

# Chapter 10

## From Nano- to Macrostructured Carbon Catalysts for Water and Wastewater Treatment



João Restivo, Olívia Salomé G. P. Soares, and Manuel Fernando R. Pereira

### 10.1 Introduction

While catalysis is widely used in a variety of industrial applications, namely, fine chemical synthesis and oil refining, its application in water treatment is yet to be fully integrated into the current industrial landscape [1, 2]. Nevertheless, catalytic emission control technologies are extensively implemented for gas effluents, in particular, downstream from combustion processes. The most common application is the use of catalytic converters in automobiles for control of CO and NO<sub>x</sub>, occasionally in combination with soot and catalytic regeneration of particle filters [3].

The lack of use of catalytic processes into water management is attributed mostly to the efficiency of the available technologies to provide sufficient treatment to comply with the applicable legislation [4]. The legislation is drawn taking into account what are the best available technologies (BTA) and is thus unlikely to significantly move forward to stricter requirements unless innovative cost-efficient technologies enter the market.

New findings in water quality have triggered interest in the development of efficient technologies that can address new rising concerns or facilitate the use or reuse of previously unavailable water sources. This includes the development of analytical techniques to detect trace organic pollutants [5–7]; the discovery of their public health and environmental impacts at very low (mg to µg per litre) concentrations [8]; the understanding of the toxicity associated with recalcitrant by-products of the degradation of emerging pollutants by conventional treatment solutions [7, 9]; and the interest in the recovery of contaminated water and recommendations for reuse of treated water where available technologies such as biological treatment may not be suitable for the intended final uses [10, 11]. The relevant authorities, faced with

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J. Restivo · O. S. G. P. Soares (✉) · M. F. R. Pereira  
Laboratory of Separation and Reaction Engineering—Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto, Porto, Portugal  
e-mail: [salome.soares@fe.up.pt](mailto:salome.soares@fe.up.pt)

the advances here described, have recently shown the intention to implement stricter legislations towards the control of target emerging pollutants in waste and drinking water [12]. Thus, the development of efficient technologies for water and wastewater treatment to remove emerging pollutants, and for the reclaiming of contaminated ground and surface water sources, is an urgent requirement to ensure adequate water management, which in turn is becoming an even more critical concern due to the rising climate emergency [13].

Advanced non-catalytic technologies exist that can mitigate or solve these issues; however, they generally rely on the concentration of the contaminants onto a different phase—usually liquid or solid. The secondary waste streams still require further handling that represents undesirable energetic and environmental costs. Several solutions are commercially available and/or topics of on-going research. Membrane processes, from micro- to nanofiltration and reverse osmosis, are regularly used as tertiary water treatment, and their efficiency in the removal of emerging pollutants is widely reported, including for those found at trace levels [14, 15]. Similarly, ion exchange is also available for the removal of ionic contaminants [16]. The use of adsorbents is also widespread in conventional water and wastewater treatment plants, typically based on high specific surface area activated carbon [17]. All these solutions result in the concentration of the contaminants in a secondary waste stream, either solid when the contaminants are adsorbed or retained from the liquid phase or liquid in the case of reverse osmosis. The concentrated secondary streams require handling for regeneration or disposal with added environmental and financial costs [18]. Biological treatment is another alternative for the removal of emerging pollutants; while this technology is already used in the large majority of wastewater treatment plants for nitrogen and phosphorous control [19], its efficiency varies with the class of pollutants and generally results in by-products that still present toxicity [20]. Moreover, biological treatment requires further handling of the activated sludge, and its use for drinking water raises concerns regarding biological risks [13].

### ***10.1.1 Catalytic Technologies for Water and Wastewater Treatment***

Catalytic technologies for water and wastewater treatment have the potential to answer the issues raised above [21], either in isolation or in combination with other treatment solutions [2], presenting several potentially interesting advantages [2, 22, 23]. Two of these characteristics are here highlighted to illustrate the potential of catalytic water treatment. On the one hand, catalysts can be tailored for the selective (e.g. in complex matrices where competition may hinder reactions) or non-selective (e.g. where conventional methods are likely to target only some of the contaminants) degradation of target pollutants. On the other hand, catalytic systems can be designed towards the complete degradation or conversion of the target pollutants,

therefore reducing the generation of secondary waste streams requiring further handling. Thus, catalytic technologies for water treatment have the potential to successfully eliminate emerging pollutants from water and wastewater without generation of concentrated secondary streams, leading to their complete mineralisation without the formation of toxic by-products. Such emerging pollutants include organic micropollutants, such as pharmaceuticals and personal care products (PPCP), pesticides, fertilisers, and detergents, and inorganic pollutants, such as nitrate, nitrite, bromate, and perchlorate. The successful implementation of catalytic water treatment technologies will likely involve their integration in urban and industrial treatment plants to help efficiently achieve water quality targets, rather than acting as a one-fit-for-all solution [2].

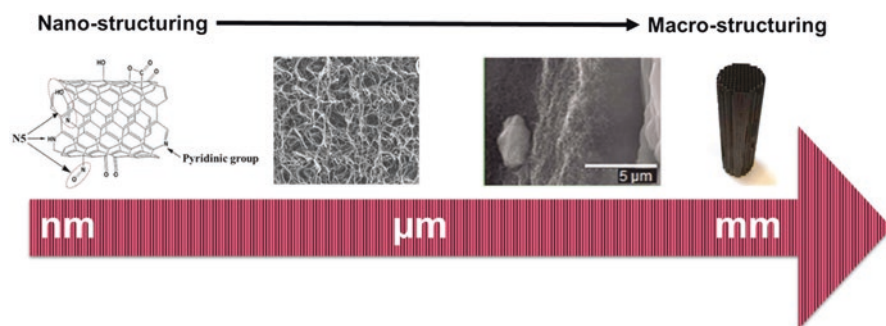
### 10.1.2 Carbon as a Catalyst

Carbon, specifically activated carbon, is extensively used as a traditional adsorbent in water treatment. Its use is very well established and firmly accepted as a methodology suitable for both waste and drinking water treatment [24]. Moreover, the capabilities of carbon as a catalyst are well-known; in particular, the appeal of carbon as a catalyst or catalyst supports resides on its easily tunable surface textural and chemical properties [25]. More recently, the structuring of carbon at the nanoscale has gained interest from researchers after the discovery and spread of materials such as graphene and carbon nanotubes [26]. In this chapter, it will be demonstrated how carbon-based catalysts can be tailored and structured at different scales (from nano to macro) towards the design of efficient systems to degrade both organic and inorganic pollutants in water.

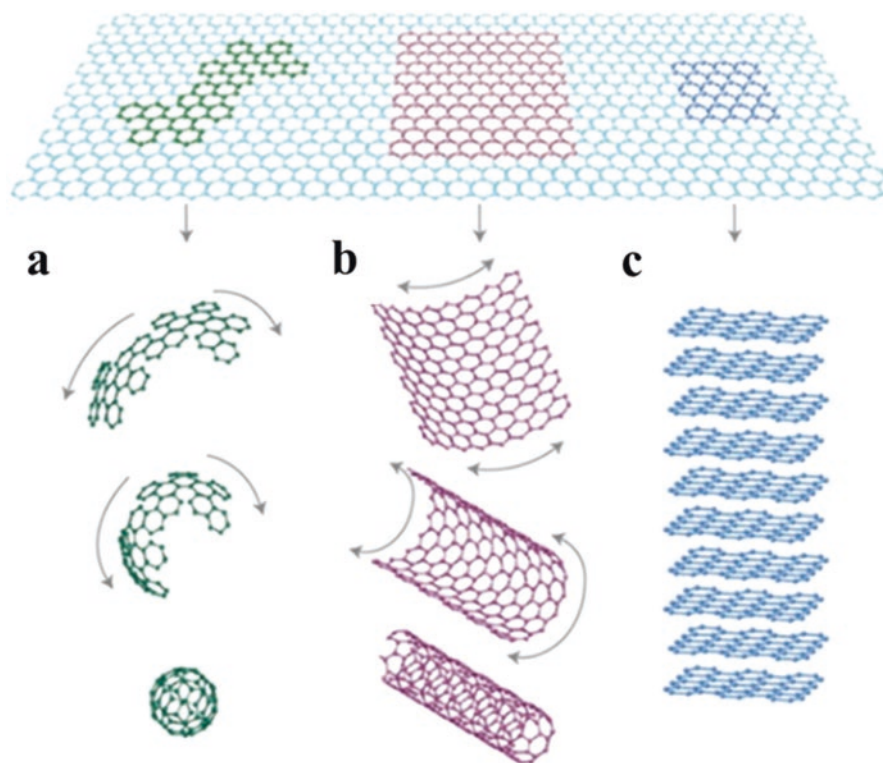
Two main approaches to catalytic technologies for water and wastewater treatment are discussed in the chapter. This distinction is closely related to different preparation methods of the carbon-based catalysts. First, the use of carbon-based metal-free catalysts in the oxidation of organic pollutants will be described and discussed in detail. Afterwards, the description of the application of carbon-based supports for active metallic phases in the catalytic reduction of inorganic ionic contaminants is presented. The description of each approach is focused on the nano- to macroscale structuring of carbon materials (Fig. 10.1), with several examples provided to illustrate the behaviour of the materials and to explain how their textural and chemical properties influence their performance.

Nanostructured carbon can be defined as materials presenting observable structures (individual particles or agglomerates) in at least one external dimension in the 1–100 nm range (or at least a set percentage of the number size distribution, usually attributed as 50%) [27]. The approach to nanostructured carbon catalysts will focus on sp<sup>2</sup> hybridised graphitic carbon nanomaterials, namely, 1D (carbon nanotubes and nanofibers) and 2D (graphene) materials (Fig. 10.2) [28].

