Modified activated carbons for catalytic wet air oxidation of phenol

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Abstract

This study aims at testing several activated carbons for the catalytic wet air oxidation (CWAO) of phenol solutions. Two commercial activated carbons were used both as received and modified by treatment with either HNO_3, $(NH_4)_2S_2O_8$, or H_2O_2 and by demineralisation with HCl. The activated carbons were characterised by measuring their surface area, distribution of surface functional groups and phenol adsorption capacity. The parent and treated activated carbons were then checked for CWAO using a trickle bed at 140 °C and 2 bar of oxygen partial pressure. The treatments increase the acidic sites, mostly creating lactones and carboxyls though some phenolic and carbonyl groups were also generated. Only $(NH_4)_2S_2O_8$ treatment yields a significant decrease in surface area. CWAO tests show that catalytic activity mainly depends on the origin of the activated carbon. The modifications generally had a low impact on phenol conversion, which correlates somewhat with the increase in the acidity of the carbons. Characterisation of the used activated carbon evidences that chemisorbed phenolic polymers formed through oxidative coupling and oxygen radicals play a major role in the CWAO over activated carbon.
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1. Introduction

Today, increasingly stringent regulations require ever more treatment of industrial effluents to generate better quality product waters that can be more easily reused or disposed of without damaging the environment. A wide range of treatment technologies is being developed and optimised for a variety of applications in many different industries. In the last few years, catalytic wet air oxidation (CWAO) has gained attention for the treatment of biologically refractory organic compounds because it can operate at mild temperature and pressure, which positively impacts to the economics of the treatment. However, the lack of stable, active catalysts has seriously hindered its development and discouraged its use in wider industrial applications [1–3].

Historically, activated carbon has been extensively used not only as an adsorbent but also as a catalyst support or even as a direct catalyst [4]. In particular, activated carbon has often been used to support active metals for CWAO [5–12]. However, in the absence of any active metal, the potential of activated carbon as direct catalytic material for CWAO has only recently been proved for the destruction of phenol and other bioxenotic organic compounds [13–15]. Activated carbon performs noticeably better than many alumina-supported metal catalysts [2]. This superior performance was believed to be due to their phenol adsorption capacity, which could enhance the oxidation environment conditions. However, the performance of the various commercial activated carbons differs significantly [16], which strongly suggests that the specific characteristics

of each activated carbon do affect their results. In addition, little attention has been paid to highlighting the role of the activated carbon in CWAO.

The adsorption capacity of the activated carbon mainly depends on its textural properties i.e. surface area, pore volume and porous structure. However, the chemical nature of its surface often plays a dominating role in its performance as adsorbent, catalyst support or catalyst [17]. The chemistry of the surface depends on the presence of heteroatoms, mainly oxygen, which form organic functional groups such as carboxylic acids, lactones, phenols, carbonyls, quinones, aldehydes, ethers, anhydrides and even others [18]. Specifically, phenol seems to interact with the activated carbon through a chemisorption mechanism based on the bonding between phenol and oxygen-containing surface groups [19], e.g. acidic groups, which can progress to form phenol-derived polymers by an oxidative coupling mechanism [20]. However, the formation of electron donor–acceptor complexes has also been proposed as the adsorption mechanism, in which the basic surface oxygen and/or carbon surface electron-rich regions act as donors, and the aromatic ring serves as the acceptor [21]. There is evidence that both adsorption mechanisms simultaneously appear in oxic conditions, though the role of the oxygen functional groups is still unclear [22–24]. Likewise, the pore structure has been shown to influence phenol adsorption capacity by controlling the accessibility to the adsorption sites [25,26].

The modification of the surface chemistry of activated carbons can be carried out by oxidation in the gas or liquid phase in order to increase the concentration of surface oxygen groups. A wide range of oxidising agents, e.g. H_2SO_4, HNO_3, $HClO_4$, $(NH_4)_2S_2O_8$, H_2O_2, ClO_2, KIO_4, $KMnO_4$, have been studied in liquid phase over a variety of carbonaceous materials. Although the trends shown for each oxidant are similar, the particular transformations mostly depend on the original characteristics of each activated carbon [17].

