Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater

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The use of carbon materials as catalytic support or direct catalyst in catalytic wet air oxidation (WAO) of organic pollutants is reviewed. The discussion covers important engineering aspects including the characterisation, activity and stability of carbon catalysts, process performance, reaction kinetics and reactor modelling. Recommendations for further research in catalytic WAO are outlined.

KEY WORDS: activated carbon; characterisation; CWAO; kinetics; modelling; organic pollutants; review; trickle bed reactor

1. Introduction

Currently half of the available freshwater is appropriated for human uses [1] indicating a high level of exploitation and contamination of the existing water resources. Large quantities of aqueous effluents arise from diverse industrial (petrochemical, chemical, pharmaceutical and agro-alimentary) or domestic activities and have to be treated before returning to the aquatic environment. The presence of highly bio-toxic and refractory organic pollutants in these effluents is challenging the traditional treatments including physical separation, incineration or biological abatement. At the same time, new regulations for the disposal and treatment of multicomponent toxic and potentially hazardous wastes are imposing lower discharge limits that are difficult to meet with the current technologies.

Significantly less contamination of water resources can be achieved *in situ* by the prevention of end-stream pollution in the specific production processes. Concepts of green chemistry and process sustainability have become issues of global importance for industrial companies. Nevertheless, the implantation of new production strategies is slowly developing in the competitively orientated industrial environment. Meanwhile, more efficient and economic solutions for end-stream treatment, avoiding high-energy input technologies [2], are imperative to produce reusable process water and environmentally friendly effluents.

A first step towards improved remediation of wastewater was the development and successful application of the Wet Air Oxidation technique (WAO) to treat sewage and other industrial effluents [3,4]. Investment and operation costs of WAO plants, however, are not favourable as WAO employs excessive temperatures between 150 and 300 °C and air pressures up to 200 bar. The effective treatment of effluents containing new highly refractory organic pollutants would make this method even more expensive.

WAO performance can be improved by the addition of homogeneous [5,6] or heterogeneous [4] catalysts at subcritical conditions or at severe 'supercritical' operating conditions [7,8]. Alternatively, low temperature oxidation processes replace oxygen by stronger oxidants such as O_3 [9,10] or H_2O_2 [9,11,12] in combination with an energy input to form reactive OH-radicals [13,14]. Several reviews on catalytic and non-catalytic WAO [4,5, 15–19], supercritical water oxidation (SCWO) [7,8, 20–22] and advanced oxidation processes (AOP) [23–25] are now available in literature.

Moreover, the intensification or integration of wastewater treatments provides superior cleaning effectiveness compared to single step oxidation processes. Examples of such new concepts are the simultaneous adsorption and oxidation [26–29] or sequential adsorption–oxidation [30] of pollutants as well as adsorption-regeneration cycles in the same reactor unit [31–34]. Better performance of a continuous trickle bed reactor (TBR) for the phenol CWAO was also achieved by applying forced periodic operation of liquid flow [35]. The integration of a chemical oxidation/reduction pretreatment step takes advantage of the partial contaminant mineralisation reducing the effluent toxicity to levels acceptable for biological end-treatment plants [36–38]. Finally, abatement techniques that appear more appropriate than CWAO should be considered for specific pollutant groups including catalytic hydrotreatment for polyphenols [39], chlorophenols [40–44] and nitrites or nitrates [42,45–48].

Over the last 10–15 years, continuous SCWO technology proved to be an extremely powerful treatment for all kinds and concentration range of toxic organic wastewater [7,8, 20–22]. Related problems with

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corrosion and plant plugging due to salt precipitation were solved on laboratory scale leading to new reactor configurations termed hydrothermal burner [49] and Transpiring Wall Reactor [50]. Long-term tests to check for the suitability of these reactors have not yet been performed [21]. The drastic operating conditions used make this technology rather expensive. Future industrial applications of SCWO will be most probably restricted to effluents that contain highly concentrated and/or extremely refractory or hazardous organic pollutants [51]. On the other hand, emerging AOPs can perform well in drinking water purification and wastewater treatment with low concentration of pollutants, corresponding to the most efficient use of the highly active oxidation species [23–25]. Ambient operating conditions result in attractive process economics, although these benefits are partially offset by the use of expensive oxidants (O_3 or H_2O_2) and the energy source required.

For wastewater containing low to medium organic concentration, batch and continuous CWAO yielded satisfactory results in laboratory studies [4,5,15–19]. Relatively mild operating conditions of temperature and pressure lead to substantially lower investment and operation cost. CWAO becomes especially attractive when coupled with a biological or physical–chemical treatment avoiding the need for a complete mineralisation of the organic pollutants often difficult to achieve under CWAO reaction conditions. The lack of stable catalysts has prevented CWAO from being widely employed as industrial wastewater treatment. The most prominent supported catalysts prone to metal leaching in the hot acidic reaction environment are Cu based metal oxides [52–56] and mixed metal oxides (CuO, ZnO, CoO) [57,58]. Expensive supported noble metal catalysts (Pt, Pd, Ru, Rh, Ir, Ag) appear much more stable, although leaching was occasionally observed, e.g. during the CWAO of pulp mill effluents over Pd and Pt supported catalysts [59,60].

A frequently overlooked catalyst deactivation was the formation and strong adsorption of carbonaceous deposits on the catalyst surface. Such catalyst fouling was detected during CWAO of phenol over Ceria, CuO/ZnO and activated carbon (AC) [61–64]. Theses studies showed that the ability of catalysts to form carbonaceous deposits strongly depends on the reactor type used. Slurry reactors with a characteristic high liquid to catalyst ratio exhibited enhanced homogeneous side reactions and thereby the build-up of such deposits [62,64] while these side-reactions were significantly reduced in TBRs [61,65,66]. During the last years considerable research efforts were focused on reducing unwanted catalyst deactivation. Stable supported catalysts with high activity towards oxidation of organic pollutants have been successfully synthesised and tested in the oxidation of phenol [66–78]. These new catalysts remain, however, relatively expensive materials and the search for cheap, active and stable CWAO catalysts continues.

Recently, activated carbon was proved to render encouraging conversions in the oxidation of phenol [26–29, 79–82]. ACs are versatile materials that entail not only excellent properties for numerous pollutant adsorption and catalyst support applications, but also catalytic activity for many reactions including hydrogenation, oxidation, halogenation, hydration isomerisation and polymerisation reactions [83–85]. A close review of the carbon and catalytic wet oxidation literature reveals that little attention has been paid to the use of carbon materials in catalytic WAO. A discussion of the recent developments in CWAO using carbon-based catalyst is required to update the current state of the art of this emerging application.

The scope of this paper is thus to review in detail the relevant literature dealing with wet oxidation studies using carbon as support or direct catalyst. Our research group has over 10 years experience in the field of CWAO of organic pollutants, pioneering the use of AC as CWAO catalyst. Main results obtained with several ACs will be presented and completed with findings of related studies. The discussion covers the most important aspects of CWAO such as catalyst performance, process operation, complex reaction kinetics and reactor modelling.

2. Application of carbon materials

Carbons are cheap materials because they can be manufactured from any carbonaceous source by physical or chemical activation and high temperature pyrolysis. The most commonly used raw materials are wood, coal, lignite and coconut shells, although synthetic polymers or petroleum processing residues serve as precursor [86] for ash free carbons. Exhaustive information on manufacture of ACs is given in literature [87–90].

A broad variety of carbons is commercially available as granulated activated carbon (GAC), carbon black powder (CB) or graphite (G). Depending on the preparation, they have specific surface areas of 10–300 m^2/g for Gs and 100–2500 m^2/g for CBs and ACs and pore size distribution including micro (<2 nm), meso (>2–50 nm) and macro pores (>50 nm). These textural properties give rise to remarkable and tuneable capacities for adsorbing many chemical species from gases and liquids. Excellent degrees of dispersion and stability were also achieved when depositing a catalytic active phase on carbon carrier. In addition, the performance of ACs as adsorbent or catalytic support is strongly affected by the presence of metal oxides in form of ashes and acidic, basic or neutral functional surface group that can interact with adsorbed species and the catalytic active phase deposited [83–85]. The surface groups mainly involve oxygen (up to 15 mol%) and hydrogen (up to 30 mol%) atoms as well as small

amounts of N, S or Cl. Clearly, the virtues of carbon materials arise both from its textural properties and its frequently overlooked surface chemistry and electronic properties. Not surprisingly, carbon materials are suitable for diverse industrial applications as listed in table 1.

2.1. Adsorption

The largest use of ACs is as adsorbent in numerous physical separation processes including water and air treatment, recovery of industrial organic solvents or metal leaches, medicinal uses and pharmaceutical industry. Following Auer *et al.* [86], the production (and consumption) in the western world of AC and CB in 1994 amounted to 373,000 and 3,336,000 T_m respectively. Thus, the efficient carbon regeneration is a feature of outmost importance for the carbon sector. The regeneration of AC by CWAO was recently reviewed by Mishra *et al.* [4] and compared to existing chemical and thermal regeneration methods by Sheintuch and Matatov-Meytal [91]. Two important conclusions are noteworthy: (1) ACs were found to enhance the CWAO regeneration process by chemical destruction of the sorbate, and (2) AC adsorbents have a bifunctional nature to fulfil: high adsorption capacity and easy regeneration. Highest affinity with sorbates is thus not always desirable because it may decrease their ability for regeneration. The surface groups of AC can enhance oxidative coupling of organic molecules (aromatic hydrocarbons) to form aromatic oligomers, which irreversibly adsorbed on the carbon surface [92–95]. Hence, the design of optimal AC adsorbents should provide suitable textural properties and surface groups.

2.2. Catalytic support

Less than 1% of the total carbon production stands for catalysts or catalyst supports [86]. Mostly, ACs and CBs are supported with noble metals (Pd, Pt, Ru, Rh, Ir, Au), metal oxides (Cu, Fe, Mo, Ce) or bimetallic catalysts (see table 1). Tuneable textural properties, particle size distribution, attrition resistance and surface chemistry of carbons are the guarantee for being excellent catalyst supports. [86]. Additional advantages are its chemical stability in both acidic and basic media, and the easy recovery of expensive precious metals by simple AC burn-off [86]. On the other hand, the easy gasification is probably the major inconvenient of carbon materials, prohibiting their use in continuous hydrogenation or oxidation reaction with temperatures above 700 K and above 500 K, respectively [84]. Typical industrial reactions that employ AC catalysts include oxidation of hydrocarbons in the liquid phase, hydrogenation of nitro-aromatics, halogenated nitro-aromatics, fatty acids as well as hydrodesulphurisation and hydrodenitrification of oil feed stocks (see table 1).

2.3. Catalyst

The catalytic properties of carbons were already reported several decades ago. Coughlin in his review [83] pointed out the intriguing fact that the catalytic activity of carbons can be correlated to its electronic properties, which range from those of a metal to semiconductor to insulator. Thus, as shown in table 1, ACs were active catalysts in diverse reactions including hydrogenation (metal conductor like catalyst), oxidation (semiconductor like catalyst) as well as polymerisation and halogenation (insulator like catalyst). The currently most important industrial use of AC as catalyst is for the production of phosgene, followed by the oxidation of nocive gases such as SO_2, NO, and H_2S in air pollution control [84,85]. The oxidative gas phase dehydrognation of alkylbenzenes over carbons also received great attention [84], although no industrial application over a carbon catalyst is reported. Unlike the catalytic purification of gaseous effluents in air control, carbon materials as active catalyst have received little attention for the abatement of organic pollutants in the liquid phase.

2.4. Perspectives

The development and progress made over the last decade in the use of carbon materials as catalytic support or direct catalyst is reflected in table 2. Most of the reviews listed there [42,83–85,96–117] are focused on distinct aspects of the catalytic application of carbons. To be mentioned are the comprehensive work of Radovic and Rodriguez-Reinoso [85] that compiles the available information on this topic until 1997 (115 pages, 480 references) as well as the extensive review of Derbyshire *et al.* [104] on carbon materials in environmental application (66 pages, 175 references). The role that may play the textural properties and surface groups of carbon materials for its catalytic activity was investigate in detail in the remarkable work of the groups of Boehm [100,117] and Radovic and Rodriguez-Reinoso [85].

These authors among others pointed out that the functional groups on the carbon surface play an important if not the key role in the heterogeneous reaction mechanism [83–85,100,108,117]. Thus, the commonly proposed correlation of catalytic activity of carbon materials and total surface area has to be revised [84]. One of the principal reasons for this lack of fundamental studies was certainly that carbon materials were little employed in oil refining and petrochemical industries which for decades controlled the attention of research in heterogeneous catalysis [100]. However, the rapidly growing interest of carbon catalysts in fuel cells, environmental and fine chemical requires a better fundamental understanding of the catalytic function and behaviour of carbons to optimise their design for a specific reaction [83–85,100].

Table 1
Applications of carbon materials

As adsorbent	As catalyst support	As catalyst (partly adapted from [83])
Separation/Elimination of • Toxic contaminants from water (organics, metal ions) and air (SO_2, NO_2, Cl_2, VOCs, mercury vapours) • Colour, taste and odour (in food industry)	Activated carbon and carbon black support Active metal phase: • Pt, Pd (mostly), Ru, Rh, Ir • Cu, Fe, Mo and Co-oxides and mixed oxides of Mo-Co, Ni-Mo, Fe-M(Co, Ni, Ru, Rh, Pd, Pt, Ir)	Involving halogen $CO + Cl_2 \rightarrow COCl_2$ $SO_2 + 5Cl_2 \rightarrow C_2Cl_6 + HCl$ $C_2H_4 + Cl_2 \rightarrow COCl_2$	Involving hydrogen $RX + H_2 \rightarrow RH + HX(X=Cl, Br)$ $HCOOH \rightarrow CO_2 + H_2$ $CH_3COHCH_3 \rightarrow CH_3COCH_3 + H_2$
Recovery of • Volatile organic solvents (all industries) • Gold leaches (mineral industry) Medicinal uses Pharmaceutical applications	Applications of metal oxides: • Hydrodesulfurization of petrol feedstocks • Hydrodenitrogenations Applications of precious metal: • Liquid phase hydrogenations of halogenated nitro-aromatic and nitro-compounds, and unsaturated free fatty acids	Oxidation/reduction: $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ $NO + \frac{1}{2}O_2 \rightarrow NO_2$ $2H_2S + O_2 \rightarrow S_2 + H_2O$ $C_6H_5C_2H_5 + \frac{1}{2}O_2 \rightarrow C_6H_5C_2H_3 + H_2O$	Isomerisation/dehydration: $3C_2H_2 \rightarrow C_2H_6$ $HCOOH \rightarrow CO + H_2O$
Storage of hydrogen and natural gas in fuel cells Biofilters in activated sludge	• Oxidation of organics in fine chemical industry • CWAO of Organic pollutions • Fuel cells	Emerging Applications • CMS for shape selectivity reactions • CWAO of organic pollutants • Gasification of Organics and Biomass	

Table 2
Recent reviews on catalytic use of carbon materials

Authors	Year	Title	Pages	Refs.
Antolini [97]	2003	Formation of carbon-supported PtM alloys for low temperature fuel cells: a review	11	81
Atamny and Baiker [98]	1998	Investigation of carbon-based catalyst by scanning tunneling microscopy: opportunities and limitations	29	240
Auer et al. [86]	1998	Carbons as supports for industrial precious metal catalysts	13	52
Augustine [99]	1996	Heterogeneous catalysis for the synthetic chemist	–	–
Boehm [100]	1994	Some aspects on the surface chemistry of carbon blacks and other carbons	11	82
Cameron et al. [101]	1990	Review of supported AC with precious metals	–	–
Coughlin [83]	1969	Carbon as adsorbent and catalyst	12	71
De-Jong [102]	1999	Synthesis of supported catalysts (carbon nanotube)	8	
De-Jong and Geus [103]	2000	Carbon nanofibres: catalytic synthesis and applications	30	175
Derbyshire et al. [104]	2001	Carbon materials in environmental application	66	21
Drago et al. [105]	1994	Deep oxidation of chlorinated hydrocarbons	13	–
Foley [106]	1995	Review on CMS	–	–
Gallezot [96]	1998	Special issue on carbon materials as catalyst supports	–	37
Jüntgen and Kühl [107]	1989	Mechanism and physical properties of carbon catalysts for flue gas cleaning	46	93
Leon y Leon et al. [108]	1992	Evidence for the protonation of basal plane sites on carbon	15	93
Lisovskii and Aharoni [109]	1994	Review on catalytic ODH hydrocarbons	15	
Reimerink [110]	1999	The use of activated carbon as catalyst and catalyst carrier in industrial applications	19	–
Lu and Rudolph [111]	1998	Special section on adsorbents and catalysts for clean energy and emissions control	–	17
Matatov-Meytal and Sheintuch [42]	2002	Hydrotreating processes for catalytic abatement of water pollutants	5	480
Radovic and Rodriguez-Reinoso [85]	1997	Carbon materials in catalysis	115	–
Radovic and Sudhakar [112]	1996	Review of patent literature	–	87
Rodriguez-Reinoso [84]	1998	The role of carbon material in heterogeneous catalysis	17	–
Rodriguez-Reinoso [113]	1995	In porosity in carbons: characterisation and applications	–	36
Sheintuch and Matatov-Meytal [114]	1999	Comparison of catalytic processes with other regeneration methods of activated carbon	8	65
Simonov et al. [115]	2000	Preparation of the Pd/C catalysts: a molecular-level study of active site formation	15	109
Serp et al. [116]	2003	Carbon nanotubes and nanofibres in catalysis	22	64
Stöhr et al. [117]	1991	Enhancement of the catalytic activity of activated carbon in oxidation reactions	14	

Table 3
Carbon as catalyst support in CWAO of phenols

Substrate	Operating conditions	Catalyst	X (%)	X_{COD} (%)	Observations	Refs.
Phenol (5 g/L)	TBR 110–160 °C, 5–8 MPa F_{AIR}/F_L = 400 m³/m³ τ = 2.0 h Liquid holdup = 0.05–0.065	0.3%Pt/CBC 0.3%Pd/CBC 0.3%Ru/CBC 0.3%Pt/SM-1 CBC SM-1 Glass beads	>99 ≈90 ≈60 ≈30	≈90 ≈80 ≈55 ≈20	Activity: Pt/CBC > Pd/CBC ≈ Ru/CBC > Pt/SM-1 > CBC > SM-1 > GB Highest formation of acetic acid for CBC, lowest for Ru/C combustion of CBC at lower T than in gas phase: 2, 3 and 6 wt.% at 393, 413 and 433 K after 8 h of use Change of surface properties (surface area, average pore diameter and porevolume) during CWAO	[118] [119]
Phenol (22 mM)	Hastelloy batch reactor 160 °C, 2 MPa of O_2 t_R = 0–3 h, C_{Cat} = 4 g/L	1.5% Ru/C 1.5%Ru–Ce/C 5%Ru/CeO₂ Blank	85 99.5 93.8 24.5	43 57 61 9	Higher specific activity for carbon supported catalyst Cerium acts as oxygen donor in Ru–Ce/C Accumulation of acetic acid No data on deactivation, AC activity and AC combustion reported	[122]
Phenol (1–10 g/L)	Batch catalyst basket reactor 160–220 °C, 2.6–4 MPa Air t_R = 100 min, 2.2 g_{Cat}	5%CuO/AC Coconut shell	35 95	15 90	60% Cu leaching as Cu-acetate, 25% loss of initial reaction rate Strong rate enhancement at pH = 12, E_a = 78.6 kJ/mol, α_{O2} = 0.5 No data on combustion of AC reported	[120] [121]
Phenol (1.3 g/L)	Slurry batch reactor 200 °C, 2 MPa O_2 t_R = 0.5–1 h, C_{CAT} = 1 c_{at}/L,	0.37%Cu/AC 0.56%Cu/AC	100 100	95 85	Chemical Vapour Deposition provides monolayer dispersion and higher specific activity compared to impregnation method No data on Cu leaching and AC combustion reported	[123]
Para-Chlorophenol (1.5 g/L)	Slurry Reactor with glass vessel 180 °C, 2.6 MPa O_2 t_R = 1 h, 1 g_{Cat} Pt, Pd, Ru = 1 wt.% Mn = 10 wt.%	None AC alone Pt/AC Pd/AC Rn/AC Pt/Al₂O₃ Pd/Al₂O₃ Ru/Al₂O₃ Pt/CeO₂ Ru/CeO₂ Mn/Al₂O₃	73.5 100 100 100 100 100 89.3 100 57.3 60.6 66.7 100	43 68.3 97.9 97.5 91.8 91.2 81.8 72.4 50.4 45.4 65.7 82.5	Strong formation of acidic intermediates without catalyst High activity of AC alone, no AC loss after run of 1 h at 180 °C Activity: Pt > Pd > Ru > Mn > Alloys, correlates well with heat of formation of MeO Support activity correlates well with BET surface area: AC (645–820 m₂/g) > Al₂O₃ (80–110 m₂/g) > CeO₂ (6.6–9.8 m₂/g) Adsorption of p-CP on support for AC. almost negliegiable for CeO₂ and Al₂O₃ Highest (acetic and chlorinated) acid destruction for Pt, lowest destruction for Ru Strong leaching of Mn	[124]

Table 4
Carbon as catalyst support in CWAO of carboxylic acids

Substrate	Operating conditions	Catalyst	X (%)	X_{COD} (%)	Observations	Refs.
Acrylic acid (52 mM)	Batch reactor 160 °C, 2 MPa of O$_2$ t_R = 0–3 h, C_{Cat} = 4 g$_{Cat}$/L	1.5%Ru/C 1.5%Ru-e/C 1.5%Ru/CeO$_2$	37 39 100	34 47 90	Low Ru/C and Ru–Ce/C activity, Accumulation of acetic acid Ce acts as oxygen donor in Ru/CeO$_2$, number of contact points between Ru and CeO$_2$ particles is key parameter for activity No data on deactivation, and AC combustion reported	[122]
Acetic acid (5 g COD/L)	Batch reactor 200 °C, 2 MPa of O$_2$ t_R = 3 h, C_{Cat} = 4 g$_{Cat}$/L (*) CO$_2$-selectivity	5%Pt/TiO$_2$ 5%Rh/TiO$_2$ 5%Ru/TiO$_2$ Mn/CeO$_2$ 5%Ru/C	6 9 42 76 97	100(*) 100 100 96 98	Low activity of Pt, Rh, Ru/ TiO$_2$ Surface Area: AC (900 m^2/g) < CeO$_2$ (200 m^2/g) > TiO$_2$ (100 m^2/g) No leaching of Ru supported on carbon after 3 h of use Significant leaching of Mn Partial oxidation of Carbon support	[125]
Acetic acid (5–20 g/L)	Batch reactor 175–200 °C, 10 MPa Air t_R = 1.5 h, m_{Cat} = 0.1–0.6 g, Graphite: 300 m^2/g AC: 850–400 m^2/g	1.2–5%Ru/C Blank Carbon support	– Negligible Negligible	100	10–40 higher rates for graphite: e$^-$-transfer from graphite to Ru reduces oxygen surface poising of Ru, diffusion limitation in AC Oxidation activity of Ru is particle size dependent Power law kinetics: E_a = 100.5 kJ/mol, α_{O2} = 0.65, $\alpha_{Acetic\ acid}$ = 0 Ru-leaching <0.05 ppm, no data on AC combustion reported	[126]
Formic acid (30–400 mM)	Slurry CSTR 9–20 °C, 0.012–0.2 Mpa O$_2$, pH = 1–13, m_{Cat} = 0.3 g	1%Pt/C			Initial reaction rate depends on C_{FA}, P_{O2}, T and has a maximum at pH = 4 (formate ion is the active species) for pH <4: decreasing concentration of active formate ion for pH >4: increasing repulsion of formate ion by catalyst Pt-leaching: 1.9 ppm (pH = 3) and 8.0 ppm (pH = 1.1) Proposed kinetic mechanism: O$_2$ + 2* ↔ 2O* HCOO$^-$ + * ↔ HCOO* HCOO* + O* ↔ CO$_2$ + OH$^-$ + *	[127]
Acetic acid	Batch reactor	1.56%Pt/AC	0	0	Formic acid > > oxalic acid > >maleic acid > > acetic acid	[71]
Maleic acid Oxalic acid Formic acid (all 5 g/L)	53–132 °C, 0.5 Mpa t_R = 1–25 h, m_{CAT} = 0.1–1.5 g	1.56%Pt/AC AC support	100 100 100 Negligible	100 100 100	High metal dispersion, uniform particle distribution and sintering stability by selective exchange of cations with carboxylic groups Pt-leaching <0.05 ppm, no data on AC combustion given	
Succinic acid Adipic acid Glutaric acid Acetic acid Propion. acid (all 5 g/L)	Batch reactor 190 °C, 1.5 MPa, t_R = 6 h, m_{Cat} = 1 g$_{Cat}$	5%Ru/C Blank		>99.5 >99.5 >99.5 >65.9 >68.5 11	TOC-abatement: SUC > GLU > ADI > PRO > ACE Power law kinetics: E_a = 100 kJ/mol, α_{O2} = 0.2, $\alpha_{Succinic\ acid}$ = 0 Addition of NaCl or HCl and H$_2$SO$_4$ decreases slightly X$_{TOC}$ At neutral or basic pH, both X and X$_{TOC}$ are greatly reduced, the dissociated carboxylate ion being difficult to adsorb and oxidise Ru-leaching <0.05 ppm, AC support partially oxidised	[128]

Table 4
(Continued)

Substrate	Operating conditions	Catalyst	X (%)	X_{COD} (%)	Observations	Refs.
Butyric acid (5 g/L)	Batch reactor with glass liner 200 °C, 0.69 MPa O_2 t_R = 2–8 h, m_{Cat} = 0.8 g	5%Ir/C AC alone Blank	53 5.1 3.1	54	AC supported Me-activity: Pt > Ir >> Cu > Ni ≈ Co ≈ AC (preparation method) Activity of Ir depends on particle size No Ir particle size change and Ir-leaching during oxidation -Methylaniline (inhibitor) suppresses acid conversion Power kinetics: $r_i = 3.2 \times 10^5\, e^{-57900/RT}\, C_{BA}\, P_{O_2}^{0.61}\, C_{Ir}^{-0.63}$ Validity: 180–220°C, 0.69–1.39 Mpa O_2, 0.2–0.8 g Ir/C No data on AC combustion reported	[129]
Butyric acid Acetic acid Propion. acid (5 g/L)	Batch reactor with glass liner 200 °C, 0.69 MPa O_2 t_R = 2–8 h, m_{Cat} = 1 g	1%Pt/C AC alone	59 60.2 75 < 5	79 93.3 99.5	TOC-Abatement: PRO > ACE > BUY (most refractory) For butyric acid: E_a = 56.7 kJ/mol No Pt-leaching detected, Pt is practically inactive below 160 °C No data on AC combustion reported	[130]

Testimony of the bright perspectives for the industrial development of carbon materials is provided by a recent review of the patent literature [112]. It was concluded that there exist many opportunities for increasing the market of carbons used in catalysis. Further indicators of the good health-state of carbon research are the rate of scientific production and development of new carbon materials. During the last decades, the diffusion of studies related to carbon as catalyst and catalyst support has grown exponentially and currently between 50 and 70 papers are published per year. Novel materials such as filamentous carbons, graphite nanotubes, carbon molecular sieves (CMS) for shape selectivity reactions and fullerenes are now available to carry out laboratory studies, although the full potential of these novel carbon materials has yet to be delineated [85].