Graphitic nanostructured carbon is understood to have properties of great interest for catalysis in general, which can be expanded to both catalytic wet air oxidation



**Fig. 10.1** Approaches to the modification of carbon materials in catalysis and their relation to structuring from the nano- to the macroscale



**Fig. 10.2** Structural relation between typical (a) 0D, e.g. buckyballs, (b) 1D, e.g. carbon nanotubes, and (c) 2D, e.g. graphene sp<sup>2</sup>-hybridised carbon nanomaterials [29]

(CWAO) and catalytic ozonation (COz). These include the high density of electrons that can potentially be delocalised and the presence of defects and edges requiring saturation with heteroatoms, thus increasing the potential for doping [26].

### ***10.1.3 Carbon Surface Nano- and Microengineering***

The modification of the surface chemistry and texture of carbons are already a classic approach to explore its potential as an adsorbent, catalyst support, or metal-free catalyst [25]. Analogous procedures have been extended to carbon nanomaterials using similar methodologies.

The textural properties, and the nature and concentration of the surface functional groups of the carbon materials, can be tailored for specific applications by the adequate preparation methods. The presence of heteroatoms, such as oxygen, nitrogen, and sulphur, bound to the edges or defects of the graphene layers in the carbon material originates from several surface functional groups (Fig. 10.3). Such elements either are present in the starting material or become chemically bound to the structure during the preparation [25]. Oxygenated groups can be introduced onto the carbon material surface by oxidative treatments, either in the gas or liquid phase [30], and can be selectively removed by thermal treatments under inert atmosphere [31]. The introduction of heteroatoms on the carbon structure allows us to control the electronic properties by introducing electron acceptors or donors, which can enhance  $\pi$ -bonding, leading to improved stability and electron transfer rate, and consequently, improved performance and durability of the catalysts. The doping of the carbon materials can be tuned to the reactions of interest (Table 10.1) [32, 33].

Activated carbons are normally characterised by their very large surface area, ranging up to a few thousand square metres per gram, and their microporosity. Some reactions may be favoured by other types of porosity, especially in cases where the small size of the pores may hurt the access of reactants to the active sites. The nanostructure of carbon materials can form porosities in the mesoporous range, which can thus facilitate the access to larger molecules, while avoiding a complete sacrifice of the large surface areas, still reaching up to several hundred square metres per gram. The mesoporous texture is present for 1D materials, such as carbon nanotubes, and emerges from the formation of empty spaces or pores within entangled bundles (Fig. 10.4) [35].

### ***10.1.4 Nanostructured Carbon Supported on Macrostructures***

The handling of nanosized powders (and powder catalysts in general) and their application in water treatment have several inherent challenges, in particular, the requirements for separation of the solids from the resulting water [36]. One potential alternative is the immobilisation of the catalysts in macrostructures that mediate

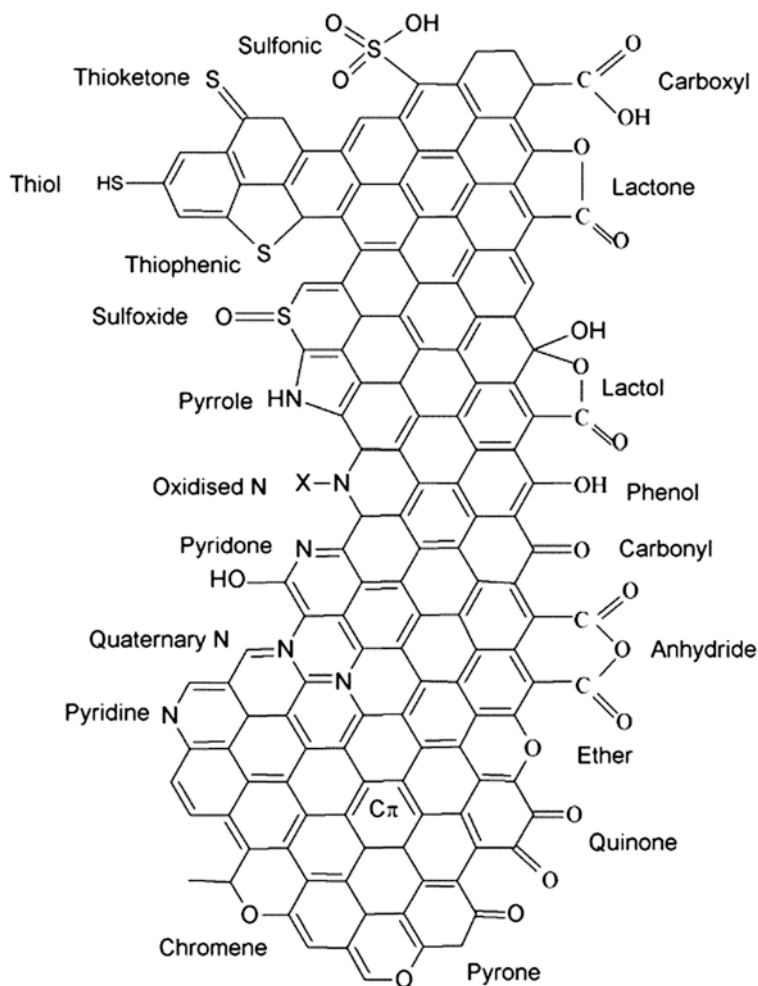


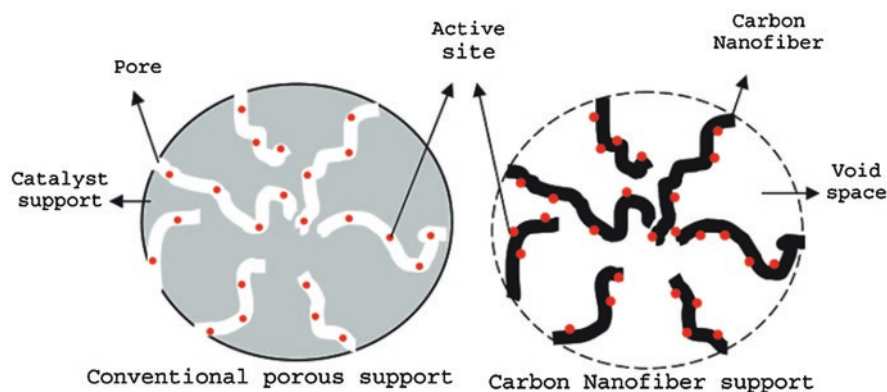
Fig. 10.3 Heteroatom functionalisation of MWCNT [34]

their contact with water and gases. Honeycomb monoliths, as a macrostructured support, have been proposed as a solution with several advantages over other configurations, including low pressure drop and the formation of favourable hydrodynamic regimes in multiphase applications [37].

Monolithic catalysts are widely used in the treatment of gas effluents, in particular, in the automotive industry [1]. However, the preparation of nanostructured carbon layers presents challenges different from those generally faced in current industrial processes. Two approaches are reported in the literature: in situ formation of a nanostructured carbon layer or coating using traditional dip-coating techniques with pre-modified nanostructured carbons [38].

**Table 10.1** Gas and liquid phase catalytic reactions catalysed by carbon and respective surface functionalities responsible for catalytic activity [34]

Reactions	Catalytic active components
<i>Gas phase</i>	
Oxidative dehydrogenation	Quinones
Dehydration of alcohols	Carboxylic acids
Dehydrogenation of alcohols	Lewis acid and basic sites
NO <sub>x</sub> reduction (SCR with NH <sub>3</sub> )	Acidic surface oxides (carboxyl, lactone) + basic sites (carbonyl or N5, N6)
NO oxidation	Basic surface
SO <sub>2</sub> oxidation	Basic sites; Pyridinic—N6
H <sub>2</sub> S oxidation	Basic sites
Dehydrohalogenation	Pyridinic nitrogen sites
<i>Liquid phase</i>	
Hydrogen peroxide reactions	Basic sites
Catalytic ozonation	Basic sites
Catalytic wet air oxidation	Basic sites

**Fig. 10.4** Illustration of the nature of the 1D carbon nanomaterial mesoporosity by comparison with the microporosity of traditional porous supports [35]

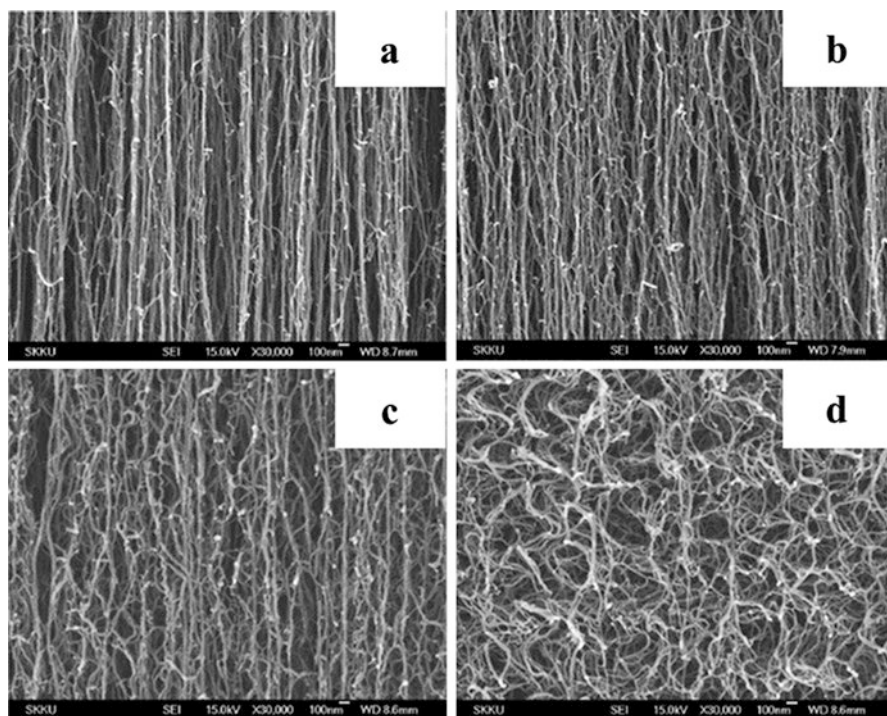
#### 10.1.4.1 In Situ Nanostructured Carbon Layer Formation