This paper checks the effect of the physico-chemical properties of several activated carbons on the performance of CWAO. Phenol was selected as the model compound representative of a family of biologically refractory substances. Prior to use, two commercially available activated carbons, made from charcoal and coconut shells, respectively, were subjected to oxidation in liquid phase using either HNO_3, $(NH_4)_2S_2O_8$, or H_2O_2 and to demineralisation by HCl treatment. The activated carbons were further characterised by BET, Boehm titration, elemental analysis and thermogravimetric analysis (TGA). Their phenol adsorption capacities at room temperature were also determined. Finally, their CWAO performance was checked at 140 °C and 2 bar of oxygen partial pressure in a trickle bed reactor.

2. Experimental

2.1. Materials

Two commercial activated carbons for industrial use, recommended for water treatment, were used. CI was purchased from Merck (ref. #2514) and CII was purchased from Warwick Benbassat (Barcelona, Spain; ref. #GH-6112). According to the manufacturers, CI is a charcoal and CII is a coconut-shell-based activated carbon. Prior to use, the activated carbons were crushed and sieved and the 25–50 mesh size particle range was separated. The above fraction was repeatedly washed to remove all the fines, oven-dried overnight at 110 °C, and stored under inert atmosphere until use.

The HNO_3, H_2O_2 and $(NH_4)_2S_2O_8$ reagents, used for the liquid oxidation of the activated carbons, and HCl, used for demineralisation, were analytical grade and obtained from Merck, as were NaOH, Na_2CO_3, and $NaHCO_3$ for the Boehm method. Analytical grade phenol was provided by Aldrich. Deionised water was used to prepare all the solutions.

BET characterisation of the parent and modified activated carbons was conducted in the Scientific and Technical Service of the University of Barcelona (Spain). Ultimate analysis and thermogravimetric analysis (TGA) were carried out in the Scientific Resources Unit of the Rovira i Virgili University in Tarragona (Spain).

2.2. Experimental set-up and procedures

Both activated carbons were subjected to liquid oxidation either with HNO_3 (referred to as –N in the figures and tables), H_2O_2 (–P) or $(NH_4)_2S_2O_8$ (–S) according to previously reported procedures [27]. They were also subjected to demineralisation with HCl (indicated as –H) following a known protocol [28]. A comparative study of the textural and chemical characteristics of the parent and treated activated carbons was then performed as described in Section 2.3. Subsequently, the catalytic performance of both parent and modified activated carbons was tested for the CWAO of 5 g/l phenol solutions.

CWAO experiments were carried out in a trickle bed reaction system in concurrent gas–liquid downflow. The reactor containing the activated carbon packed bed consists of a stainless steel tube (20 cm in length and 1.1 cm i.d.), which is placed in a controlled temperature oven (±1 °C). Typically, about 7.5 g of activated carbon were loaded into the reactor and the liquid flowrate was then calculated to give a space time of 0.12 h, i.e. a liquid WHLV of 8.2 h^{-1}. The oxygen partial pressure was always 2 bar, while the air flowrate was kept constant at 2.4 ml/s STP, which is well beyond the stoichiometric oxygen uptake. All the experiments were run at 140 °C.

Fifty hours tests were completed for each of the activated carbons tested. Exited liquid samples were periodically withdrawn and analysed to determine phenol conversion and COD reduction. At the end of the test, the used activated carbon was carefully collected and dried overnight at 150 °C in an oven to remove any physically adsorbed phenol. Weight change was then obtained using a balance.

The phenol concentration of the exited samples was determined by HPLC following an analytical procedure described elsewhere [29]. COD was measured following the standard method 5220D [30]. A complete scheme of the experimental apparatus and a more detailed description of the procedures can be found in the literature [13,16,31].