3. Carbon materials in CWAO

As for CWAO of organic pollutants in general, most of the research studying carbon catalysts aimed to assess its catalytic activity. Little attention was given to catalyst characterisation and deactivation phenomena or kinetic modelling. The available information on process operation and reactor modelling is even scarcer. The first part of this review summarises thus CWAO results, distinguishing between the use of carbon materials as support or catalyst. In the second more general part, recent advances made in kinetic and reactor modelling as well as process operation are discussed.

3.1. Carbon as catalytic support for CWAO

Tables 3 to 7 presents a total of about 30 papers published over the past decade on the use of carbon as catalyst support in CWAO [71,118–146]. No exhaustive survey of patent literature was attempted, but the relatively small number [140–143] of patent application found indicates that CWAO (over carbon catalysts) is still in a developing stage. However, carbons are also increasingly tested in laboratory for the abatement of organic pollutants via hydrogenation [39,45, 147,148] or hydrodechloration [40–44,149–153] and low temperature photocatalysis [25].

3.1.1. Preparation and characterisation

Carbon supported CWAO catalysts contain noble metals (Pt, Pd, Ru, Ir, Rh, bimetallic Pd–Bi and Pt–Ru) and less frequently metal oxides (CuO) or mixed oxides. The carbon support of choice is activated carbon followed by carbon black and graphite (see tables 3–7). Among the available techniques of catalyst preparation, incipient wetness impregnation was mostly employed followed by ion exchange. In the latter, the carbon support is pre-oxidised with a sodium hypochlorite solution to create exchangeable carboxylic groups on the carbon surface [126]. The presence of these

Table 5
Carbon as catalyst support in CWAO of alcohols and trace organic compounds

Substrate	Operating conditions	Catalyst	X (%)	X_{COD} (%)	Observations	Refs.
Glyoxal	Batch slurry reactor	Pt/C	100		Selective partial oxidation at mild conditions	[131]
Glucose (1.7 M)	40 °C, 0.1 MPa, pH = 9	Pd/C PdBi/C	100		Selectivity of intermediates is controlled by correct choice of noble metal catalysts and reaction conditions (basic pH-value)	[132]
Glycerol (1 M)	60 °C, 0.1 MPa, pH = 10–11	Pt/C Pd/C	100		Bismuth doping prevents oxygen poisoning of Pt and Pd surface. No Metal leaching observed	[133]
Cyclohexanol (5 g/l)	150 °C, 5 Mpa	PtBi/C	100		Mineralisation (complete oxidation) is possible by slightly higher temperature and pressure	[134]
Trichloro-ethylene (0.05 g/L)	Fixed bed reactor (ε_L = 0.28) 90 °C, τ = 5.04 min liquid saturated at 0.6 MPa O_2	5.4 wt% Pt/C Pt–Ru/C		>98	Trichloroethylene: E_a = 14.7 kJ/mol (90–102 °C), pore diffusion limitations in micropourous carbon (S_A = 1800 m^2/g)	[135]
		Ru = 5 wt.% Pt = 20 wt.%		>96	No catalyst degradation observed due to HCl or Cl_2 formation Attrition and partial oxidation of the AC support is reported Phenol: E_a = 33.8 kJ/mol (35–65 °C), pore diffusion	[136]
Methylene Blue (0.02 g/L)	Fixed bed reactor (ε_L = 0.28) 30 °C, τ = 0.4 min liquid saturated at 0.6 Mpa O_2	Pt–Ru/C Pt–Ru/C			limitations in micropourous carbon (S_A = 1800 m^2/g)	
Phenol (0.015 g/L)	Fixed bed reactor (ε_L = 0.28) 60 °C, τ = 5.04 min liquid saturated at 0.6 Mpa O_2	Pt–Ru/C		>98		
Alcohols	0.016–0.018 g/L TOC (alcohol)			98–99.5	Deep oxidation of organic traces is achieved in a Fixed bed reactor at mild operating conditions of temperature of 125 °C	
Carbox. Acids	0.018 g/L TOC (Carbox. Acids)			99.5		
Triethylene-tetramine	0.015 g/L TOC (Triethylene-tetramine)			98.5	Primary products of deep oxidation of organic chlorine, nitrogen and sulphur are HCl, N_2 and H_2SO_4	
Benzyl alcohol	0.08 g/L TOC (Benzyl alcohol)			97.5		
Dimethyl phthalate	0.062 g/L TOC (Dimethyl phthalate)			99.8		
Urea	0.06 g/L TOC (Urea)			93–98		

Table 6
Carbon as catalyst support in CWAO of ammonia

Substrate	Conditions	Catalyst	X (%)	X_{COD} (%)	Observations	Refs.
Ammonia (1–2.6 g/L)	Batch reactor 130–190 °C, 0.75–1.6 MPa t_R = 1–12 h Using several unsupported modified activated carbons HNO$_3$ oxidation, H or N reduction	C (carbon) COX (oxidised) CH (reduced) CHO COH CON	Activity 0.58 mM/g/h 0.66 mM/g/h 1.02 mM/g/h 0.75 mM/g/h 1.55 mM/g/h 1.50 mM/g/h		Surface area = 900–1000 m^2/g, V_{meso} = 0.045–0.05 cm^3/g Correlation of activity with amount of quinonic surface groups Carbon Quinonic Activity (a.u./g) (mM/g/h) CO used 0.21 0.75 CH 0.78 1.02 CON 2.11 1.50 COH 3.12 1.55	[137]
Ammonia (0.95 g/L)	CSTR 150–180 °C, 1.5 MPa, t_R = 2 h O$_2$/NH$_3$ = 0.3 mol/mol	5%Pt/Graphite 5%Pt/C 5%Pd/C 5%Ru/C 5%Pt/Graphite	12 (150 °C) 10 4 2 45 (180 °C)		Me-activity: Pt > Pd > Ru > Mn > Co, but Pd, Ru more selective to N$_2$ Support activity and selectivity: Graphite > AC > TiO$_2$ > ZrO$_2$ 20 (TiO$_2$) and 50 (ZrO$_2$) higher Me-area for both graphite and AC Activity and N$_2$-selectivty are sensitive to O$_2$, deficit O$_2$ avoids oxygen poisoning (overoxidation) of metal surface No data on Me-leaching or graphite/AC combustion reported	[138]
Ammonia (1 gN/L as (NH$_4$)$_2$SO$_4$)	Batch reactor 200–230 °C 0.3 MPa O$_2$ t_R = 1.67 h, pH = 12 m_{Cat} = 0.8–1.0 g	AC alone 5%Cu/AC 2%Co/AC 5 %Mo/AC 5 %Mn/AC 5%Ru/Al$_2$O$_3$ 0.5 %Ru/AC 0.5 %Pt/AC Pt(opt)/AC	10 13 18 20 20 30 59 79 88 (220 °C) (200 °C)		Me-activity: Pt/AC > Ru/AC > Ru/Al$_2$O$_3$ > Base metals/AC Support: AC (1200 m^2/g) > Al$_2$O$_3$ > TiO$_2$ > MCM-41 (1400 m^2/g) N$_2$-selectivity: >7% for Pt/AC and >95% for Ru/AC For optimised Pt(opt)/Ac catalyst: Strong effect of pH$_0$ and T on conversion (X): Low X at pH$_0$ = 5.6 (as NH$_4^+$), high X at pH$_0$ = 12 (as NH$_3$) X = 20% at 180 °C, X = 80% at 220 °C lower P$_{O_2}$ increase significantly NH$_3$ conversion (at higher O$_2$ pressure over-oxidation of Pt surface occurs) 20% initial deactivation for reused Pt(opt)/AC, then stable activity during two catalyst reuse	[139]
Ammonia (N) + Phenol (COD)	N(mgN/L)/COD(mg/L): 500/1000 (0.34 MPa O$_2$, 200 °C) 1000/4000 (1.04 MPa O$_2$, 200 °C) 1500/8000 (1.93 MPa O$_2$, 200 °C)	Pt(opt)/AC Pt(opt)/AC Pt(opt)/AC	N 71 49 53	COD >98 >96 >95	Ru-leaching: 0.6–4.2 ppm, no Pt-leaching detected No data on AC combustion reported	

groups guarantees a strong anchorage of the metal particles to the carbon surface providing high dispersion, homogeneous particle distribution and stability to sintering. In a particular case, chemical vapour deposition of copper on AC was performed to produce active monolayer catalysts (confirmed by X-ray diffraction, XRD) with a low metal content of 0.3 to 0.5 wt.% Cu [123]. These synthesised catalysts were then proved to yield high activities for phenol CWAO, comparable to those obtained over a commercial CuO/AC catalyst containing 5 wt.% of impregnated copper [120,123].

Different preparation methods and support types lead to distinct catalytic properties and catalyst characterisation becomes necessary for a better fundamental understanding of its function and behaviour during the CWAO process. Available techniques to characterise the metal-support surface are XRD, transmission electron microscopy (TEM or STEM) and XPS. Textural properties of the support including surface area, porosity and pore size distribution can be obtained by N_2 adsorption isotherms and mercury porosimetry. Temperature Programmed Reduction (TPR) and Oxidation (TPO) techniques give useful information on the catalytic redox properties and the carbonaceous surface deposits on spent catalyst, respectively.

The comparison of AC, Al_2O_3, CeO_2 and TiO_2 supports (surprisingly SiO_2 is never used) showed superior activity for the carbon support in the oxidation of phenol [118,119], carboxylic acids [123] and ammonia [138,139]. Suitable support properties provided by the carbons used may account for these findings. TEM analysis revealed 10 times higher metal dispersion and surface area [138] as well as a uniform metal particle size distribution [126] for the tested carbon supports. High surface area graphite further outperformed (microporous) AC in the oxidation of acetic acid and ammonia [126,138]. The 10 to 40 times greater activities observed in case of Ru-particles supported on graphite were partially attributed to a less hindered access of reactant molecules to the active metal sites in the mesoporous graphite structure [126]. In addition, a support effect involving electron transfer from the graphite structure to the small Ru-particles was postulated to take place leading to a better resistance of the metal surface to oxygen poisoning. In the same work, TEM examination of 1.2 and 4 wt.% Ru/C showed metal particle sizes of < 1 and 2 nm, respectively and a nine times higher specific reaction rate for the 2 nm particles. The authors related the size effect to the higher adsorption enthalpies of oxygen on small metal particles resulting in a higher surface coverage and inactivation by strongly adsorbed oxygen.

Doping of noble metal catalysts with oxygen donors such as Ce [122] or Bi [132] was also found very effective in promoting their oxidation power. The donor atoms preferentially crystallise in the vicinity of the noble metal particles creating a high number of contact points that ensure both an excellent oxygen transfer and protection of the noble metal surface against over-oxidation [122]. The promoting effect of bismuth doping was demonstrated in the WAO of glucose to gluconic acid. Under otherwise same operating conditions (pH = 9, 40 °C, air flow rate 1.51 L/min) the Pd–Bi/C catalyst achieved complete conversion after 4 h against a small 10% conversion for the untreated Pd/C catalyst [132].

As far as the carbon support is concerned, changes in textural and chemical surface properties as well as carbon support oxidation during the continuous exposure to oxygen at CWAO conditions were experimentally evidenced [118,119,128,135]. These phenomena will be discussed more in detail in the following sections.

3.1.2. Catalytic activity, stability and deactivation

Mostly, single component solutions were investigated in CWAO of organic contaminants including phenol and derivatives, carboxylic acids resulting from phenol oxidation, alcohols and low molecular weight polar compounds (in very small amounts) found within humidity condensates, urine distillates and crew personal hygiene wastewaters. (see tables 3–5). In addition to effluents of the dyeing and textile industry, catalytic wet ammonia oxidation was also investigated. Experiments with ammonia both pure or mixed with other organic pollutants (phenol, cresol and different aromatic hydrocarbons) were conducted to simulate effluents that are frequently encountered in a variety of chemical industries (see tables 6, 7)

3.1.2.1. Phenolic compounds. From table 3 it follows that phenol oxidation over noble metal (Pt, Pd Ru) or metal oxide (Cu) supported on carbon was extensively studied during the last decade. Experiments were conducted at temperatures between 120 and 220 °C and total pressures up to 8 MPa. Under these conditions complete conversion of phenol and high degrees of mineralisation between 85 and 98% were readily attained over diverse carbon supported noble metals catalysts. As illustrated in figure 1, Trawczynski [118,119] observed in trickle bed runs at 120–160 °C and 8 MPa the following order of activity for Carbon Black Composite CBC supported catalysts of 0.3 wt.% metal loading: Pt > Pd ≈ Ru. Platinum exhibited thus superior activity, although ruthenium and palladium were reported to be slightly more selective towards carboxylic acid destruction and CO_2 formation. In all studies listed in table 3, the accumulation of refractory acetic acid occurred during the oxidation leading to an undesired corrosive reaction medium with pH values close to 3. Carbon supports and noble metal catalysts are known to be stable at low pH values and effectively, severe leaching was only reported for supported Cu [120,121] and Mn [124,125] catalysts. It can be concluded that the use of carbon as support gave good results in CWAO of phenolic compounds.

Table 7
Carbon as catalyst support in CWAO of industrial effluents

Substrate	Operating conditions	Catalyst	X (%)	X_{COD} (%)	Observations	Refs.
Petroleum refinery water (Cresol, NH_3 and phenol)	120 °C, 2.0 MPa, t_R = 12 min COD: 2.6 g/L Phenol: 0.6 g/L NH_3: 0.05 g/L	CoMoS/AC NiWS/C	44 (NH_3) 46 (PhOH) 14 (NH_3) 83 (PhOH)		US Patent: US 5,552,063 Metal leaching not given	[140]
Ammonium sulphite solution (Sulphide, PhOH, Aromatic HCs)	145 °C, 0.7 MPa, t_R = 120 min Total: 1.75 wt.% Phenol: 0.84 g/L HCs: 0.5 g/L	MSCPC/C	99 (Total) 89 (PhOH) 100 (HCs)		US Patent: US 5,207,927 Metal leaching not given MSCPC = Monosulphonated Cobaltphtalocyanine	[141]
Acetic acid solution (M, E, A, P, B, EE) Formamide Thiourea	120 °C, 0.34 MPa, t_R = 3 min Acetic acid: 0.1 g/L TOC Solution: 0.14 g/L TOC Formamide: 0.1 g/L Thiourea: 0.45 g/L	Pt/AC		100 100 100 100	US Patent: US 5,460,734 US Patent: US 5,698,488 Stable activity (100 h) A: aniline; B: butanol; E: ethanol; M: methanol; P: propanol	[142] [143]
Dyeing process wastewater	Batch slurry 200 °C, 2.6 MPa, t_R = 2 h m_{Cat} = 2 g in 1.4 L COD: 11.1 g/L, TOC: 2.5–3.2 g/L	TiO_2 MnO_2 PtO_2 Fe_2O_3 CuO CuO/Al_2O_3 12 %Cu/AC	45 50 52 55 60 60 72	90	Cu/AC appears most active for dyeing wastewater AC support gives better oxidation results than Al_2O_3 support Structure and texture of the AC support is not much altered by Cu impregnation, also the state of immobilised Cu (elemental or oxide) has little effect on the catalytic activity Particle size <0.35 mm reduces pore diffusion limitations No data on Cu-leaching and AC combustion given	[144] [145] [146]

Moreover, some carbon supports alone revealed catalytic activities comparable to those of the corresponding supported metal catalysts tested in the oxidation of phenol ([118] and figure 3) and *p*-chlorophenol [124]. A major inconvenient of carbon supports, however, is their combustion that can take place during the oxidation process. For example, 2, 3 and 6 wt.% loss of CBC was measured at 120, 140 and 160 °C, respectively after eight hours of continuous CWAO due to the preferential oxidation of the binder material [118].

Two copper catalysts tested in batch runs (commercial 5 wt.% Cu/AC [120] and 0.3–0.5 wt.% Cu/AC prepared by chemical vapour deposition [123]) showed also high TOC destruction of 85–95% for initial phenol concentrations below 2.4 g/L. In contrast, for a high initial phenol loading of 10 g/L, phenol concentration apparently levelled off, as illustrated in figure 2, although fresh 5 wt.% Cu/AC catalyst and enough reactants were still available. For this catalyst, up to 60% of the initial copper amount was leached after 6 repeated runs (see figure 2). However, this cannot explain the activity loss observed since dissolved copper ions were shown to be very active in the homogeneous oxidation of phenol. The authors ascribed the unexpected catalyst deactivation to complete pore blocking caused by deposits of organocupric polymers formed on the carbon surface [121]. Catalyst stability against leaching, fouling and support oxidation is a key issue for successful application of CWAO. More studies under continuous operation are required to assess data on catalyst life-time (stability and deactivation) that are useful, if not imperative before moving CWAO to pilot plant or industrial process scale.

Little information exits on CWAO of substituted phenols and aromatic hydrocarbons using carbon supports. Qin *et al.* [124] studied the batch oxidation of *p*-chlorophenol over different noble metals supported on AC, Al_2O_3 or CeO_2 at 180 °C and 2.6 MPa of oxygen partial pressure. Almost complete COD destruction (98%) of a 1.5 g/L *p*-chlorophenol solution was achieved after 100 min with 1 wt.% Pt/AC. The following order of activity for supported noble metals resulted: Pt > Pd > Ru > Mn > Pt–Pd. The catalytic potential of the noble metals could be correlated with the heat of formation of the respective metal oxide except for Ru supported on CeO_2. The smaller the heat of formation of the metal oxide, the more active was the noble metal. Conversely to phenol oxidation, Pt showed highest acid destruction rate and Ru lowest. The carbon support tested provided the most effective support for the noble metals (AC > Al_2O_3 > CeO_2). Their catalytic efficiency observed was in line with their total surface area that decreased by one order of magnitude from AC to Al_2O_3 to CeO_2, respectively. However, the authors suggested that the ability of the support to adsorb *p*-chlorophenol (strong for AC, negligible for Al_2O_3 and CeO_2) should also play an
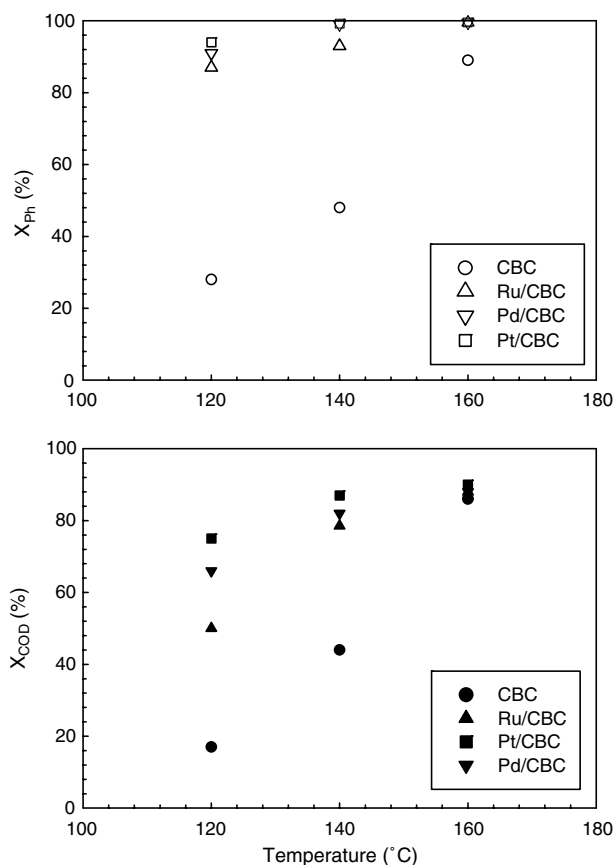

Figure 1. Phenol and COD conversion as function of temperature for CBC and different CBC supported catalysts: $P = 8$ MPa, LHSV = 0.5 h^{-1} [118].

important role in the oxidation of *p*-chlorophenol. Finally, the acidity build-up in the course of *p*-chlorophenol (1.5 g/L) oxidation was even more pronounced due to the additional release of chlorinated acids leading to pH values as low as 2.5.

3.1.2.2. Carboxylic acids. Table 4 illustrates that considerable research efforts were directed to CWAO studies of carboxylic acids that may form during the oxidation of aromatic and phenolic compounds. The carboxylic acids tested clearly fall into two groups of oxidation refractoriness. Formic acid, oxalic acid and maleic acid (Formic ≫ Oxalic ≫ Maleic) were completely destroyed under relatively mild operating conditions of 53 °C and 0.1 MPa of O_2 in case of formic and oxalic acid and 132 °C and 0.5 MPa of O_2 in case of maleic acid [71]. On the other hand, succinic acid, adipic acid, glutaric acid, propionic acid, acetic acid and butyric acid required significantly higher temperatures (200 °C) and oxygen partial pressures (2 MPa) to achieve satisfactory COD destruction efficiency [126, 128–130]. The order of TOC abatement using a 5 wt.% Pd/C catalyst was as follows: succinic > glutaric > adipic > propionic > acetic > butyric. It was impossible to completely mineralise acetic acid and
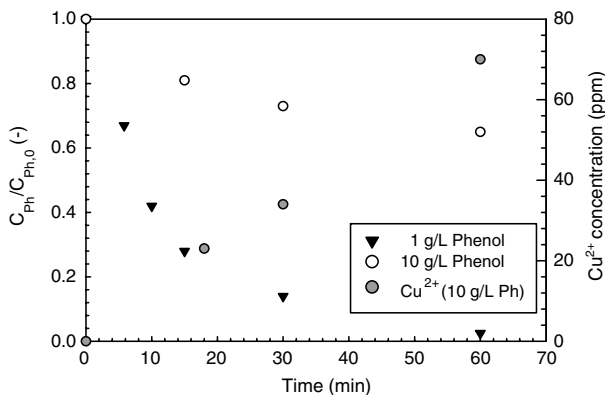
Figure 2. Phenol removal and copper leaching during phenol oxidation over 5 wt.% CuO/AC: $P = 3.6$ MPa, $T = 180$ °C, $m_{Cat} = 11$ g/L [121].

butyric acid, thus butyric acid must be considered as refractory to CWAO as acetic acid.