The in situ growth of nanostructured 1D carbon on a macrostructured support is an adaptation of the chemical vapour deposition (CVD) method for the growth of carbon nanotubes and nanofibers [39]. A supporting layer with adequate chemistry and porosity may be coated onto the support beforehand (when required), after which the metallic growth catalyst is dispersed on the support in the form of nanoparticles. The growth of the carbon nanofibers or tubes is then promoted by the decomposition of a carbon source at temperature [40]. The resulting nanostructured layer is often called a carbon nanotube/fibre forest, in particular when their alignment is

promoted during growth [41], as it is formed by several individual tubes or fibres (Fig. 10.5).

The growth conditions can be modified to obtain carbon nanostructures with the desired characteristics, either in their morphology or chemical properties. The methods available to promote these modifications are similar to those used for the synthesis of carbon nanomaterials in powder form and are based on changing the growth catalyst (choice of metal, particle size and shape, and crystalline structure), the carbon source, and the growth parameters (temperature and time) [43]. Furthermore, the carbon nanostructures can be doped with heteroatoms by mixing a precursor with the carbon source, for example, ammonia for N-doped carbon [44]. However, this doping procedure is known to cause changes in the yield of carbon nanostructures, limiting the thickness of the layers, and to affect the structure of the carbon (from nanotubes to bamboo-like structures for example).

Post-growth modification of the carbon nanostructure layers can also be used to modify their surface chemistry and texture to an extent. Similar methods as those used to powder materials are applicable, with the required adaptations to accommodate the macrostructures. Nevertheless, the efficiency of these is highly dependent on the macrostructure and layer thickness and structure [45]. Additionally, the in situ methodology for formation of a nanostructured carbon layer is not compatible



**Fig. 10.5** Example of carbon nanotube layers grown in situ with different orders of alignment (from **a** to **d**) with changing growth catalyst particle size [42]



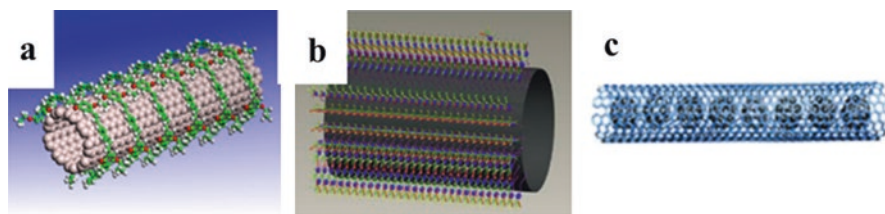
with mechanical methodologies for modification of the chemical and textural properties of carbon nanomaterials. The potential of these methods is further detailed in Sects. 10.2 and 10.3.

#### 10.1.4.2 Coating with Pre-modified Nanostructured Carbon

The limitations to the modification of carbon nanomaterials grown in situ motivate the development of methods to create coatings with pre-modified materials. This approach has specific challenges related to the handling of the nanomaterials and the formation of the catalytic layer. On one hand, the dispersion of carbon nanomaterials in water, while preferable from a process point of view, is not readily achieved in most cases. Modification of the nanomaterials can improve their solubility and help form slurries that can be coated onto macrostructures. This can be achieved by chemical or physical surface functionalisation: chemical functionalisation refers to the covalent linkage onto the carbon scaffold, while physical functionalisation refers to non-covalent interactions with chemical functionalities (Fig. 10.6) [46]. The use of the former to enhance the catalytic performance of carbon materials is thoroughly described in Sect. 10.2.1. However, the latter (or a combination of both) is understood to be more successful for the coating of macrostructures with nanostructured carbon layers.

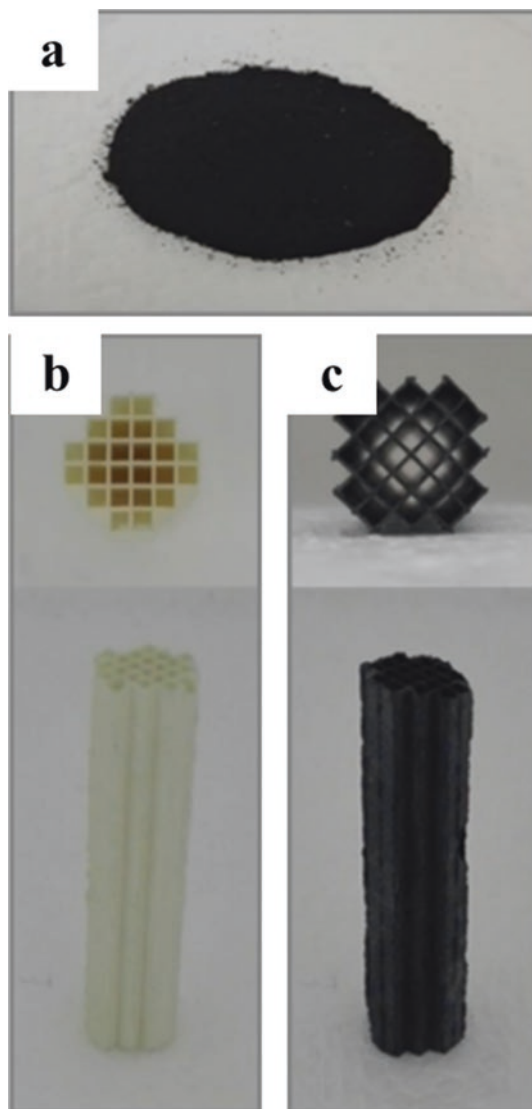
The use of polymers has the advantage of, besides resulting in stable dispersions, providing an organic polymeric framework upon coating that maintains the nanostructured layer integrity. This method is used effectively in preparing ceramic and steel macrostructures using a variety of polymeric binders such as glucose (Fig. 10.7) [47–50] and sucrose or dextrin [51, 52].

The use of polymeric wrapping of carbon nanotubes to create nanocomposite layers can create issues with the access of reactants to the catalytic surface. The carbonisation of the polymers can produce a separate carbon phase wrapping the carbon nanomaterials. The new carbon wrapping can be active on itself; in fact, this method is often used to create activated carbon coatings for catalytic applications [53]. Nevertheless, this type of carbon material is distinct from the actual nanomaterials in the coating. A compromise between stability and activity can be achieved



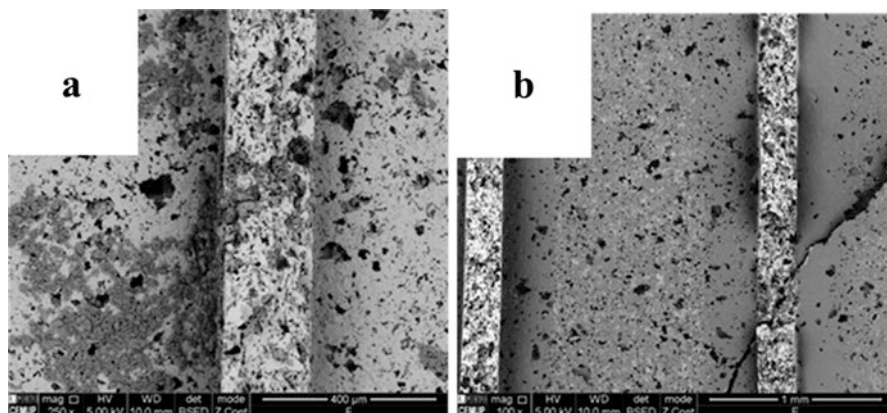
**Fig. 10.6** Physical functionalisation of carbon nanotubes by (a) polymer wrapping, (b) surfactant adsorption, and (c) endohedral method [46]

**Fig. 10.7** Preparation of a macrostructured N-doped carbon nanotube catalyst from (a) N-doped carbon nanotubes in powder form and (b) cordierite bare support, resulting in (c) the carbon nanotube covered cordierite structure [47]



through optimisation of the process to maximise the availability of the catalytic active sites in the carbon nanomaterials.

Surfactants have also been successful in creating carbon nanotube dispersions to coat cordierite macrostructures [54]. Surfactants adsorb on the carbon nanomaterial surface, forming a hydrophilic barrier that hinders agglomeration and stabilises the suspension in water. The formation of a homogeneous coating was found to be significantly improved when mechanical means (ball milling and ultrasonication) was used to reduce the size of the original nanomaterial bundles, improving the



**Fig. 10.8** Carbon nanotube coating (dark) on cordierite (light) top view: (a) as-received carbon nanotube and (b) ball-milled carbon nanotubes [54]

interaction between the carbon and the cordierite substrate (Fig. 10.8). Other methods available include covalent bonding of graphene to surface functionalities anchored on cordierite used to form catalytic nanostructured graphene layers, taking advantage of the 2D graphene structure [55, 56] and electrophoretic formation of a carbon nanotube layer on a conducting macrostructure [57].

