed bed reactor attached to an IR spectrometer. Gaseous ozone flow: 4000 ppmv ozone in N_2/O_2 (1:1:3) stream. Ozone exposure: 3 h. Temperature: 60 °C	Not evaluated	Four surface oxygen groups were identified as formed by ozonation: carbonyl, carboxylic acid, lactone, and anhydride.	Specific concentrations of the four groups were calculated by combining TPD and DRIFTS information	[68]
Granular AC obtained from cherry stones (BET surface area 604 m^2/g)	Oxidation conditions: Fluidized bed reactor. Gaseous ozone flow: 25 L/h of an air-ozone mixture with 1.5% vol ozone. Exposure time: 1 h. Room temperature	Unlike other oxidizing agents (nitric acid, hydrogen peroxide and air), ozone barely affected the textural properties of the AC.	Ozone treatment resulted in the fixation of acidic SOGs and the removal of basic SOGs. As a result, the PZC was considerably lower in the oxidized sample (4.3) than in the untreated AC (8.8)	Functionalization of the AC by ozone treatment improved the adsorption of Cu(II) and Co(II) ions.	[67]

2. Activated carbon treatments

2.1. Oxidation treatments

2.1.1. Hydrogen peroxide and nitric acid treatments

Tables 1 and 2 list selected studies [1,2,4–18,93] on the oxidation treatment of different ACs with H_2O_2 and HNO_3, summarizing the experimental conditions used to prepare the materials and the textural and chemical modifications, with relevant observations.

Hydrogen peroxide and nitric acid oxidation treatments can be both performed in various forms of AC, from pellets to granular or cloth ACs. Oxidation reaction is achieved at temperatures close to 100 °C although, when H_2O_2 is used, it can also take place at close to room temperature, which offers evident advantages [1]. On the other hand, a study of nitric acid treatments demonstrated that the temperature applied during oxidation has a major influence on the chemistry of the carbon, finding an increase in oxygen complexes with higher temperature [4].

Table 4
Sulfurization treatments.

Raw material	Treatment	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
Black Pearls 1300 (Cabot Corporation) and Pittsburgh CPB (Calgon Corporation).	HT/S/CS$_2$ (washing)	1123–1173 K, 7–8 h/748 K, 3 h/24 h.	Not evaluated	Not evaluated	After the sulfurizing treatment, the S content was 48 wt.% for Black Pearls 1300 and 43.0 wt.% for Pittsburgh CPB. After CS$_2$ washing, S content was 12.8 and 7.9 wt.%, respectively.	[69]
Three ACs: A, B, and C. Particle sizes: A, 0.5–2.38 mm; B, 1.0–2.0 mm; and B, 1.0–2.38 mm.	(1) A,B,C-H$_2$O$_2$ (AO, BO, CO), (2) (A,B,C), (AO, BO, CO)-CS$_2$/HT/CS$_2$ (washing); (AS, BS, CS), (AOS, BOS, COS).	(1) 298 K, 1 week (2) 873 K, 6 h, He saturated with CS$_2$ at 288 K/773 K, He.	As an example, S_{N2} (m^2/g): AO, 836, AOS, 776; BO, 1049, BOS, 824; CO, 1034, COS, 854. $V_P(\phi > 75\,\text{Å})$ (cm^3/g): AO, 0.23 AOS; 0.22; BO, 0.60, BOS, 0.53; CO, 0.15, COS, 0.26.	Sulfur content increased between 6.68% and 10.91%. Surface sulfide and hydrosulfide groups were present in the sulfurized carbons, as analyzed by the catalyzed decomposition reaction of sodium azide by iodine.		[77]
AC (Merck, Darmstadt), average particle size, 1.5 mm; $S_{BET} = 921$ m^2/g).	(1) SO$_2$-T, (2) H$_2$S-T, (3) SO$_2$/N$_2$, (4) H$_2$S/N$_2$, (5) SO$_2$/H$_2$S/N$_2$, (6) SO$_2$/H$_2$S/N$_2$-T.	(1) and (2), 1173 K; (3), (4) and (5), 303 K; (6), 473 K.	S_{BET} (m^2/g): virgin carbon, 921; SO$_2$-T, 831; H$_2$S-T, 785; SO$_2$/H$_2$S/N$_2$-T, 764. The S_{BET} decreased by ≤17%.	The presence of C–S, S–S, C=S, and S=O bonds was detected in sulfurized AC samples by FT-IR spectroscopy.	The sulfur content of the sulfurized carbons ranged from 2.1 wt.% for the H$_2$S/N$_2$ treatment to 17.2 wt.% for the SO$_2$-T treatment. SO$_2$ interacted very strongly with the carbon. At room temperature, the retention of SO$_2$ was high but its stability was low, since most of it was removed by transport with nitrogen.	[78,83]
Bituminous coal-based AC (Calgon Carbon Corporation, Pittsburgh, PA), 4 × 10 and 12 × 30 U.S. mesh sizes; 988–1026 m^2/g.	S	873 K, 2 h.	S_{BET} reduced by 19.7%.	S was as S$_8$ rings in a commercially available S-impregnated carbon and as S$_2$ and S$_6$ chains in the AC-S impregnated product.	The S content of S-impregnated carbon was 10.0%. S as S$_8$ was weakly bonded in macropores, whereas S as S$_2$ and S$_6$ was strongly bonded in micropores.	[73]
Bituminous coal-based AC (Calgon Carbon Corporation, Pittsburgh, PA), 4 × 10 and 12 × 30 U.S. mesh sizes, 988–1026 m^2/g.	S	873 K, 2 h.	S_{BET} decreased by 12–20%.	Sulfur content increased from 0.5 to 0.7% for virgin AC to 12.5–12.9% for sulfur-impregnate carbon. The major sulfur forms on the carbon surface were assumed to be short linear-chain sulfur allotropes.	Maintaining a stagnant inert atmosphere during the impregnation process improved sulfur deposition.	[74]
Bagasse pith	(1) Carbonization (C-200), (2) Using C-200, activation-sulfurization.	(1) 473 K, 2 h. (2) Steam, H$_2$S; steam, SO$_2$; steam, SO$_2$, H$_2$S; 673 K.	The surface area slightly decreased, V_{me} significantly increased, and V_{ma} markedly decreased.	The sulfur content was 7.8–8.9 wt.% for sulfurized carbons. For the SO$_2$-H$_2$S treated product, C=S, S=O and S–S bonds containing sulfur surface groups were formed.	pH$_{pzc}$ was lower for the sulfurized products.	[79]
Lignite (150–250 μm), after demineralization (5N HCl, 22 N HF, 12 N HCl), pyrolisis (N$_2$;1073, 1173 K, 0.5 h) and activation (CO$_2$; 1073, 1173 K, 6 h).	S	873 K, 2 h.	N$_2$ and CO$_2$ adsorption capacities, S_{BET}, and total micro-mesopore volume decreased.	Not	Sulfur addition was mainly affected by the impregnation temperature and less by the sulfur/carbon ratio and residence time.	[75]
Coconut shell AC (Active Carbon Ltd., Hyderabad, India), S content, 0.56 wt.%; S_{BET}, 1000 m^2/g.	Na$_2$S	Heating until dryness.	S_{BET} (900 m^2 g^{-1}) slightly decreased.	The S content increased from 0.56 wt.% for the virgin carbon to 7.86 wt.% for the sulfur-enriched carbon.–C=S, S=O and S–S bonds containing surface groups were identified by FT-IR analysis.		[78]

Table 4 (*Continued*)

Raw material	Treatment	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
BPL (Calgon Carbon Corporation, Pittsburgh, PA), 16×50 US mesh size, microporous carbon, $S_{BET} = 1067\,m^2/g$.	H_2S	673–1073 K.	A slight change in the pore volume in the 10–20 Å range after sulfurization.	Sulfurization at higher temperatures resulted in larger sulfur content and more stable sulfur species. The presence of H_2S during the cooling process increased the final sulfur content, especially with relatively unstable species.	H_2S was likely added on active sites at <600 °C and directly reacted with the carbon at higher temperatures, due to decomposition of (oxygen) surface functionalities and the creation of more active sites for sulfur bonding. At higher temperatures, sulfur species were also more stable.	[81]
A commercial AC (CAC): 80–230 mesh size, $S_{BET} = 1287\,m^2/g$, $V_t = 0.79\,cm^3/g$), and a nut shell-H_3PO_4 activation product (PAC): 80–230 mesh size, $S_{BET} = 1557\,m^2/g$, $V_t = 0.93\,cm^3/g$).	SO_2	Room temperature, 4 h.	S_{BET} decreased by ≈19%. The average pore radius (Å) increased from 11.95 to 13.08. V_t decreased from 0.93 cm^3/g to 0.82 cm^3/g.	Infrared absorption at 1160 cm^{-1} for the sulfurized PAC was assigned to the stretching (C=S) vibration mode.		[80]
AC prepared from coconut shells (Shanghai AC Co., Ltd., Shanghai, China), $S_{BET} = 1884\,m^2/g$.	S	473–873 K, 2 h.	For the carbon impregnated at 673 K (ACS-400), S_{BET} decreased by about 2/3, to 646 m^2/g.	Depending on the temperature, sulfur could either directly deposit on AC surface or react with its carbon matrix to produce sulfur species such as thiophene, sulfoxide, and sulfone.	For ACS-400, the sulfur content increased from nearly zero to around 34%.	[76]

Table 5
Nitrogenation of AC. Higher N content and nitrogen functionalities.