In agreement with the results for phenol oxidation, among different metals (Ru, Pt, Rh, Ir, Cu, Mn, Ni and Co), Ru supported on carbon exhibited superior activity towards carboxylic acid decomposition without metal leaching after 3 h of use [125]. Not surprisingly, partial oxidation of the carbon supports occurred during the oxidation of diverse refractory carboxylic acids, the temperature of reaction being as high as 200 °C [125,128]. Pt also showed a good oxidation potential, but sems to be completely inactive at temperatures below 160 °C [71,130]. Furthermore, the nature of the support was found to influence the catalytic activity. Different supports in the presence of Ru were investigated in the oxidation of acetic acid [125,126]. The resulting activity of the Ruthenium catalysts ranked in the following order depending on the support: Graphite (300 m^2/g) $\gg$ AC (900 m^2/g) > CeO$_2$ (200 m^2/g) > TiO$_2$ (100 m^2/g). Catalyst effectiveness can be apparently related to surface area of the support with exception of graphite. As for the oxidation of phenol [126], less hindered pore diffusion in the mesoporous graphite and electron transfer from its surface to the deposited metal particles may additionally enhance the activity of the Ru/graphite catalyst.

The influence of the support properties, which are not textural in nature, was also noticed in the oxidation of acrylic acid over Ru/C and Ru/CeO$_2$ catalysts [122]. Under the reaction conditions used, the Ru/CeO$_2$ catalyst performed 90% COD destruction against 34% measured for the high surface area Ru/C catalyst. The poor activity demonstrated by the Ru/C catalyst was attributed to different adsorption capacity of the supports. Acrylic acid is believed to strongly adsorb on the carbon support, reducing the number of free sites for oxygen adsorption and thereby the transfer of adsorbed oxygen to the Ru particles. Acrylic acid also preferentially adsorbs to the CeO$_2$ surface, but CeO$_2$ itself acts as

a powerful oxygen donor providing reactive species for oxidation through a high number of contact points between the metal and support. Finally, carbon as direct catalyst did not show noticeable activity for the oxidation of refractory carboxylic acids [126,128,129].

3.1.2.3. Polyalcohols and low concentrated organic compounds. CWAO of concentrated polyalcohol solutions is sought to offer an environmentally friendly technology for the manufacture of fine and speciality chemicals with non-polluting endstream effluents [131–134]. At atmospheric pressure and 40 to 60 °C, Pt and Pd supported on carbon proved to partially oxidise glyoxal, glucose and gylcerol into valuable intermediates without cleavage of C–C bonds (see table 5). The intermediate selectivity could be controlled by the correct choice of the noble metal catalyst and operating conditions (high pH values). In particular, doping of platinum and palladium with bismuth atoms highly promoted their activity so that the oxygen mass transfer limited the reaction rate rather than the intrinsic activity of the catalyst [132]. The catalysts could be recycled without loss of activity and selectivity and metal particles were not leached from the catalyst during reaction and recycling. The authors concluded that the bismuth particles strongly held on the metal surface acted as a co-catalyst because of its higher affinity towards oxygen, thereby preventing the poisoning of palladium and platinum by over-oxidation. Additional experiments showed that the oxidation of these polyalcohols may proceed to the formation of carbon dioxide and water under slightly more severe conditions than those required for partial oxidation.

The oxidation of unwanted or toxic dissolved organic contaminants in trace amounts is another example for the successful application of low temperature heterogeneous oxidation catalysis. Using bimetallic Ru–Pt/C catalyst, Atwater et al. [135,136] studied the CWAO of a broad variety of low molecular weight polar compounds found in very low concentrations within humidity condensates, urine distillates and crew personal hygiene wastewaters. The selected model contaminants included alcohols, diols, carboxylic acids, urea and thiourea (see table 5). Oxidation experiments conducted in a TBR at 125 °C with TOC feed solution values ranging from 6 to 19.4 ppm yielded high 93–99.8 TOC conversions within short residence times of 5 min. The same catalyst was tested on trichloroethylene, benzene, phenol and methylene blue to simulate industrial wastewater effluents. As seen from table 5, almost complete destruction of these molecules was performed over the studied temperature range of 60–130 °C. The reactivity of the four compounds to undergo oxidation was found as follows: phenol > trichloroethylene > benzene > methylene blue. No catalyst deterioration due to the (low) formation of HCl or Cl$_2$ could be detected, but attrition and

partial oxidation of the carbon support at temperatures as low as 125 °C was evidenced during the CWAO experiments.

3.1.2.4. Ammonia and industrial effluents. Table 6 gives an overview of the recent work dealing with the CWAO of ammonia over carbon supported catalysts. As for acetic acid, ammonia is a stable intermediate formed during the oxidation of nitrogen-containing compounds. Ammonia is frequently present in diverse industrial effluents that contain aromatic hydrocarbons in low concentrations. These effluents are very refractory to oxidative destruction and catalysts that give satisfactory results for aromatic oxidation may not very active in ammonia decomposition [11–13 in 139, 140].

Uktropec *et al.* [138] and Cao *et al.* [139] studied the CWAO of 1–1.5 g/L ammonia solutions in a CSTR and Batch reactor at temperatures of 180 and 230 °C, respectively. Among different active metals (Pt, Ru, Pd, Mn, Mo, Co, Cu) and supports (Graphite, AC, Al_2O_3, TiO_2, ZrO_2, MCM-41) tested, platinum and graphite proved to be the most active metal-support combination, although palladium and ruthenium may perform slightly better N_2-selectivity [138,139]. Under the given conditions, conversions of about 40–50% resulted for the 5 wt.% Pt /Graphite [138] and 88% for the 0.5 wt.% Pt/AC [139]. The same Pt/AC catalyst also exhibited a remarkable and constant phenol destruction efficiency (95–98%) when tested on several simulated industrial effluents that contained phenol and ammonia in increasing concentrations [139]. On the contrary, the conversion of ammonia decreased from 71 to about 50% for an increase of ammonia concentration from 500 to 1500 mg N/L. In order to maintain the $(NH_3 + COD)/O_2$ ratio constant in each experiment, the oxygen partial pressure was raised from 0.34 to 1.93 MPa. These results indicate that CWAO activity of Pt/AC catalyst is sensitive towards oxygen pressure. The authors attributed the oxygen dependence to the over-oxidation (poisoning) of the platinum surface that was readily promoted at higher oxygen concentrations. The same conclusion was reached by Uktropec *et al.* [138] who found that the conversion and N_2-selectivity in ammonia oxidation was favoured by conditions of oxygen deficit, i.e. lower oxygen pressures. The superior activity observed for the graphite and AC support may result from their 20–50 times higher metal surface area and metal dispersion provided [138]. High surface area in case of AC may account for this situation, although it cannot satisfactorily explain the overall activity since the highest surface area support MCM-41 (1400 m^2/g) performed the lowest destruction rate in ammonia oxidation [139]. As noticed in the oxidation of acetic acid, the graphite support with a very low BET area of 15 m^2/g gave even a slightly better ammonia conversion than did the AC support (1200 m^2/g). Under the same

reaction conditions the AC support alone was not very active in ammonia degradation giving a low 10% conversion at 200 °C.

Leaching of platinum was not detected during the experiments, but depending on the pH value of the reaction solution, dissolved ruthenium ions were detected in concentrations ranging from 0.6 to 4.2 ppm [139]. Cao *et al.* [139] further tested the stability of the 0.5 wt.% Pt/AC catalyst through repeated use of the same catalyst sample. The catalyst suffered an initial 20% decrease of conversion, but then maintained a stable activity during two further runs. Partial oxidation of the carbon supports is very likely to occur under the high reaction temperatures employed, however no data on long-term stability of the catalyst was given in the works of Cao *et al.* [139] and Uktropec *et al.* [138].

As shown in table 7, CWAO over carbon supported catalyst of industrial effluents only recently attracted attention leading to several patent applications for diverse process wastewater [140–143]. Yan [140] patented a process to effectively clean wastewater streams from the petroleum refinery containing aromatic hydrocarbons (phenol, cresol) and small amounts of ammonia The authors used several metal compounds deposited on carbon supports with both high porosity and surface area. Low temperatures and pressures of 120 °C and 2 MPa were employed in the catalytic oxidation runs. The tested catalysts exhibited phenol conversions ranging from 46 to 83% but only moderate activity towards ammonia degradation. Under similar operating conditions, Birbara [142,143] demonstrated that platinum supported on AC achieved quasi-complete destruction of acetic acid, solutions of numerous oxygenated compounds as well as nitrogen based molecules (formamide, thiourea). Catalyst lifetime experiments confirmed stable activity over 100 h of continuous use. Monosulphonated cobalt phtalocyanine supported on activated carbon was also highly active at 145°C and 0.7 MPa for the destruction of ammonium sulphide effluents contaminated with phenols and aromatic hydrocarbons [141]. It is noteworthy to underline the promising potential of the patented catalysts supported on activated carbon exhibiting high destruction efficiency at relatively low temperatures of 120–145 °C. The currently running CWAO plants using precious metals supported on titania–zirconia carrier for the treatment of industrial effluents require about 100 °C higher temperatures to achieve comparable process performance [154–157].

Yue *et al.* [144–146] studied various metal oxides and metal oxide supported catalysts for the treatment of dyeing process water from the textile industry at 200 °C and 2.6 MPa. Among these metal oxides, activated carbon coated with CuO performed a superior 72% COD conversion. The authors did not investigate the stability of the copper based catalyst against metal

leaching, despite these catalysts were reported to readily dissolve in the harsh reaction environment.

3.2. Carbon as direct catalyst for CWAO

The ability of active carbon to oxidise diverse organic compounds was already reported in the late seventies in studies related to the regeneration of spent activated carbon via WAO [158]. The regeneration efficiency was found to depend positively on temperature and oxygen pressure as did the loss of AC due to combustion. Repeated regeneration produced noticeable modification in texture and surface composition of treated AC. A critical temperature of 200 °C was recommended to provide satisfactory carbon clean up without excessive AC loss during WAO regeneration [159]. 30 years later, the use of carbon as catalyst for environmental oxidation processes is starting to develop. Excluding the patent and scientific literature on AC regeneration via WAO, about 25 papers were published during the last 10 years on catalytic wet oxidation using carbons as direct catalyst [26–29,35,61,79–82,160–173]. Strictly, half of these studies was devoted either to low temperature oxidation employing AC and H_2O_2 or O_3 oxidants [166–173] or partial oxidation for fine chemical synthesis [80–82] rather than to CWAO. Tables 8–10 summarise the most important data of these studies.

3.2.1. Preparation and characterisation

Among the available carbon materials, mostly AC and CB were selected as CWAO catalysts. Currently, activated carbons are manufactured by chemical or physical activation from suitable precursors [86]. The former technique uses the simultaneous carbonisation and activation of the (wood) raw material at 600–800 °C. The activating agent, i.e. H_3PO_4, $ZnCl_2$ or NaOH, is added to the raw material before the heating process. Physical or steam activation starts with the precarbonisation of the carbonaceous precursor by thermal decomposition at 600–800 °C in absence or under controlled admission of air. The posterior activation step is usually performed by steam and/or CO_2 at 800–1100 °C. The final products show different properties, but typically a microporous network of highly disordered graphitic material bearing surface oxide groups is developed. Carbon blacks are synthesised by high temperature pyrolysis (1400 °C) of hydrocarbons such as natural gas or oil fractions from petroleum processing [86]. Quenching immediately behind the reaction zone to 200–250 °C suppresses further reaction of the carbon black with oxidising components of the furnaces gases, e.g. steam or CO_2. This preparation process rather produces mesoporous carbons with lower surface area, less amounts of surface oxide groups and very low ash contents (<1%).

Prior to use in adsorption or catalytic reactions, the carbons as received were often subjected to specific liquid and gas phase treatments. Liquid phase modification employs demineralising (HCl, HF) or oxidising agent with increasing strength (H_2O_2, $(NH_4)_2S_2O_8$, HNO_3). Washing with HCl or HF attempts to eliminate catalytic active impurities (ashes) that can alter the performance of the carbon [79,83,84,166]. Oxidation in the liquid phase unselectively introduces surface oxides (mostly carboxylic and lactone groups) without a significant change of textural properties, except for stronger oxidants under harsh treatment conditions [82, 174–176]. However, modification of the carbon surface does not only depend on the expected oxidising power of the chemicals used. Their controlled access to the pores and diffusion within the pores also plays an important role. Thus, treatment temperature and time, concentration of the agents, initial carbon pore size distribution, and interaction of solvent and agent molecules with surface oxide groups already may account for the different and sometimes conflicting results observed in liquid phase treatments [176].

Gas phase treatments under controlled temperature and air or oxygen admission develop microporous structures and high amounts of surface oxide groups by partial carbon burn-off [80–82,174]. Further exposure of oxidised carbons to CO_2, N_2 or H_2 during temperature rating up to 1177 °C can progressively eliminate specific (acid) surface oxide groups to obtain carbons with basic properties [82,100,167,174,177,178]. High temperature N_2-reduction produced basic but re-oxidisable surfaces at room temperature, whereas a reducing H_2-atmosphere provided stable basic carbon surfaces [177]. Summarising the current knowledge on surface groups, surface oxides, in particular carboxylic, lactone, lactol, and phenolic groups, are mainly responsible for acidic carbon properties. Basic properties are related to chromene and pyrone groups as well as to Lewis type sites in the graphite carbon matrix itself [100,108,177–179].

Diverse organic precursors, manufacture and posterior surface modification being possible, characterisation of carbons is imperative to understand their function and behaviour in heterogeneously catalysed (oxidation) reactions. As for carbon supports, scanning techniques used are TEM, XPS, and FTIR (DRIFT) analysis. Surface area, pore size distribution and porosity are measured by means of N_2-adsorption isotherms (BET) and mercury porosimetry. Complementary techniques of temperature programmed adsorption or desorption (TPA and TPD) as well as Boehm titration allow determining the distribution of acidic and basic surface functionalities. Elemental analysis gives information of the total content of C and heteroatoms (O, H, N, S) atoms present in the carbon. Finally, electrostatic properties, i.e. surface charge, of immersed carbons depending on solution pH can be predicted by measurement of the Point of Zero Charge (PZC, titration) or the Isoelectrical Point (IEP, electrophoresis) of carbons.

Table 8
Carbon as catalyst in CWAO of phenolic compounds

Substrate	Operating conditions	Origin	S_A (m^2/g)	Ash (%)	X (%)	X_{COD} (%)	Observations	Refs.
Phenol (5 g/L)	TBR 120–160 °C, 0.1–0.9 MPa O$_2$ τ = 0.05–0.6 h, 7 g of AC	Wood	1000	4	>99	≈85	Stable activity during 10 days at 140°C and 0.2 MPa O$_2$	[26]
		Wood (CI)	1000	4	40		E_a = 70 kJ/mol, α_{Ph} = 1, α_{O2} = 1 (0.1–0.2 MPa)	[27]
		Coco (CII)	600	1	15		No obvious correlation of activity with surface area	[160]
		Mineral	960	15	8		and adsorption capacity, accumulation of acetic acid	[161]
Phenol (0.2–7 g/L)	Slurry batch reactor 100–160 °C, 0.35–0.95 MPa O$_2$ t_R = 6 h, 1–4 g of AC	Wood	1000	4	50–99		Deactivation due to carbonaceous deposits on surface E_a = 37 kJ/mol, α_{Ph} = 1, α_{O2} ≈ 0.0 (0.35–0.95 MPa)	[61]
Phenol (1 and 5 g/L)	Fixed bed reactor (upflow) 160 °C, 1.6 MPa, pH = 3.5 τ = 0.03–0.3 h, 3.5–7 g of AC	IndReact	745	(64)*	>99	≈85	Correlation of activity with mesoporous surface area and content of CO surface groups, but not with adsorption capacity. Accumulation of acetic acid. No data on AC combustion given. Important Cu-leaching: 88 ppm at τ = 0.3 h	[162]
		Centaur	931	(50)	>99			
		RTA180	1333	(40)	≈88			
		Cu/AC	960	(16)	≈85			
		*Mesoporous surface area						
Phenol 2-amino phenol Salicylic acid 5-sulfo salicylic acid (all 5 g/L)	TBR 125–175 °C 1–7 MPa O$_2$ (+H$_2$O vapour) VLHSV = 1–20 h^{-1}	Charcoal	1049	—	>99 >99 40 40		Carboxyl and S-group deactivates phenol molecule. Higher rates (10^3) obtained in Batch Reactor performance of TBR depends on reactor hydrodynamics (catalyst wetting, mass transfer) and reaction rate. Gas reactant limited: partial wetting favours conversion. Liquid reactant limited: full wetting favours conversion. Periodic operation of TBR enhances conversion	[28] [29] [35] [79]
Phenol (5 g/L)	Slurry batch reactor 110–160 °C 3–5 MPa O$_2$ (+H$_2$O vapour) t_R = 3 h, 0.1–1 g of AC	Chezacarb	950	Ni 0.25	>99		Strong effect of T: no induction period at 160 °C at pH$_0$ = 2 low formation rate, at pH$_0$ = 10 high formation rate of dicarboxylic acids	
		Charcoal	1049	Fe: 0.016 V: 0.08 —	>99		Metal traces promote carboxylic acid destruction	
Phenol (5 g/L)	TBR 110–160 °C, 5–8 Mpa F_{AIR}/F_L = 400m^3/m^3 τ = 2.0 h Liquid holdup = 0.05–0.065	CBC	70.1	—	>99	≈85	High formation of acetic acid for CBC 2, 3 and 6 % combustion of CBC at 120, 140 and 160 °C after 8 h of use. Change of surface properties (surface area, average pore diameter and pore volume) during CWAO	[118]
Phenol (20 g/L)	Fixed bed reactor (upflow) 400 °C, 25 Mpa τ = 2.6 s, 0.9 g of AC	Without carbon			7	1	High combustion rate for bamboo, coconut and fibre 1–2 order lower for coke and graphite, respectively weak pore diffusion limitation reported for supercritical reaction conditions	[163,164]
		Coconut	430	0.33	63	50		
		Bamboo	42.7	1.53	30	18		
		Coke	12.4	10.0	38	28		
		Graphite	0.003	4.14	22	17		
		Fibre	0.6	1.99	40	29		

Table 8
Continued

Substrate	Operating conditions	Origin	S_A (m²/g)	Ash (%)	X (%)	X_{COD} (%)	Observations	Refs.
Para-chlorophenol (1.5 g/L)	Slurry reactor with glass vessel 180 °C, 2.6 MPa O_2, t_R = 1 h	AC	645–820	–	100	68.3	Strong formation of acidic intermediates No AC loss after run of 1 h at 180 °C Strong adsorption of p-chlorophenol on AC	[124]
Para-nitrophenol	Fixed bed reactor 150–180 °C, 0.718 MPa O_2, t_R = 3.5–6.5 h load: 0.178 gNP/g AC	Darco	450	—	>90		Carbon catalyses wet oxidation of p-nitrophenol: E_a = 135 kJ/mol for WAO, E_a = 99 kJ/mol with carbon 20–30% loss of initial surface area after regeneration 80% of initial adsorption capacity after regeneration	[165]

Numerous modification and characterisation techniques are available to analyse the catalytic behaviour of carbons. Tables 8 to 10 illustrate however, that the potential of these techniques is currently being little used to elucidate the role that the carbon plays in catalytic oxidation reactions. Huang et al. [167] and Lücking et al. [168] studied the low temperature wet peroxide oxidation of p-chlorophenol over carbons of different origin and preparation. Huang et al. [167] stated that the treatment of Filtrasorb300 carbon with HNO_3 caused a 2-fold lower surface area and 4-chlorophenol adsorption capacity. At the same time the modified carbon performed a five times higher dechlorination rate than that of the HCl or H_2O_2–HCl treated parent carbon. Lücking et al. [168] tested graphite and several activated carbons on the destruction of 4-chlorophenol using H_2O_2 oxidant. The graphite carbon exhibited higher activity towards 4-chlorophenol decomposition than did the ACs. The authors ascribed the differences observed to the electronic properties of the internal graphitic structure that can act like a metal electron donor or acceptor. Khalil et al. [169] characterised in detail 12 activated carbons prepared from solid olive oil mill wastes and tested on H_2O_2 composition. The highly developed AC obtained by impregnation with H_3PO_4 and heat treatment at 300–700 °C showed only low to moderate catalytic action for the decomposition of H_2O_2. The extent of H_2O_2 conversion for these carbons apparently followed an inverse function of textural properties including external non porous surface area, pore size and porosity. Carbons activated with steam or NH_4Cl leading to more basic carbon surfaces, demonstrated to be distinctly better H_2O_2 decomposers. The NH_4Cl carbon treated at 600 °C exhibited a slurry pH of 9.5 and rate constant of 0.0036 min^{-1}, whereas the P-75 carbon (70%H_3PO_4 and 500 °C) with pH of 5.0 gave a 4 times lower rate constant of 0.00085 min^{-1}. All the authors pointed out the carbon surface chemistry as the prevailing factor in affecting the extent of 4-chlorophenol and H_2O_2 degradation, but no attempt was made to analyse the nature of the acidic and basic surface groups involved.