## 10.2 Metal-Free Structured Catalysts for Water Treatment

The application of carbon (mostly activated carbon—AC) as a catalyst in advanced oxidation processes (AOPs) for water treatment is a relatively well-established research topic within the relevant community. In the past twenty years, several works have been published on the topic. Two highlights are the applications of AC in catalytic wet air oxidation (CWAO) [24] and in catalytic ozonation (COz) [58]. More recently, both processes have been expanded to include nano- and macroscale structured carbons. The discussion concerning the application of metal-free catalysts will mostly focus on these two processes, where some overlapping exists with the work previously carried out with AC.

While differing in targets and overall process design, CWAO and COz are fundamentally related in their reaction mechanism. Both achieve oxidation of organic contaminants by the action of highly reactive and non-selective radicals, formed upon the interaction of an oxidant with the carbon surface [58–61]. The main difference between these processes lies in the oxidant applied; CWAO uses oxygen, while COz uses ozone. CWAO requires high working pressures and/or temperatures and is generally applied in effluents with high organic loadings [62]. COz operates at room temperature and pressure, but requires in situ ozone generation, and usually targets effluents with recalcitrant pollutants at lower levels [63]. Moreover, the

combination of ozonation and a catalyst looks to improve the process's total mineralisation rates, whereas wet air oxidation is combined with a catalyst to achieve efficient performance at lower operating temperatures and pressures.

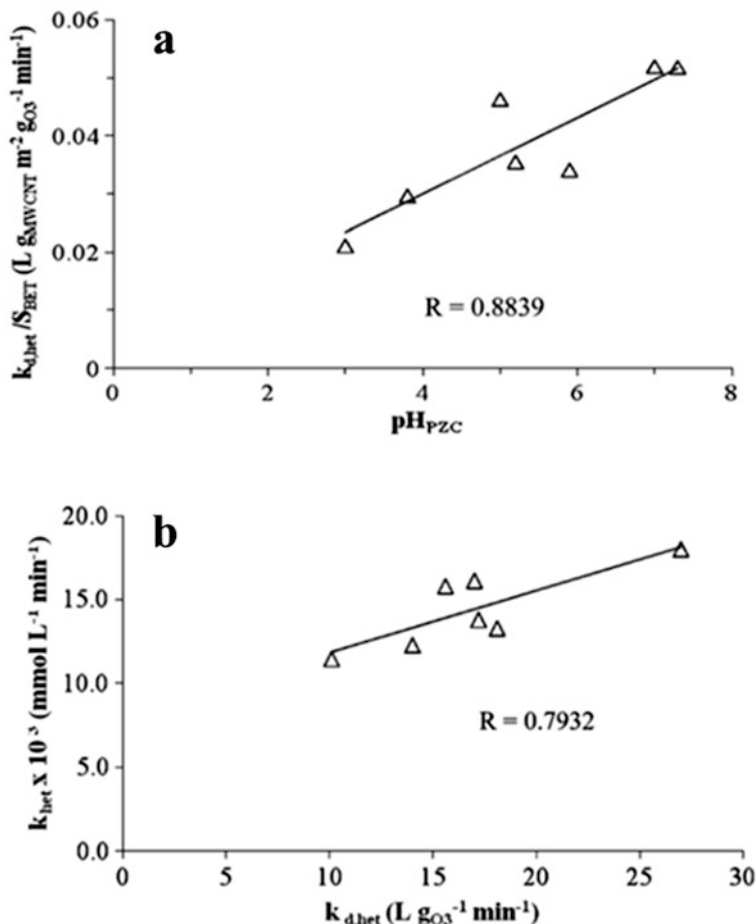
### 10.2.1 Surface Chemistry and Catalytic Performance

The acid or basic character of multi-walled carbon nanotubes (MWCNTs) plays a major role in their performance as a catalyst in ozonation. The surface charge, as measured by calculation of the pH at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ), is linked directly to the type and amount of O-containing functionalities (Table 10.2). As per the seminal study detailing the relation between CO and  $\text{CO}_2$  released during thermally programmed desorption (TPD) experiments and the nature of the surface functionalities on AC [31], a similar relationship is found for MWCNT. Nitric acid oxidation is then expected to introduce similar oxygen-containing groups (e.g. carboxyl, hydroxyl, and carbonyl groups) on the MWCNT surface [64], which are then selectively removed during thermal treatment [63].

The effect of the acid/basic character of MWCNT in its catalytic performance is made clear when tested in the ozonation of oxalic acid (OxAc). OxAc is a carboxylic acid, recalcitrant to molecular ozonation, and often found as a final product in the oxidation of many organic contaminants; moreover, a sufficiently concentrated oxalic acid solution hinders the spontaneous decomposition of dissolved ozone into hydroxyl radicals, thus serving as an ideal model to study the performance of catalysts in ozonation [58]. Figure 10.9 shows the improvement in specific surface area (SSA) normalised rate constants for ozone decomposition and oxalic acid degradation with  $\text{pH}_{\text{pzc}}$  increase [63]. More basic samples are increasingly efficient in the decomposition of ozone into non-selective highly active radicals, which in turn results in a faster degradation of oxalic acid. Heat treatment with hydrogen gas has been found to be even more efficient in emphasising the basic character of MWCNT, improving their performance in catalytic ozonation of oxalic acid beyond that of nitrogen gas heat-treated materials [65].

**Table 10.2** Textural and chemical characterisation of modified MWCNT samples (nitric acid modified, with subsequent thermal treatment at 400, 600, and 900 °C and with  $\text{O}_2$  and  $\text{H}_2\text{O}_2$ ). [63]

Sample	$\text{CO}_2$ ( $\mu\text{mol g}^{-1}$ )	CO ( $\mu\text{mol g}^{-1}$ )	% $\text{m}_\text{O}$	pH ( $\text{pzc}$ )	$\text{S}_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )
Original	25	478	0.84	7.0	331
$\text{HNO}_3$	1514	2435	8.7	3.0	476
$\text{HNO}_3$ 400	561	2350	5.6	3.8	483
$\text{HNO}_3$ 600	125	1494	2.8	5.9	504
$\text{HNO}_3$ 900	15	308	0.54	7.3	529
$\text{O}_2$	91	1339	2.5	5.2	508
$\text{H}_2\text{O}_2$	150	466	1.2	5.0	337
AC	63	579	1.1	8.5	909



**Fig. 10.9** Correlation of normalised rate constants for heterogeneous ozone decomposition (a) and oxalic acid degradation (b) with modified MWCNT surface charge [63]

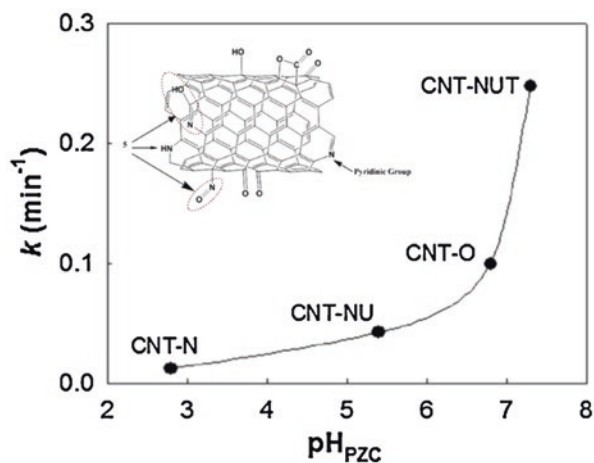
The comparison of MWCNT and AC performances further highlights the potential of graphitic carbon materials to act as catalysts for COz. In the same conditions and with a much higher SSA than any MWCNT sample, AC was not able to completely degrade OxAc after 180 min; the unmodified MWCNT almost completely degrades OxAc in 60 min, with the most basic sample achieving complete mineralisation in 60 min. The improved performance of MWCNT is attributed to the higher amount of delocalised  $\pi$ -electrons on their surface [32, 33], highlighted by the behaviour of the more basic samples [58, 66], and the significant decrease of internal mass transfer resistances due to the mesoporous character of MWCNT vs. the microporous character of AC [67]. The re-utilisation of the basic catalysts showed a tendency of the catalytic performance towards what was seen for the most acidic samples. Ozone is known to oxidise the MWCNT surface by introducing oxygen

functionalities, and thus, this behaviour is in agreement with the expected performance of the materials as a function of their surface properties.

Nevertheless, other works have found a different trend in ozone degradation vs. surface oxygen content on MWCNT. Despite the low reactivity of carboxylic groups with molecular ozone [68], it has been suggested that deprotonated carboxylic groups in neutral pH suspensions might enhance  $O_3$  reactivity with adjacent aryl or alkene moieties, as those possibly found in the sidewalls of oxidised MWCNT [69]. Another interpretation suggests that hydroxyl radicals may be reacting with carbon centres in MWCNT sidewalls, which become less available for the reaction when occupied with oxygen groups formed during oxidation [70]. However, most of such reports are not able to clearly identify the mechanisms for ozone interaction with the oxygen surface groups, as other factors might be influencing the performance of the oxidised MWCNT, such as the creation of surface defects in the carbon lattice, formation of amorphous carbon materials, or improvements in the dispersion of the hydrophilic oxidised MWCNT [69].

A similar approach to MWCNT acid/basic character modification by surface oxygen introduction showed the same trend in their performance in CWAO [71] (Fig. 10.10). Similar to  $CO_z$ , a mechanism for basicity enhanced performance is proposed for CWAO [71], while more complex reaction systems occasionally report a benefit in the presence of carboxylic acids [72].