Treatment	N content, wt.% (mol.%)	Nitrogen functional groups
NH_3	3.74 [88], 2.23 [89], 4.4, 16.0 [90], (5.8) [92], 3.83 [97], 2.3 [100], 4.5 [103], 1.63 [105], 2.1 [107].	• Amine groups and nitrile and/or pyridine-like nitrogen [89]. • Imide-, amide-, and lactam-type surface species [90]. • Amides and amine [91]. • Lactams and imides (transformed by further heat treatment into pyridine and pyrrole groups) [92]. • Pyridine and pyridine-N-oxide structures [95]. • Amides [97]. • Amino groups [98]. • Surface C–N and C=N groups [102]. • N-6, N-5, N-Q and N-X [107]. • NH and CN groups, cyclic amides, and aromatic amines [108].
NH_3-air	3.8 [90] 2.6 (2.8) [92] 7.1 [113] 7.4 [114]	• Imide-, amide-, and lactam-type species [90]. • Amides [92]. • Imines, amines, amides, N-5, N-6, pyridine-N-oxides and N-Ox [113].
HCN C-dmea C-dmpa	3.87 [89] 3.2 [92] 7.9 [92]	• Amine groups and nitrile and/or pyridine-like N • Tertiary amine groups. • Tertiary amine groups.
HNO_3		• Nitro and nitrate groups [93]. • Pyridine structures and pyridine-N-oxide species [95]. • NO_2^-, NO_3^-, and pyridine-N-oxide [86].
Urea	3.4 [100] 9.3 [101] 5.1 [86] 8.55 [111]	• Pyridinic, pyrrolic/pyridone, quaternary N, and pyridine-N-oxide groups [86].
Urea-air MM MM-urea DCD DMF EDA	5.6 [85] 6.0 [104], 5.9 [86] 5.4 [104] 4.6 [100] 1.9 [100] 10.29 [112]	• N-6, N-5, imine, amine, amide, pyridonic N and N-Q. • Pyridinic, pyrrolic/pyridone, quaternary N, and pyridine-N-oxide groups. • Pyridine-like and quaternary-like N. • C–Cl, C=S, S=O and N–H bonds and CON.

Table 6
Nitrogenation treatments.

Raw material	Treatment	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
AC prepared from sulfonated styrene-divinyl-benzene comopymer (Ambersorb XE-348, Rohm and Hass), 20 × 50 mesh.	NH_3	875 K, 1.5 h	Not evaluated	The N content increased substantially from 0.38 wt.% to 3.74 wt.%. Much of this N would be located at edge sites.	As a result of reaction in NH_3, the surface of the carbon became less negatively charged, with an isoelectric point of 5.7.	[88]
AC produced from peat (Anthralur).	(1) NH_3; (2) HCN	573–1173 K, 4 h (NH_3), 1 h (HCN).	At 1173 K, the accessible micropore volume increased with NH_3 treatment and decreased with HCN treatment	The N content of the carbon (0.71%) markedly increased after treatment with NH_3 (2.23%, at 1173 K) or HCN (3.87%, at 973 H). N was chemisorbed as amine groups and nitrile and/or pyridine-like nitrogen.	N was distributed homogeneously for NH_3-treated carbons and significantly more at the surface than in the bulk for HCN-treated carbons	[89]
Four ACs: RB0.8, RA+0.8, RH0.8, and C (Norit N.V., Amersfoort).	(1) NH_3-air; (2) HNO_3 (A); (3) A/NH_3-air; (4) A/HT; (5) A/NH_3(B); (6) B/HT	(1) 503 K, 2.5 h; (2) reflux, 4 h; (4) A/473–873 K, 2.5 h; (5) A/473 K, 2.5 h	Virtually unchanged pore structure.	The amount of N introduced into the AC was significantly higher when amination and ammoxidation were performed after HNO_3-oxidation. The N content was usually <4.4% for nitrogenated ACs. Imide-, amide-, and lactam-type surface species were probably formed. These surface groups could be converted to aromatic nitrogen species by HT >873 K.	Ammoxidation and amination resulted in a different surface chemistry from that of NH_3 treatment at high temperatures (800–1173 K).	[90]
A peat-based microporous gas AC (Norit N.V., Amersfoort, the Netherlands) and an H_3PO_4-activated mesoporous AC (Norit C-Granular).	(1) HNO_3/NH_3; (2) $Ca(ClO)_2$/NH_3	NH_3 treatment: 473 K, 2.5 h	Not evaluated	The carboxylate groups appeared to be converted to amides, whereas hydroxylmethyl groups yielded amines.	With HN_3 at relatively low temperatures, basic carbon surfaces were formed with relatively large ion exchange capacities.	[91]
ACs from Norit N.V., Amersfoort.	(1) HNO_3/NH_3/HT (C-NA); (2) NH_3-air (C-Am); (3) HNO_3/N,N-dimethylethanolamine (C-dmea), N,N-dimethyl-1,3-propanediamine (C-dmpa)/HT.	(1) Boiling, 3 h/503 K, 2.5 h/673–1273 K, 10 min. (2) 693 K; (3) 406 K/673 K.	Not evaluated	The N content (mol%) was: C-dmpa (7.9) > C-NA (5.8) > C-dmea (3.2) > C-Am (2.6). Ammoxidation led to amides, amination to lactams and imides, and further heat treatment to pyridine and pyrrole groups. Reaction of pre-oxidized carbons with organic amines resulted in the attachment of tertiary amine groups.		[92]
An almond shell-derived AC (carbonization: 1173 K, 1 h; activation: 1123 K, 1–8 h steam; 0.15–0.25 mm).	HNO_3	353 K until dryness	A larger decrease in internal surface area and micropore volume with increasing degree of steam activation of the original AC.	Introduction of surface nitro and nitrate groups.		[93]
A commercial AC (D43/1, Carbo-Tech Aktivkohlen GmbH, Essen, Germany), 1131 m^2/g.	HNO_3/NH_3	353 K, 3 h/1170, 1070, 2 h	A slight increase in micropore diameter/increase in micropore volume and size.	Formation of pyridine and pyridine-N-oxide structures at the expense of pyrrolitic moieties/increase in concentrations of pyridine and pyridine-N-oxide groups.	Higher concentration and strength of acidic structures/enhancement of the basic properties at the expense of acidic properties.	[95]

Table 6 (*Continued*)

Raw material	Treatment	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
A coconut charcoal (CG-10, Futamura Chemical Ind., Lt.).	$(CH_3CO)_2O$, H_2SO_4(conc.), HNO_3 (fuming)/28% aqueous NH_3, $Na_2S_2O_4$.	<278 K, 19 h/Room temperature, 24 h.	Amination caused no appreciable changes in surface area, pore volume, or pore size.	Surface nitro groups introduced by nitration were reduced to amino groups by treatment with NH_3/NaS_2O_4.	Nitration and/or amination of the carbon raised its surface basicity and acidity.	[98]
AC, 1288 $m^2 g^{-1}$	NH_3	473–873 K, 3 h	S_{BET} and V_{mi} decreased with NH_3 treatment. S_{BET} was reduced by 14.3% in the product treated at 873 K.	The total N content increased from 0.24% to 0.70–3.83%. High concentration of amides at 673 K and of basic quinones at 873 K.	New acidic groups and basic sites were created.	[94,97]
ACs from different sources.	Urea, NH_3, dicyanodiamine, *N,N*-dimethylformamide.	In autoclave under pressure at 573 K.	The modification of porosity by N introduction into the carbon was more marked in materials with a narrow porosity. The reduction in S_{BET} and V_{mi} was greater with the urea treatment.	Urea favored the introduction of N into the carbons. In these carbons, the N content was 3.4, 3.0 and 2.2%. Mainly pyridinic-like and quaternary-like N or only pyridinic-like N were present in the N,N-dimethylformamide-treated ACs.		[100]
Four ACs prepared from wood (BAX, Westvaco), coconut shell (S208, Waterlink Barnabey and Sutcliffe), bituminous coal (BPL, Calgon), and coconut shell (PCB, Norit).	(1) Urea (saturated aqueous solution); (2) HT.	(1) Stirring, 48 h; (2) N_2, 723 or 1223 K, 1 h	The effect on surface area and pore volumes depended on the AC origin and heat treatment temperature.	The N content increased from 0.19% to 9.30% for BAX, 0.44% to 3.65% for BPL, 0.12% to 1.67% for S208, and 0.11% to 0.70% for PCB. N was higher in the product nitrogenated at 723 K.	After the urea treatment and heat treatment, an increase in the pH values of carbons was observed.	[101]
A commercial AC (CWZ-35, Gryfskand Co. Ltd., Poland; 1323 m^2/g).	NH_3	473–1273 K, 2 h	Not evaluated	Surface C–N and C=N groups were introduced into the carbon.		[102]
AC prepared from a bituminous coal: Oxidation in air 447 K for 24 h; pyrolysis in N_2 at 1173 K for 1h; activation in CO_2 at 1123 K for 16.5 h;	(1) 50% HNO_3/Melamine/HT; (2) Melamine-urea/HT	(1) 4 h/5 h/Ar, 1123 K, 0.5 h (SBC-M1); (2) 923 K, 1123 K (SBC-M2.	The surface area decreased by ≈ 22% for SBC-M1 and 22% for SBC-M$_2$.	N content increased from 1.0% for SBC to 6.0% for SBC-M1 and 5.4% for SBC-M2.	The content of basic groups (meq/g) was 0.05 for SBC, 0.35 for SBC-M1, and 0.72 for SBC-M2.	[104]
Two commercial ACs: wood-based (Macro, Westvaco Inc.) and coal-based (F400, Calgon Corp.), 30–40 mesh size, 1035, 1569 m^2/g.	NH_3	573 K, 1 h; 673 K, 1 h; 1073 K, 2 h.	In comparison to previously HNO_3-oxidized precursors, high temperature NH_3 treatment increased S_{BET} by 151% for Macro and 46% for F400.	N content increased from 0.7% to 8.6% for Macro and from 0.5% to 7.5% for F400.	High temperature NH_3 treatment of oxidized carbons increased the basicity and N content. pH_{pzc} increased from 1.9 to 6.9 for Macro and to 8.5 for F400.	[103]
A bituminous granular AC (Superior Adsorbents Inc., Emlenton, PA), 874 m^2/g.	NH_3	500–800 °C, 1 h	S_{BET} and V_{mi} and V_{me} increased with increasing HTT to 973 K. Pores were created, mostly between 5 and 30 Å.	An increase in N content from 0.64% to 1.61–1.63% and in H content from 0.64% to 0.87%.	The carbon surface became more positively charged at higher pH, as shown by surface charge densities, pH_{pzc} and pH_{IEP}	[105]
A commercial AC (ROW 0.8 Supra (Norit, The Netherlands),	NH_3-O_2	673 K	S_{BET} of the ammoxidated carbon was 1024 m^2/g.	The total N surface concentration increased to 2.1%. The types of N distinguished in the modified material were: N-6 (pyridinic), N-5 (pyrrolic and pyridonic), N-Q (quaternary N) and N-X (N oxides, pyridine-N-oxides).		[107]