Rivera-Ultrilla and Sanchez-Polo [166] provided a more fundamental investigation of the catalytic role of carbon surface groups. The authors selected several commercial activated carbons with different physical and chemical surface properties to study the ozonation of 1,3,6-naphtalenetrisulphonic acid (NTS). The carbon samples were texturally and chemically characterised using N_2-adorption isotherms, mercury porosimetry, pH_{PZC}, selective neutralisation and elemental analysis. The findings of this work are summarised in table 9. Carbons with high intrinsic macropore volumes mostly favoured NTS removal, although no clear relationship was observed between NTS ozonation rate and total surface area. The macropores should facilitate the access of ozone to the carbon surface, thereby reducing pore

Table 9
Carbon as catalyst for low temperature oxidation using H_2O_2 or O_3 oxidants

Substrate	Conditions	Origin	Treatment	BET (m²/g)	V_{Mic} (ml/g)	V_{Mac} (ml/g)	Elemental %N	O %	Ash %	Acid	Basic (µeq/g)	PZC	Conversion (%) Org	Conversion (%) TOC	H_2O_2	Refs.
1,3,6-naphtalene trisulphonic acid (0.045 g/L)	Slurry batch reactor 25 °C, pH₀ = 2.3, t_R = 0–4 h, 0.5 g_{AC} liquid presaturated with ozone	Ceca GAC	As received	966	0.13	0.29	0.73	19.6	12	323	99	6.8	91	50		[166]
		Ceca AC40	id	1201	0.07	0.39	0.53	10	8.3	438	102	5.3	67	59		
		Witco	id	808	0.04	0.09	0.00	4.2	0.3	183	253	6.8	55	75		
		Filtasorb 400	id	1075	0.11	0.36	0.80	11	6.6	234	570	7.9	87	75		
		Merck	id	1301	0.09	0.35	0.72	9	5.2	114	582	7.9	89	75		
		Sorbo	id	1295	0.06	0.43	0.61	10	5.9	88	1713	9.4	91	75		
		Norit	Id	968	0.10	0.52	0.70	10	4.8	139	2050	9.2	91	75		
P-chloro phenol (0.5 mM)	Batch flask 25 °C, 0.1 Mpa t_R = 70 h 4–20 mM H_2O_2	Filtrasorb-GAC1	HCl for 24 h	983	0.28				Low			4.2	40		High	[167]
		Filtrasorb-GAC2	9.8 M H_2O_2 +	1023	0.26				Low			3.5	40		Medium	
		Filtrasorb-GAC3	HCl for 24 h 13.9 N HNO_3	556	0.11				Low							
P-chloro phenol (1 g/L)	Brown flask 30 °C, 0.1 MPa t_R = 6–800 h, pH = 3 5.3 g/L H_2O_2	Graphite	As received	–					–			3.2	52		Small	[168]
		F-300 (Chemvir.)	id	1000					< 8			after 96 h	90	25	25	
		Darco (Norit)	id (hard coal)	1000					< 8			after 800 h	85	25	50	
		ROW 0.8 (Norit)	id (peat)	950					< 6			after 800 h	80	25	80	
		RFZ 1 (Norit)	impregnated with Fe(OH)₂	800					15–20			after 800 h	80	25	98	
												after 200 h	80	40	100	
H_2O_2 (0.802 M)	Glass cells 30 °C, 0.1 Mpa t_R = 70 min carbons prepared from milled olive stone residuals	P-33 300 °C and	30%H_3PO_4	310	0.061	0.218			Low			slurry pH: 5.7			3.2	[169]
		P-37 700 °C and	30%H_3PO_4	408	0.096	0.241			Low			5.2			6.2	
		P-55 500 °C and	50%H_3PO_4	675	0.182	0.223			Low			5.1			1.9	
		P-65 500 °C and	60%H_3PO_4	750	0.173	0.257			Low			5.4			3.3	
		P-75 500 °C and	70%H_3PO_4	506	0.117	0.272			Low			5.0			4.0	
		P-57 700 °C and	50%H_3PO_4	598	0.142	0.288			Low			4.9			2.4	
		S600 600 °C and	Steam Pyrol	171	0.040	0.068			Low			7.6			6.6	
		S700 700 °C and	Steam Pyrol	270	0.121	0.105			Low			7.7			7.8	
		SN 850 °C and	Steam/N_2	90	0.026	0.024			Low			8.1			7.1	
		Sd 850 °C and	Steam/CO_2	113	0.021	0.061			Low			8.7			7.8	
		NH_4Cl 600°C and	NH_4Cl	199	0.065	0.026			Low			9.5			9.3	

Table 10
Carbon as catalyst for partial oxidation in fine chemical synthesis

Substrate	Conditions	Origin	Treatment	BET (m²/g)	V_{pore} (mL/g)	%O	%N	Acidic	Basic	Rate (mM h⁻¹ g⁻¹)	Refs.
								Groups (mM/g)			
Cyclo-hexanone (5 g/L)	Slurry batch reactor 140°C, 5 mPa Air t_R = 6 h, 0.2 g of AC	HMT	As received	530	0.62	1.7	0.8	0.13	0.50	6	[80]
		HMT-49C (49% burn off of carbon)	in CO₂ at 1123 K	1260	1.20	1.8	0.1	0.35	0.78	22.5	[81]
		HMT-55C	in CO₂ at 1123 K	1470	1.37					28.5	
	HMT = novolac resin, crosslinked with hexamethlenetetramine	HMT-30A	in Air at 723 K	874	0.90	18.9	0.7	2.35	0.24	19.5	
		HMT-30A-N873	+ N₂ at 873 K					1.20	0.58	25.5	
		HMT-30A-N1173	+ N₂ at 1173 K							10.5	
	FU = novolac resin with urea and cross linked with formaldehyde	FU	as received	650	0.67	1.5	0.4	0.19	0.50	7.5	
		FU-23C (23% burn-off of carbon)	in CO₂ at 1123 K	997	0.92	1.1	0.4	0.34	0.53	18	
		FU-55C	in CO₂ at 1123 K	1477	1.33	1.1	0.4	0.89	0.38	28.5	
		FU-23C-AM	+ Air at 573 K	1042		6.8	0.3			16.5	
		FU-55C-AM	+ Air at 573 K	1353		5.1	0.5			15	
		FU-23C-AM-N873	+ N₂ at 873 K							18	
		FU-23C-AM-N1173	+ N₂ at 1173 K	1123		0.45	<0.2			15	
PMIDA (0.17 M)	Slurry batch reactor 95 °C, pH₀ = 1.5 t_R = 3 h, 3 g of AC	4S (wood AC)	As received	1164	0.88		0.03	0.2		2.8	[82]
		4S/NaOCl/RT	NaOCl at 20 °C	1243				1.3		1.5	
		4S/HNO₃/RT	HNO₃ at 20 °C					2.9		1.1	
		4S/N₂/900 °C	in N₂ at 900 °C	940	0.7		0.05	≈ 0		4.0	
		4S/NH₃/900 °C	in NH₃ at 900 °C	1501	1.14		4.20			5.1	
		CBP (wood AC)	as received	146	0.05					0.3	
		CBP/NH₃/900 °C	in N₂ at 900 °C	462	0.20					5.1	
		AC40 (wood AC)	as received	1300						1.5	
		HSAG (graphite)	id	364	0.05					0.1	
		Vulcan (carbon black)	id	295	0.06					0.5	
		SX1G (peat AC)	id	1055	0.73		0.34			4.0	
		SNK (synthetic AC)	id	1112	0.46		2.10			4.0	

diffusion limitation. The carbons that gave best activity for NTS destruction were those with basic pH_{PZC} values and both highest and lowest concentrations of basic and acidic surface groups, respectively (see table 9). The authors related the basic carbon sites to basal plane π-electrons away from the cyrstallite edges and oxygenated surface groups (chromene and pyrone) as advanced by Radovic *et al.* [180].

A similar conclusion was reached by Pinel *et al.* [82] in the oxidative decarboxylation of aqueous solution of N-phosphonomethyliminodiactic acid (PMIDA) to synthesise glyphosate over diverse commercial and synthetic activated carbons (see table 10). The increase of acidic surface groups due to NaOCl or HNO_3 treatments reduced at the same time the specific activity of the Ceca carbon (4S) by a factor of 3. In contrast, the activity of carbon catalysts were greatly enhanced by either nitrogen containing groups or the presence of basic sites and/or absence of acidic sites. As seen in table 10, the carbons that have high intrinsic nitrogen content (SNK1, Norit SX1G) or nitrogen incorporated by treatment with NH_3 vapour at 900 °C (Ceca/NH/ 900 °C) exhibited the largest specific and surface area rates for the oxidative decarboxylation of PMIDA. Thermal treatment of the original Ceca carbon (0.02 wt.%N) at 900 °C under nitrogen atmosphere suppressed all acidic surface groups, leading also to a 2-fold higher surface area based activity than that of the parent Ceca carbon. This may indicate the presence of distinct nitrogen free basic sites that probably were inactive in the vicinity of acidic surface groups [82]. Similar results were obtained in the WAO of aqueous H_2SO_3 over activated carbon [117]. In this study, Stöhr *et al.* subjected activated carbon to gas phase treatment with NH_3 and HCN at elevated temperatures of 600– 900 °C followed by reduction in hydrogen or nitrogen atmosphere. The catalytic activity for the oxidation of diluted aqueous H_2SO_3 was enhanced upon the introduction of nitrogen that was assigned to amine groups and nitrile or pyridine-like nitrogen. A further increase of activity was even noticed when most of the nitrogen chemisorbed was removed by subsequent heating to 700–900 °C under nitrogen or hydrogen. The results of XPS surface characterisation and thermal oxygen desorption suggested the existence of superoxide species (O_2^-). The author related the catalytic activity shown by the carbons to the O_2^- species assuming that their formation was facilitated by the chemisorbed nitrogen atoms, even in trace amounts.

Only a few oxidation studies attempted to discern the type of surface group responsible for the catalytic activity of carbons. Besson *et al.* used synthetic carbons derived from phenolic resins in the partial oxidation of cyclohexanone to C_4–C_6 dicarboxylic acids (adipic, glutaric and succinic) [80,81]. Heat treatments of these carbons in nitrogen at different temperatures were carried out to selectively eliminate oxygenated surface groups formed during CO_2 or air activation. The changes of surface chemistry produced were followed by means of Boehm titration, TPD and XPS. Analysis of textural properties showed that surface area and surprisingly microporosity favoured carbon activity. Furthermore, the partial elimination of carboxyl/lactone groups under N_2 admission at 600 °C caused a noticeable 10–30% improvement of both activity and selectivity. It is worth to note that the loss of acidic groups was accompanied by a 2-fold increase in the amount of basic sites. The subsequent elimination of carboxylic/ lactone groups and most phenolic/quinone type groups via N_2 reduction at 900 °C, however, reduced activity and selectivity, in particular for the HMT carbon series. The authors concluded that phenolic or more probably quinone surface groups were the active sites in the mechanism of activation of molecular oxygen involving the redox equilibrium between quinone and hydroquinone surface groups. A good correlation of the catalytic activity and the surface concentration of quinone groups was also obtained in the gas phase oxidative dehydrogenation of ethylbenzene (ODH) over activated carbon catalyst [181]. Aguilar *et al.* [137] investigated the catalytic wet oxidation of 1000–2600 ppm aqueous NH_3 solution over several HNO_3 oxidised or H_2 reduced activated carbons. The surface group distribution was determined by means of Boehm titration, FTIR spectroscopy and TPD analysis. The liquid phase oxidation with 6 M HNO_3 at 80 °C increased all kinds of oxygenated acid surface groups. Hydrogen reduction at 400 °C for 10.5 h produced basic activated carbons with mainly high-temperature anhydride, phenol and quinone surface groups. The authors found out that the activated carbons containing carboxylic, lactone and anhydride groups performed both strong ammonia adsorption and low catalytic activity. Under CWAO conditions (130–190 °C, 7–16 bar O_2), the catalytic activity of the activated carbons correlated well with the amount of quinone surface groups, but not with that of the carbonyl-phenolic type groups. The results of all these studies strongly suggest that the active sites for catalytic oxidation are related to the quinone surface groups of activated carbon.

Pure CWAO studies of organic pollutants over carbon catalyst, essentially ignored the influence of surface chemistry on catalytic activity. Most research dealing with the wet oxidation of phenolic compounds [26–29,35,61,79,118,124,160–165] only considered total carbon surface area, given by the manufacturer or measured by N_2-adsorption isotherms. As indicated in table 8, the total surface area of activated carbons used ranged from 600 to 1400 m^2/g, but no clear correlation of catalytic activity and surface area was observed. Yustos *et al.* [162] additionally determined the surface area related to mesoporosity for three activated carbons and one supported Cu/AC catalyst. Two interesting findings arise from this study (table 8). First, the

mesoporous surface area only made up a small 2–10% of the usable surface area of the microporous activated carbons, and second the catalytic activity increased with mesoporous surface area. This may suggest that the access to micropores and pore diffusion of reactants can limit the overall reaction rate. On the other hand, the authors reported very similar adsorption isotherms for the four catalysts, which are rather difficult to explain solely with textural differences. Surface oxide groups should also play a role in the adsorption and surface reaction of phenol molecules. Additional TPD experiments confirmed that the catalytic activity of the active carbon improved with the amount of CO containing surface groups, but the authors gave no quantitative results.

Recently, two activated carbons recommended for water treatment were tested in our laboratory on the continuous CWAO of phenol at 140 °C and 2 bar of oxygen partial pressure. According to the manufactureres, the carbons were prepared from wood (CI) and coconut shell (CII) precursors. Following previously tested procedures [182], modification of parent carbons was performed by liquid phase oxidation with H_2O_2, $(NH_4)_2S_2O_8$ or HNO_3 and demineralisation with HCl. The treated activated carbons were characterised by means of N_2-adsorption isotherms, elemental and TG analysis, Boehm titration, oxic phenol adsorption at 20 °C, slurry pH and ability for generating oxygenated radicals from dissolved molecular oxygen. tables 8 and 11 give some textural properties and the chemical surface group distribution of the parent and modified activated carbons. Figure 3 presents their catalytic activity observed in 50 h tests of continuous phenol oxidation. The two parent carbons (CI and CII) exhibited distinct total surface areas, amounts of N and S heteroatoms, ash contents and phenol conversions of 47 and 10% for CI and CII, respectively. High (microporous) surface area of CI carbon does not necessarily mean high activity as highlighted before. Phenol adsorption experiments at room temperature showed similar high specific adsorption capacity for the two carbons. If the capacity however is related to their surface areas, CII was superior to CI, respectively 0.51 to 0.37 mg/m^2. This suggests that a significant part of the CI microsurface area would not be accessible for the adsorption (and oxidation) of phenol molecules due to the small pore sizes.

The greater activity of CI demonstrated might be related to its intrinsically higher amount of heteroatoms (four times for N and ten times for S). Unfortunately, little is known about the nature of heteroatom containing surface groups to safely conclude on their eventual effect in carbon catalyst. HCl treatment reduced the ash content of parent carbons to low residual values smaller than 1 wt.%. At the same time, the phenol conversion dropped down to 25% for CI and 2% for CII. Thus, the activity of CI and CII depends to some extent upon their

ash content. It was also reported that the retention of some chemisorbed chlorine could decrease the pore size thereby influencing the catalytic performance of the carbon [182]. However, other factors should play a role since oxidation treatments for example of CI carbon comparably suppressed the ash content (< 1 wt.%), but not the phenol conversion (between 35 and 38%) as can be depicted from figure 3. A main cause for the different CI and CII activity observed could be due to the given capacity of the carbons for generating radicals. The CI carbon was shown to produce hydrogen peroxide in HCl acidified and oxygenated water at a rate one order of magnitude higher than CII did. Thus, the catalytic function of the parent carbons must fairly be attributed to (basic) surface groups that were capable of hydrogen abstraction.

The oxidation treatments practically did not affect the surface area of parent CI and CII carbons, with exception of a significant 20 to 30% loss in weight observed in case of $(NH_4)_2S_2O_8$. The initial distribution of chemical surface groups (table 11) was seen to be similar for parent CI and CII carbons. Phenolic surface groups predominated over lactone and carboxylic groups being almost absent. In addition, basic slurry pH values and high amounts of basic sites were detected for both non-modified activated carbons. The oxidative treatments, particularly with $(NH_4)_2S_2O_8$ and HNO_3, resulted in a sensible increase of the number of oxygen chemical groups. As expected, more carboxylic and lactone groups were introduced with increasing oxidation strength of the chemical agents used. Surprisingly, H_2O_2 and HCl under the treatment conditions applied exhibited a very similar oxidation power with respect to the generation of carboxylic and lactone groups. For CI the number of phenolic groups was only noticeably altered by $(NH_4)_2S_2O_8$. In contrast, CII showed considerably more new phenolic sites after treatment with $(NH_4)_2S_2O_8$, H_2O_2 and HCl. The introduction of acid surface groups was always accompanied by an important destruction of the basic sites excepting for H_2O_2. Possibly, H_2O_2 was capable to introduce some recognised basic groups as quinones, chromenes or pyrones [183] due to its rather soft oxidation strength.

The diverse modifications effected within a carbon series made evident a correlation of activity and initial basicity or non-acidity strength of the carbon surface. Various indicators including carbon slurry pH, amount of acidic and basic groups and oxygen content (see table 11) confirmed that the catalytic activity of these carbons towards phenol oxidation declined with a parallel increase/decrease in surface acidity/basicity. A particular good correlation was found for the CI series when plotting the phenol conversion over the ratio of phenolic groups to carboxylic and lactone groups as shown in figure 4. The lower activity observed in case of the HCl treated CI carbon was probably caused by the elimination of ash content that additionally reduced the

Table 11
Distribution of chemical surface groups for parent and treated carbons CI and CII

Active Carbon	Surface groups (meq/g)			Total (meq/g)			Elemental (%)			[a]Q_ads (mg/g)	X_Ph (%)
	Phenolic	Lactone	Carboxylic	Acidic	Basic	PH	N	S	O		
CI	0.84	0.09	0.04	0.96	2.31	8.3	0.4	1.0	8.4	425	47
CI–N	0.96	0.17	0.28	1.42	1.27	3.0	1.1	0.8	15.0	190	37
CI–S	1.23	0.28	0.15	1.66	1.25	2.7	0.4	1.5	20.8	350	37
CI–P	0.82	0.27	0.03	1.13	2.80	5.9	0.4	1.2	11.0	410	37
CI–H	0.76	0.16	0.18	1.09	1.25	7.2	0.4	1.2	8.9	380	25
CII	0.65	0.00	0.00	0.65	1.22	11.3	0.1	0.1	8.4	310	10
CII–N	0.52	0.03	0.51	1.06	0.69	4.2	0.7	0.1	14.3	370	2
CII–S	1.04	0.03	0.53	1.60	0.97	3.8	0.3	0.1	14.9	220	2
CII–P	0.82	0.08	0.15	1.33	1.33	7.5	0.1	0.1	9.7	475	2
CII–H	0.76	0.09	0.18	1.25	0.66	7.7	0.1	0.1	9.7	340	2

[a]Adsorption capacity for phenol.

phenol conversion. It is important to note that Boehm titration does not allow distinguishing between ether type oxygen, carbonyl and phenolic groups. However, TG analysis indicated a significant weight loss at higher temperatures that could be assigned to CO release from phenolic groups but also carbonyls and quinone groups. In agreement with the different oxidation studies described before [80–82,181], it is expected that the quinone groups rather than the phenolic ones are responsible for the catalytic action of the CI activated carbon, however a satisfactory experimental proof is still lacking. On going research in our laboratory is dedicated to elucidate the role that these specific groups play in the CWAO of aqueous phenol solution.

3.2.2. Catalytic activity, stability and deactivation

This section analyses the activity and stability of carbon catalysts depending on the compound treated and oxidation conditions employed. Mainly aromatic pollutants including phenols and substituted phenols were studied as target compounds in CWAO. Occasionally, complex industrial effluents containing textile process residuals were tested using a combination of low temperature, ozone oxidant and granulated active carbon. Special attention will be given to frequently overlooked aspects related to stability and deactivation of the carbon catalysts that can occur during the oxidation process.

3.2.2.1. Low temperature oxidation over activated carbon using H_2O_2 or O_3 oxidants. The use of stronger oxidants like hydrogen peroxide or ozone combined with the catalytic effect of activated carbon is an appropriate solution for purification of drinking water or remediation of low concentrated organic wastewater. For example, hydrogen peroxide oxidant and diverse carbon materials allowed for 80 to 90% degradation of a 1000 ppm *p*-chlorophenol solution at 25 °C [168]. Noteworthy, the graphite catalyst gave superior performance than that of an iron impregnated activated carbon. However, TOC conversions measured remained small (25–40%) and reaction times were excessively large ranging from 96 h for graphite to 800 h for activated carbons. Information on the stability of carbons was not given in these works. Another example is the ozonation of a 45 ppm 1,3,6-naphtalenetrisulphonic acid aqueous solution over activated carbon (0.5 g). NTS was readily destroyed within 4 h of reaction in solutions saturated with ozone at 25 °C
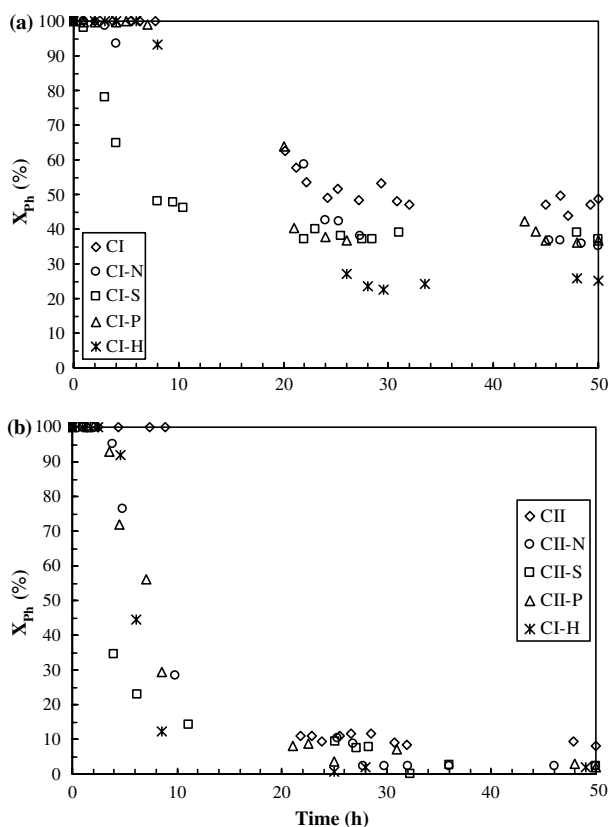
Figure 3. Evolution of phenol conversion during CWAO over parent and modified activated carbons: (a) CI series, (b) CII series; $P_{O2} = 0.9$ MPa, $T = 140$ °C, LHSV = 8.2 h^{-1}.

[166]. The activity was found to depend upon the origin of the activated carbon, the most basic Norit carbon yielding the best 91% conversion and 75% TOC destruction.

The catalytic effect that result from the presence of carbons (AC or CB) in ozonation processes was examined in detail by Jans and Hoigné [173]. The authors investigated the mechanism and kinetics of the transformation of aqueous ozone into OH-radicals catalyzed by small amounts of AC or CB (2–4 mg/L) at ambient temperature. The AC used (Chemviron) had a BET surface area of > 1300 m^2/g and an ash content of 7.9% containing Fe < 7 mg/g. Tests were also done with 3 CBs (Degussa): FS 101: d_p = 95 nm, S_A = 20 m^2/g; Printex-60: d_p = 21 nm, S_A = 115 m^2/g; FW-2: d_p = 13 nm, S_A = 460 m^2/g. The kinetic measurements revealed that already small amounts of AC or BC acted as an heterogeneous initiator for the radical-type chain reactions proceeding in the bulk solution and accelerated by a factor 3 the transformation of ozone into secondary oxidants such as OH-radicals. The rate enhancement found was comparable to that observed for systems in which ozone was transformed at either elevated pH, by addition of H$_2$O$_2$ or by UV initiation [Hoigné, 1997 in 173]. According to the authors, AC therefore seems to represent an alternative 'clean' reagent to enhance ozone-based AOP while being easier to apply than the other catalyts mentioned before.

Jans and Hoigné [173] reported that the initiation of ozone transformation is preceded by adsorption of ozone on the carbon surface, where catalytic sites, i.e. oxygen containing surface groups, start the radical-type chain reactions. No attempt was made to determine the nature of the active surface groups involved, but it was observed that the reaction rate for ozone depletion increased linearly with the BET surface area of the three different CBs tested. Stability of the active carbon during ozone transformation was also assessed. A series

of aqueous solution containing 20 mg/L of AC was first contacted with different dosages of ozone (9.5, 19, 38 mg/L). Subsequent standard experiments with these pretreated AC samples confirmed then that the preozonation did not affect the activity for transforming ozone. This result is in line with the work of Dussert and Kovacic [Dussert and Kovacic, 1997 in 173], who reported that the oxidation state and the chemical structure of GAC did not change during an extended exposure to an ozone containing water. Moreover, Jans and Hoigné mentioned the possibility that a fraction of ozone produces some surface sites on the carbon skeleton (e.g. further radicals) that contribute to the initiation of the radical-type chain reaction.

On the other hand, Alvarez et al. [184] subjected a GAC (AQ-40 Chemviron) to gas phase ozonation at 25 °C in a gas–solid fixed bed reactor. The virgin and treated carbons were characterised by BET surface area, micropore volume, acidic and basic surface functions, pH$_Z$ and adsorption isotherms for phenol, p-nitrophenol and p-chlorophenol. Minor changes were observed in textural properties including surface area and micropore volume as a result of AQ-40 ozonation. In contrast, the organic adsorption capacity of the ozonated carbon was found to decrease about 50 to 100% in all cases. The smaller adsorption capacities were related to the formation of new acid sites on the treated carbon surface, rising from 0.23 to 1.54 meq/g during ozonation. Since these oxygenated groups possess electron withdrawing properties they can reduce the electron density on the basal plane of the carbon, thereby weakening the adsorption interaction between adsorbate and carbon itself. In contrast to liquid phase ozonation processes, exposure to gaseous ozone thus introduces changes in the carbon surface that can affect its (catalytic and adsorptive) long-term performance. This is in agreement with previous studies showing that in the gas phase the depletion of ozone is due to both stoichiometric oxidation of the carbon and catalytic transformation [Stephens et al., 1986, Rakitskaya et al., 1994 in 173].

Lin et al. [170–172] treated two textile process wastewater by means of low temperature wet ozonation in fixed and fluidised beds (FLB) of GAC. The textile effluents contained diverse dyestuffs (ADMI colour index = 650–1250) and amounts of COD and suspended solids ranging from 250 to 1800 mg/L and 50 to 300 mg/L, respectively. The authors observed a significantly enhanced ozonation rate in presence of activated carbon, performing up to 90% COD removal. The COD destruction was very sensitive to the ozone flow rate (bed fluidisation) and the impeller speed in the gas induced fixed bed reactor, clearly highlighting the importance of mass transfer on the overall reactor performance. It was also reported that in a steady state run, exhausted GAC got regenerated in situ via ozonation of adsorbed species. Repeated use of the same GAC batch for five times caused a only slight loss in
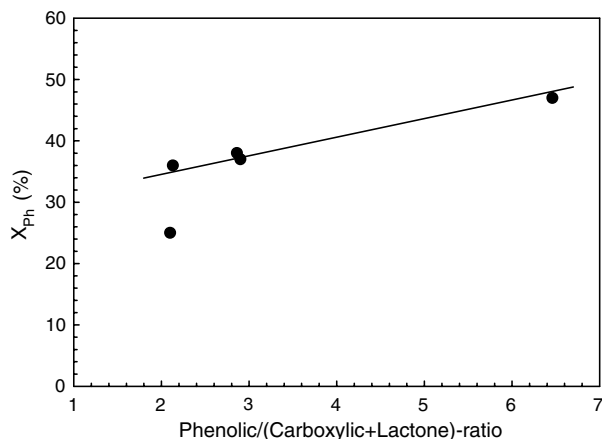

Figure 4. Phenol conversion as a function of phenolic groups to carboxylic and lactone groups ratio for parent and modified CI carbons; 0.9 MPa of O$_2$, 140 °C, LHSV = 8.2 h^{-1}.