The introduction of N-containing functionalities by doping with nitrogen precursors was shown to increase the basicity of MWCNT further; thus, an improved performance with these materials was found for both  $CO_z$  and CWAO with  $OxAc$  and phenol [73]. An exception was found for S-containing MWCNT in CWAO; while these samples had an acidic character, their performance in CWAO of phenol was above that of more basic samples. The high operating temperature and pressure



**Fig. 10.10** Correlation of initial rate constants of oxalic acid degradation by CWAO with modified MWCNT surface charge [71]

of CWAO promote the formation of sulphonic radicals from surface S-containing functionalities. Sulphonic radicals react promptly with phenol, but are not able to further mineralise phenol intermediate oxidation products such as oxalic acid [73]. Thus, the S-containing MWCNT samples do not act as a true catalyst and the relationship between catalytic performance and basic character is maintained.

Solvent-free mechanical techniques (namely, ball milling) have also been used as an easy methodology to introduce large amounts of heteroatoms onto MWCNT [74]. While ball milling also affects the textural properties of the materials (discussed in next section), this method further highlights the effect of heteroatom doping in the MWCNT catalytic performance (Fig. 10.11), as seen in N-doped MWCNT in both CWAO and COZ [75]. The role of N-, P-, and B-containing surface groups is explored in the CWAO of OxAc beyond the acid/basic character of the materials. Mechanisms proposed for the enhanced performance of the MWCNT include electron donation by N-groups with unpaired electrons [47] and higher affinity to oxygen due to the effect of P and B atoms in the electroneutrality of the graphitic structure [74], enhancing the interaction with oxygen.

Graphene underwent a similar approach towards the tuning of its surface chemistry. Reduced graphene oxide (rGO) samples doped with nitrogen using melamine and urea as precursors, with an increased basic character when compared with the pristine rGO, were again found to have enhanced catalytic performance both in COZ and CWAO [76, 77]. However, the most basic samples were not necessarily the most active, showing how other factors can affect the performance of N-doped samples (textural properties, nitrogen amount, and nature of nitrogen groups).

The remarkable performance of MWCNT and rGO in COZ and CWAO prompted their use in the treatment of more complex pollutants. Numerous instances are found in the literature, from traditional pollutants like organic dyes [78, 79] or phenolic wastewaters [73, 80] to emerging organic pollutants [81–84]. Since conventional water and wastewater treatment solutions are generally efficient at degrading large organic molecules at sufficiently fast rates for their efficient removal from

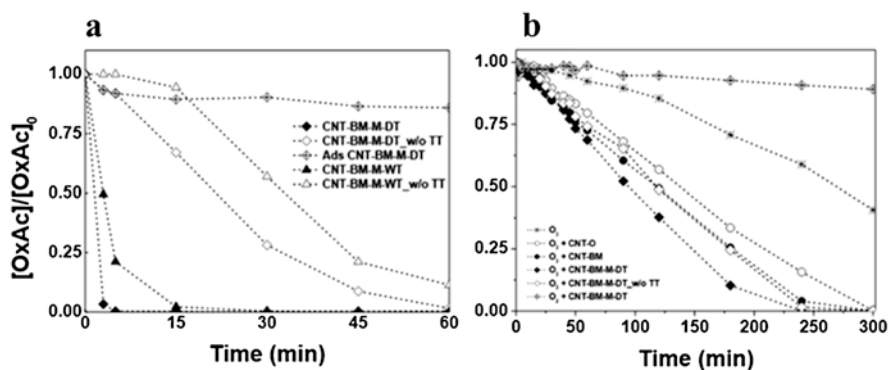
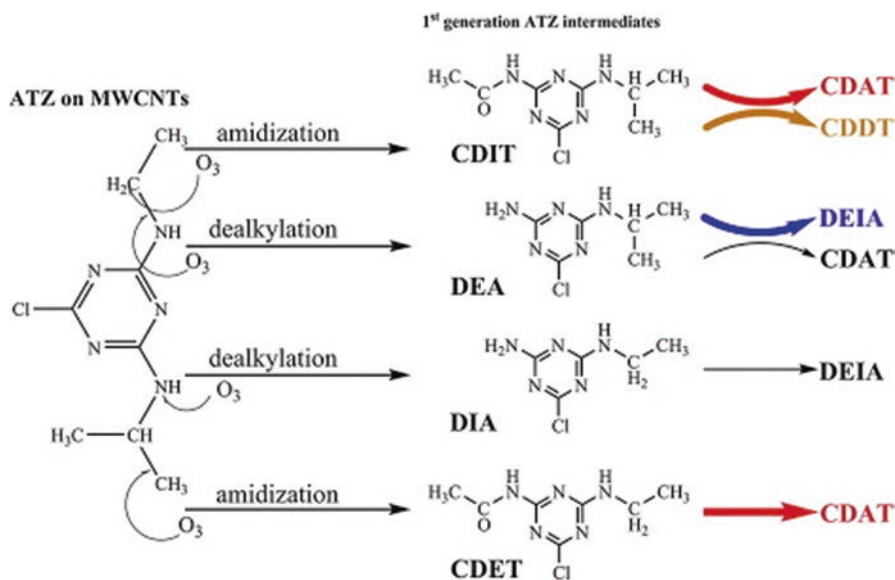


Fig. 10.11 Dimensionless concentration of oxalic acid during (a) CWAO and (b) COZ experiments carried out using MWCNT doped with nitrogen using ball milling [74]

water and wastewater, the main concern of these studies lies on the total mineralisation of the contaminants. CO<sub>2</sub> studies carried out with the pesticide atrazine (ATZ) have shown how molecular ozone readily reacts with ATZ, but leads to the accumulation of a series of recalcitrant intermediate products, often more toxic than the parent compound (Fig. 10.12) [85].

A similar behaviour is found for many other emerging micropollutants. Addition of a catalyst might even decrease the rate of degradation of the parent compound due to the decomposition of ozone and the unselective nature of the formed active radicals [82–84]. Nevertheless, these radicals are able to enhance the efficiency of the process, either by complete mineralisation of the contaminants into water and carbon dioxide or decomposition into less toxic by-products [82]. The complex nature of the involved reaction pathways means that it is not advisable to generalise on the mechanisms of their catalytic oxidation. In fact, it is found that besides leading to higher mineralisation degrees, the reaction pathways often change due to the tuning of the catalysts through surface modification [85]. Both CO<sub>2</sub> and CWAO using several different variations of rGO and MWCNT have been tested towards the treatment of a large range of emerging organic pollutants [81, 85–97].



**Fig. 10.12** Reaction of molecular ozone with atrazine (ATZ) and accumulation of first generation intermediates recalcitrant to direct ozonation (desethylatrazine (DEA), desisopropylatrazine (DIA), desethyldeisopropyl-atrazine (DEIA), 2-chloro-4-acetamido-6-isopropylamino-1,3,5-triazine (CDIT), 2-chloro-4-ethylamino-6-acetamido-1,3,5-triazine (CDET), 2-chloro-4-acetamido-6-amino-1,3,5-triazine (CDAT), and 2-chloro-4,6-diacetamido-1,3,5-triazine (CDDT)) [85]



### ***10.2.2 Textural Properties and Catalytic Performance***

The specific surface area and pore characteristics also play a key role in defining the catalytic potential of carbon materials. This effect has been widely studied for an extensive range of catalytic reactions, including CWAO and CO<sub>2</sub>, using more traditional carbon materials such as activated carbon and carbon black [25, 59, 98].

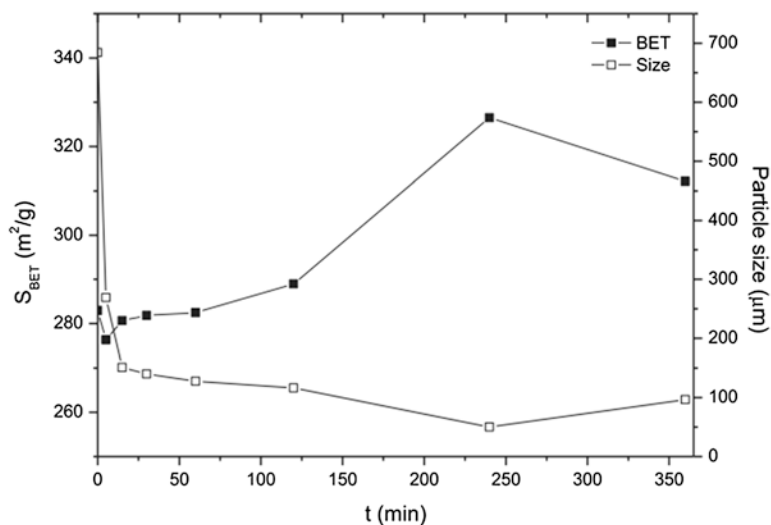
A larger surface area allows for more existing active sites for reaction and thus can be expected to increase the catalytic performance of carbon materials. One of the main selling points of AC is, in fact, its potential to easily obtain high specific surface areas, up to 3000 m<sup>2</sup> g<sup>-1</sup> [99]. However, the microporous nature of AC can restrict the access of large molecules to active reaction sites or create additional internal diffusion and mass transfer resistances [100].

While 1D carbon nanomaterials, such as MWCNT, typically present a lower surface area than AC, their porous structure consists mainly of mesopores [35, 67]. Treatments for modification of surface chemistry generally result in changes to the surface area and pore structure. It is not always straightforward to decouple the simultaneous effect on surface chemistry and texture of these modification methods. On the other hand, ball milling without any heteroatom precursor can produce changes in textural properties without significantly changing the surface chemistry [101]. A correlation between ball-milling parameters and catalytic performance of MWCNT in CO<sub>2</sub> was found, which in turn translates into a correlation between MWCNT morphology and surface textural properties and performance (Fig. 10.13).