Table 6 (*Continued*)

Raw material	Treatment	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
Carbonization and KOH-activation products prepared from a Polish brown coal (Konin mine).	Urea/air	623 K, 3 h	S_{BET} was reduced, but the product still had a well-developed surface area.	The amount of N introduced into ACs ranged from 4.8 wt.% to 5.6 wt.% depending on carbonization temperature. N was incorporated into the carbonaceous products mainly in form of N-6 and N-5 and imine, amine, and amide groups. Pyridonic nitrogen and N-Q were formed by activation of nitrogen-enriched carbons.	Coal treatments enabled preparation of microporous ACs (S_{BET} $\approx$ 3000 m^2/g) considerably enriched with N.	[85]
Three commercial ACs (CWZ-11, CWZ-30, CWZ-35; Gryfskand Co Ltd., Poland), 680–1323 m^2/g.	NH$_3$	873–1073 K, 2 h	S_{BET} and V_{mi} decreased to an extent that depended on the starting AC. The S_{BET} reduction ranged between % for CWZ-30 and % for CW-35.	Infrared bands were associated with NH and CN groups, cyclic amides and aromatic amine groups.	The formation of N groups was favored at higher HTTs (800 °C).	[108]
A coal based AC (F400, Chemviron, USA).	HT/(CH$_3$CO)$_2$O, H$_2$SO$_4$, and HNO$_3$/Na$_2$S$_2$O$_4$-NH$_3$ (aqueous solution).	1173 K, 3 h/< 283 K; 293 K, 24 h; (2) 24 h.	Micropores were enhanced, whereas the pore size distribution in the meso- and macropore regions was not affected.	The N content was 0.45 wt.% for F400 and 1.06 wt.% for the aminated product.	The aminated AC had the lowest pHpzc and pH$_{IEP}$.	[109]
A granular AC (Fitrasorb 200, Calgon, Pittsburgh, PA), 500–850 mμ, S_{BET} = 671 m^2/g.	Polyaniline	10 min	The chemical modification did not produce pore blockage or change in S_{BET}, which was 671 m^2/g for the chemically treated carbon.	An increase in electron-rich aromatic ring structures and nitrogen-containing functional groups.	The surface positive charge density was markedly increased in acidic solution.	[110]
A wood origin AC (BAX-1500, MeadWestvac), 2176 m^2/g.	(1) BAX, 50% HNO$_3$ (BAX-O); (2) BAX, BAX-O; urea (U) or melamine (M) suspension; (2) HT, N$_2$ (BAX-U, BAX-M, BAX-OU, BAX-OM.	(1) 4 h; (2) 5 h; (3) 1223 K, 0.5 h.	The modified products of BAX possessed a markedly reduced surface area and porosity.	The N content increased from 0.2% for BAX to 5.1% (BAX-U) and 8.0% (BAX-OM). Quaternary N, pyridine, pyrrolic/pyridone and pyridine-N-oxide were formed. The presence of oxygen groups on the surface before treatment with urea and melamine favored formation of quaternary N and pyridine-N-oxide. Oxidation incorporated N in form of nitric oxides, nitrate-NO$_3^-$, and pyridine-N-oxide.	Similar types of groups were formed with urea and melamine, although the relative amounts of the groups differed	[86]
A commercial AC (CarboTech D45/2, DMT Modern Fuels Unit, Essen, Germany), particle size reduced to <180 μ; N content, 0.37 wt.%; 1003 m^2/g, V_{mi} (CO$_2$ adsorption), 0.252 cm^3/g.	Urea carried by He	723 (U1), 1073 (U2) K; 1 h	A decrease in S_{BET} of 34% for U1 and of 29% for U2. V_{mi} increased by 22.5% for U1 and by 48.8% for U2.	The N content increased to 8.55 wt.% for U1 and to 6.52 wt.% for U2.		[111]
AC (Norit Darco), 20 × 40LI, 650 m^2/g.	Nitric acid/thionyl chloride/ethylenediamine.	313 K, 7 h/343 K, 5 h/363 K, 24 h.	Not evaluated	The nitrogen content increased from 2.10% to 10.29% due to the AC treatment. C–Cl, C=S, S=O and N–H bonds and CON were identified by FT-IR spectroscopy.	Functional groups containing Cl, S, or N were introduced into the carbon surface. The product obtained was more acidic than the virgin AC. pH$_{pzc}$ was 2.55 and 9.6, respectively.	[112]

Table 6 (*Continued*)

Raw material	Treatment	Experimental conditions	Textural modifications	Chemical modifications	Observations	Reference
A Polish high volatile bituminous coal (Kazimiers-Juliusz mine) (KJ).	The demineralized precursor (KJD), carbonization product (KJDC), and AC (KJDCA) were treated in an NH_3-air mixture at ratio of 1:3.	623 K, 5 h	Major development of surface area with dominant presence of micropores.	The largest amount of N was introduced into demineralized coal (16 wt.%), followed by the AC (7.1%) and carbonized coal (6.7%). Nitrogen was introduced mainly in the form of imines, amines, and amides, N-5 and N-6. Oxidized nitrogen species were formed.		[113]
ACs prepared from brown coal (L), sub-bituminous coal (S), bituminous coal (B) and anthracite (A) by demineralization with concentrated HCl and HF, carbonization (Ar, 973 K, 1 h) and activation: (KOH, 973 K, 0.75 h).	NH_3-air mixture at a ratio of 1:3.	573 or 623 K, 5 h	Ammoxidation produced either decreases in surface area and pore volume or textural improvement, depending on its application to AC or to the precursor and carbonized product (pre-activation).	The N content in the nitrogenated ACs ranged from 4.0 wt.% to 7.4 wt.%.	ACs ammoxidated at the stages of precursor and carbonized product were acidic in character, whereas those ammoxidated after activation were basic.	[114]

The majority of the reviewed studies concluded that H_2O_2 treatment produces minimal textural modifications [1,3,5,6], although both increases [7] and decreases [8] in surface area were reported. Most studies on the influence of HNO_3 treatment on carbon texture showed stronger effects at higher acid concentrations due to the destruction of pore walls [6], which decreases the surface area and pore volume of the treated carbons. Severe oxidation conditions might even lead to complete destruction of the carbon texture [9]. The surface chemistry can influence the texture of the oxidized material through the blocking of pore entrances by oxygen functional groups [10].

Table 7
Functionalization treatments of ACs.

Raw material	Coordinated ligand functionalization	Textural modifications	Chemical modifications	Reference
Commercial Norit Darko	Nitric acid oxidation and $SOCl_2$ treatment.	The modified AC appeared to have a smoother surface.	Potentiometric titration showed that the modifications introduced more negative surface charges, favoring cation sorption	[117]
Comercial Filtrasorb Tl 830	Zyrconyl nitrate adsorption from aqueous phase	Surface area and pore texture similar after treatment.	XAS data at the Zr K-edge suggest that the structure of the zirconyl nitrate coating is constructed from chains of edge-sharing ZrO_8 trigonal dodecahedra bound to each other through two double hydroxyl bridges.	[118]
Commercial Superdarco	Iron and quaternary ammonium surfactants adsorption from aqueous phase	The iron (hydr)oxide diminished porosity primarily in the 4–15A° range, indicating that these iron hydr(oxide) nanoparticles were 4–15A° in size. The pyridinium surfactant (an alternative to Arquad 2C-75–) occupied pores throughout the 4–500A° width range; and there was an 0.3 mL/g reduction in these pore volumes for the 17.8% pyridinium surfactant loading;	Increasing the positive charge may align the mesopores and macropores of an AC.	[119]
Commercial AC Merck K24504014)	N-(4-Amino-1,6-dihydro-1-methyl-5-nitroso-6-oxopyrimidin-2-yl)-N0-[bis(2-aminoethyl)]ethylenediamine dichlorhydrate (2.2HCl) adsorption from aqueous solution	Not evaluated	Adsorption of ligands on the ACM sorbent provides a route to develop $H_2N–(CH_2)_2–NR–(CH_2)_2–NH_2$ functionalities on its graphitic surface.	[120]
Commercial AC	Ethylenediamine adsorption from aqueous solution	Not evaluated	Elemental analysis indicated 59.10% carbon, 7.818% nitrogen and 2.904% hydrogen in modified AC.	[121]
Commercial AC	1-(2-thiazolylazo)-2-naphthol adsorption from aqueous solution	Not evaluated	Not evaluated	[122]

Table 7 (*Continued*)