COD and colour removal, proving a good resistance of the GAC towards deactivation. Moreover, FTIR spectrophotos taken for fresh and regenerated GACs showed a strong similarity given further support to the hypothesis of *in situ* regeneration of the spent GAC. As stated before, ozonation in the liquid phase is favourable for AC stability and FLB or fixed bed reactor configuration that can provid complete wetting of AC are suitable for reducing the loss of activated carbon by combustion. However, more studies in continuous reactor systems are required to quantitatively assess catalytic deactivation since such data is very useful for industrial application purposes.

3.2.2.2. Partial oxidation over activated carbon for fine chemical synthesis. In fine chemical synthesis, both activity and selectivity of carbon catalysts towards partial intermediates play a role. For glyphosate (from PMIDIA) and dicarboxylic acid (from cyclohexnone) synthesis, mild temperatures of 100 to 140 °C, air pressures up to 50 bar and eventual basic pH adjusting yielded satisfactory selective oxidation activities, i.e. almost 100% conversion within 3–6 h of reaction (table 10). The effect of pressure and temperature on selectivity was not studied in detailed. Selectivity (and activity) of carbon catalysts towards intermediate products were strongly enhanced in the presence of basic surface groups as reported before. All the experiments were conducted batchwise that made it difficult to obtain precise information on catalyst stability and deactivation under the given reaction conditions. To this end, Pigamo *et al.* [82] tested an activated carbon in the oxidation of 5 g/L cyclohexanone in a continuous microreactor (0.5 g carbon, 0.06 L/h) at 120 °C over a period of one month. Promising stable behaviour of the catalyst resulted without any significant change in conversion and selectivity. Figure 5 shows the SEM pictures of the fresh and used synthetic carbons after the experiment [185]. The author reported only a weak loss of carbon in the spent catalyst, although the surface texture was drastically modified, making it prone to attrition (see figure 5). Attrition of carbons was also observed by Trawczynski [118] in the oxidation of phenol over CBC. The authors attributed the loss in CBC weight mainly to the oxidation of the binder material leading to a subsequent weaker mechanical strength of the composite. It can be speculated that such drastic changes in the carbon texture (see figure 5) also modified the distribution of surface groups. Actually, to explain the stable activity and selectivity demonstrated in the cyclohexanone oxidation, the authors [82] suggested that the surface oxide groups at the origin of the reaction, if consumed in the earlier stage of the reaction, were continuously regenerated by oxygen attack of the carbon surface.

3.2.2.3. CWAO of phenolic compounds over carbon catalysts. Catalytic activity: Table 8 indicates that most of the CWAO studies were devoted to the oxidation of phenol and substituted phenols. Special effort was made to assess the catalytic activity, stability and reactor performance rather than to elucidate the role of textural properties and surface groups in the oxidation reaction. As described before, the origin and preparation of the carbons essentially determine the activity towards phenol oxidation. Fortuny *et al.* [26] reported a 40, 15 and 8% phenol conversion in trickle bed experiments at 140 °C and 9 bar of O_2 for a wood (CI), mineral and coconut (CII) based activated carbon, respectively (table 8). In particular, basic surface groups and their ability to generate oxygenated radicals are thought to play a key role in the reaction mechanism.

New experiments in our laboratory also proved that a low surface area graphite (not functionalised) was not active giving zero phenol degradation. A promising result was obtained with an activated carbon prepared from sewage sludge and demineralised with HCl prior to use. Figure 6 plots the phenol conversion of parent and treated sludge-based carbon observed in 50 h trickle bed runs at 140 °C and 2 bar of oxygen. Under these conditions 15% destruction of phenol was achieved with the HCl treated sludge based carbon. The observed performance was similar to that of the Centaur activated carbon (figure 6), which already demonstrated to effectively oxidise phenol in fixed bed reactor at 160 °C and 16 bar [162]. The use of sewage sludge based activated carbon also gave good results in the catalytic gas phase oxidation of H_2S and the biological activated suldge treatment [186,187]. Ongoing research work in collaboration with the LEQUI group from the university of Girona is exploring the possibility to convert sewage sludge into a catalytic active carbon for the oxidation of phenolic wastewater.

The diverse batch and continuous CWAO studies listed in table 8 reported almost 100% phenol conversion and 85% TOC or COD destruction at 160 °C, 2–45 bar O_2 and space or reaction times of about 0.3 h or 3–6 h, respectively. Tested under similar reaction conditions, a CBC achieved similar performance in a TBR, although for one order of magnitude higher space-time of 2 h [118]. All the carbon catalysts used exhibited accumulation of refractory acetic acid, which mainly accounts for the remaining 15% of TOC or COD measured in the liquid phase. The accumulation of acetic acid is not critical from an environmental viewpoint since it is easily biodegradable. However, acetic acid build up caused pH values as low as three requiring reactor materials (and catalysts) that can withstand the hot and corrosive reaction conditions.

When compared to recently developed supported metal and metal oxide catalysts tested on phenol oxidation, our CI activated carbon displayed comparable or even better catalytic performance at 160 °C and significantly lower oxygen partial pressure of 2 bar (table 12). Additionally, the CI carbon showed stable activity over 10 days on stream at 140 °C and 2 bar of
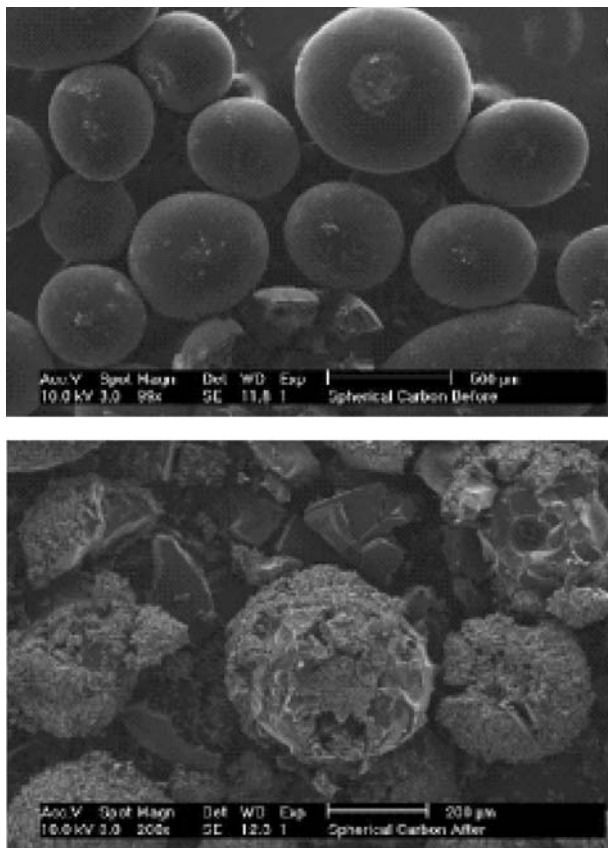
Figure 5. SEM pictures of synthetic mesoporous carbon: (above) fresh catalyst, (below) catalyst used for 4 weeks in cyclohexanone oxidation at 120 °C in a TB reactor [185].

O_2 [27] that was only surpassed by the Cu/Ni/Al-hydrotalcite catalyst [66,70]. In contrast, for supported catalysts deactivation and/or metal leaching frequently occurred during the oxidation process. It must be noted that in several studies catalytic (long-term) stability of supported catalysts was not monitored at all (table 12).
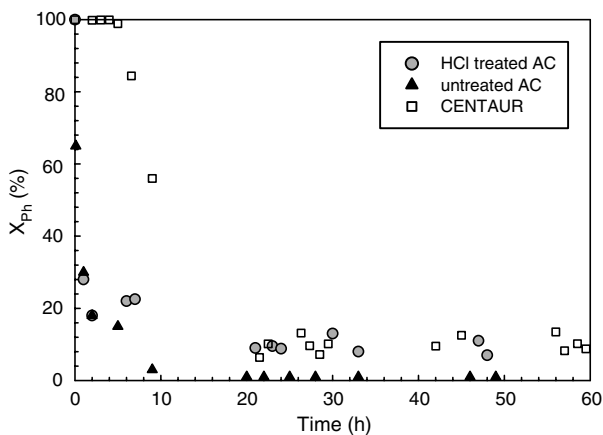

Figure 6. Phenol conversion using Centaur® carbon or parent and HCl treated carbons prepared from sewage sludge; 140 °C, 2 bar O_2, $C_{Ph,0} = 5$ g/L, LHSV = 8.2 h^{-1}.

Table 12
Performance of diverse catalysts in CWAO of phenol

Catalyst	Reactor type	C_{Ph} (g/L)	T (K)	P_{O_2} (MPa)	X_{Ph} (%)	X_{TOC} (%)	Catalyst stability	Refs.
Cu/Ni/Al	Batch slurry	5	423	0.9	>99	~99	Stable in TBR runs for 15 days on stream	[66]
Hydrotalcite	Trickle bed				>75	>67		[70]
Active Carbon	Trickle bed	5	433	0.2	>99	~85	Stable in TBR runs for 10 days on stream at 140 °C and 2 bar of oxygen	[27] [160]
CeO$_2$	Semibatch-slurry	5	453	1.5	~95	~75	deactivation reported	[188]
CuO/AC	Spinning basket	2.4	453	3.6	>99	~70	After 6 runs: 60% of Cu-leaching, X drops from 99 to 80%	[120] [121]
Ru–CeO$_2$/AC	Batch slurry	2.2	433	2.0	>99	57	Deactivation not tested	[122]
Cu/Zn/Co–oxides	Trickle bed	3.0	423	0.7	~50	~47	Leaching: Cu (20%), Co (15%) and Zn (10%)	[189]
K–Mn–Ce–O	Batch slurry	1.0	383	0.5	>99	~99	2% X-loss after 3 runs	[68] [69]
Pt/TiO$_2$	Batch Slurry Trickle Bed	1.2	473	0.8	~99	~95	In TBR: X drops from 80 to 60% after 140 g of phenol passed	[190]
CuO/MCM-41	Batch slurry	1.3	473	3.4	>99	~90	Not tested, important Cu leaching reported	[60]
CuO–CeO$_2$	Semibatch–Slurry	1.0	432	0.73	>99	~90	Not tested, important Cu leaching reported	[77] [78]
CuO–2(CuO)–Cr$_2$O$_3$	Fixed bed	1.2	433	1.6	>99	~70	10% Cu leaching after 160 h of operation	[56] [191]

Currently, the use of activated carbon was merely considered for the oxidative degradation of substituted phenols. Studied compounds included p-chlorophenol [124], 2-aminophenol, salicylic acid and 5-sulphosalicylic acid [28]. The activated carbons employed exhibited almost complete conversion of the chloro and amino substituted phenols at the given reaction conditions. The carboxy and sulpho group of salicylic acid and 5-sulphosalicylic acid apparently deactivated the phenol molecule leading to a low 40% degradation. In order to obtain a clearer picture of the substituent effect in CWAO, we tested the CI carbon on diverse aromatic pollutants. 50 h on stream experiments were conducted in a small-scale TBR at 140 °C and 9 bar of oxygen partial pressure. The target compounds encompassed phenol as well as substituted phenols and aromatics: m-xylene, o-cresol, o-chlorophenol, p-nitrophenol, aniline, nitrobenzene and sulfolane. Inlet organic concentration was set to 5 g/L, except for less soluble m-xylene and nitrobenzene having 0.2 and 2 g/L, respectively. Figure 7 depicts as an example the evolution of conversion monitored for o-cresol, o-chlorophenol, p-nitrophenol and sulpholane. The residual conversions achieved after 50 h operation on stream are given for all compounds in table 13.

Two distinct trends in conversion can be deduced from the results obtained. The CI carbon was capable to readily destroy m-xylene, o-cresol, o-chlorophenol and phenol, whereas aromatic compounds containing nitrogen and sulphur groups proved very refractory to CWAO. The following reactivity order was observed: m-xylene (99.8%) > o-cresol (83%) > o-chlorophenol (74%) > phenol (70%) > aniline (15%) > p-nitrophenol (9%) > sulfolane (5%) > nitrobenzene (<1%). The mechanism of oxidative phenol destruction is complex, but it is generally accepted that the liquid phase oxidation of phenols and substituted phenols by molecular oxygen is an electrophilic reaction that follows a heterogeneous–homogeneous free radical chain mechanism [65,192–194]. According to the postulated mechanism, the easiness of the organic to form free radicals is a key parameter that can be inferred from critical oxidation [92] or halve-wave potentials [192]. Available literature values of the respective potentials are given in table 13. The relative easiness of oxidation should be favoured by the increase of steric crowding in ortho position and higher electron-releasing (or lower electron-withdrawing) ability of substituents in ortho and para positions. This tendency was confirmed by our results. Activating Cl and CH_3 groups in o-chlorophenol and o-cresol have lower oxidation potentials than that of phenol explaining the noticeable higher conversion observed in CWAO. In turn, p-nitrophenol (and nitrobenzene) contains a strongly deactivating NO_2 group that increased considerably its oxidation potential and refractoriness to CWAO (table 13). Aniline has a potential close to that of phenol but exhibited a low conversion of about 15%.

The amino group significantly activated the benzene ring compared to the NO_2 group in nitrobenzene, although its electron-donor capacity must be much weaker than that of the OH group in phenol. The low activity demonstrated by sulpholane should be attributed to the stabilising effect of the sulpho group itself. A marked difference consisted also the small adsorption capacity of the activated carbon observed for this latter molecule.

Summarising, it can be concluded that the concept of electron-donor/acceptor groups is also useful to predict the CWAO activity of aromatic compounds, if the oxidation mechanism essentially follows an electrophilic substitution attack. However, it must be kept in mind that heterogeneously catalysed oxidation of organic compounds over activated carbon involves adsorption of both organic and oxygen molecules that can strongly interfere in the reaction mechanism and the resulting activity.

Stability and deactivation of carbon catalysts: Activated carbon as a catalyst proved to possess high activity towards the WAO of diverse organic pollutants. One key issue for the development and application of any CWAO process is the stability and deactivation of catalyst used under the given conditions. As for CWAO in general, this important aspect is currently being scarcely addressed in the available open literature on carbon catalysts. However, frequent catalyst deactivation, i.e. leaching of active phase and sintering, can be discarded since activated carbons are stable in both acidic and basic medium. In addition, CWAO temperatures employed are too mild to provoke sintering or solid state transformation. However, activated carbon exposed to oxygen can react and not surprisingly carbon loss due to combustion was reported by various authors [26,27,118,163,164]. Extremely high combustion rates of 15–60 mg/min were observed for diverse activated carbons when subjected to supercritical water conditions of 400 °C and 25 MPa [163,164]. The use of activated
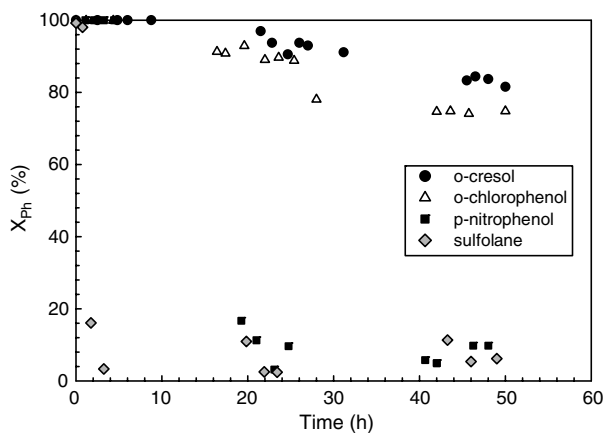

Figure 7. CWAO conversion of diverse substituted aromatic pollutants obtained in TBR using CI activated carbon at 140 °C, 9 bar O_2, $C_{org,o}$ = 5 g/L and LHSV = 8.2 h^{-1}.

carbon, although strongly promoting the non-catalytic oxidation of phenol [163], is thus questionable under such harsh conditions of supercritical water. Moreover, it appears that the combustion of activated carbon proceeds at a significantly higher rate in the liquid phase than in the gas phase. Temperatures as low as 120–160 °C and oxygen pressure of about 9 bar were found sufficient to induce slow but noticeable carbon burn-off [26,118] that in turn continuously reduced phenol conversion achieved [26,27]. On the contrary, no weight change was found at any time when the activated carbon was exposed to air in the absence of water and phenol under otherwise same temperature, oxygen pressure and air flow rate [26]. Carbon consumption only occurring in aqueous phase confirmed that water plays a fundamental role in the carbon oxidation process. The dilemma is that catalitically active carbons can also undergo fast combustion under WAO conditions. The supercritical water oxidation of phenol over diverse carbon additives provided one extreme for this situation [163]. Active bamboo and coconut carbons as well as carbon fibre demonstrated both high phenol conversion and combustion rates, while less active coke carbon and graphite gave one order lower combustion rate.

One efficient mean to avoid the unacceptable carbon loss is to control the temperature and the oxygen concentration at the carbon surface. The temperature range being fixed within 120–160 °C to ensure acceptable activity, Fortuny et al. [27] varied oxygen partial pressure from 1 to 9 bar in trickle bed oxidation of phenol conducted under 140 °C and 10 days on stream operation. Each catalyst sample was recovered after the run and prior to weighting kept for several hours at 400 °C under nitrogen atmosphere to remove any physically adsorbed phenol. During the life-time experiments a continuous decline in phenol conversion was observed for 9 and 4 bar of O_2, whereas 2 and 1 bar of O_2 allowed for reaching a conversion plateau after 1 days on stream. The trend in conversion was in line with the measured CI carbon consumption revealing a final 33 and 16% loss of the original weight for 9 and

4 bar, respectively. For 2 bar the CI load (increase of 3%) was constant, while even gaining 16% in weight at 1 bar after use. Thus, temperature of 140 °C and oxygen partial pressure of 2 bar can perform stable activity without any significant loss in the carbon catalyst.

Inlet phenol concentration also strongly influenced the extent of CI carbon consumption. First experimental evidence was provided in a continuous experiment at 9 bar of O_2 but without phenol in the feed. The CI carbon was completely oxidised after only 9 days on stream indicating a substantially higher combustion rate in the absence of phenol [26]. Additional 100 h on stream trickle bed experiments were recently conducted in our laboratory by feeding different phenol inlet concentration at 160 °C to induce consumption of the CI carbon used. The on stream conversions measured for different phenol inlet concentration are illustrated in figure 8. Final phenol conversion and weight of recovered and heat treated CI samples are given in table 14. This table also lists the time needed to saturate the CI fixed bed and the respective oxygen excess. An inspection of table 14 highlights that CI carbon consumption is a strong function of inlet phenol concentration. Low inlet concentrations greatly promoted carbon burn-off reducing the original carbon load by a factor 5 in case of 1.0 g/L phenol feed solution. In contrast, a 33% carbon weight gain was noted for the highest phenol feed concentration of 10 g/L tested. For 7.5 and 10 g/L of phenol, figure 8 shows a sudden drop of conversion right after the bed saturation zone, most probably due to the presence of oxygen mass transfer limitation rather than the non-linear nature of the reaction with respect to phenol concentration. High phenol concentrations produce an increase in reaction rate. At the same time the oxygen excess is significantly reduced for constant air flow rate (see table 14) that can lead to oxygen depletion in the liquid phase. The demonstrated sensitivity of carbon combustion to inlet phenol concentration further suggests that adsorbed phenol molecules and/or reaction products protect the carbon surface from being attacked by dissolved molecular oxygen. Smallest phenol feed concentrations resulted in large bed saturation times of 20 to 50 h (table 14 and figure 8) and low equilibrium coverage at the same time, thereby exposing the unprotected carbon surface to prolonged harmful oxygen contact. The highest phenol feed concentration of 10 g/L not only suppressed the carbon combustion providing short saturation time (2 h) and densely crowed phenol surface, but also produced a considerable irreversible weight gain as reported above. Activated carbon is well known to catalyse phenol coupling reactions [92–95] forming condensation products that can strongly adsorb onto the carbon. Not surprisingly, a batch study testing the CI carbon on phenol WAO [61] deduced from liquid and gas phase carbon balances the deposit of important amounts of carbonaceous matter on the carbon surface. Dynamic batch experiments of phenol adsorption on CI

Table 13
Chemical oxidation potential and CWAO conversion of several aromatics obtained with CI carbon after 50 h on stream at 140 °C, 9 bar O_2 and LHSV = 8.2 h^{-1}

Compound	O_{rg} (%)	COP[a] (mV)
m-xylem	99.8	–
o-cresol	83	556
o-chlorophenol	74	625
Phenol	70	1004
Aniline	15	1135
p-nitrophenol	9	1433
Sulpholane	5	–
Nitrobenzene	< 1	–

[a]Taken from [92, 194].

carbon gave additional evidence of the presence of coupling reactions in the phenol-AC system. During the adsorption runs under oxic conditions, temperature was stepwise increased from 25 to 120 and then to 160°C. The phenol adsorption capacity of the CI carbon measured at room temperature first decreased when heating the slurry solution to 120 °C, as expected from the exothermic nature of physical phenol adsorption. For a further rise to 160 °C however, the CI carbon restored almost all of its capacity performed at 25 °C indicating the strong adsorption of phenol dimers and oligomers formed by accelerated coupling reactions.

During phenol CWAO carbon textural and surface properties as well are likely to undergo modifications. On one hand, the deposit of carbonaceous material on the carbon surface can physically block the pores giving rise to undesired catalyst fouling. On the other hand, the soft attack of oxygen, if not leading to important burn-off, may continuously produce new surface oxide groups altering the original catalytic activity of the carbon. Continuous monitoring and/or characterisation of spent carbons can detect such changes as will be described below. The impact of long-term oxygen exposure on the carbon morphology was impressively visualised by Besson and Gallezot [185] taking SEM pictures (figure 5) of fresh and spent carbon catalysts used for 4 weeks in TBR cyclohexanone oxidation at 120 °C. Qin et al. [124] reported a 20–30% loss of surface area and p-nitrophenol adsorption capacity after WAO regeneration of the spent Darco activated carbon. Probably, adsorbed p-nitrophenol coupling products irreversibly blocked the access to the pores thereby causing an apparent reduction of the available surface area. Trawczynski [118] assessed the acid strength distribution of CBC before and after phenol oxidation runs by means of NH_3–TPD measurements. The distributions obtained confirmed marked differences between a fresh and spent catalyst in the concentration of sites with
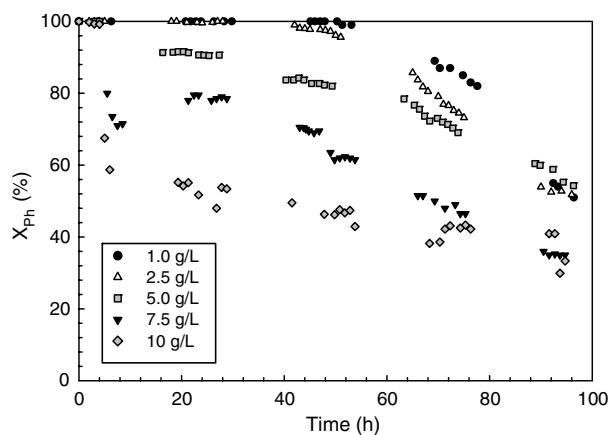
Table 14
CWAO phenol conversion, CI weight and oxygen excess for different phenol inlet concentration: 100 h on stream at 160 °C, 2 bar O_2, 7.5 g_{AC} and LHSV = 8.2 h^{-1}

$C_{Ph,In}$ (g/L)	X_{org} (%)	W_{AC} (g)	Excess (%)	$^*t_{sat}$ (h)
1.0	51	1.5	1600	50
2.5	53	2.5	580	20
5.0	55	5.7	250	8
7.5	35	7.1	135	4
10.0	38	9.9	75	2

$^*t_{sa}$: bed saturation time.

equal acidic strength, although the total acidity did not change significantly. Based on their results, the authors assumed that slow oxidation of the CBC support under WAO conditions was responsible for the development of surface functionalities with weakly acidic character, e.g. lactone and phenolic groups. In all these studies, no attempt was undertaken to clarify the mechanism of how the carbon loss and modification of the surface group distribution affected the performance of the carbon black catalyst.