2.3. Characterisation of the active carbons

Surface area was determined by nitrogen adsorption at 77 K in a Micromeritics Model ASAP 2000. Thermogravimetric analysis (TGA) was carried in a Thermobalance Perkin–Elmer model TGA7, TCA7. The sample was first kept at 100 °C for 20 min and then heated up to 900 °C under He flow at a heating rate of 10 °C/min. The samples were previously dried overnight in an oven at 150 °C. Ash content was obtained by calcination in an oven at 650 °C (±5 °C) following ASTM D-2866. Ultimate analysis was also performed to determine the content in hydrogen, carbon, nitrogen and oxygen.

Boehm titrations were carried out following a procedure described elsewhere [27,32,33]. The number and type of acidic sites were calculated by considering that NaOH neutralises carboxylic, lactonic and phenolic groups, that Na_2CO_3 neutralises carboxylic and lactonic groups, and that $NaHCO_3$ neutralises only carboxylic groups. Carboxylic groups were therefore quantified by direct titration with $NaHCO_3$. The difference between the groups titrated with Na_2CO_3 and those titrated with $NaHCO_3$ was assumed to be lactones and the difference between the groups titrated with NaOH and those titrated with Na_2CO_3 was assumed to be phenols. Basic sites were determined by titration with HCl. The pH of the carbon suspension was determined with a pH meter by equilibrating 1 g sample in 25 cm^3 of deionised water.

Phenol adsorption isotherms of the active carbons were obtained at 20 °C (±2 °C) in oxic conditions following a standard protocol [20].

3. Results and discussion

3.1. Characterisation of the activated carbons

The surface area and ash contents of the activated carbons tested are summarised in Table 1. The original carbon CI shows a relatively high surface area of over 1100 m^2/g. This is much greater than that of CII, which is around 600 m^2/g. This is a distinctive trend for the two commercial activated carbons tested. For both CI and CII, HNO_3 and H_2O_2 treatments do not significantly change their surface area within the experimental error of BET determinations. These results contrast with the surface areas obtained after $(NH_4)_2S_2O_8$ treatment, which were remarkably lower. This decrease is close to 30% for CI and about 18% for CII. This effect of oxidising treatments on surface area seems to depend strongly on the source and treatment conditions [34,35] and can increase or decrease the surface area.

With regard to ash content, there is a clear difference between the parent activated carbon since CI contains a remarkable amount of mineral matter i.e. 4.5% ash content. All the treatments effectively eliminate mineral matter and the resulting activated carbons have an ash content of around 1%. The treatments remove almost no mineral matter from CII because its initial content is already low.

The distribution of chemical surface groups for both parent and treated CI and CII is shown in Table 2. This table also shows the pH given in solution. Phenolic groups predominate in both parent activated carbons; lactones and carboxylic groups are almost negligible. Note the large number of basic sites obtained for both non-modified activated carbons. Apparently, CI is more functionalised than CII because the total amount of acidic groups is 32% higher for CI and its number of basic groups is almost twice as high. However, referred to surface area, CII is more acidly functionalised than CI, though basic sites are similar.

As expected, treatment with oxidants increases the number of oxygen groups. Treatment with $(NH_4)_2S_2O_8$ leads to the highest rise in total acidic sites, which is 73% higher for CI and almost threefold greater for CII. Treatment with HNO_3 also renders a significant increase, 48% and 63% higher, respectively, than the original CI and CII. The effect of H_2O_2 is slight for CI, with an increase of only 18%. For CII, this increase is more than twofold after treatment. Demineralisation with HCl produces a negligible change for CI but a more marked change for CII. Thus, the number of acidic sites almost doubles although the new sites are mainly phenolic. Overall, treatment with HNO_3 mostly generates lactones and carboxylic groups, while the phenolic group concentration is less affected. On the other hand, liquid treatment with $(NH_4)_2S_2O_8$ creates phenolic groups, though the increase in lactones and carboxylic sites is also noticeable. Note that on the whole the number of lactones and carboxyls is almost identical for CI after treatment with HNO_3 and $(NH_4)_2S_2O_8$, but that carboxyls are predominant for HNO_3 and lactones were predominant for $(NH_4)_2S_2O_8$. This can be explained by the greater density of phenolic groups for $(NH_4)_2S_2O_8$,