Raw material	Coordinated ligand functionalization	Textural modifications	Chemical modifications	Reference
Commercial AC	2-((2-aminoethylamino)methyl)phenol adsorption from aqueous solution	Not evaluated	Comparison of the IR spectrum of AC-AMP with AC-COOH; the new peak at 1451.44 – cm⁻1 resulted from ₋CH2 and stretching vibrations of aromatic C C bonds. A strong band at 754.20 cm⁻1 was caused by ₋C–H of the aromatic ring in 2-((2-aminoethylamino)methyl)phenol. The intensive feature at 1564.41 cm⁻1 was assigned to ₋C C, confirming that AC was successfully modified by 2-((2-aminoethylamino)methyl)phenol.	[123]
Commercial AC (CMK-33)	Carboxymethylated polyethyleneimine (CMPI) adsorption from aqueous solution	There was no significant change in the unit cell parameter ($a0 = 2 \times 3 - 1/2\, d1\, 0\, 0$) calculated from the (1 0 0) interplanar spacing, which remained 9.71 nm after surface treatment of CMK-3 with CMPEI.	Surface modification of CMK-3 with CMPEI was investigated by FT-IR. CMPEI/CMK-3 exhibited a trend for the small band at 1400 – cm⁻1 to become much sharper and for the band around 1600 to shift to higher energy *versus* CMK-3, indicating the presence of CMPEI on the surface of CMK-3.	[124]
Commercial AC Merck K24504014	L-glutamic acid-pyrimidine derivative adsorption from aqueous solutions.	Not evaluated	The comparison of N1s bands in XPS diagrams of the pure solid ligand with those of the corresponding hybrid AC-ligand revealed a slight but informative shift to higher energy values (0.3 eV) in the spectrum of AC-ligand. Because this band comprises contributions from five planar nitrogen atoms (those in the pyrimidine ring or directly connected to it), this shift indicates an increase in the electronic shielding of the pyrimidine moiety, suggesting some pi-electron donation from arene centers to the pyrimidine nucleus.	[125]
Rice husk-based AC (RHC)	Poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) adsorption from aqueous phase on nitric treated AC.	The surface area of the resulting PDMAEMA-RHC was reduced from 1347 to 789 – m² g⁻1, and the average pore size decreased from 4.1 to 3.8 nm	Using TGA analysis, it was concluded that the content of PDMAEMA in the composite materials was around 12 wt.%.	[112]
Commercial AC	Polypyrrole-impregnated porous carbon was readily synthesized using vapor infiltration polymerization of pyrrole monomers.	The pore size shift from 22.5 to 17.5 nm was confirmed in the pore size distribution analysis of porous carbon and functionalized porous carbon, which was coincident with the pore wall increase in TEM analysis. Hence, modification of the pore wall surface was successfully achieved.	The FT-IR spectrum of PPy-impregnated porous carbon exhibited characteristic PPy bands at 1546 and 3452 cm⁻1, due to C–N stretching and N–H stretching, respectively (Fig. S2). These representative peaks of PPy demonstrated that the increase in N originated from the amine group of the introduced PPy layer. Based on one nitrogen atom per pyrrole molecule and the ratio of carbon and nitrogen in PPy (C/N = 3.4), the EA results showed the amount of PPy (43 wt.%) in the functionalized porous carbon.	[127]
Multiwall carbon nanotube	Ethylenediamine	Unknown	FTIR, TGA and elemental analysis showed an increase in N content	[129]

Studies have generally shown that the surface chemistry of materials is affected by H_2O_2 oxidation treatment, mainly by introducing surface oxygen groups (SOGs) [1,3,5,7,8,11], such us carboxyl, ketone, and ether groups [3]. Nitric acid oxidation usually produces marked chemical modifications, with a high amount of SOGs, including carboxyl, carbonyl, phenol, and lactone groups [6,12]. The formation of acidic groups on the surface of the treated material tends to increase the total acidity of the carbon, with some studies reporting a three-fold rise [8,10,13,14].

2.1.2. Ozone treatment

Ozone is a powerful oxidizing gas ($E^\circ = 2.07$ V), far more potent than oxygen molecule, which finds applications in various fields, including medicine, water treatment, bleaching, and manufacturing and food industries. Because of its chemical structure, the ozone molecule can react selectively with numerous organic and inorganic compounds through cycloaddition, electrophilic attack, electron transfer and oxygen transfer reactions [19]. Under certain conditions, ozone can also decompose into free radical species with high oxidizing capacity, including the hydroxyl radical (HO•), which is the second most potent oxidant ($E^\circ = 2.8$ V) after fluorine. The reactivity between ozone and carbon materials has long been known [20–22]. It was proposed that gaseous ozone is chemisorbed at room temperature on the AC surface rather than being physically adsorbed. Two types of adsorption centers can be considered: (i) centers where the abstraction of an oxygen atom takes place; and (ii) centers where ozone is added to form an ozonide according to Criegge's mechanism. The products of both reactions can suffer

Table 8
AC modified by hydrogen peroxide, nitric acid or ozone oxidation as adsorbent for water treatment.

Adsorbent	Contaminant	Adsorption conditions	Observation	Reference
Commercial, manufactured from coal particles through carbonization and steam activation at 850 °C; oxidized using HNO_3 and H_2O_2 at 100 °C during 1 h and washed until neutral pH. Adsorbents after dried at 120 °C during 2 h.	Cr (VI).	AC (0.025–0.15 g) was added to 25 mL of sodium chromate ($Na_2CrO_4 \cdot 4H_2O$) solutions. Initial pH was adjusted from 1 to 9 using 1N HCl. Flasks were sealed and then agitated (80 strokes/min) from 0.5 to 3 h at 25 C; reaction mixture was after filtered and the adsorbed amount of Cr (VI) was evaluated.	Application: wastewater decontamination. Adsorption capacity increased after oxidation and heat treatment. Interaction between adsorbate ion and adsorbent surface was found to be chemical in nature.	[11]
5 g of commercial AC oxidized using concentrated HNO_3 (50 cm^3), heated at 80 °C until dryness, washed with distilled water and dried overnight at 110 °C; adsorbent was finally heated at 600 °C under N_2 flow during 2 h.	Cr(III); Cr(VI).	Adsorption isotherms of Cr(III) and Cr(VI) were obtained using sealed flasks containing 0.15 g of carbon in 50 cm^3 of aqueous solutions of $Cr(NO_3)_3 \cdot 9H_2O$ and $(NH_4)_2,CrO_4$, respectively; one electrolyte (NaCl) was present in the solution. Flasks were agitated at 25 °C during 48 h and after concentrations were measured.	Application: metal adsorption. Adsorption of both Cr(III) and Cr(Vl) was enhanced by the presence of acidic surface oxygen complexes.	[13]
Coconut shell activated in steam at 900 °C, and washed with water; after oxidized in HNO_3 solution for 4 and 48 h, extracted with water until constant pH extract and dried at 75 °C.	Cd(II).	Adsorption: solutions containing AC and cadmium nitrate were maintained at 25 °C during 48 h; the carbons were filtered and rinsed with water (0 °C). Desorption: using Soxhlet extraction during 24 h.	Aplication: metal adsorption; Cd(II) adsorption capacity was strongly enhanced after oxidation and significantly reduced after heat treatment due to the decomposition of surface oxygen functional groups. Adsorption capacity increased with the increase of oxidation time, due to the incorporation of more oxygen functionalities.	[16]
Commercial Filtrasorb 200 (Calgon Corp.) ground into particles with 20–32 mesh size, oxidized using HNO_3 (1 g/10 mL) with different concentrations; and after washed using deionized water.	Copper (chosen as a typical toxic metal).	AC (0.01–2.5 g) added to 100 mL of buffered $CuCl_2$ solution (1×10^{-3} M) of pH 4.9 containing sodium acetate (NaAc) 0.07 M and acetic acid (HAc) 0.03 M; one electrolyte (sodium chloride 0.01 M) was also added. The solution was agitated and maintained at 25 °C during 48 h.	Application: metal adsorption; Treated AC showed good adsorption. Most of the copper ions adsorbed rapidly in the first 2 h; adsorption equilibrium was established in around 8 h.	[12]
AC prepared from olive stones, carbonized at 1100 °C during 1 h under nitrogen flow; 4 g of AC were oxidized using 80 cm^3 of concentrated HNO_3 (15 M) under agitation at ambient temperature during 24 h, washed with distilled water until neutral pH, separated by filtration and dried under vacuum at 50 °C during night.	*p*-nitrophenol.	After weighted, AC samples were kept at 110 °C in air overnight; AC (100 mg) was contacted with 100 mL of concentrated solutions of pNP. Flasks were shaken at 25 °C during 1 week; p-nitrophenol solutions were then separated from adsorbent by sedimentation.	Application: adsorption of substituted phenols. The presence of CO-evolving groups showed no influence on *p*-nitrophenol uptakes. The presence of carboxylic groups, which thermally decompose into CO_2, inhibited *p*-nitrophenol adsorption.	[2]
9 g of commercial Norit ROX 0.8 were oxidized using 200 cm^3 of HNO_3 (5 M) heated to boiling temperature; the reflux was maintained for 3 h. AC was then washed with distilled water till neutral pH and dried in air at 110 °C during 24 h.	Anionic dyes Cationic dyes Real textile dyes.	AC (50 mg) crushed to minimize mass transfer resistance was mixed with 50 cm^3 of dye solution (600 mg/dm^3); the suspension was agitated at 20 °C during 48 h. The adsorbent was separated by centrifugation and the dye solution was further analyzed.	Application: dye removal. The adsorbent treated with HNO_3 showed poor performance for anionic dyes adsorption, but good performance for cationic dyes. Color removal from textile wastewaters was higher using basic thermally treated ACs.	[6]
Microporous steam-activated coconut-based AC treated with ozone in a fluidized bed reactor (see Table 1 for conditions)	2-methylisoborneol.	Adsorption isotherms were obtained.	The adsorbent affinity for 2-methylisoborneol decreased with the oxidation treatment.	[61]
Filtrasorb 400 (Calgon Carbon Corp) treated with ozone in a fixed bed reactor (see Table 1 for conditions)	Methylene blue.	Methylene blue adsorption index was measured.	The amount of methylene blue adsorbed decreased with longer ozonation time.	[28]

Table 8 (*Continued*)

Adsorbent	Contaminant	Adsorption conditions	Observation	Reference
Filtrasorb 400 (Calgon Carbon Corp) treated with ozone in a fixed bed reactor (see Ref. 28 in Table 1 for conditions).	Cd(II) and Hg(II).	Adsorption isotherms were measured at pH 6. Additional equilibrium adsorption experiments were carried out in the 2–12 pH range.	Ozonation treatment enhanced the adsorption capacity of AC for Cd(II) but prevented to some extent the adsorption of Hg(II).	[130]
Filtrasorb 400 (Calgon Carbon Corp) treated with ozone in a fixed bed reactor (see Ref. 28 in Table 1 for conditions).	Naphthalenesulfonic acids.	Adsorption isotherms were measured at pH 6. Additional equilibrium adsorption experiments were carried out in the 2–12 pH range.	A significant reduction in adsorption capacity of aromatic sulfonic compounds was observed with the ozone treatment of AC. Adsorption of naphtalensulfonic acids takes place mainly by π–π dispersion interactions.	[132]
Filtrasorb 400 (Calgon Carbon Corp) treated with ozone in a fixed bed reactor (Ref. 28, Table 3).	Cr(III).	Adsorption isotherms were measured at pH 6. Additional equilibrium adsorption experiments were carried out in the 2–12 pH range.	The adsorption capacity and affinity of the adsorbent for Cr(III) increased with the increase in acidic SOGs created by the ozone treatment.Electrostatic interactions prevail in the adsorption process.	[131]

further surface changes, including the generation of CO and CO_2, leaving oxygen containing groups on the carbon surface. It was later suggested that ozone may also decompose to oxygen on carbon materials *via* catalysis [23]. A recent kinetic study carried out with 20 granular ACs with different textural and chemical surface properties confirmed the coexistence of catalytic and non-catalytic pathways of ozone decomposition [24]. The fact that ozone decomposes rapidly on AC has led to its use in air cleaners or even building materials to remove ozone from indoor air [25–27].