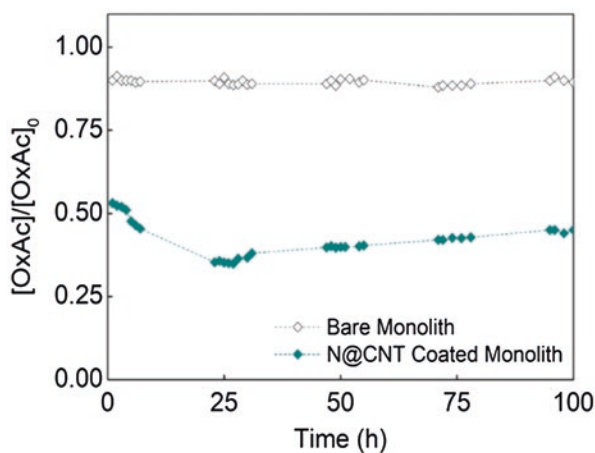
### ***10.2.3 Macrostructured Catalysts***

Macrostructured supports covered with carbon nanotubes or nanofibers have been used extensively as catalysts for the oxidation of organic pollutants. Most of these studies focus on continuous water treatment processes. Various examples can be found in the literature, including catalytic ozonation [102] and catalytic wet air oxidation [47]. The catalysts were found to translate the expected performance of the powders, including N-doped carbon nanofibers grown on cordierite macrostructured supports.

Ex situ prepared nanostructured carbon layers on macrostructured supports have also been successfully used in both CWAO (Fig. 10.14) [47] and CO<sub>2</sub> of organic pollutants [54].



**Fig. 10.13** Changes to specific surface area and particle size of MWCNT for increasing ball-milling time [101]



**Fig. 10.14** Dimensionless oxalic acid concentration during continuous CWAO experiments carried out using ex situ prepared N-doped CNT coated onto a cordierite macrostructure [47]

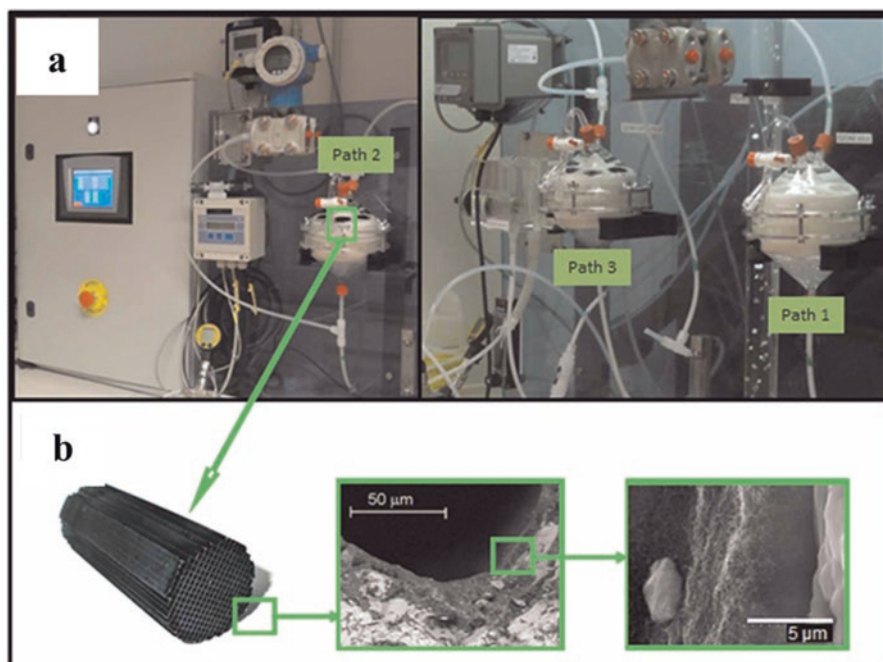
### 10.2.4 Application in Real Conditions

The advances described here have mostly been achieved at the laboratory scale, using model compounds that allow the direct evaluation of the catalytic performance of the materials being tested. This is particularly relevant when targeting

emerging organic micropollutants, as they are found with relevant impacts even at concentrations in the ppb or smaller ranges.

The use of carbon nanomaterials in a catalytic ozonation pilot plant (Fig. 10.15) has been demonstrated in the degradation of 5 selected organic micropollutants: atrazine, bezafibrate, erythromycin, metolachlor, and nonylphenol [22]. The plant was designed to compare the removal efficiency of the non-catalytic and the catalytic ozonation process. Teflon reactors holding carbon nanotube covered macrostructures were used to contact the catalyst with the effluent with or without pre-saturation with ozone. Each reactor held 6 macrostructured catalysts, each with 22 mm diameter and 60 mm length. The system showed that the catalytic process was efficient at removing the selected pollutants.

The influence of a real water matrix in the catalytic ozonation process over carbon nanotubes has also been investigated [82]. The influence of typical real water components was assessed, and the main inhibitors of the catalytic activity were identified.  $\text{HCO}_3^-$  is proposed to act as a radical scavenger in solution;  $\text{SO}_4^{2-}$  is also proposed to act as a radical scavenger, besides affecting the dissolution of ozone in water;  $\text{Ca}^{2+}$  was found to form precipitates when interacting with the organics in the effluent, resulting in blocking of the active sites available for the catalytic reaction.



**Fig. 10.15** Pilot-scale experimental set-up for the testing of carbon nanotube covered ceramic macrostructures in a catalytic ozonation process: (a) overview of set-up and teflon reactors holding 6 catalysts in parallel and (b) detailed view of each catalyst by SEM imaging of the nanostructured carbon layer [22]

Nevertheless, the catalytic process was still found to largely present good performances. Moreover, long-term testing of the catalysts has shown these to be stable after an initial period of deactivation due to ozone surface oxidation [82].

While CWAO has been tested at different scales using different catalysts, there are no reports on large-scale applications and/or with real effluents using carbon nanomaterials [103]. The EU funded FP7 project FREECATS culminated in the formulation of a business plan laying out the development of a continuous CWAO reactor using N-doped carbon nanomaterials as catalysts [104]. The stability of the carbon nanomaterials has been assessed in long-term experiments again, showing that the catalysts deposited on macrostructures maintain their activity under reaction conditions [47].

### **10.2.5 Outlooks**

The use of carbon nanomaterials as metal-free catalysts for environmental applications has matured immensely in the past 20 years, showing great potential to tackle current urgent issues in water treatment. The research and development of nanomaterials with tailored properties have contributed largely for their application, but further research is required to overcome the constraints that limit their use in water treatment plants. The current research towards the adoption of the technology for practical applications focuses on the scaling-up of the process (from material manufacture to operation) and its integration in water and wastewater treatment plants to guarantee their performance and durability.

## **10.3 Carbon as a Catalyst Support in Water Treatment**

Another opportunity for the development of catalytic technologies for water remediation exists for waters contaminated with inorganic pollutants. The contamination of drinking water sources with nitrate, which is metabolised into nitrite in the human body, requires the development of efficient solutions. Nitrite is known as a potential carcinogenic and is also related to the development of the blue baby syndrome and hypertension [105]. The diffuse sources of surface and groundwater contamination by nitrate, such as fertiliser run-off, cannot be tackled by treatment of effluents feeding into the natural water sources. Alternative technologies for nitrate removal such as ultrafiltration or reverse osmosis are effective but result in a concentrated effluent that requires further handling. Biological denitrification is widely used in wastewater treatment; however, it is yet not or rarely applied for drinking water due to its complexity and concerns regarding possible bacterial contamination, the presence of residual organics in treated water, and the possible increase in chlorine demand of purified water [106]. Bromate is also a reoccurring contaminant in both water and wastewater, which is a good candidate target for catalytic reduction. Besides being

found in natural waters from diffuse sources such as sweater intrusion and, again, pesticide and fertiliser run-off, bromate is also formed during ozonation of bromide containing waters in drinking water plants. Bromate in drinking water is a public health concern due to its carcinogenic potential, and thus, efficient technologies for its removal are required. The available technologies are biological treatment, photocatalysis, electrochemical reduction, and catalytic reduction. The catalytic route presents advantages in terms of efficiency and rate of removal, without producing secondary waste streams with the accumulated remnants [107].

As is the case for metal-free catalytic applications, carbon is highly attractive as a support for an active catalytic phase. While carbon can be used to replace and avoid the use of often expensive metals for the reactions described in the previous section, other applications still require the use of an active metallic phase. The chemical reduction of inorganic pollutants generally requires a mono- or bimetallic catalyst able to activate the reduction agent (e.g. hydrogen or formic acid [108]) and to adsorb the pollutant to promote its reduction on the catalytic surface [23, 109]. The characteristics of carbon materials of interest for use as catalyst support largely overlap with those of metal-free catalysis, namely, their very high surface area suitable for metal particle dispersion, access to active sites, and potential for surface chemical and textural modification. The cost of activated carbon is also attractive when compared with other standard catalyst supports [25].