Table 1
Properties of the parent and treated activated carbons CI and CII

	Activated carbon									
	CI	CI–N	CI–S	CI–P	CI–H	CII	CII–N	CII–S	CII–P	CII–H
S_{N2} (m^2/g)	1142	1160	806	1110	1089	602	617	496	639	617
Ash (%w/w)	4.5	1.0	1.1	1.0	1.0	1.0	0.8	1.3	0.9	1.0

Table 2
Chemical surface groups for the parent and treated activated carbons CI and CII

Activated carbon	Total					
	Phenolic[a]	Lactone	Carboxylic	Acidic	Basic	pH
	Surface groups density[b]					
CI	0.84	0.09	0.04	0.96	2.31	8.3
CI–N	0.96	0.17	0.28	1.42	1.27	3.0
CI–S	1.23	0.28	0.15	1.66	1.25	2.7
CI–P	0.82	0.27	0.03	1.13	2.80	5.9
CI–H	0.76	0.16	0.18	1.09	1.25	7.2
CII	0.65	0.00	0.00	0.65	1.22	11.3
CII–N	0.52	0.03	0.51	1.06	0.69	4.2
CII–S	1.04	0.03	0.53	1.60	0.97	3.8
CII–P	1.10	0.08	0.15	1.33	1.33	7.5
CII–H	1.03	0.09	0.18	1.30	0.66	7.7

[a] Also including carbonyls.
[b] In meq/g AC.

which leads to their condensation with the carboxyls to form lactones, and therefore also decreases the density of carboxylic groups [36]. The effect of treatment with H_2O_2 depends on which activated carbon is considered. For CI, only an increase in the lactones is observed. On the other hand, there is a large increase in the phenolic groups for CII with only slight changes for lactones and carboxylic groups.

In general, all the treatments, except the treatment with H_2O_2, leads to a destruction of basic sites. The greatest destruction is observed for HNO_3, which is recognised as the strongest oxidant of all those used. Surprisingly, H_2O_2 is also able to create new basic sites in addition to acidic groups. Possibly, H_2O_2, because of its gentler oxidant character, could be able to render some recognised basic groups as quinones, chromenes or pyrenes [37]. This effect is comparable for both activated carbons since the number of basic sites increases 21% for CI and 9% for CII. This could be related to the lower surface area of CII, which suggests that its surface is more available for attack by the oxidants. The different behaviour must be ascribed to the fact that oxidising power is not the only factor to affect the extent of oxidation. Pore diffusion, oxidant concentration, temperature, pH, exposure time and even the original characteristics of the activated carbon can drive the final result [38]. With regard to pH, both activated carbons are basic in origin, though CII is considerably more alkaline than CI. All treatments lowered pH, especially

HNO_3 and $(NH_4)_2S_2O_8$, due to the increase in the acidic groups and probably also to the destruction of basic sites.

The increase in surface oxygen groups in the treated activated carbons is also demonstrated by the ultimate analyses in Table 3. As it can be seen for CI, the oxygen content goes from 8.4% to 15.0% after HNO_3 treatment and to 20.8% after $(NH_4)_2S_2O_8$ treatment. There is a significant decrease in carbon content when surface area was also reduced. The higher nitrogen content after HNO_3 treatment is probably due to the formation of nitrogen-containing species attached to the aromatic ring structure of the activated carbon, as Salame and