A further potential utilization of the interaction between ozone and carbon is the functionalization of the material with SOGs to enhance its adsorption and/or catalytic properties. Extensive

Table 9
Sulfurized AC as adsorbent for water treatment.

Adsorbent	Contaminant	Adsorption conditions	Observation	Reference
Three ACs (A, B, C) were used; particle sizes: A, 0.5–2.38 mm; B, 1.0–2.0 mm; C, 1.0–2.38 mm. treated with A,B,C-H_2O_2 (AO,BO,CO) (A,B,C) and (AO,BO,CO)-CS_2/HT/CS_2 (washing).	$HgCl_2$	Temperature: 298 K Equilibration time: 1 weak Adsorptive solution: unadjusted pH and buffered with HCl/KCl (pH range 1.0–2.2) and with K_2HPO_4–$3H_2O$/KH_2PO_4 (pH range 5–7).	Mercury adsorption was increased by the introduction of surface sulfur on the carbons, although not all sulfur complexes exhibited the same adsorption behavior towards mercury.	[77]
AC (Merck, Darmstadt), average particle size, 1.5 mm; S_{BET} = 921 m^2/g) treated with SO_2, H_2S, SO_2-H_2S.	Hg(II)	Temperature: 298 K Equilibration time: 9–173 h.	Mercury adsorption substantially increased when sulfurized in H_2S at 1173 K and successively in SO_2 and H_2S at 303 K and transported with N_2 at 473 K. However, treatments in SO_2 at 303 K and at 1173 K markedly decreased the adsorption.	[78]
AC (Merck, Darmstadt), average particle size, 1.5 mm; S_{BET} = 921 m^2/g) treated with H_2S, SO_2-H_2S	Pb(II), Cd(II)	Temperature: 298–318 K Equilibration time: <7 days, Pb(II); 6–140 h, Cd(II) Adsorptive solution: pH, 5.5 or 2.0 for Pb(II) and 6.2 or 2.0 for Cd(II). pH 2 was fixed with concentrated $HClO_4$ solution.	After treatments of AC, the adsorption of metallic ions, especially Pb(II), increased at unchanged solution pH and at 298 K. A decrease in solution pH markedly reduced Pb(II) adsorption. Cd(II) adsorption depended on the adsorbent. A change in adsorption temperature generally decreased Pb(II) and Cd(II) adsorption. Adsorption kinetics depended on the adsorption system, pH, and temperature.	[83,133]
AC (Merck), average particle size, 1.5 mm, S_{BET} = 921 m^2/g, treated with H_2S, SO_2-H_2S	Hg(II), Cd(II), Pb(II)	Temperature: 298 K Equilibration time: different depending on the adsorbent Adsorptive solution: pH, 2.0 and 4.4 for Hg(II), 6.2 for Cd(II) or 5.4 for Pb(II).	Much higher adsorption for Hg(II) than for Cd(II) and Pb(II). Adsorption of Hg(II) was drastically reduced at pH 2.0.	[133]
AC (Fluka) 100–150 μm, 1100 m^2/g) treated with sodium dietyl dithiocarbamate (SDDC).	Cu(II), Zn(II), Cr(VI)	In the adsorption experiments, fixed bed modified activated columns were used. The flow rate was maintained at 2 mL min^{-1} with a contact time of about 8 min.	Treatment of AC with SDDC increased the adsorption capacity four-fold for Cu(II) and Zn(II) and two-fold for Cr(VI).	[99]
Bagasse pith treated: (1) Carbonization: 473 K; (2) ctivation-sulfurization: steam, H_2S; steam, SO_2; steam, H_2S.	Hg(II)	Temperature: 303–333 K Equilibration time: 4 h Adsorptive solution: pH, 2–10; ionic strength adjusted to 0.001–0.5 mol L^{-1} with NaCl.	The uptake of Hg(II) was influenced by the sulfurization treatment in the order SO_2-H_2S > SO_2 > H_2S. Optimum pH range of Hg(II) adsorption was 4–9 if the carbon contained sulfur and 6–9 if it did not. A decrease in ionic strength and increase in adsorption temperature improved the Hg(II) uptake.	[79]

Table 9 (*Continued*)

Adsorbent	Contaminant	Adsorption conditions	Observation	Reference
AC (Merck; 1.5 mm, $S_{BET} = 921\,m^2/g$) treated by SO_2, SO_2-H_2S	Cd(II), Pb(II)	Temperature: 298 and 318 K Equilibration time: 15 h–130 h. Adsorptive solution: pH, 6.2 and 2.0 for Cd(II) and 5.4 and 2.0 for Pb(II).	For Cd^{2+}, the various sulfurizing treatments of the carbon had no significant effect on the adsorption kinetics but increased the adsorption capacity. By heating AC in SO_2 at 1173 K, adsorption of Cd(II) was increased by 70.3% with respect to the virgin AC. Adsorption also increased with a rise in adsorption temperature from 298 K to 318 K. The introduction of sulfur slowed the adsorption rate of of Pb^{2+} and markedly increased its extent. Adsorption kinetics and extent were favored by partial removal of sulfur from the sulfurized products. The process was also faster at higher adsorption temperature.	[134,135]
Coconut shell-based granular AC (Active Carbon Ltd., Hyderabad, India), S content, 0.56 wt.%; S_{BET}, $1000\,m^2/g$, treated with Na_2S	Pb(II)	Batch studies: Temperature: 310 K Equilibration time: 20 h Adsorptive solution: pH, 5. Dynamic column study: Bed height: 0.3–0.5 m Hydraulic loading rate: $7.5\,m^3/(hm^2)$.	Adsorption of Pb(II) increased by 35.0% on the Na_2S-treated AC.	[82]
Commercial AC (CAC): 80–230 mesh size, $S_{BET} = 1287\,m^2/g$, $V_t = 0.79\,cm^3/g$), and a nut shell-H_3PO_4 activation product (PAC): 80–230 mesh size, $S_{BET} = 1557\,m^2/g$, $V_t = 0.93\,cm^3/g$), treated with SO_2.	Cd(II)	Temperature: 298–303 K Equilibration time: 4 h	Adsorption was higher at pH 8–12. Maximum removal was 92.4% for the PAC sulfurized product, with a 37.1% increase in adsorption capacity.	[80]
AC prepared from coconut shells (Shanghai AC Co., Ltd., Shanghai, China), $S_{BET} = 1884\,m^2/g$, treated with S.	Hg(II)	Temperature: 298 K Equilibration time: 24 h Adsorptive solution: pH fixed at 5.5 with NaAc/HAc and ionic strength controlled with $NaNO_3$.	Impregnation at 673 K produced the largest equilibrium uptake of Hg(II) (800 mg/g) at pH 5.5. At C_0 (initial mercury concentration) = 43 mg/L, removal ratios were >98% in pH range 2–11.	[76]

research has been done on the characterization and identification of SOGs fixed on carbon surfaces by ozonation, with papers on the ozonation of chars [28–31], carbon blacks [20,32–36], carbon fibers [37–39], carbon cloths [40], carbon nanotubes [41–43], graphite [35,36,44,45], fullerenes [46–48], glassy carbons [49,50], fly ash carbons [34,51], soot particles [52], and ACs.

Table 3 compiles studies published over the past decade that analyzed the textural and/or chemical properties of ACs after exposure to gaseous ozone. There have been a few other reports on the interaction of aqueous ozone with ACs, but their objective was not the functionalization of AC but rather the removal of residual ozone from treated water [53] or, more frequently, enhancement of the effectiveness of ozone oxidation to remove aqueous pollutants by generating secondary oxidants such as hydroxyl radicals [54–59]. Although the AC surface can be oxidized with aqueous ozone, this process is far less effective than gaseous ozone treatments due to the low solubility of ozone in water.

The studies in Table 3 generally report that ozonation drastically increases the number and type of acidic oxygen-containing surface groups. However, its impact on the textural properties are more controversial, with some authors finding only minor effects of ozone on the AC surface area and pore volume [60,61] and others observing a decrease in surface area and destruction of microporosity [28,31,62]. The impact of ozone on the texture of ACs appears to be highly dependent on the dose, since a low dose can even produce an increased surface area due to carbon gasification, whereas high ozone doses destroy pore walls and fix large amounts of SOGs at the entrance of micropores, markedly reducing the surface area [28,62,63].