Fortuny et al. [26,27] monitored also the change of CI carbon weight and BET surface area produced during 240 h of trickle bed phenol oxidation at 140 °C and 9 bar of O_2. The results of 8 runs with increasing on stream times are illustrated in figure 9. The phenol conversion is apparently complete during the first 10 h due to the saturation of the CI fixed bed, then conversion gradually dropped down to reach a final value of 50%. At the same time, the CI carbon exhibited a 20% maximum weight gain and 30% surface loss that coincided with the end of the saturation period. Then, a smooth decrease to 66 and 36% of its respective starting values occurred. The sharp initial change of carbon weight and surface area was attributed to the formation of irreversibly adsorbed phenol condensation products since they could not be desorbed under nitrogen heat treatment at 400 °C. The performance of the CI carbon seemed to be governed by the simultaneous modification of surface area and carbon weight. To this end, the experimental data of figure 9 were fitted to a plug flow reactor model assuming kinetic regime and first order of reaction with respect to phenol. The kinetic rate constant was then calculated for each X_{Ph}, W and a_s set, resolving the differential phenol mass balance:

$$k = \frac{Q}{W a_s} \ln\left(1 - \frac{X_{ph}}{100}\right), \tag{1}$$

where k denotes the kinetic constant ($L/m^2_{AC}/h$), Q the volumetric liquid flow rate (L/h), W the actual CI carbon weight in the reactor (g), a_s the actual surface area of CI carbon (m^2/g_{AC}) and X_{Ph} the phenol conversion.

The resulting rate constants are plotted in figure 10, revealing only small fluctuations around a mean value of

Figure 8. Stream-line conversion of phenol as a function of phenol inlet concentration obtained with CI activated carbon at 160 °C, 2 bar O_2 and LHSV = 8.2 h^{-1}.

about 1.8×10^{-5} L/(m$^2_{AC}$ h). The assumption of kinetic regime and first order of reaction for phenol proved thus reasonable. This means that the activated carbon remaining in the reactor conserved its original intrinsic catalytic activity despite the drastic alteration of surface area and weight suffered during the CWAO experiment.

As to possible changes in surface groups, TG curves were recorded for both the fresh and spent CI and H_2O_2, $(NH_4)_2S_2O_8$, HNO_3 and HCl modified CI carbons in extra experiments of phenol oxidation at 140 °C and 2 bar of O_2 (figure 11). The weight change during TGA was notably greater for the used parent and modified activated carbons than those shown by the fresh CI series except for CI-S. A more detailed inspection of figure 11 evidenced a pronounced release of gaseous species in case of the spent CI carbon series for temperatures ranging from 200 to 700 °C. This reveals that during the liquid phase oxidation of phenol new carboxylic, lactone and probably some phenolic groups were introduced on the carbon surface by the continuous oxygen attack. The rate of weight loss of spent CI carbons was little altered for $T > 700$ °C indicating the same amount of more stable carbonyl/quinone groups. A particular peak was detected above 400 °C, which is the starting temperature of hydrocarbon cracking, providing further support for the existence of a carbonaceous layer on the CI carbon. The second conclusion suggested by figure 11 is that the difference in surface (groups) seemed to vanish during the phenol CWAO runs, the TGA curves being very similar for all treated carbons. Such a gradual homogenisation of the carbon surface was also detected during the ODH of ethylbenzene [195].

From these findings a complex reaction mechanism arises for the heterogeneously catalysed phenol oxidation over the CI activated carbon. The main path is undoubtedly the degradation of phenol cascading through diverse reactive quinone intermediates to more stable ring opening products (carboxylic acids) to final products including water and carbon dioxide or refractory acetic acid. The consecutive-parallel destruction reaction network is accompanied by the oxidation of the carbon matrix itself as well as coupling reaction of phenol molecules to form carbonaceous products that can irreversibly adsorb on the carbon surface. The complex mechanism is far from being completely understood, but a dynamic component is introduced by the slowly proceeding side reactions. It can be speculated that during the heating and carbon bed saturation period, coupling reactions and chemisorption of phenol and coupling products prevailed over the carbon combustion, explaining the parallel weight gain and surface area loss of the CI carbon observed. Also, HPLC and COD analysis detected no oxidation intermediates during the saturation period giving further experimental support to this hypothesis. When complete bed saturation is achieved, phenol, coupling products and free carbon sites start to compete for the free radicals that are sought to be essentially generated by basic surface groups of the activated carbon itself. In this stage, the phenol destruction pathway will become dominant and not unexpected an immediate decrease in phenol conversion and release of partial oxidation intermediates was observed by HPLC analysis. Depending on the operating conditions (T, P_{O2}, $C_{Ph,0}$) applied, different rates of coupling and combustion reaction will result leading to the apparently contradictory situations observed of carbon weight gain, stable weight or weight loss.

The same temporal evolution of conversion, carbon weight and surface area was reported for the gas phase ODH of ethylbenzene over activated carbon, as shown in figure 12. The authors characterised in detail the activated carbon and concluded that the surface coke layer formed was active in ODH. According to their results, the continuous attack of oxygen homogenised
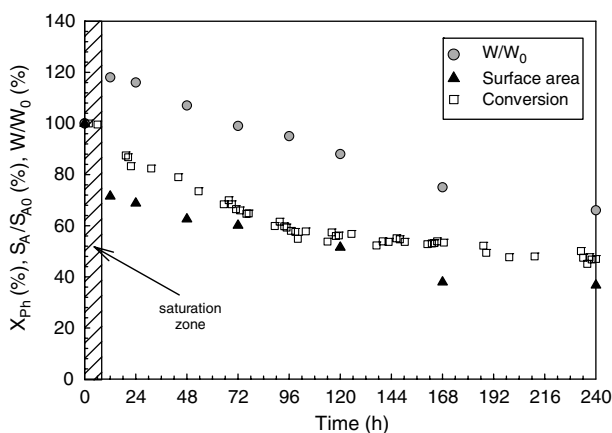

Figure 9. Evolution of phenol conversion, CI carbon weight and surface area during trickle bed CWAO at 140 °C, 9 bar O_2 5 g/L inlet phenol and LHSV = 8.2 h^{-1} [27].
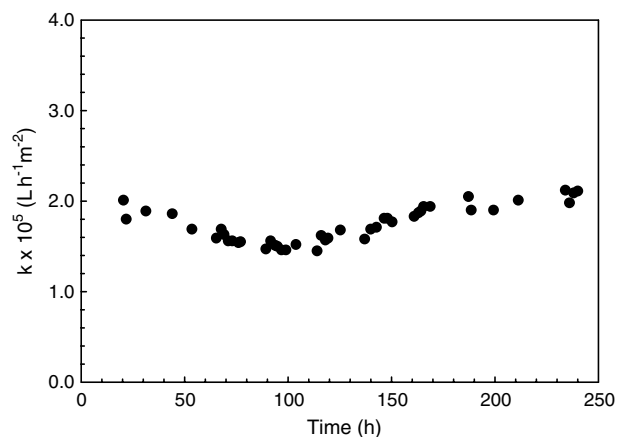

Figure 10. Temporal variation of kinetic rate constant during phenol oxidation over CI activated carbon at 140 °C, 9 bar O_2, 5 g/L inlet phenol and LHSV = 8.2 h^{-1} [27].
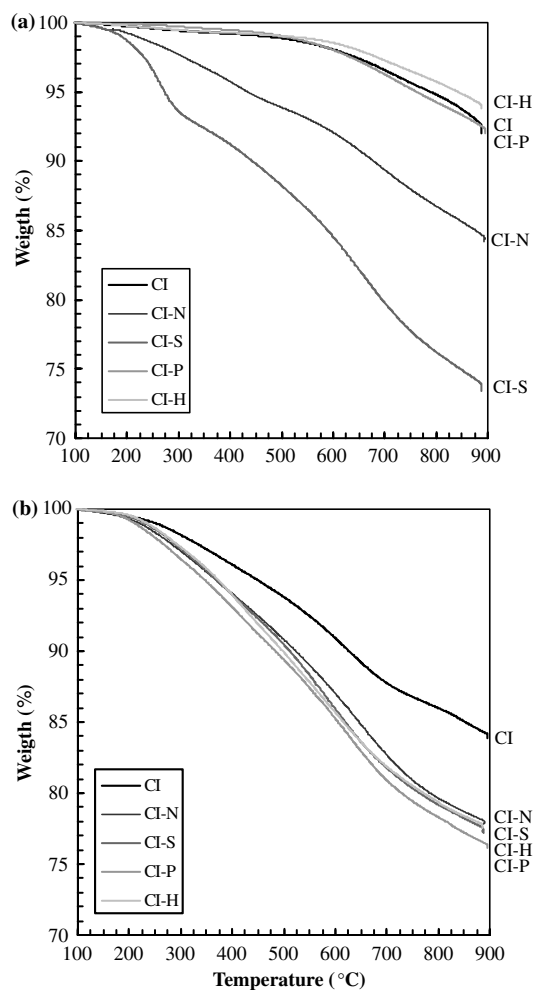
Figure 11. TGA profiles of the parent and modified CI activated carbons of (a) fresh sample (b) after being used for 50 h in phenol CWAO.

the carbon surface during the reaction. New non-quinone-like groups more reactive for carbon combustion than for coke formation were gradually created on the surface causing the observed maximum in carbon weight and its subsequent smooth but inevitable decline until the carbon mass balance becomes negative. It would be of interest to clarify if the detected carbonaceous deposits could play a similar role in the CWAO of phenol. Differences will certainly arise due to the presence of water in CWAO. For instance, the rate of carbon combustion was greatly enhanced in the liquid phase. Also, HPLC analysis of phenol CWAO samples detected up to 60 minor peaks [196] revealing a much more complex reaction mechanism than that proposed for the ODH of Ethylbenzene.

4. Process consideration and modelling of CWAO

The last section is dedicated to the engineering aspects of CWAO for the treatment of organic wastewater. The pathways and mechanism governing CWAO have been mainly assessed in case of pure compounds including phenolic compounds and carboxylic acids. Due to the complexity of reactions involved in wet oxidation processes, lumped kinetic models, particularly for industrial effluents, were preferred over detailed kinetic studies. The latter models however are very useful as they can lead to a more reliable design and operation of CWAO reactors. Similarly, only a few CWAO studies were dealing with the selection of adequate continuous reactor configuration and operation strategies. Finally, the use of comprehensive reactor modelling and its application in process scale-up is even less frequent indicating that CWAO engineering is still in a developing stage. Our special interest is focused on CWAO over carbon catalysts and the essential information of related work will be summarised in the following subsections.

4.1. Process consideration

4.1.1. Reactor type and operation

In most cases, CWAO should be designed for continuous operation given the range of volumetric flow rates commonly to be treated. Four main categories of gas–liquid–solid catalytic reactors can be considered: mechanically agitated slurry CSTR reactor, SBC, FBR and finally fixed bed reactors [196]. A common characteristic of the former three reactor configurations is the substantially lower catalyst to liquid ratio compared to the fixed bed reactor.

Batch slurry tests on phenol oxidation over metal supported catalysts [62–64] demonstrated the negative impact of low catalyst concentrations on reactor performance. Under such conditions, heterogeneous–homogeneous phenol condensation reactions were strongly enhanced leading to fast catalyst deactivation by irreversible adsorption of the condensation products formed. A comparative study of batch slurry and continuous TBRs came to the same conclusion for the phenol oxidation over the CI carbon [61]. Figure 13 gives the
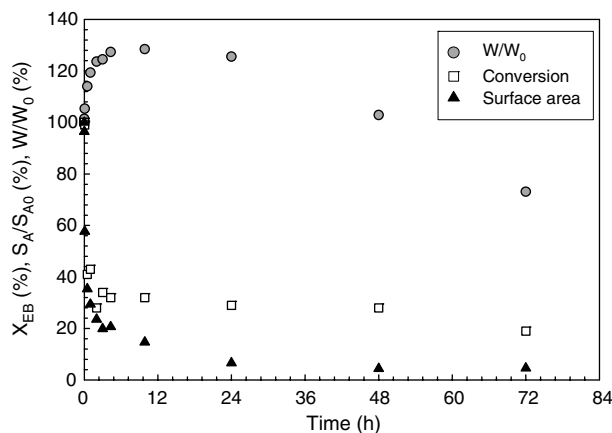
Figure 12. Ethylbenzene (EB) conversion, carbon weight and surface area during oxidative EB dehydrogentation: 350 °C, 0.023 bar EB, 0.203 bar O_2 [192].

phenol concentration and kinetic rate constant obtained with the two reactors at 140 °C, 5.5 bar of O_2 and different normalised residence times. The slurry system rendered extremely fast initial rates of phenol destruction even in case of aged CI carbon previously used for 50 h in the trickle bed reactor (figure 13b). Then, the slurry rate constant was seen to immediately drop down by one to two orders of magnitude, in contrast to that of the trickle bed reactor exhibiting a constant value. It must be pointed out that during the batch slurry runs the phenol concentration also levelled off for higher residence times (figure 13a), although enough phenol and oxygen reactants and fresh catalyst were available. These results and the impossibility to close the carbon mass balance over the liquid and gas phase indicate the formation and irreversible adsorption of carbonaceous deposits on the carbon surface. Due to its enhancing catalyst fouling properties, the slurry or FLB type reactor configuration cannot be recommended for the oxidation of phenols and aromatic compounds because of their ability to undergo homogeneous condensation reaction in the liquid phase. On the other hand, the worse performance of fixed bed reactors regarding heat and mass transfer is not critical for the treatment of wastewater since relatively low intrinsic reaction rates and heat release result from the highly diluted organic pollutant concentrations. This situation outlines the fixed bed reactor as a priority choice for the CWAO of organic compounds.

Within the fixed bed configuration two flow directions of the gas and liquid phase are of interest for CWAO operation: co-current downflow (TBR) or co-current upflow (Packed Bed Column). The mode preferred in industry is the TBR [196] allowing for a variety of flow regimes depending on the gas and liquid flow rates employed. The same situation holds for CWAO, however only a few of the available studies attempted to experimentally assess the impact of gas–liquid hydrodynamics and mass transfer on reactor performance under CWAO conditions [28,29,56,191, 197]. Non-idealities in TBR operation during CWAO were detected by various researchers. Tukac et al. [28,29] observed decreasing phenol conversion at higher residence times and attributed this result to the insufficient wetting of catalyst particles at lower liquid through puts. The dilution of 4 mm activated carbon catalyst particles with 1 mm fine inerts increased the catalyst wetting and suppressed the non-idealities of liquid maldistribution and uneven catalyst wetting. In contrast to the common belief, the dilution of catalyst bed caused a substantial decrease in the mean reaction rate value when raising the reaction temperature form 129 to 168 °C. A higher reaction temperature shifted the reaction system to the gas-limited region and fully wetted catalyst particles lead to additional resistance for gas–liquid oxygen mass transfer. Santos et al. [56,191] conducted phenol oxidation runs in a fixed bed reactor at different catalyst concentrations mixing
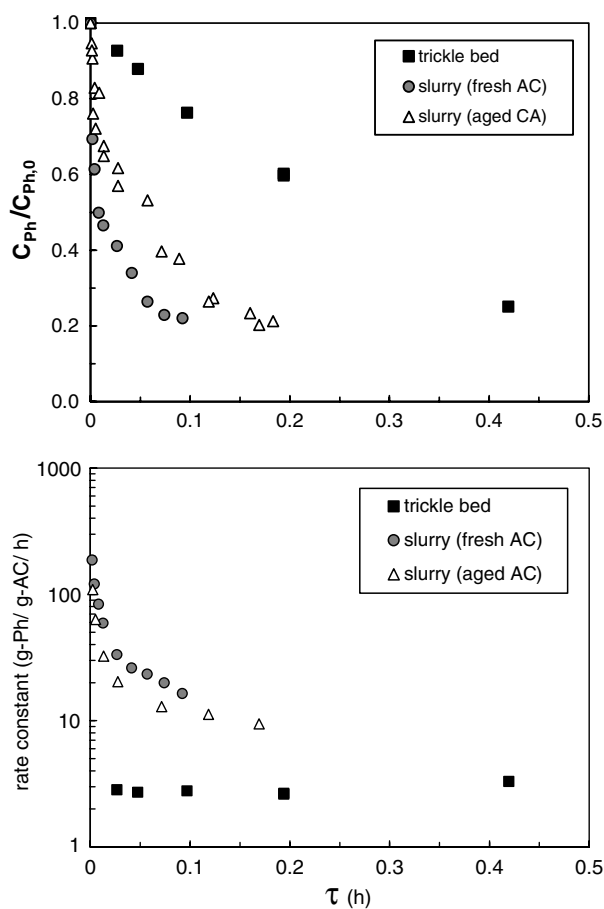

Figure 13. Evolution of phenol concentration and rate constant during slurry batch and trickle bed phenol oxidation: 140 °C, 5.5 bar O_2 5 g/L phenol [61].

inert and catalytic particle of same size. The authors reported a critical catalyst concentration below which the apparent reaction rate was not longer proportional to the catalyst concentration because of a significant homogeneous contribution to the reaction. Eftaxias et al. [196] compared in our laboratory the performance of up and downflow mode for the phenol oxidation over the CI carbon under typical CWAO temperatures of 120 to 160 °C and 2 bar of oxygen partial pressure. The phenol concentration-space time profiles assessed for both flow directions are plotted in figure 14. Clearly, the downflow operation yielded noticeable higher reaction rates, i.e. lower outlet phenol concentrations, for all temperatures tested. The same situation was found for COD concentrations. The CI carbon has a proven high activity towards phenol destruction leading to strong external oxygen mass transfer control in case of fully wetted catalyst, i.e. upflow operation. Thus, two options are available to conveniently modify, if necessary, the gas–liquid hydrodynamics of CWAO fixed bed reactors: dilution of catalyst and gas–liquid flow direction.

Finally, Kakildar et al. [198] provided a unified criterion to diagnose on the appropriate flow direction

or dilution of fixed bed reactors. The authors proposed the following definition of the γ reactant flux ratio:

$$\gamma = \frac{D_L^{eff} C_L}{\nu D_G^{eff} C_G}, \tag{2}$$

where D^{eff} is the effective gas or liquid diffusion coefficient of the reactant in the catalyst particle, C is the respective gas or liquid reactant concentration and ν the stoichiometric coefficient of the gaseous reactant.

According to the authors [198], when $\gamma \gg 1$, the reaction is gas-reactant limited and downflow mode is recommended to obtain higher conversions. Conversely, $\gamma \ll 1$ corresponds to the liquid-reactant limited situation, where the upflow mode should provide a better reactor performance. This criterion successfully predicted the performance of selective hydrocarbon hydrogenation and partial alcohol oxidation reactions when tested in both up and downflow mode [198].

The application of the criterion to CWAO conditions gave also good results. The calculated γ values for the study of Eftaxias et al. [197] ranged from 17 to 34, thus trickle bed operation with partial wetting are the preferred mode as was confirmed by the subsequent experiments. The conditions used in the work of Tukac et al. [28] gave a considerably lower γ value of 2.5 indicating smaller oxygen reactant limitation. This can explain the only slightly reduced phenol conversion observed at lower temperatures with a fully wetted catalyst fixed bed. Overall, the criterion proved to yield reliable predictions of reactor performance in diverse situations offering thus an effective and simple tool for the appropriate set-up of fixed bed reactor operation under steady state conditions.

Unsteady state operation can further enhance the performance of fixed bed reactors. Forced periodic operation of liquid flow must be considered as a new promising operation concept. Silveston and Hanika [199] lately reviewed periodic operation of TBRs pointing out the good results obtained for reactions including the wet oxidation of SO_2 over activated carbon [200] and the catalytic hydrogenation of a-methylstyrene [201,202] or crotonaldehyde [203]. Essentially, periodic operation consists in controlled ON–OFF liquid feed flow modulation to induce forced pulsing flow regime in the reactor. The pulses create transient temperature and pressure waves throughout the catalytic fixed bed and thereby dynamic behaviour of gas–liquid hydrodynamics, mass and heat transfer and chemical reaction or adsorption. The most important parameters to adjust in the system are the feed cycle period length and its split value. In a recent work, Tukac et al. [35] tested periodic operation of a TBR for the CWAO of phenol over activated carbon catalyst at 150 °C and 5 MPa of system pressure (pure oxygen). The conversion measured under pulsing flow regime at the same average feed rate was reported to be over 10% higher than that
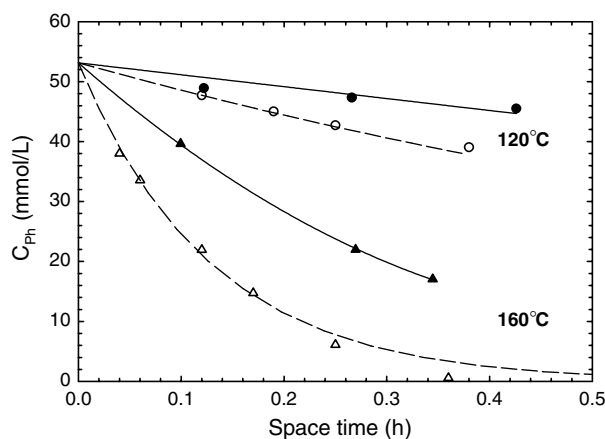

Figure 14. Phenol concentration for downflow (filled symbols) and upflow (open symbols) oxidation over CI carbon at 2.0 bar O_2, lines indicate trends.

attained in the steady state regime. Optimal results resulted for a period length comparable to the true liquid residence time based on dynamic liquid holdup determined by liquid draining. The authors concluded that future experiments have to be planned using longer catalytic fixed bed where pulse attenuation can occur. Also, aspects of phenol mineralisation, intermediate distribution and catalyst stability are of research interest to delineate the potential of dynamic operation of CWAO reactors.

4.1.2. Operating conditions

The previously discussed studies on CWAO recommended the continuous fixed bed reactor for the effective treatment of organic waste dissolved in water. Thus, it is of interest to establish a safe operation window for active carbon catalysts with temperature, oxygen partial pressure and phenol inlet concentration as basic coordinates. To reduce eventual catalyst loss caused by wet carbon combustion to acceptable levels, process temperature and partial oxygen pressure have to be kept as low as possible. An optimum must be found because the selected conditions should also provide satisfactory catalytic activity, if not excessive carbon weight or space times will result. Temperatures between 120 and 160 °C and low oxygen pressures of 2 bar proved to match these requirements for stable continuous operation using the CI carbon. Depending on the inlet phenol concentration, temperature and pressure values may be varied since high phenol concentrations were found to protect the carbon from being burnt off. More flexibility to this end can also give the appropriate modification of the carbon surface chemistry to yield more active carbons at lower temperatures. This is an important open aspect of activated carbon catalyst that has to be addressed by future research efforts.

Promotion of CWAO destruction power was also achieved in our laboratory by the addition of small

quantities of H_2O_2 oxidant to the organic feed solution [204]. These oxidation tests were conducted with reduced catalyst weight under higher temperature and oxygen pressure of 170 °C and 3.4 bar to maintain appreciable organic conversions at shorter experimental run times. Figure 15 reflects the conversion results that were performed by CWAO of phenol and p-nitrophenol over the CI carbon feeding different H_2O_2 amounts. A clear enhancement of phenol and p-nitrophenol conversion is visible on H_2O_2 addition. Moreover, the improvement in COD destruction (not shown in figure 15) corresponded to the quantity of H_2O_2 oxidant added. It can be speculated that the activated carbon plays the role of concentrating and decomposing the H_2O_2 molecules to very active hydroxyl radical. The radicals essentially formed at the carbon surface can then immediately react with adsorbed organic molecules explaining the very effective H_2O_2 use observed. In this way, the oxidation of CWAO resistant p-nitrophenol could be greatly enhanced to give high conversion and COD destruction of 75% and 70%, respectively with a feed containing 40% of H_2O_2 stoichiometric demand. The combination of activated carbon and H_2O_2 seems attractive since substantial loss of H_2O_2 oxidant was reported to be one of the major drawbacks of this advanced oxidation technology. Further CWAO studies should investigate the promotion of H_2O_2 and its effect on the combustion of activated carbon catalyst.

If formation of acetic acid is a critical design parameter in order to avoid low pH values, the carbon catalysts should be coated with noble ruthenium or palladium metals, although this will inevitably lead to higher running costs. Activated carbon alone seems not capable to attack C3–C4 carboxylic acids or refractory acetic acid. The formation of diverse intermediates of distinct toxicity in the oxidation of organic compounds arises the question of the severity or mineralisation required in CWAO treatment. Probably, the most cost attractive use of CWAO is that in combination with a biological end-treatment allowing for incomplete mineralisation in CWAO. In return, the required severity of CWAO treatment has then to be established. Currently, the biodegradability of exiting CWAO streams was scarcely analysed. Santos *et al.* [205] proposed the bioassay method using luminescent marine bacteria (photobacterium phosphoreum) for the toxicity determination of organic loaded wastewater samples. The tests are based on the 50% reduction of intensity of light emission measured after 15 min of contact time of the bacteria with the toxic compound. EC_{50} values can be obtained indicating the effective nominal concentration of toxicant required for 50% light emission reduction. Their results confirmed that phenol (EC_{50} of 16.7 mg/L) and ring intermediates formed in the first stage of phenol oxidation including catechol (8.32 mg/L) and particularly hydroquinone (0.041 mg/L) and p-benzoquinone (0.1 mg/L) have low EC_{50} toxicity concentra-

tions. On the other hand, ring opening products, i.e. carboxylic acids, were less toxic showing substantially higher EC_{50} values in the range of 130 mg/L for acetic acid to >450 mg/L for oxalic acid. CWAO was always capable to reduce the toxicity of the phenol feed by completely destroying the ring intermediated, However, the EC_{50} measurements cannot give a precise information on the necessary mineralisation degree since they are not based on biomass populations of running biological plants that may exhibit different sensitivity to the toxic partial oxidation products.