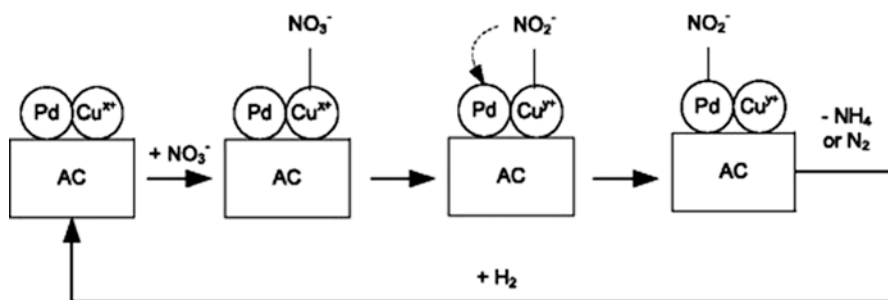
Nanostructured carbon materials have added advantages compared to traditional carbon supports, like activated carbon, due to their unique properties, while retaining the high surface area and surface textural and chemical tunability. Besides the modified pore structure detailed in Sect. 10.2, the electronic properties of the sp<sup>2</sup> hybridised structure are particularly relevant to their role as catalyst support. The high electrical conductivity can promote specific metal-support interactions that directly affect the catalyst activity and selectivity [26].

The most common method for the preparation of nanostructured carbon supported metallic catalysts is through impregnation using the appropriated precursor salts for the desired metal. The improvement in activity of carbon nanotube supported catalysts has been demonstrated for monometallic catalysts supported on multi-walled carbon nanotubes for the catalytic reduction of bromate under hydrogen when compared with those using activated carbon as a support [110]. An improvement in the turn-over frequency (TOF, moles converted per available metallic surface area per unit time) of ~30 times was measured on average for Pd, Pt, Rh, and Ru monometallic catalysts. While the mesoporous structure of MWCNT is expected to contribute to the improvement in the activity, it has also been suggested that the intrinsic contribution of the support (i.e. discounting the contribution of the diffusion effects) is still higher for MWCNT when compared with other supports in the reduction of nitrite [111, 112]. It is suggested that the graphitic surface provides an additional site for anionic compound adsorption and reaction with spilled-over hydrogen formed on the metallic sites. This is in agreement with findings in other catalytic reactions over supported metallic catalysts, such as the hydrogenation of cinnamaldehyde [113]. The adsorption of spilled-over hydrogen on graphitic carbon has also been reported for non-catalytic cases [114, 115]. However, it has also been

reported that addition of MWCNT to carbon nanofibers as a support for Pd catalyst improved the reduction of nitrite by promoting the formation of smaller metallic nanoparticles and thus improving the available metallic surface for reaction [116].

The hydrogenation of nitrate into nitrogen in water requires a bimetallic catalyst. Unlike bromate and nitrite, which can adsorb on the noble metal or graphitic planes, nitrate is preferentially adsorbed onto transition metals. However, transition metals cannot dissociate hydrogen, and thus, a combination of a noble metal and a transition metal is a necessary condition for the reduction of nitrate to nitrite, which is then further reduced on the noble metal (Fig. 10.16). This mechanism is well-understood with several reported examples using a variety of carbon and metal oxide supports [117–119]. The main challenge in the process is the selectivity towards ammonia, which is also a harmful pollutant. It is proposed that a combination of factors affects the selectivity to ammonia, ranging from the concentration of nitrite ions in solution to the spatial distribution of the metallic phases and including metal-support interaction effects [106].

Unlike with bromate and nitrite, the graphitic carbon in carbon nanotube supports cannot directly participate in the nitrate reduction reaction mechanism, as seen when monometallic catalysts are tested in the reaction. However, a very large impact on the catalyst activity and selectivity is still found. The effect varies with the metal pair chosen, the weight ratios between both, the calcination and reduction temperatures of the prepared catalysts, and the surface chemistry of the supports [121]. For the 1%Pd/1%Cu pair, the nitrate removal of the catalyst prepared with activated carbon was only matched with a surface-modified carbon nanotube support. On the other hand, the selectivity to nitrogen was improved with three of the eleven carbon nanotube supported catalysts tested. The same experiment carried out with the pair 1%Pt/0.3%Cu was very different, with five of eleven carbon nanotube supported catalysts outperforming activated carbon in nitrate reduction. This pair, on the other hand, resulted in much worse selectivity to nitrogen, independent of the support used. The kinetics of nitrate reduction over 1%Pd/1%Cu were studied in detail and suggested that the structured support was able to improve mass transfers



**Fig. 10.16** Schematic reaction mechanism for nitrate catalytic reduction under hydrogen over bimetallic catalysts supported on carbon [120]

happening near the metallic catalyst surface, resulting in improved selectivity to nitrogen [122].

Another approach to the use of carbon nanotube as support for an active bimetallic phase is the formation of confined catalysts. Ag-cut carbon nanotubes were used to confine Pd-Cu alloyed particles on the internal and external surface of the nanotubes, with the former showing better nitrate conversion and selectivity to nitrogen [123]. It is suggested that the main driver for the improved activity was the electron deficient internal surface of the carbon nanotubes, leading to donation of electrons from the bimetallic catalysts, which in turn hinders nitrate adsorption on the metallic surface.

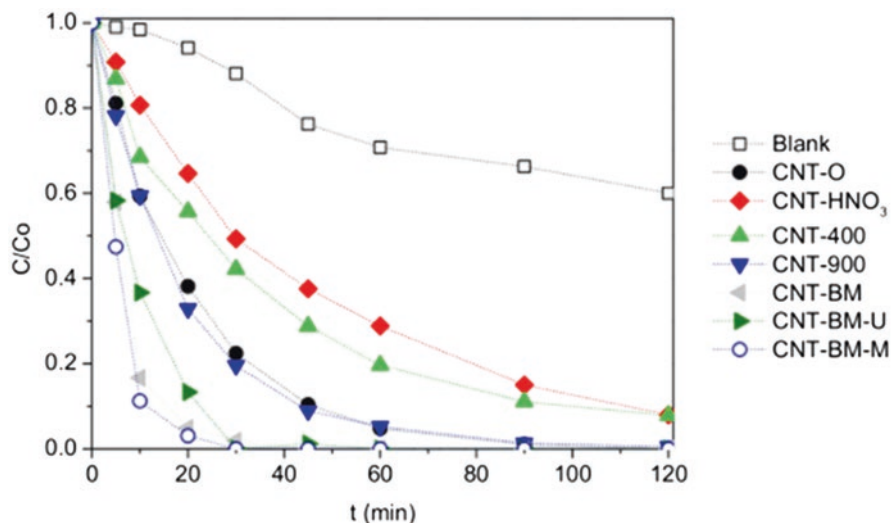
Graphene has also been used as a support for bimetallic catalysts for the reduction of nitrate using zero-valent iron as an electron source to form hydrogen in water and reduce nitrate, with similar results as with carbon nanotubes [124].

Similar techniques to those used in the development of metal-free catalysts for water and wastewater treatment can be used towards the modification of nanostructured carbon supports.

### ***10.3.1 Support Surface Chemistry and Catalytic Performance***

The effect of the surface chemistry of the nanocarbon supports on the catalytic performance of mono- and bimetallic catalysts has been studied for bromate and nitrate reduction.

Carbon nanotubes oxidised with different surface oxygen content were prepared and used as supports for Pd/Cu and Pt/Cu bimetallic catalysts at optimised ratios for nitrate reduction [121]. The carbon nanotubes were used as-received, after oxidation with 7 M HNO<sub>3</sub>, and after thermal treatment under inert atmosphere at 400 °C post-oxidation. The activity of the oxidised carbon nanotubes as support for the Pd/Cu catalyst was found to be below that of the as-received supports, except for high calcination and reduction temperatures. In the as-received supports, the increase of the preparation temperature above 200 °C resulted in a decrease in activity due to the sintering of the metallic nanoparticles and alloy formation. The preparation of the catalysts on the oxidised support at temperatures below 200 °C could not form metallic particles from the precursor salts. In fact, thermal programmed reduction (TPR) experiments reveal that the oxidised support has a much less reducing character when compared with the as-received carbon nanotubes, thus requiring high temperatures to form a dispersion of metallic particles [125]. It is also suggested that the interaction of copper with surface oxygen can hinder the interaction with the palladium particles. A good compromise in the role of oxygen-containing surface functionalities is found for the catalyst prepared using oxidised carbon nanotubes subject to thermal treatment under inert gas at 400 °C prior to metal impregnation. The heat treatment at 400 °C removes only part of the acid oxygen-containing groups from the support surface. The oxygen still present on the surface promotes the anchoring and dispersion of the metals on the support surface [126],



**Fig. 10.17** Dimensionless concentration of bromate in catalytic reduction experiments over Pd mono-metallic catalysts supported on carbon nanotubes with different surface properties (as-received (CNT-O), nitric acid treated (CNT-HNO<sub>3</sub>) and subsequent thermal treatments at 400 and 900 °C (CNT-400 and CNT-900), ball-milled (CNT-BM), and heteroatom doped with nitrogen precursors urea and melamine (CNT-BM-U and CNT-BM-M)) [127]

offering a compromise offset with the negative contribution of surface oxygen in the reduction of the metals or the interaction between palladium and copper, as seen for the support with the highest content of surface oxygen.

When similar supports were used in the preparation of monometallic Pd catalysts for bromate reduction (as received, HNO<sub>3</sub> oxidised, and subsequently thermally treated at 400 and 900 °C), the activity was directly related to the amount of surface-oxygen groups (Fig. 10.17) [127].

Basic supports were also prepared using a mechano-thermal approach by adding a nitrogen precursor during the ball milling of carbon nanotubes. The morphological and textural effect is discussed in detail in the next section; however, it is clear that the more basic supports shown an increased activity when compared with their counterparts with no nitrogen doping. The nitrogen heteroatoms increase the electronic density on the carbon surface and consequently its reducibility, acting then as promoters of the formation of metallic dispersions on the carbon surface.