SOGs have been identified on ozonated ACs by FTIR spectroscopy, XPS, elemental analysis, and titration methods. Although there is a consensus that ozonation of AC leads to the fixation of acidic SOGs and the removal of basic SOGs, there is disagreement on their concentration, type, and relative distribution. Valdés et al. [28] found linear relationships between the dose of ozone applied to the AC Filtrasorb 400 and the numbers of acidic groups formed and basic groups removed. On average, 1 mmol of ozone was consumed in the formation of 16 µeq/g of acidic sites and removal of 3.2 µeq/g of basic sites. Similar figures were found by Álvarez et al. [64] using the same commercial AC. However, the consumption of ozone appears to be highly dependent on the properties and any pre-treatment of the AC [24,65]. Most of the studies describe carboxylic acids as the main SOG fixed on AC by ozonation, making the carbon surface more hydrophilic [66]. As a result, the pH of the point of zero charge (pH_{PZC}) of the AC markedly decreases [28,64,67].

The temperature of ozone treatment was below 250 °C in all investigations reviewed, since ozone decomposes into oxygen above this temperature [30], and most studies were conducted at room temperature. The effect of ozonation temperature was investigated by Considine et al. [61] and Álvarez et al. [64], who found that it plays a role in the ozone-AC reaction mechanisms and therefore affects the type of SOG fixed on the AC. At 25 °C, carboxylic acids were the main SOG formed, while a more even distribution of carboxylic, hydroxyl, and carbonyl SOGs was observed at 100 °C, when the gasification effect of ozone was also more evident. Jaramillo et al. [67] compared treatments of a cherry stone-based AC with various oxidizing agents. They found that ozone, unlike nitric acid, hydrogen peroxide, or air, barely affected the textural properties of the virgin AC but led to the fixation of large amounts of acidic surface groups on the mesopore structure, leaving the non-polar surface of micropores practically unaffected. The authors suggested that ozone-treated ACs might be bifunctional with a hydrophobic microporous structure and a hydrophilic external surface due to the presence of acidic SOGs.

It can be concluded from the reviewed literature on AC oxidation treatments that surface oxygen complexes are the predominant type of surface functional group generated on AC. Surface oxygen complexes on AC can be created by two main oxidation methods, dry and wet oxidation. Dry oxidation involves reactions with oxi-

Table 10
Nitrogenated AC as adsorbent for water treatment.

Adsorbent	Contaminant	Adsorption conditions	Observation	Reference
Commercial AC (D43/1, Carbo-Tech Aktivkohlen GmbH, Essen, Germany), 1131 m^2/g, treated with HNO_3, NH_3.	Cu(II)	Temperature: 298 K Equilibration time: Adsorptive solution: at different pHs, adjusted with H_2SO_4 or NaOH.	Adsorption depended on the nature and quantity of surface acid–base functionalities and on the pH.	[96]
A coconut charcoal (CG-10, Futamura Chemical Ind., Lt.) treated with $CH_3CO)_2O$, H_2SO_4(conc.), HNO_3 (fuming)/28% aqueous NH_3, $Na_2S_2O_4$.	Benzoic acid	Temperature: 298 K Equilibration time: 24 h.	Adsorption decreased after amination of the AC.	[98]
AC (Fluka), 100–150 μm, 1100 m^2/g, treated with Tetrabutyl ammonium iodide.	Cyanide	In the adsorption experiments, fixed bed modified activated columns were used. The flow rate was maintained at 2 mL min^{-1}	Removal capacity increased around five-fold *versus* plain carbon.	[99]
Two commercial ACs: wood-based (Macro, Westvaco Inc.) and coal-based (F400, Calgon Corp.), 30–40 mesh size, 1035, 1569 m^2/g, treated with NH_3.	Dissolved natural organic matter (DNOM).	Temperature: 295 K Time: 2 weeks.	Marked enhancement of DNOM uptake was mainly associated with the increase in accessible surface area and surface basicity.	[103]
A bituminous granular AC (Superior Adsorbents Inc., Emlenton, PA), 250–180 μ, 874 m^2/g, treated with NH_3.	Perchlorate	Temperature: 293 K Equilibration time: 24 h.	973 K was the most favorable NH_3 treatment temperature for the most positively charged surface at near neutral pH and the highest ClO_4^- adsorption	[105]
AC treated with O_2-NH_3/HNO_3.	Pb(II), Hg(II), Cd(II)	Equilibration time: 48 h Adsorptive solution: at pH 1.33, adjusted with HNO_3.	The order of adsorption capacity was Hg(II)> Pb(II) > Cd(II).	[107]
A coal-based AC (F400, Chemviron, USA), treated with HT/$(CH_3CO)_2O$, H_2SO_4, and HNO_3/$Na_2S_2O_4$-NH_3 (aqueous solution).	Atrazine	Temperature: 298 K Equilibration time: 7 days Adsorptive solutions: at pH 5, adjusted with H_2SO_4 and NaOH.	Sorption of atrazine depended on the pore size distribution and surface functionality.	[109]
Three commercial ACs (CWZ-11, CWZ-30, CWZ-35; Gryfskand Co Ltd., Poland), 680–1323 m^2/g, treated with NH_3.	Phenol	Temperature: 298 K Equilibration time: 3 h.	Enhanced adsorption of phenol from water depended on the HTT in NH_3 and the porous structure; optimum HTT was 973 K. The adsorption of phenol was greater on carbons with higher micropore volumes.	[108]
Commercial granular AC (Fitrasorb 200, Calgon, Pittsburgh, PA), 500–850 mμ, 671 m^2/g, treated with Polyanilina.	As(V)	Temperature: 298 K Equilibration time: 48 h Adsorptive solution: pH adjusted with $HClO_4$ or NaOH and ionic strength fixed to 0.05 M with $NaClO_4$.	The maximum adsorption capacity at an optimal pH of 5.5 was enhanced by 84%. The arsenic concentration, which ranged from 120 to 1910 ppb, was reduced to <10 ppb. The presence of humic acid had no major impact on arsenic adsorption dynamics.	[110]
Commercial AC (CarboTech D45/2, DMT Modern Fuels Unit, Essen, Germany), particle size reduced to <l180 μ; N content, 0.37 wt.%; 1003 m^2/g, V_{mi} (CO_2 adsorption), 0.252 cm^3/g, treated by urea and carried by He.	Phenol	Temperature: 293 K Equilibration time: 8 days Adsorptive solution: buffered with sodium hydrogen phosphate.	Enhancement of phenol adsorption of phenol was due to the basic character of the urea-treated AC.	[111]
Commercial AC (Norit Darco), 20 × 40LI, 650 m^2/g, treated using nitric acid/thionyl chloride/ethylenediamine.	Hg(II)	Temperature: 298 K Equilibration time: 24 h Adsorptive solution: acidified with HNO_3 and buffered with KH_2PO_4-NaOH and NaAc-HAc.	Hg adsorption was faster (<30 min), greater (>200%), and occurred over a wider pH range (4–10 *versus* 5–7).	[112]

dizing gases (e.g., steam, CO_2, ozone, etc.) at high temperatures, while wet oxidation involves reactions between AC surfaces and oxidizing solutions (e.g., aqueous solutions of HNO_3, H_2O_2, and O_3) under relatively mild reaction conditions (20–100 °C). In addition, various authors have addressed the oxidation of AC by using O_2, Cl_2, ClO^-, ClO_2, $S_2O_8^{2-}$, MnO_4^-, $Cr_2O_7^{2-}$, H_2SO_4, and oxygen plasma, among other agents [1,3,11,13,15,50,63,68].

2.2. Sulfuration treatments

The ability of carbons to bind sulfur on their surface has been known for almost a century [69]. During this time, carbon–sulfur complexes have been reported on a wide variety of carbonaceous materials, including AC. There is controversy related to the carbon–sulfur complexes formation, their high thermal stability, the manner and the form in which they can decompose their influence on the surface behavior of carbons, and the nature of the carbon surface structure, among other factors [70]. The amount of sulfur introduced into carbons by sulfurization can be as high as 40–50% [70]. Puri et al. [71,72] suggested that sulfur was fixed partly by addition at unsaturated sites and partly by substitution *via* reactions with certain oxygen- and hydrogen-containing groups. They also concluded that the fixed sulfur was in the form of sulfides, which catalyze the oxidation of azide ion by iodine. The surface sulfur complexes of carbons show many similarities in regard to their non stoichiometric character and chemical–physical behavior. They cannot be extracted with solvents or completely decomposed by heat treatment in vacuum at 1273 K, but they can be completely

Table 11
AC funcionalized with coordinated ligands as adsorbent for water treatment.