To continuously control and monitor the biodegradability of CWAO effluents containing biotoxic organic compounds, respirometry may offer a time saving and reliable method among other available tests including biochemical methane potential or BOD_5 measurements. Preliminary respirometry assays were conducted in our laboratory to test the toxicity of synthetic o-cresol solutions. The effluent was treated in trickle bed CWAO over CI carbon at 140 °C, 2 bar of oxygen partial pressure and space time of 0.1 h. The experimental protocol to measure the oxygen consumption of the micro-organisms during the respirometry test was established according to Guisasola *et al.* [206]. The selected control substrate was a synthetic easily biodegradable wastewater with a COD value of 3250 mg/L. The local urban wastewater treatment plant of Tarragona pro-
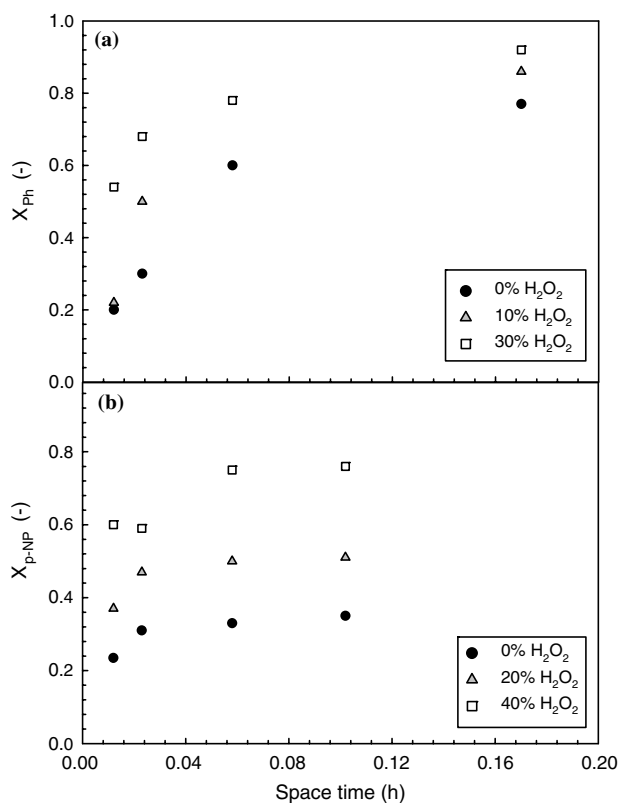

Figure 15. H_2O_2 promoted CWAO of (a) phenol and (b) p-nitrophenol over CI carbon at 170 °C, 3.4 bar O_2 and 5 g/L inlet concentration.

vided the non-acclimated active sludge. In this facility only aerobic treatment is performed with a biomass containing mainly heterotrophic micro-organisms. During the experiments different volumes of control substrate, untreated and CWAO treated o-cresol solutions were added to the bioreactor to adjust an initial COD pulse of 50 mg/L. The measured profiles of oxygen consumption are illustrated in figure 16. Two important conclusions can be withdrawn from the inspection of this figure. The untreated o-cresol feed solution was not biodegraded at all by the micro-organisms after several hours, but showed a toxic and inhibition effect on the active biomass. The CWAO treated effluent with a small 30% o-cresol conversion showed an important biodegradable fraction, in line with a reduced toxicity and inhibition potential. Thus, respirometry technique offers a relatively simple means to follow up the severity of CWAO treatment. Ongoing research work in collaboration with another research group from the University Autonoma of Barcelona is aiming to determine the optimal severity of CWAO as a precursor for the biological remediation of diverse organic model and more complex industrial effluents.

4.2. CWAO kinetic modelling

Kinetic modelling is a prerequisite for the reliable design and modelling of CWAO reactors. Based on the pioneer work of Devlin and Harris [207] on phenol WAO, detailed oxidation pathways of pure phenol [64,65,79,119,122,125,160,208–211], phenolic compounds [64,124,212] and carboxylic acids [72,122,125,127,130] were experimentally assessed for different catalysts including activated carbon [79,160] and activated carbon supported Ru, Pt, Pd metals [119,122,125,127,130,211]. The distribution of partial oxidation products obtained in phenol CWAO essentially involved the same species as those found by Devlin and Harris. Moreover, the oxidation of multicomponent solutions and/or industrial effluents was described by using lumped magnitudes of COD or TOC.

The advanced description of intermediate distribution is currently not reflected in the related kinetic modelling. Many kinetic studies, in view of the complexity of the reaction system, applied only lumped models in combination with rate equations of power law type [197]. This concept was recently extended to account for catalyst deactivation by the use of Langmuir–Hinshelwood–Hougen–Watson rate equations [213,214]. The lumping strategy can give good fits of the experimental data, but the empirically calculated kinetic parameters should not be used for extrapolation purposes. Homogeneous polymer formation [64,191] and catalyst deactivation [215] were successfully described by combined homogeneous and heterogeneous rate equations. The few models that involve mechanistic aspects proposed the use of free radical mechanism

based rate equations or Langmuir–Hinshelwood and Eley–Redeal type rate equations. A simple but generally accepted free radical chain mechanism for phenol oxidation was given by Pintar and Levec [64]. The mechanism postulated a heterogeneous initiation step on the catalyst surface followed by a homogeneous propagation and either heterogeneous or homogeneous termination reactions. Recent efforts by Rivas et al. [216] were driven to develop more detailed radical based networks for the WAO of phenol. These models established several tens of radical reactions and should be more reliable when extrapolated beyond the conditions considered in data fitting. Such fundamental knowledge is necessary for a better understanding of the CWAO process since it can lead to significant improvements in the design and operation of CWAO reactors. However, the difficult mathematical handling of such mechanistic models makes them not very attractive for applied engineering studies.

The most sophisticated CWAO kinetic studies account for the heterogeneous nature of solid catalysed oxidation reactions involving adsorption, surface reaction and desorption of reactants and products. To properly describe these phenomena, Langmuir–Hinshelwood rate
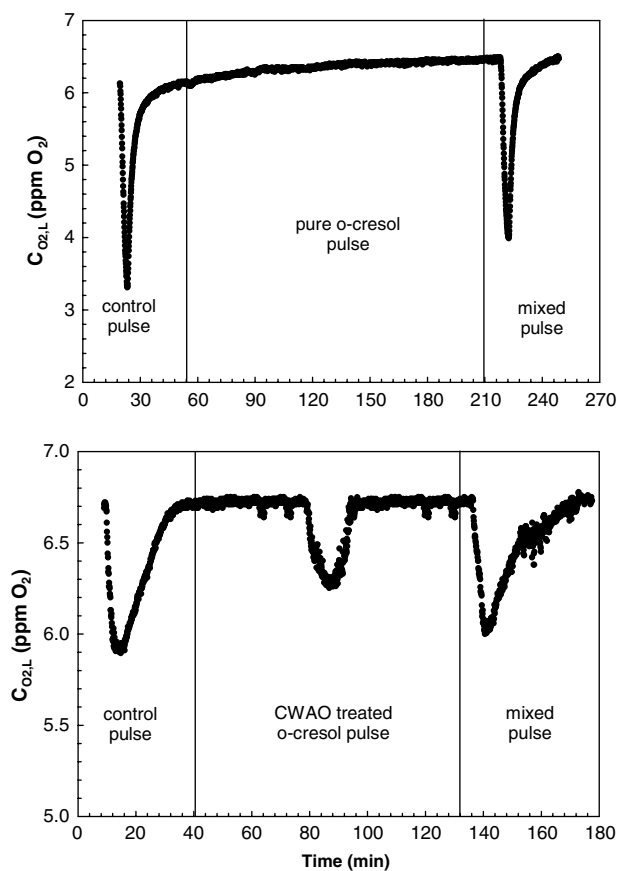

Figure 16. Respirometry profiles of dissolved oxygen for untreated (above) and CWAO treated (below) o-cresol effluents: 140 °C, 2 bar O_2, $X_{cresol} = 0.3$.

equations were developed and successfully tested on the oxidation of the initial reactant. A wide scenario of L-H expressions can be established, although the most popular used in CWAO considered only the competitive adsorption of organic reactants on the same active site, ignoring the existing adsorption of dissolved molecular oxygen. More realistic kinetic models including the participation of adsorbed oxygen in the mechanism were also reported [127,217,218]. For example, Harmsen et al. [127] proposed a detailed kinetic model of several elementary steps for the CWAO of formic acid over a carbon supported platinum catalyst at ambient temperatures. The adsorption isotherms were assumed to be of the L-H type and the surface reaction occurred between adsorbed oxygen atoms and free formate ions in the liquid phase. The application of heterogeneous rate equations to complex reaction networks was less frequently attempted in kinetic studies. Beziat et al. [72] successfully tested a comprehensive model of six individual reactions on the CWAO of succinic acid in a TBR. Similarly, Eftaxias et al. [197,219,220] used this approach to comprehensively describe the catalytic oxidation of phenol over CuO supported on alumina accounting for eight identified main compounds and eight reactions. Such detailed reaction networks present an important progress in the kinetic modelling of CWAO, although they involve a high number of unknown parameter translating the kinetic parameter estimation into an extremely difficult task. Eftaxias [197] conducted additional TBR experiments of phenol oxidation over CI carbon in our laboratory. The study aimed to determine the intermediate distribution by detailed HPLC analysis for a subsequent comprehensive kinetic modelling. The most important findings of this work will be summarised and discussed below.

4.2.1. Kinetic modelling of phenol CWAO over activated carbon

CWAO kinetic studies were generally conducted in agitated slurry or spinning basket reactors to avoid mass and heat transfer limitation by rigorous stirring and correct choice of particle size. In case of phenol and phenolic compounds, fast catalyst deactivation due to carbonaceous deposits invalidates the use of this reactor configuration. Pintar and Levec [64] reported that the kinetic expressions developed from batch phenol oxidation experiments could not match the phenol concentration profiles obtained in a TBR study. Stüber et al. [61] found 50–100 times higher initial rates and low activation energy of 37 kJ/mol for phenol oxidation over the CI carbon in slurry batch reactor. Clearly, the extrapolation of these kinetic data to continuous fixed bed reactor would inevitably lead to erroneous design of such continuous CWAO units. Alternative kinetic studies employed liquid full fixed bed reactors with oxygen pre-saturated liquid feed streams [65,221,222]. High flow rates were necessary to operate the reactor in differential kinetic regime at conversions smaller than 10% in this way avoiding oxygen depletion. For phenol conversion of this magnitude, the progress of oxidation and intermediate distribution cannot satisfactorily be monitored.

The drawbacks of differential mode can be overcome by integral fixed bed reactor studies provided a careful verification of kinetic reaction control under the given operating conditions. In CWAO of organic pollutants, the favourable reactant dilution leads to low intrinsic reaction rates. For this reason mass and heat transfer resistance should be less important in CWAO reactors. Gas–liquid hydrodynamics, i.e. liquid maldistribution and partial catalyst wetting are additional factors that have to be addressed and the correct selection of operating conditions is imperative to assess true kinetic data in a continuous fixed bed reactor.

4.2.1.1. Determination of kinetic regime. The CWAO experiments of phenol over CI carbon were conducted in a fixed bed reactor ($W_{AC} = 7$ g, $d_P = 0.5$ mm) operated either in downflow or upflow mode [197]. Temperature, oxygen partial pressure and space-time were ranged from 120 to 160 °C, 1–2 bar and 0.04–0.6 h, respectively. Under this conditions it was verified with the help of three-phase reactor flow maps that the reactor operates in trickle downflow [223] or bubble upflow [224] regime. The possible influence of gas–liquid hydrodynamics including partial wetting, axial dispersion and liquid maldistribution as well as external and internal mass transfer parameters was first checked by the diagnose criteria established for three-phase catalytic reactors [224]. The criteria values calculated for the highest temperature of 160 °C using appropriate high-pressure literature correlations for the calculation of wetting efficiency [225,226], gas–liquid [227] and solid–liquid [228,229] oxygen mass transfer coefficients are given in table 15. Under the conditions employed, only the possibility of oxygen mass transfer limitation was considered since the oxygen concentration in the liquid phase ranged from 1 to 2 mmol/L being 25 to 50 times smaller than the inlet phenol concentration of 53 mmol/L. The high values of the γ reactant flux ratio of 17 and 34 confirmed the condition of oxygen as the limiting reactant. Table 15 infers that mass transfer should not limit the overall reaction rate. The α_{gl}, α_{ls} and Weisz–Prater Φ_{WP} criteria based on observed reaction rates showed all low values close to the limit values established for the absence of the respective mass transfer contribution [224]. For the catalyst particle size of 0.5 mm used in the trickle bed experiments, Stüber et al. [61] additionally assured the absence of internal mass transfer limitation in a batch agitated reactor at 140°C and 9 bar of oxygen partial pressure. Effects of liquid axial dispersion and excessive wall flow were suppressed by the correct choice of

particle and reactor geometry ($L_R = 20$ cm, $D_R = 1.1$ cm and $d_P = 0.5$ mm). The relevant criteria of L_R/d_P and D_R/d_P have values of 400 and 20, respectively that meet the critical value of 20 established for safe operation [224].

The estimation of the wetting efficiency with high-pressure correlations [225,226] gave important partial catalyst wetting in the range of 0.25 to 0.5 for the liquid flow rates used. This situation was expected from the calculated low external [230] and static [231] liquid hold up taking values between 0.06 and 0.1. Partial catalyst wetting varying with the liquid flow rate used transforms the kinetic study into a delicate task. The high γ values calculated indicate that trickle bed flow is preferred over upflow mode. The latter would be limited by strong gas–liquid oxygen mass transfer limitation as demonstrated before by figure 14 revealing substantially higher outlet phenol concentrations in case of fully wetted upflow operation for all temperatures and liquid flow rates studied. Strictly, a comprehensive TBR modelling including catalyst wetting and mass transfer phenomena must thus assess the influence of different catalyst wetting on conversion. Such numerical verification was undertaken and the results will be presented in the section on reactor modelling of CWAO processes. However, there exist additional results that support the validity of our kinetic modelling. No decrease of phenol conversion at low liquid flow rates due to liquid maldistribution was observed during the experiments as was reported by Tukac and Hanika [28]. The preliminary kinetic analyse of phenol conversion data at different temperatures showed clear Arrhenius behaviour giving an activation energy of 70 kJ/mol that is a typical value obtained for phenol CWAO conducted under kinetic control [197]. Finally, our model was also capable to precisely predict experimental phenol oxidation conversions assessed in a different CWAO reactor at 170 °C and 3.4 bar [204]. Thus, the model established proved reliable even beyond the fitting conditions providing a powerful tool for modelling, design and optimisation of CWAO trickle bed reactors. Moreover, it would be of interest to implement the TBR kinetics in a fixed bed upflow reactor model and compare model prediction and experiments.

4.2.1.2. Intermediate distribution and reaction pathway. During the CWAO of phenol, HPLC analysis of liquid samples detected between 15 and 60 peaks. Most of these peaks had retention times closes to quinone or phenolic compounds and very small areas. Among all peaks, five main intermediate compounds could be identified as 4-hydrobenzoic acid (4-HBA), benzoquinone, maleic acid including its isomer fumaric acid, formic acid and acetic acid. Hydroquinone, catechol and oxalic acid were also found in trace amounts. The closure of HPLC and COD carbon mass balance was always better than 90%, mostly being fulfilled above 95%. It can be speculated that many of the unknown peaks were associated to trace amounts of compounds probably resulting from the combustion of the polymer layer formed during the initial stage of carbon bed saturation. The obtained concentration-space time profiles are plotted in figures 17, 18 and 19 for a partial oxygen pressure of 2 bar. A close inspection of these figures reveals that phenol oxidation follows a complex pathway of parallel-consecutive reactions. A maximum in all intermediate concentrations is observed, except for refractory acetic acid that accumulates in the system explaining the remaining 15% COD at highest phenol conversion of $> 99\%$. The formation of 4-HBA must also be pointed out as an interesting result since it was not reported before in related CWAO kinetic studies. Moreover, it seems that benzoquinone and formic acid are formed at earlier space times than 4-HBA and maleic acid, respectively. This suggests that phenol oxidation over the CI carbon may proceed by two parallel routes, the 4-HBA destruction path being a new route in the Devlin and Harris reaction scheme of phenol WAO [207]. The complete network proposed from the experimental data for the CWAO of phenol over the CI carbon can be depicted from figure 20. This scheme, among others, was tested in the subsequent detailed kinetic modelling.

4.2.1.3. Kinetic model and multiparameter estimation. To develop a reliable kinetic model for the CWAO of phenol accounting for all detected intermediates, a hierarchical model building with increasing complexity was adopted as described in Eftaxias *et al.* [220]. Several reaction schemes either variation of that given in

Table 15

Estimation of oxygen mass transfer limitation and partial catalyst wetting for phenol CWAO over CI carbon at 160 °C and $C_{Ph,0} = 53$ mM

P_{O_2} (bar)	$C_{O2,L}^{eq}$ (mM)	[a] $(ka)_{gl}$ (s^{-1})	[b]$(ka)_{ls}$ (s^{-1})	[c]α_{gl} (–)	[c]α_{ls} (–)	[c]Φ_{WP} (–)	[d]f_w (–)	γ (–)
1	0.91	1.2	0.5–3	0.15	0.05–0.3	0.19	0.25–0.5	34
2	1.8	1.0	0.5–3	0.13	0.05–0.3	0.38	0.25–0.5	17

[a]From [227].
[b]From [228, 229].
[c]From [224].
[d]Wetting efficiency from [225, 226].

figure 20 or based on the classical Devlin and Harris network were considered in the optimisation procedure. If complex reaction networks are fitted to experimental data, the number of kinetic parameter involved to be estimated increases drastically. In this case, classical non-linear parameter estimation based on the gradient method (Levenberg–Marquardt algorithm) often fails due to its sensitivity to starting guess values and the inevitable convergence to local minima solution. For this reason the use of a global optimisation approach was tested. The Simulated Annealing algorithm was selected given both its simple computational programming and proven robustness in applications of combinatorial [232] and kinetic multiparameter optimisation [220]. This stochastic method randomly scans the entire parameter space defined and theoretically converges to the global minimum provided an infinite number of function evaluations. However, starting the gradient method from the solution previously obtained by the stochastic method is very useful since it allows for statistical confidence calculations and discrimination of rival models achieving similar fits [233].

The laboratory trickle bed reactor used for the kinetic study was modelled assuming isothermal plug flow, kinetic regime and constant oxygen partial pressure throughout the activated carbon catalytic fixed bed. The

Figure 18. Concentration profiles of benzoquinone and 4-hydrobenzoic acid using CI carbon at 2 bar; TBR experiments: (○) 120 °C, (■) 140 °C, (△) 160 °C}, Model: (–).

net production rates of the involved species were defined according to the reaction pathway proposed for the kinetic parameter optimisation. The reactor model was numerically integrated with a fourth order Runge–Kutta algorithm. The rate equations of the individual oxidation reactions were taken as Langmuir–Hinshelwood type to account for organic compound adsorption on the CI carbon. The reaction order with respect to oxygen concentration was optimised, but oxygen adsorption was not accounted for in the model. In preliminary kinetic calculation it was observed that the phenol degradation profiles could be well described by both power law and Langmuir–Hinshelwood rate equations, probably due to the high adsorption capacity of phenol on the CI carbon. Overall, the tested kinetic models involved up to seven reactions and five adsorbed organic compounds leading up to 31 parameters to be identified.

The best fit was obtained with the reaction scheme given in figure 20. For comparison with experimental data, the predicted phenol, intermediate and COD concentration profiles were also plotted over figures 17, 18 and 19. The average fit error was calculated to 8.5% being only 4.4% for phenol and COD, which is a very good result in view of the given complexity of the reaction system. The kinetic model proposed from experimental observation thus described not only reasonably well the concentration profiles of phenol and
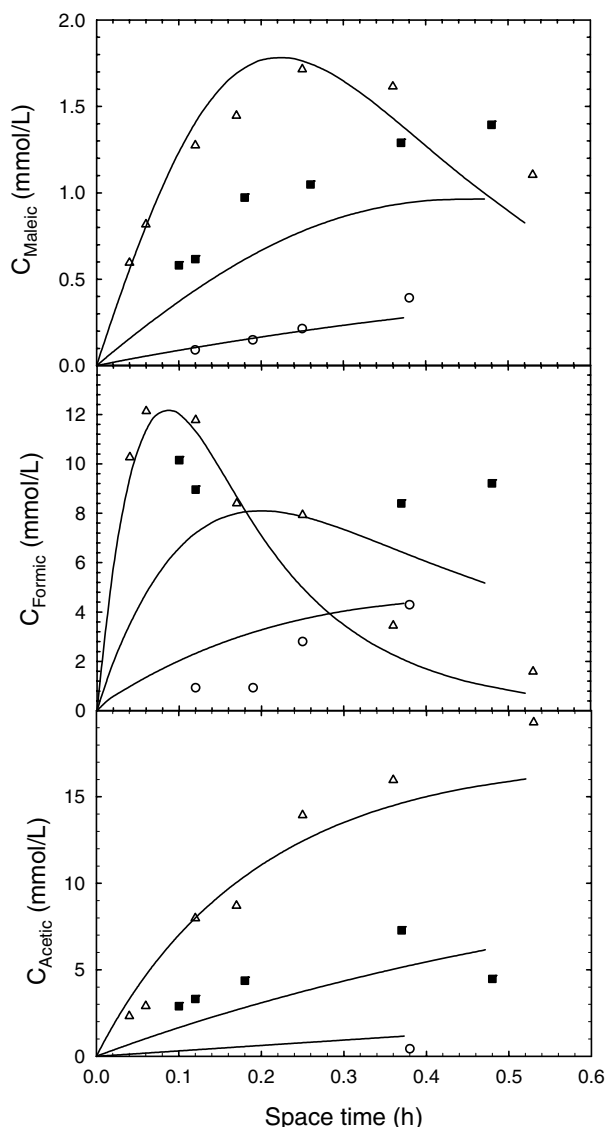

Figure 17. CWAO concentration profiles of phenol and COD using CI carbon at 2 bar; TBR experiments: (○) 120 °C, (■) 140°C, (△) 160 °C, Model: (—).

Figure 19. CWAO concentration profiles of maleic, formic and acetic acid using CI carbon at 2 bar; TBR experiments: {(○) 120 °C, (■) 140 °C, (△) 160 °C}, Model: (—).
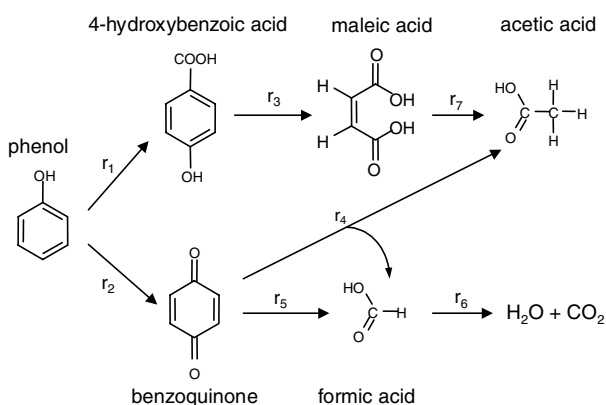

Figure 20. Reaction network proposed from intermediate distribution for CWAO of phenol over CI activated carbon.

COD but also those of the intermediate products as can be appreciated in figures 17, 18 and 19. The values of all kinetic and adsorption parameters determined seem to have physical meaning. The activation energies took values between 55 and 118 kJ/mol that can be expected for CWAO of phenol and carboxylic acids under kinetic control. Also, the reaction order of dissolved oxygen concentration ranged from 0.5 to 1.0, commonly encountered in reaction involving molecular oxygen. Finally, all heats of adsorption were small but negative in agreement with the commonly encountered exothermic nature of adsorption of organic compounds on activated carbon. Summarising the results, CWAO of phenol over the CI carbon also follows a complex parallel-consecutive reaction network. Phenol seems to be destroyed via two routes, the first and dominating one leads to the formation of benzoquinone. The second route proceeds through 4-hydroxybenzoic acid, which is not reported in the phenol oxidation networks published in literature. However, the complexity of phenol CWAO over activated carbon requires further in-depth kinetic studies. It would be of interest to refine the kinetic model by a better identification of the remaining unknown phenol degradation intermediates. Moreover, the current model is not capable to explain the formation of 4-hydroxybenzoic acid that may be related to the carbonaceous layer formed on the activated carbon. The next generation of kinetic models for the CWAO of phenol should attempt to include these phenomena to achieve a better understanding of the global reaction mechanism of catalytic phenol oxidation in the presence of activated carbon.