### 10.3.2 Support Textural Properties and Catalytic Performance

The textural properties of carbon supports were also found to affect the performance of mono- and bimetallic catalysts supported on carbon nanotubes in the reduction of bromate [127]. Carbon nanotubes after ball milling were found to drastically



improve the catalytic activity of both Pd (Fig. 10.14) and Pd/Cu catalysts. This effect was attributed to the increase in the surface area due to the opening of the carbon nanotubes. This effect is very prominent with bromate as reactions on the surface of the carbon support of the adsorbed bromate with spilled-over hydrogen from the metallic catalyst are possible, in addition to reactions exclusively on the metallic surface.

### ***10.3.3 Macrostructured Nanocarbon Supports for Metallic Phases***

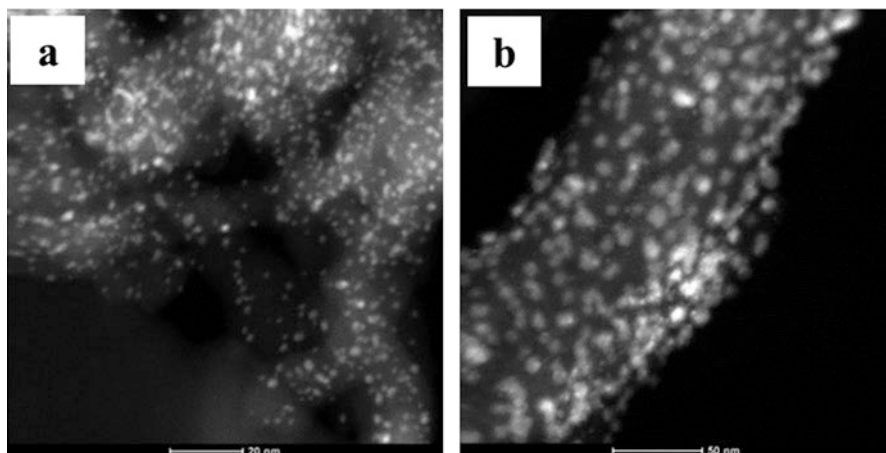
Macrostructures containing carbon nanomaterials as support for active metallic phases have been developed and applied in catalytic reduction of inorganic contaminants in water.

The most common method for coating macrostructures with nanostructured carbon layers for catalytic reduction applications is still chemical vapour deposition (CVD). However, unlike in the case of metal-free catalysis, the impregnation of the nanostructured carbon materials with the active metallic phase is an additional challenge in the process. Incipient wetness impregnation, when applied to powder materials, offers excellent fine control of the uptake of the metallic precursor salts by the carbon supports, achieved by tuning the solution volumes used to the support pore structures. However, and since the impregnation step needs to be carried out following the CVD growth of the nanostructured carbon layers, it is not as straightforward to achieve a uniform contact of the carbon supports with the precursor solution using a limited optimised volume. Thus, most methods rely on impregnation from solution by excess [128, 129]. An alternative approach using *ex situ* catalyst preparation and subsequent coating is possible, but the post-deposition thermal treatments significantly affect the performance of the catalyst, leading, for example, to the sintering of metallic nanoparticles. Thus, some optimisation of those methods is still required to achieve an efficient methodology [52].

Nevertheless, despite the difficulties in optimising the preparation method, several different types of macrostructured supports have been successfully applied to the catalytic reduction of inorganic pollutants.

Three types of macrostructures have been used thus far in bromate and nitrate continuous removal, using different mono- and bimetallic catalysts prepared using a nanostructured carbon layer: activated carbon fibres [128, 130, 131], sintered metal filters (Fig. 10.18) [132], and honeycomb ceramic monoliths [110, 132].

Besides the effects found for the catalysts in powder form, additional effects are found for the different types of macrostructures used both in bromate and nitrate reduction. A comparison between activated carbon filters and sintered metal filters found that the latter promoted more favourable hydrodynamic conditions [128]. Honeycomb monolithic catalysts also promote formation of favourable



**Fig. 10.18** STEM images of (a) Pd/Cu and (b) Pd/Sn catalysts supported on carbon nanofibers grown on sintered metal fibres [128]

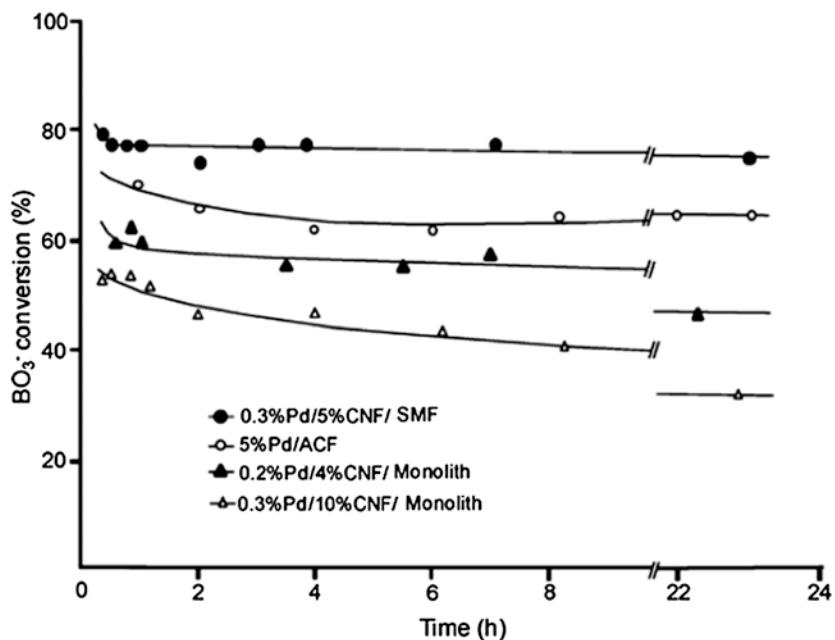
hydrodynamic conditions (Taylor or slug flow), which resulted in very good bromate conversion rates [110].

### 10.3.4 Application in Real Conditions

Carbon nanofibers coated on activated carbon filters and sintered metal filters have been prepared with Pd mono-metallic and Pd/Sn bimetallic catalysts for continuous and simultaneous bromate and nitrate reduction [133]. A bubble-reactor was designed to contact an effluent sequentially with mono- and bimetallic catalyst, achieving conversions capable of bringing their concentrations below the legal limits when used in polluted industrial and natural waters (Fig. 10.19).

The behaviour of the catalysts has also been studied using natural waters. Nitrate reduction was found to be affected by high conductivities and hardness, due to precipitation of calcium salts and poisoning of Pd by sulphur [134]. In another study, using polluted groundwater contaminated with nitrate over a Pd/Cu catalyst on carbon nanotubes, it was reported that all water components besides sulphates actually had a negative impact in the performance of the catalysts due to competitive adsorption on the catalytic active sites [135]. The effect of water components is thus likely to be specific to the concentrations in which they are present and the specificities of the catalysts.

As of today, there are not reported large-scale applications of catalytic reduction for the removal of nitrate or bromate from water. One on-going project supported by the Portugal—University of Texas in Austin collaborative programme includes the development of a pilot scale plant for reduction of nitrate, bromate, and perchlorate.



**Fig. 10.19** Bromate conversion during long-term continuous reactions over carbon-supported Pd catalyst (carbon nano fibre (CNF), sintered metal filter (SMF), and activated carbon felt (ACF)) [133]

### 10.3.5 Outlooks

The use of nanostructured carbons as supports in the catalytic reduction of inorganic contaminants in water over mono- and bimetallic catalysts containing noble metals results in very promising increases in activity when compared with the same process using other traditional carbon supports.

The modification of carbon nanotubes by mechanical methods (e.g. ball milling) in particular is seen to greatly improve their performance in bromate reduction. Methods to make use of the mechanically modified carbon nanomaterials in macrostructured reactors need optimisation since thermal treatment affects the performance of the catalysts. On the other hand, the nitrate removal is particularly sensitive to the catalyst used in terms of selectivity to ammonia, suggesting that practical applications will require custom-designed solutions rather than a “one-size-fits-all” solution. Nevertheless, reactor design can also be used to tune the selectivity of the catalytic process towards nitrogen formation. As with metal-free environmental catalysts for water treatment, the gap between the laboratory experimental results and the application to a real case needs to be completed with further research into catalyst and reactor scaling-up and integration in water and wastewater treatment plants.

## 10.4 Conclusions

An introduction into the structuring of carbon from the nano- to the macroscale and its application in catalytic water treatment is provided to those seeking to have an overall picture of recent advances. The role of catalytic water treatment and its integration into the wider water management strategies for pollution control and mitigation is described, in particular for the removal of emerging organic and inorganic contaminants.

The catalytic processes are divided into those making use of metal-free catalysts (where the carbon is an active catalyst) and those requiring an active metallic phase (where carbon is used as a support). The discussion is focussed on 1D sp<sup>2</sup> hybridised carbon (carbon nanotubes and nanofibers) as their properties are particularly interesting for the applications described here. Several examples are provided to illustrate how the properties of the carbon nanomaterials affect the performance of the catalysts. Succinctly, the general case is that basic and mesoporous carbon nanomaterials tend to offer the best performances as both a catalyst and a catalyst support.

The challenge of transferring the catalysts developed in powder form to systems suitable for practical applications is described where the macrostructuring of the carbons is approached. Reported applications in real or approximated conditions are used to provide insight into what can be expected from these technologies in the future. Pathways for future research are briefly suggested, focussing on the translation of the catalytic water treatment solutions to practical real-world applications.

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