Adsorbent	Contaminant	Adsorption conditions	Observations	Reference
Commercial activated carbon treated with zirconyl nitrate adsorption from aqueous phase.	Arsenate	Temperature: 298 K Equilibration time: 8 days Adsorptive solution: Not Buffered.	Zr K-edge EXAFS data indicate that arsenate tetrahedra form monodentate mononuclear surface complexes with free hydroxyl groups of zirconyl dodecahedra, whereby each bidentate nitrate group is exchanged by up to two arsenate groups. The inner-sphere arsenate binding to the Zr-AC surface sites constrained with the spectroscopic results was used in the formulation of a surface complexation model that successfully described the adsorption behavior of arsenate in the pH range 4-12.	[118]
Iron and quaternary ammonium surfactant adsorption from aqueous phase by commercial activated carbon	Arsenate and perchlorate	Temperature: 298 K Equilibration time: 24 h Adsorptive solution: acidified with HNO_3 and buffered with KH_2PO_4-NaOH and NaAc-HAc	Results indicated that when ACs are impregnated with iron and quaternary ammonium surfactants, they offer considerable potential for remediating groundwater that contains both arsenic and perchlorate *via* simultaneous removal mechanisms.	[119]
N-(4-Amino-1,6-dihydro-1-methyl-5-nitroso-6-oxopyrimidin-2-yl)-N0-[bis(2-aminoethyl)]ethylenediamine dichlorhydrate (2_2HCl) adsorption from aqueous solution by commercial activated carbon	Cobalt, nickel, and copper	Temperature: 298 K Equilibration time: 48 h Adsorptive solution: 4–10 adjusted with KOH	Results demonstrated that the adsorption capacities of the AC–ligand hybrid material for the three metalions studied correlated with the stabilities of the tri-amine-metal-ion bonds formed during the adsorption process.	[120]
Ethylenediamine adsorption from aqueous solution by commercial activated carbon	Chromium, mercury, iron, and lead	Temperature: 298 K Equilibration time: 48 h Adsorptive solution pH: 4–10.	Maximum static adsorption capacity of the sorbent under optimum conditions was 39.4, 28.9, 60.5, and 49.9 mg g^{-1} for Cr(III), Fe(III), Hg(II), and Pb(II), respectively. Time to 94% adsorption of target metal ions was <2 min.	[121]
Commercial activated carbon treated with 1-(2-thiazolylazo)-2-naphthol adsorption	Mercury	Temperature: 298 K Equilibration time: 48 h Adsorptive solution pH: 6 adjusted with ammonium acetate.	The new material removes traces of mercury(II) in the pH range 6.0 ± 0.2. Other parameters that influence quantitative recovery of mercury(II), i.e., %concentration of TAN in AC, amount of TAN–AC, preconcentration time, and volume of aqueous phase, were varied and optimized.	[122]
Commercial activated carbon treated with 2-((2-aminoethylamino)methyl)phenol	Cu(II), Fe(II) and Pb(II)	Temperature: 298 K Equilibration time: 48 h Adsorptive solution pH: 1–6 adjusted with HCl and NaOH.	The adsorption capacity of AC-AMP was 12.1, 67.1, and 16.2 mg g^{-1} for Cu(II), Fe(III), and Pb(II), respectively.	[123]
Commercial activated carbon treated with Carboxymethylated polyethyleneimine (CMPI)	Uranium	Temperature: 295 K Equilibration time: 24 Adsorptive solution: 4 adjusted with HCl NaOH.	Adsorption of uranyl ions on the functionalized carbons followed the Langmuir isotherm model. The maximum uranium adsorption capacity of the adsorbent (by Langmuir model) was 151.5 mg U/g adsorbent. The loading stability of uranium on the adsorbent was examined at pH 4.	[124]
Commercial activated carbon treated with L-glutamic acid-pyrimidine derivatives.	Cu(II)	Temperature: 298 K Equilibration time: 24 h Adsorptive solution pH: Adjusted with KOH and HCl	In the 2.5–6.5 pH range, the uptake of the adsorbate was markedly reduced with higher pH value, related to ligand deprotonation. The ligand uptake is proposed to take place *via* p–p interactions between the planar pyrimidine moiety of the ligand and the arene centers of the carbon surface, explaining the irreversible character of these adsorption processes. Ligand adsorption develops carboxyl functionalities at the carbon surface, thereby endowing the carbon material with enhanced adsorption capacity for Cu2+ ion *versus* the non-functionalized AC in the 2.5–6.0 pH range.	[125]
Chitosan flakes were suspended in methanol (100 mL), and a 25% aqueous glutaraldehyde solution was added. Cross-linked chitosan flakes were treated with 25 mL of 14% NaOH and 1 mL CS2	Pb(II)	Temperature: 298 K Equilibration time: 4 h Adsorptive solution pH: 2–6 Adjusted with HCl	Maximum adsorption was observed at both pH 4 and 5. The adsorption data followed both Freundlich and Langmuir isotherms. Langmuir isotherm gave a saturated capacity of 322.6 ± 1.2 mg/g at pH 4. FTIR spectra analysis indicated that xanthate and amino groups participate in the adsorption process. The procedure was developed and successfully applied to remove lead ions from real battery wastewater samples.	[126]
Polypyrrole-impregnated porous carbon was readily synthesized using vapor infiltration polymerization of pyrrole monomers.	Hg(II), Ag(I) and Pb(II)	Temperature: Not measured Equilibration time: Not measured Adsorptive solution Not measured	The PPy-coated layer enhanced the adsorption capacity for mercury, lead, and silver ions and opened up the possibility of a filter for heavy metal ions. The introduced PPy-functionalized layer and retained porous structure yielded an adsorbent with 20-fold greater adsorption capacity *versus* that with different amine groups.	[127]

Table 11 (*Continued*)

Adsorbent	Contaminant	Adsorption conditions	Observations	Reference
The chemical modification of chitosan (CHS) *via* Schiff base reaction, through the covalent immobilization of (2[-bis-(pyridylmethyl)aminomethyl]-4-methyl-6-formylphenol) BPMAMF ligand.	Cu(II), Cd(II), Ni(II)	Temperature: 298 K Equilibration time: 3000 min Adsorptive solution Na_2HPO_4/KH_2PO_4	The maximum adsorption was at pH 6.0 for Cu(II) but at pH 2.0 and 3.0 (acidic media) for Cd(II) and Ni(II), respectively. Pseudo-first-order and pseudo-second-order equation models were used to study the kinetics, and the equilibrium data were analyzed with Langmuir and Freundlich isotherm models. The adsorption kinetics fitted the pseudo-second-order equation for all studied systems. This mechanism suggests that the adsorption rate of metal ions by CHS–BPMAMF depends on the number of ions on the adsorbent surface and on their number at equilibrium. The best interpretation for the equilibrium data was provided by the Langmuir isotherm, giving maximum adsorption capacities of 109 mg g^{-1} for Cu(II), 38.5 mg g^{-1} for Cd(II), and 9.6 mg g^{-1} for Ni(II).	[128]

removed as hydrogen sulfide by heat treatment in hydrogen at 973–1046 K [70].

As shown in Table 4, various methods have been used to introduce sulfur surface complexes into ACs, maintaining the sulfurizing agent in contact with an AC for a given time at room or higher temperatures. The process has been carried out in a single stage or in successive stages in the atmosphere of various sulfurizing agents. Frequently, an end-transport or washing operation was also carried out to remove surface sulfur deposits or weakly retained sulfur species present in the carbon after its sulfurization. Sulfurization treatments of ACs have used S [69,73–76], CS_2 [77], SO_2 [78–80], H_2S [78,79,81], and Na_2S [82].

Generally, sulfurization had a detrimental effect on the porous structure of AC, reducing the S_{BET} slightly [79,82] or by 12–20% [73,74,78,80], with Wang et al. observing a two-thirds decrease [76]. However, a significant increase in the volumes of mesopores [79] and macropores [77] has also been occasionally reported. Following the sulfurization of AC, a large amount of sulfur can be incorporated into the carbon, obtaining increases in sulfur content of 34% [76] or 43–48% [69]. Sulfurization resulted in the formation of surface sulfur complexes such as sulfide and hydrosulfide groups [77], C–S, S–S, C=S, or S=O bond-containing groups [79,80,82,83], S_8 rings or S_2 and S_6 chains [73], short linear chain sulfur allotropes [74], and sulfur deposits or thiophene, sulfoxide or sulfone groups [76].

2.3. Nitrogenation treatments

Nitrogen modification (nitrogenation) of AC is applied in a wide range of settings: to protect the natural environment by removing sulfur compounds, nitrogen oxides, and carbon dioxide; in catalysis as catalyst or catalyst supports; and in electrochemistry for the manufacture of electrodes for electrochemical capacitors, cells, and batteries to upgrade their capacity parameters [84–116]. This is because the nitrogenation of AC can increase its basicity, which is a required property in adsorption and catalysis processes. The introduction of nitrogen into carbon significantly increases the polarity of its surface and hence its specific interaction with polar adsorptives. Moreover, reactions such as NO_x reduction, SO_2 oxidation, and dehydrohalogentation can be catalyzed by nitrogen-basic active sites containing carbons [87].

As shown in Tables 5 and 6, NH_3 has been by far the most frequently used reagent to introduce N into AC, used alone or after preoxidation of the carbon with HNO_3 (amination) or NH_3-air gas mixtures (ammoxidation) [90]. HCN, HNO_3, N,N-dimethylethanolamine, N,N-dimethylpropanediamine, urea, dicyanodiamide, N,N-dimethylformamide, melamine, and polyani-

line have also been used in AC nitrogenation treatments. Depending on the reagent used, the process was conducted either in gas (ammonia, hydrogen cyanide, and amines) or liquid (nitric acid, urea amines, and ammonia) phase. Generally, the process consisted of a single nitrogenation stage or of two successive stages in which an AC substratum was first oxidized in liquid phase and then nitrogenated in gas or liquid phase.

The nitrogenation treatment of AC not only affected its surface chemical nature, as expected, but also its porous structure, in a form and to an extent that depended on the starting AC, the chemical agent, and the experimental method used. Development of the surface area and microporosity has frequently been reported with NH_3 [89,95,103,106,109]. The increase in S_{BET} was as high as 151% for a wood-based commercial AC in comparison to the HNO_3-oxidized precursor [103]. There have been only rare reports of the porous structure remaining unchanged [90,98] or of a reduction in surface area and microporosity [94,97,108]. For the NH_3-air gas mixture, the pore structure remained virtually unchanged [90], and the surface area became highly developed [113] or decreased [114]. With nitrogenating agents other than NH_3 and NH_3-air (i.e., HCN, HNO_3, urea, melamine, and malamine-urea), decreases in surface area and micropore volume were reported [85,86,89,93,104,111]. As two exceptions to the rule, these textural parameters either increased or decreased, depending on the carbon, with urea, NH_3, dicyanodiamine, and N,N-dimethylformamie [100] and showed no modifications with polyaniline [110].

Various nitrogen functional groups were formed as a consequence of the nitrogenation of ACs. For comparative purposes, they are compiled separately for each nitrogenating agent in Table 5, together with the nitrogen contents and literature sources.

2.4. Coordinated ligand functionalization treatments

Table 7 lists some significant studies on the functionalization treatments of ACs by using coordinated ligand s, summarizing the experimental conditions used to prepare the materials and the textural and chemical modifications observed. Different coordinated ligands have been used to modify the textural and chemical properties of ACs and increase their adsorption properties (Table 7). Results reported show that coordinated ligand anchorage on the AC surface modifies its textural and chemical properties, although research to date has largely focused on the application of these materials for the adsorption of heavy metals. Only a few articles [117–125,112,126–129] analyzed the effect of coordinated ligand anchorage on textural properties (surface area and porosity), of AC reporting a decrease in surface area and micro- and mesoporosity. The chemical modifications

of AC depend on the composition of the ligand used. Studies have demonstrated that coordinated ligand anchorage on the AC surface increases surface basicity, negative charge, and N, Cl, and S contents [117–125,112,126–129]. Further details on the effect of coordinated ligand functionalization of the AC surface can be found in Table 7.