4.3. CWAO reactor modelling

Most laboratory studies of CWAO were carried out in slurry, spinning basket reactors or differential fixed bed reactors. However, industrial scale applications including hydrotreating and hydrogenation processes [223] commonly prefer the use of continuous fixed bed or sparged catalytic reactors since they offer both high catalyst to liquid ratio and easy mechanical handling. Catalytic fixed bed reactors were also advocated as the best choice for CWAO of organic pollutants showing a high potential for homogeneous polymerisation reactions [61,64,65]. Tukac and Hanika [28] experimentally studied the effect of catalyst wetting for phenol CWAO over activated carbon and concluded that incomplete catalyst wetting facilitated oxygen transfer through direct contact between gas and catalyst. A complex scenario of gas–liquid hydrodynamics and mass and heat transfer coupled with the chemical surface reaction arises from the operation of catalytic three-phase systems. Experimental studies are imperative to obtain trends for reactor operation, but only the comprehensive modelling of the underlying physical and chemical phenomena involved can improve our fundamental

understanding of these three-phase systems. In return, the development of reliable kinetic and reactor models to predict process performance is of transcendent importance providing a useful tool for the design, optimisation and scale up of any CWAO process.

Modelling of continuous CWAO reactors aiming to predict integral performance was only attempted in a few studies [19,30,189,190,221,234–238]. The available publications primarily focused on steady state operation of TBRs. Transient reactor modelling was considered to describe phenol adsorption-oxidation/regeneration sequences in a TBR [30,33] or periodic operation of TBR for the catalytic oxidation of aqueous SO_2 solution over activated carbon [237]. The major findings of these works will be summarised below.

To end this last section on CWAO, we will present OUR results on a comprehensive TBR model developed in collaboration with the Larachi group FROM Laval university [236] for the CWAO of phenol over the CI carbon [238].

4.3.1. Steady state reactor modelling

Smith and co-workers modelled the oxidation of formic acid [234] and acetic acid [221] in a TBR. The underlying reaction kinetics used were previously obtained operating the same reactor in a differential mode, i.e. with low catalyst loading. The authors developed an isothermal one-dimensional axial dispersion model accounting for external and internal mass transfer, ignoring catalyst wetting. The gas to liquid and liquid to solid mass transfer coefficients were obtained by correlating experimental data at 25 °C and 0.1 MPa and can be found in [228]. The model systematically over-estimated the experimental conversions measured for both acids. The relative importance of transport resistances according to this model, in decreasing order was: gas to liquid, intraparticle diffusion, liquid to particle and axial dispersion. In case of CWAO of acetic acid [221] higher deviations were observed at low liquid flow rates, what the authors attributed to liquid channelling. Pintar et al. [189] essentially followed the same approach to model the CWAO of phenol in a TBR. The authors used more realistic Langmuir–Hinshelwood rate equations obtained from kinetic experiments in a differential liquid full packed bed reactor [65]. Although they calculated low wetting efficiencies of 0.6–0.7, they did not account for it in the model. Their simulations predicted 50% lower phenol conversions than the experimental ones. Surprisingly, the model deviation remained when all mass transfer control was suppressed in the model. Very recently, Maugans and Akgerman [190] established a TBR model for the CWAO of phenol over a Pt/TiO_2 catalyst, accounting for external and internal diffusion and catalyst deactivation. The model predictions of conversion profiles matched well experimental observations. It is noteworthy that in this case

the kinetics assessed in batch slurry assays could be successfully transferred to the fixed bed reactor, contrary to the studies of Pintar and Levec [65] and Stüber et al. [61]. All the previous CWAO modelling did not consider partial catalyst wetting, although it was proven a key parameter for a better model prediction of trickle bed operation mode [239].

The issue of reactor screening has been attended from a theoretical standpoint. Larachi et al. [235] and Iliuta and Larachi [19] modelled the performance of different reactor types with non-deactivating and deactivating catalysts for the CWAO of phenol. They considered four different reactor types including TBR, packed bubble column (PBC), SBC and FLB. In all simulations the effectiveness factor was calculated by solving the diffusion-reaction equation in the pellet. The TBR and PBC model equations incorporated the effect of mass transfer from the dynamic liquid to the stagnant liquid. For the SBC an additional equation was added to account for the longitudinal distribution of the solids. The simulation results indicated that under the conditions of liquid reactant limitation studied, the PBC outperforms the TBR partial wetting being harmful for conversion in this situation.

4.3.2. Transient reactor modelling

Transient modelling is useful to describe dynamic processes that either are imposed or occur naturally during CWAO. Actually, the works of Larachi and Iliuta presented above [19,235] must be considered as unsteady state modelling since transient terms were incorporated in the underlying model equations. With the help of these dynamic models, the authors could demonstrate that the TBR and the PBC were less prone to catalyst deactivation, while the SBC suffered more severe deactivation than the FLB.

Forced liquid flow interruption, i.e. periodic operation, is another example for dynamic behaviour of TBR. Periodic operation was experimentally studied for the catalytic oxidation of phenol [35] and SO_2 [200,240] over activated carbon. Proper adjusting of feed cycle period length and its split value was shown to increase conversion if the reaction system is limited by the gaseous reactant. According to the review of Silveston and Hanika [228], modelling of periodic flow interruption or flow variation received much attention, leading to the development of macroscopic, one-dimensional, dynamic models [237,241–243]. The authors pointed out that these models were capable to represent well the transient outlet reactant and product concentrations, but not so the temperature waves travelling throughout the fixed bed. Given their accuracy for the prediction of time-average performance, these models should be useful for optimising periodic flow interruption and exploring new applications of periodic flow forcing. Finally, the authors concluded that the need for further model improvement is in the description of steady-state

flow maldistribution at low flow rates and the dynamic of changes imposed either by abruptly decreasing or increasing the liquid flow rate. The time and position-averaged models currently adopted seems not capable to tackle this situation, and the authors recommended the use of percolation theory for this model extension.

Process intensification in wastewater treatment was tested combining adsorption and oxidation of organic pollutants over activated carbon as support or direct catalyst in the same reactor unit [30,33]. This implies dynamic reactor operation in sequential adsorption-oxidation or gas phase regeneration cycles. Matatov-Meytal *et al.* [33] studied both experimentally and theoretically the periodic liquid phase adsorption and gas phase regeneration of phenol and *p*-chlorophenol over activated carbon modified with metal oxide catalysts at temperatures of 250–290 °C. The authors reported a full recovery of the adsorbate in the case of phenol whereas only poor regeneration was achieved with *p*-chlorophenol. During the regeneration of activated carbon the transient effluent CO_2 concentration were recorded. In the subsequent modelling different models with various kinetics were compared with the dynamic regeneration data enabling to the authors to extract parameters including activation energies and rate constants. Such kinetic data are very useful for the optimisation of the regeneration process.

The Toulouse group of Prof. Delmas in collaboration with our research group proposed and patented a cyclic low temperature adsorption-high temperature oxidation sequence for the treatment of phenolic solutions over the CI carbon [30,244]. The process was described by transient modelling of the adsorption and oxidation step conducted in the same TBR unit. First, the activated carbon bed is saturated with the flowing phenol feed solution at ambient temperature taking advantage of the higher adsorption capacity. After bed saturation the phenol feed is stopped to recycle a fixed volume of phenol feed in a closed loop at high flow rate to approach differential operation of the TBR. At the same time, the reactor is heated to 140 °C and pressurised with air at 4 MPa to start the oxidation reaction. Adsorption isotherm and reaction rate of phenol oxidation at 140 °C were either measured or taken from [61], respectively. Using only 80% of the ambient adsorption capacity, the dimensions of the reactor, catalyst loading (m_{cat}) and running time of the adsorption step were first determined. Then, the duration of the oxidation step was calculated at 140 °C assuming a perfectly well-mixed reactor model accounting simultaneously for oxidation and adsorption equilibrium:

$$-r m_{cat} = m_{cat} \frac{dq_{Ph,eq}}{dt} + V_L \frac{dC_{Ph,L}}{dt}, \qquad (3)$$

$$r = k_1 C_{Ph,L}, \qquad (4)$$

where $q_{Ph,eq}$ is the phenol equilibrium adsorption capacity, C_{Ph} the phenol concentration in the liquid phase, V_L the loop liquid volume, m_{cat} the catalyst loading, $C_{Ph,L}$ the liquid phenol concentration and k_1 the rate constant of phenol oxidation.

Table 16 lists the calculated run times for the adsorption and oxidation step at a fixed volumetric flow rate of 2 m³/L and varying initial phenol inlet concentrations. Reactor size and catalyst loading were quite important ($L_R = 11$ m, $D_R = 0.84$ m, $m_{cat} = 2920$ kg) due to the very low liquid velocity of 0.001 m/s selected in the calculation of the adsorption step. The combined sequential process seemed particularly attractive for the treatment of diluted phenol solution with concentrations smaller than 1000 ppm. Under these conditions the running time of the adsorption step was one order of magnitude higher than the oxidation step. Moreover, for highly concentrated phenolic wastewater, running times of the two steps were still comparable and continuous treatment can be assured by operating two TBRs in parallel. The second important result was related to the final level of degradation to be achieved by oxidation treatment. The simulations showed that residual phenol concentrations of about 1000 ppm after oxidation at 140 °C were sufficient to provide very small new phenol equilibrium concentration of about 20 ppm when the treated liquid volume is cooled down to ambient temperature. Thus, the sequential two-step adsorption-oxidation process can offer a very attractive solution for the purification of phenolic containing effluents. On going research work is focused both on optimising the adsorption velocity required and extending the dynamic modelling of the oxidation step. A more realistic model is under development that accounts for the adiabatic heating period as well as the mass transfer between phases and eventual catalyst wetting. Also, a pilot plant was constructed in the laboratory of the Delmas group and experimental will be available for comparison with model prediction. Additionally, the economics of the process proposed should be compared to the costs of classical adsorption-regeneration in order to evaluate its industrial feasibility.

4.3.3. Modelling of phenol CWAO over activated carbon in TBR

Unlike the modelling of TBRs for hydrotreatment and selective hydrogenation or oxidation processes, the influence of partial wetting on reactor performance was essentially ignored in most of the works on CWAO reactor modelling. The same situation holds for aspects of non-isothermal TBR operation, which is of importance for industrial application due to possible energy savings. To this end, Eftaxias *et al.* [197,236] developed in collaboration with the group of Larachi a comprehensive phenomenological non-isothermal model for CWAO of phenol. The model was successfully tested

with a $CuO/\gamma\text{-}Al_2O_3$ catalyst [236]. However, this catalyst was shown to undergo important catalyst leaching [52] and thus cannot be recommended for catalytic oxidation treatment of phenolic wastewater. An attractive substitute offers the CI activated carbon that gave even better catalytic activity than the copper-based catalyst.

4.3.3.1. Model description and solution. The TBR model developed is based on previous work of Iliuta and Larachi [19] and Rajashejharam *et al.* [245]. It was further extended to incorporate: (1) a modified effectiveness factor that addresses both the gas limiting and liquid limiting reactant situation and (2) the heat balance equation to study non-isothermal reactor operation. Mathematical description of the underlying phenomena were done on three length scale, i.e. molecular scale (reaction kinetics), pellet scale and reactor scale. The model can thus predict the axial concentration profiles of all species involved in the gas phase (oxygen), liquid bulk, catalyst surface and within the catalyst pores. For non-isothermal operation the temperature variation along the catalytic fixed bed is calculated accounting for water evaporation. The important assumptions made in the model were

- Existence of static and dynamic liquid portions.
- Constant partial catalyst wetting throughout the reactor.
- Catalyst completely internally wetted.
- Backmixing in the dynamic liquid phase.
- External and internal mass transfer between phases according to film model.
- Absence of radial concentration and temperature gradients.
- Instantaneous water vapour–liquid equilibrium.
- Stable catalyst activity and surface oxidation reaction.

The reaction kinetics and network used in the model were those presented before in section 4.2.2 and figure 20, respectively. Physical properties of the bulk phase were obtained from the estimation methods included in Reid *et al.* [246] assuming the bulk phase to be pure water. The Henry constant for oxygen solubility in water was taken from Himmelblau [247]. The most important hydrodynamic and mass transfer parameters can be found in table 15 of Section 4.2.1. Additionally, the gas–solid oxygen mass transfer coef-

ficient across the dry pellet was assumed to be one order of magnitude higher than the gas–liquid mass transfer coefficient in agreement with the observation of Lu *et al.* [248]. The liquid phase axial dispersion coefficients were determined from the work of Piché *et al.* [249] and finally, the effective pore diffusion coefficients were calculated with a tortuosity factor equal to three.

The complete differential and algebraic equation system, given in [197,236] was solved according to the method of orthogonal collocation on finite elements [250]. The number of collocation points used was eight both for reactor and pellet length scale. In most cases it was possible to obtain a stable numerical solution with one element, except for complete wetting or very low effectiveness factors where two elements in the reactor model were required to achieve convergence.

4.3.3.2. Model validation. In a first step, the sensitivity of the model parameters was examined under isothermal conditions. The calculated high γ reactant flux ratios of 17 and 34 indicated the positive influence that partial wetting should have on reactor performance. Not surprisingly, increasing the catalyst wetting efficiency in the model was found to decrease the reactor conversion. It is noteworthy to state that wetting efficiency was found to have an On–Off effect on phenol conversion. A small portion of dry catalyst surface can already provide enough oxygen on the catalyst surface through fast direct gas–solid mass transfer, by-passing the external gas–liquid and liquid–solid mass transfer resistances. Internal mass transfer also had a strong effect that could be expected from the particle size selected for the kinetic study. Axial dispersion and external mass transfer were not influent at all under realistic conditions of partial wetting. When assuming fully wetted catalyst particle in the model, the external mass transfer of oxygen, in particular between the gas and liquid phase, then proved to be important. Overall, the sensitivity analyses reflected a coherent behaviour of the comprehensive TBR model.

In a second step, the TBR model was tested against the experimental Trickle Bed data used for the kinetic modelling study. Thus, the prediction of the TBR model should match the experimental data when assessed in the kinetic regime. The close agreement of the transport-reaction model with both the simple kinetic model and the experimental data, as shown in figure 21 for phenol

Table 16
Influence of initial phenol concentration on adsorption and oxidation time: 140 °C, 4 MPa, $C_{Ph,fin} = 1.0$ g/L, $F_L = 2$ m^3/h, $L_R = 11$ m, $D_R = 0.84$ m, $m_{CAT} = 2920$ kg [30]

Initial phenol concentration (ppm)	500	1000	2000	3000	5000	10000
Adsorption time (h)	145.2	105.6	71.8	55.9	40.3	25.4
Oxidation time (h)	10.3	12.7	14.9	15.8	17.0	17.1

concentration, gave a convincing prove for the validity of the kinetic and comprehensive TBR models. However, the TBR model should be further tested against experimental data that were obtained under conditions of external mass transfer control.

4.3.3.3. Operation strategies for phenol CWAO. With the help of the reliable TBR model, different operation strategies of CWAO reactors can be simulated as it was already done in case of phenol CWAO over the CuO/alumina catalyst [236]. At typical CWAO conditions, the oxidation of phenol may be either gas or liquid reactant limited. For a given inlet phenol concentration, the isothermal TBR model can recommend adequate operating conditions and flow direction that should optimise the phenol conversion. For the high γ reactant flux ratio of 17 and 34, oxygen in the gas phase will be always the limiting reactant even for high conversions, thus down-flow operation with partial catalyst wetting will favour the phenol conversion. If the particle size has to be scaled up or down, the model was shown to be a useful mean in screening an optimal combination of pressure drop and conversion. The build-in of the detailed reaction network, accounting for the main partial oxidation products, only slightly altered phenol degradation profiles. However, the distribution of intermediates that determines toxicity and pH values of the effluent was seen to be affected in the presence of strong mass transfer limitations.

Finally, non-isothermal simulations evidenced that water evaporation must be considered in the design of adiabatically operated CWAO reactors. As illustrate in figure 22, neglecting evaporation, especially at high conversions, can lead to erroneous results of both too high adiabatic temperature rise and outlet conversions of phenol. The adiabatic temperature rise was further shown to strongly depend on the superficial gas flow rate. In agreement with experimental observation for adiabatic WAO processes, the ATR exhibited a maximum at oxygen excess flow rates of about 10–20% yielding at the same time favourable phenol conversion in adiabatic CWAO.

5. Conclusions

Different reviews on carbon materials prognostic an increasing catalytic use of activated carbon and carbon black given the wide range of existing commercial processes and potential application in fine chemicals, fuel cells and environmental friendly technologies. To meet with this encouraging prognostic, two crucial prerequisites has to be addressed by future research: a better fundamental understanding of the catalytic function of carbon materials and the controlled manufacture of carbons tailored to the specific needs of the application.
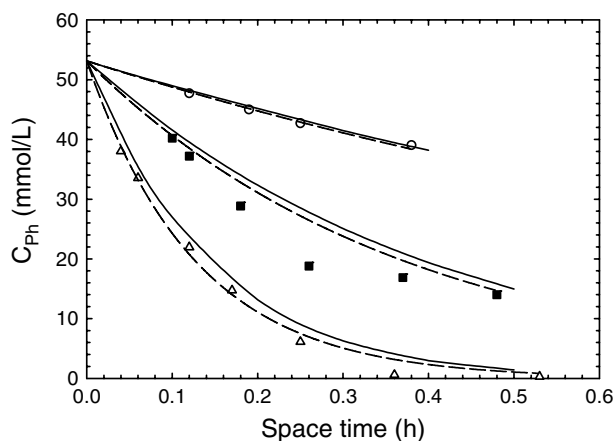

Figure 21. Prediction of comprehensive TBR model and kinetic model for the CWAO of phenol over the CI activated carbon at 0.2 MPa. Experiments: (○) 120 °C, (■) 140 °C, (△) 160 °C}, Solid lines: TBR model, Dashed lines: Kinetic model.

The fate of carbons in the treatment of organic wastewater pollutants is at one extreme the mere use as a support for precious metal and metal oxide catalysts more resistant to leaching of the active phase in the acidic CWAO environment. At the other extreme carbon itself emerges as a promising active oxidation catalyst. Considerable progress was made in the characterisation of the relevant physical and chemical surface properties of carbon materials. It appears that these high surface area materials give a superior support performance than commonly employed Al_2O_3, TiO_2 and ZrO_2 supports do. The main virtue of providing a high surface area is the high initial monolayer dispersion even at high metal loading. The often desirable strong interaction between the carbon surface and the metal particles to avoid active phase leaching and overoxidation can be achieved by increasing the number of adsorbing sites, i.e. COO^- groups, through HNO_3 treatment. The challenge then is to maintain a high and clean surface area during continuous use: in this regard, carbonyl groups are the more effective dispersion-maintaining agents. Moreover, among the available carbon supports, high surface area graphite may offer a better choice since the graphite structure can stabilise the anchored metal particles via an electron-donor effect. Thus, high activity as well as unwanted catalyst leaching, sintering and overoxidation can be controlled under typical CWAO with the currently available supported catalysts.

The catalytic function of unsupported carbon is less understood. It is now recognised that the carbon surface chemistry is at the origin of activity rather than the carbon texture that, however, mainly controls the access of the reactants to the active surface sites, thus being of equal importance. Preparation and subsequent modification of carbons by gas phase and liquid phase treatments allow readily designing a given surface chemistry. The problem is that in many cases we do
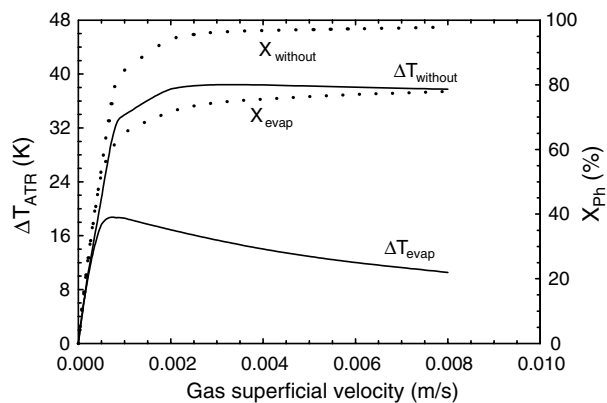
Figure 22. TBR model prediction of adiabatic temperature rise (ATR) (—) and phenol conversion (···) as a function of gas superficial velocity: $u_l = 0.4$ mm/s, $T_0 = 140$ °C.

not know exactly what type of functionalised surface chemistry is the optimal one. CWAO and related oxidation studies have shown that basic carbons containing quinone groups are active as oxidation catalysts for organic wastewater pollutants probably due to their ability to form reactive free radicals by hydrogen abstraction. There remain however several open questions requiring in-depth research studies. The opportunity of tailoring pore size distribution and thereby activity and selectivity has been realised, but has not been often tested in catalytic applications of carbon materials. Moreover, it is important to assess the changes that can undergo the texture and surface of carbon catalyst when continuously contacted with dissolved oxygen and organic compounds at typical CWAO conditions. Carbons are resistant to acidic and basic pH, but partial combustion of carbon in the liquid phase has been observed at temperatures as low as 120 °C. Thus, the catalyst designer has to worry about the affinity of oxygen for carbon. Optimisation of surface chemistry must develop carbons more active at lower temperatures and more resistant to oxygen attack because excessive loss of carbon may prevent the process from being commercialised. In a next step, these optimised carbons should then be tested on frequently encountered organic pollutants as well as more complex industrial effluents.

The design of catalyst is only one of the engineering aspects that has to be addressed simultaneously. The choice of appropriate continuous reactor and operation conditions including catalyst geometry is crucial for efficiently moving the optimised (powder) catalyst potential to industrial scale applications. The lack of extensive literature references and patent applications demonstrates that CWAO engineering is still in a developing stage. Comparative kinetic experiments of CWAO showed that bio-toxic and refractory organic wastewater pollutants have a high potential for polymerisation reactions advocating fixed bed reactors as a good choice due to their favourable high solid to

liquid ratio provided. Catalytic three-phase fixed bed reactors are characterised by the coupling of gas–liquid hydrodynamics, mass and heat transfer and heterogeneous surface reaction of adsorbed species. The few CWAO reactor studies highlighted the strong influence of catalyst wetting and gas–liquid mass transfer on the performance of this reactor configuration. A simple but reliable reactant flux criterion that determines the limiting reactant can help to decide on the gas–liquid flow direction or catalytic fixed bed dilution for obtaining optimal pollutant conversion. Several promising operation strategies have been proposed to increment the efficiency of fixed bed reactors including adiabatic operation, forced periodic flow interruption, sequential adsorption-oxidation cycles in the same unit as well as the integration of CWAO as a precursor in a traditional biological treatment facility.

It is evident that further experimental research is necessary in this regard, but only the comprehensive modelling of fixed bed reactor can provide the fundamental knowledge required for a safe design, optimisation and eventual scale-up of CWAO processes. More realistic models that better describe the phenomena prevailing on the reactor length scale, in particular the hydrodynamics of the gas–liquid flow have to be tested. Aspects of non-isothermal and transient operation should also be accounted for in this next generation of models. To this end, the designer of CWAO processes can take advantage of the important progress made in the characterisation of gas–liquid flow in catalytic fixed beds applied to hydrogenation and partial oxidation reactions. Finally, the current state of the art in CWAO kinetic modelling has to be updated. The frequently used COD or TOC lumping strategies may no longer be appropriate when a more precise knowledge of the effluent toxicity is desired. The distribution of reaction intermediates can be conveniently assessed by available analysis techniques. So far, only the reaction pathways of not catalytic and catalytic phenol and carboxylic acids oxidation are known in detail. Other organic compounds containing nitrogen, chloro and sulphur heteroatoms are of interest, although it may be often impossible to characterise the composition in complex industrial effluents. The subsequent kinetic modelling should then consider the complete reaction network including the adsorption of organic pollutants and oxygen preceding the surface reaction in heterogeneously catalysed processes. On the other hand, detailed models involve a high number of unknown kinetic parameters translating simple parameter estimation into a hard mathematical task of non-linear multiparameter identification.

It can be concluded that the global design of CWAO (or any heterogeneously catalysed processes) should entail optimisation studies on three different process length-scales. On one hand, the extrapolation of the intrinsic (powder) catalyst potential to the pellet size and finally to the reactor size offers many opportunities for

the designer. On the other hand, the approach that simultaneously deals with all these aspects within a group of experts certainly gives a much better result than the traditional strategy that employs sequential optimisation studies.

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