3. Applications of modified activated carbons in water treatments. Adsorption of pollutants.

3.1. Oxidated activated carbon

Table 8 lists selected studies on applications of modified ACs (oxidized by H_2O_2 and HNO_3 or O_3) as adsorbents for water treatment, summarizing the target contaminants, the specific applications, the AC used, and relevant observations. In all these treatments, as discussed above, oxidation treatments can alter the textural and chemical parameters of the AC surface and exert a major influence on the adsorption of substances from aqueous solution. Studies have specifically assessed the effect of oxidation treatment on the adsorption of organic and inorganic water pollutants on AC.

As a rule, oxidation treatment increased the concentration of acidic oxygen groups on the AC surface, thereby increasing the polarity and decreasing the pH of the point of zero charge. Adsorption of metallic ions on the oxidized AC was therefore enhanced by electrostatic interactions between the negatively charged AC surface ($pH_{solution} > pH_{PZC}$) and the positively charged metal species in solution. Moreover, acidic oxygen groups can behave as ion-exchange centers, retaining metallic species and releasing protons to aqueous solution, giving rise to the formation of metal-ligand surface complexes [130,131].

Regarding the adsorption of organic compounds from aqueous solution, most of the studies were on aromatic compounds such as phenol, substituted phenols naphthalenesulphonic acid and benzothiazole. Aromatic compounds can adsorb on AC through dispersive interactions between the π electrons of the aromatic ring of the solute and those of the graphene layers of the carbon surface. The presence of electron-withdrawing acidic SOGs on oxidized-treated ACs produces the removal of π electrons from the graphene layers of carbon, which weakens π–π dispersive interactions and prevents to some extent the adsorption of aromatic compounds [132]. This effect was systematically observed in the reviewed studies.

3.2. Sulfurized activated carbons

ACs sulfurized by various methods have been tested as adsorbents of a large number of metal chemical species ($HgCl_2$, Hg(II), Cd(II), Pb(II), Cu(II), Zn(II), and Cr(VI)), in aqueous solution. These species usually have a high affinity for sulfur, as demonstrated by their natural occurrence as metal sulfides [103], and have a strong environmental impact due to their numerous industrial applications and high toxicity. Studies in Table 9 show that the sulfurization of AC has an important beneficial effect on the extent of metal adsorption. The AC used, sulfurizing agent, and sulfurization method all have a marked influence on the adsorption process and on its dependence on the solution pH and adsorption temperature. Gómez-Serrano et al. [133], who used the same AC in a series of sulfurization treatments, reported that mercury adsorption increased on samples treated at 1173 K in H_2S and at 303 K successively in SO_2 and H_2S, whereas it decreased on products treated at 303 or 1173 K in SO_2. However, adsorption of Cd(II) and Pb(II) was markedly higher on SO_2-treated AC at 1173 K than on virgin AC [133–135] and lower of H_2S-treated AC at 1173 K. Krish-

nan and Anirudhan [79] reported the order of Hg^{2+} adsorption to be AC-SO_2-H_2S > AC-SO_2 > AC-H_2S. With regard to the relative adsorption of metallic ions, it was found to be higher for Hg(II) than for Cd(II) and Pb(II) [133] and for Cu(II) and Zn(II) than for Cr(VI) [99].

Adsorption of Hg(II) and Pb(II) on H_2S-treated AC at 1173 K greatly decreased when the pH of the adsorptive solution was lowered from the pH of the initial solution (i.e., 4.4 for Hg(II) and 5.4 for Pb(II)) to pH 2.0 [83,133]. In the case of Cd(II), however, adsorption was practically insensitive to the pH change [136]. For the adsorption of Hg^{2+} on bagasse pith-derived sulfurized ACs, the optimum pH was 4–9 [79], while the adsorption of Cd(II) on SO_2-treated ACs was higher at pH 8–12 [80]. Elevated Hg(II) removal ratios were obtained on S-sulfurized AC at pH 2–11 [76].

3.3. Nitrogenated activated carbons

Nitrogen-modified ACs have been used in catalytic oxidation reactions in aqueous medium [89] and in adsorption/oxidation reactions of highly volatile organic compounds such as mercaptans (thiols), which are responsible for disagreeable odors [104,115]. Nitrogenated ACs have also been frequently employed as adsorbents in water decontamination treatments (Table 10). NH_3 has been the preferred nitrogenating agent to date in AC treatments [96,98,103,106–109]. AC samples treated with NH_3 and other nitrogenating agents have been used as adsorbents of a wide spectrum of toxic and detrimental chemical species, including: metal ions (Cu(II), Pb(II), Hg(II), and Cd(II)), anions (CN^-, ClO_4^-, AsO_4^{3-}), organic substances (benzoic acid, phenol, atrazine), and natural organic matter. Despite differing widely in size, charge, polarity, among other relevant properties affecting the adsorption process, their adsorption was generally enhanced on nitrogenated versus virgin ACs. Thus, after nitrogenation, cyanide adsorption increased around five-fold [99] and mercury adsorption more than two-fold [112]. The effectiveness to remove pollutant species from waters by adsorption was associated with: the acid–base character of the carbon surface [96,106,109], and with the porous structure of the carbon, i.e., its, surface area [103], micropore volume [108], and pore size distribution [109]. As an exception to the rule, the adsorption of benzoic acid decreased after amination of the AC [98].

3.4. Activated carbons functionalizated with coordination ligands

ACs modified by anchoring coordinated ligands on their surface are mainly used as adsorbents of heavy metals. All published findings have demonstrated an increase in metal adsorption rate and capacity when ligands are anchored on the AC surface, due to the formation of coordination complexes between ligands and metal species. The results obtained also showed that (i) there is no leaching of the ligand to the solution, and (ii) AC adsorption properties can be readily regenerated after treatment, increasing the benefits of this technology. Table 11 lists relevant studies on this topic.

4. Conclusions

The majority of the reviewed studies concluded that H_2O_2 treatment produces minimal textural modifications in the activated carbons, although depending on the raw material of activated carbon, both increases and decreases in surface area have been reported. It has been generally shown that the surface chemistry of AC is affected by H_2O_2 oxidation treatment, mainly by introducing surface oxygen groups such us carboxyl, ketone, and ether groups. Nitric acid oxidation usually produces marked chemical modifications, with a high amount of SOGs, including carboxyl, carbonyl, phenol, and lactone groups. Most studies on the influence of HNO_3 treatment on activated carbon texture showed stronger

effects at higher acid concentrations due to the destruction of pore walls, which decreases the surface area and pore volume of the treated carbons. Severe oxidation conditions might even lead to complete destruction of the carbon texture. The studies generally report that ozonation drastically increases the number and type of acidic oxygen-containing surface groups. SOGs have been identified on ozonated ACs by FTIR spectroscopy, XPS, elemental analysis, and titration methods. Although there is a consensus that ozonation of AC leads to the fixation of acidic SOGs and the removal of basic SOGs, there is disagreement on their concentration, type, and relative distribution., The impact of ozonation on the textural properties of activated carbons is more controversial, with some authors finding only minor effects of ozone on the AC surface area and pore volume and others observing a decrease in surface area and destruction of microporosity. Generally, sulfurization has a detrimental effect on the porous structure of AC, slightly reducing the S_{BET}. However, a significant increase in the mesopore and macropore volumes has also occasionally been reported. The sulfurization of AC generates a large amount of sulfur incorporated into the carbon, obtaining increases in sulfur content of 34–48%. Sulfurization resulted in the formation of surface sulfur complexes such as sulfide and hydrosulfide groups, C–S, S–S, C=S, or S=O bond-containing groups, S_8 rings or S_2 and S_6 chains, short linear chain sulfur allotropes, and sulfur deposits or thiophene, sulfoxide or sulfone groups.

As a rule, oxidation treatment increases the concentration of acidic oxygen groups on the AC surface, thereby increasing the polarity and decreasing the pH of the point of zero charge. Hence, adsorption of metallic ions on the oxidized AC is enhanced by electrostatic interactions between the negatively charged AC surface (solution $pH > pH_{PZC}$) and the positively charged metal species in solution. Moreover, acidic oxygen groups can behave both as ion-exchange centers, retaining metallic species and releasing protons to aqueous solution, and as ligands, giving rise to the formation of metal-ligand surface complexes.

Nitrogenation treatments of AC affect not only the chemical nature of its surface, as expected, but also its porous structure, depending on the original AC, the chemical agent, and the experimental conditions of the treatment. Despite widely differing in size, surface charge, polarity, among other relevant properties, nitrogenated ACs generally possess a higher adsorption capacity in comparison to the virgin products.

Heavy metals such as (Hg(II), Cd(II), Pb(II), Cu(II), Zn(II), and Cr(VI)) usually have a high affinity for sulfur, as demonstrated by their natural occurrence as metal sulfides, and have a strong environmental impact due to their numerous industrial applications and high toxicity, thus the sulfurization treatment of AC has an important beneficial effect on the extent of metal species adsorption. The AC used, sulfurizing agent, and sulfurization method all have a marked influence on the pollutant adsorption process and on its dependence on the solution pH and adsorption temperature.

Different coordinated ligands have also been used to increase the adsorption capacity of ACs. Results obtained indicate that coordinated ligand anchorage on the AC surface modifies its textural and chemical properties, although this research has largely focused on the use of these modified materials to remove heavy metals from water by complex formation. All published findings have demonstrated an increase in metal adsorption rate and adsorption capacity when ligands are anchored on the AC surface, due to the formation of coordination complexes between ligands and metal species. Moreover, the results obtained also showed that (i) there is no leaching of the ligand to the solution, and (ii) AC adsorption properties can be readily regenerated after treatment.

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