Table 3
Ultimate analysis of the parent and treated activated carbons CI and CII

Activated carbon	C (%)	H (%)	N (%)	S (%)	O (%)[a]
CI	89.8	0.3	0.4	1.0	8.4
CI–N	82.7	1.1	1.1	0.8	15.0
CI–S	76.1	0.4	0.4	1.5	20.8
CI–P	86.9	0.3	0.4	1.2	11.1
CI–H	89.1	0.3	0.4	1.2	8.9
CII	91.2	0.2	0.1	0.1	8.4
CII–N	84.1	0.8	0.7	0.1	14.3
CII–S	84.2	0.5	0.3	0.1	14.9
CII–P	89.9	0.2	0.1	0.1	9.7
CII–H	89.9	0.2	0.1	0.1	9.7

[a] By difference.

Bandosz [29] already observed. Nitro groups cannot be detected by the Boehm method but they do account for during TGA determination. As expected, demineralisation with HCl does not essentially change the ultimate analysis in comparison with that of the original activated carbon.

Fig. 1a shows the weight loss for both parent and treated CI during the TGA carried out between 100 and 900 °C. Since no TPD was done, TGA interpretation is conducted in accordance with the study by Figueiredo et al. [39], which assigns each temperature zone to the desorption of a particular surface group or groups. Several studies agree with this interpretation [40–42]. In general, the evolution of CI, CI–H, and

Fig. 1. TGA profiles of the parent and modified activated carbons: (a) CI and (b) CII.

CI–P is similar. There is almost no loss up to 500 °C. Then there is a zone with a marked drop in weight. The low content of carboxylic groups agrees with this result. However, taking into account the previously reported data for oxygen, some difference should be expected between CI and CI–H or CI–P. The uncertainty in the Bohem titrations can probably explain the similarity. In turn, CI–N and CI–S show a first zone of rapid release of gaseous species between 200 and 300 °C, with a peak at around 250 °C. This zone could belong to the CO_2 from the decomposition of carboxylic groups present in all the activated carbons. Later, a broad zone of continuous loss is seen, extending from 300 to 800 °C. This zone peaks at around 650 °C and could be assigned to CO_2 from the lactones and to CO from the phenolic groups, carbonyls and other minor groups. Similar trends can be drawn from the TGA performed on the CII samples, which are shown in Fig. 1b.

The total weight loss for each sample of both activated carbons is summarised in Table 4. The results are generally consistent with those that could be predicted from the Boehm titrations and ultimate analysis, if the differences are just ascribed to the new oxygen groups. The biggest weight loss for CI, 26.5%, is provided by the treatment with $(NH_4)_2S_2O_8$. This was unexpectedly large, more than three times higher than for the original CI, which is only 8.0%. This increase is in the same order of magnitude as for the ultimate analysis for oxygen.

The same trend is observed for the treatments with HNO_3, for which there is a significant weight loss of 16.0%. For treatments with H_2O_2 and HCl, weight loss was negligible. In these cases, the mass increase due to the addition of oxygen groups can be offset by the loss in volatile carbonaceous matter that is also released during TGA. This effect, which also occurred with the HNO_3 and $(NH_4)_2S_2O_8$ treatments, is masked by the much greater presence of surface oxygen groups and even nitro groups for CI–N. The trends are the same for CII, though the differences are not so marked. CII produces an inferior weight loss than CI, which is in agreement with its lower original oxygen content.

Fig. 2a and b shows the phenol adsorption isotherms at room temperature for CI and CII, respectively. Table 5 collects the maximum phenol adsorption capacity for each activated carbon. Both parent activated carbons exhibit a high capacity for phenol adsorption. The higher adsorption capacity shown by CI could be attributed to its higher surface area. However, if their capacity is related to their respective surface areas, CII is superior to CI (0.51 mg/m^2 compared to 0.37 mg/m^2), though the influence of pore diffusion is not considered in the comparison. This difference could be related to the higher intrinsic alkalinity of CII, which rather indicates an adsorption mechanism via the formation of electron
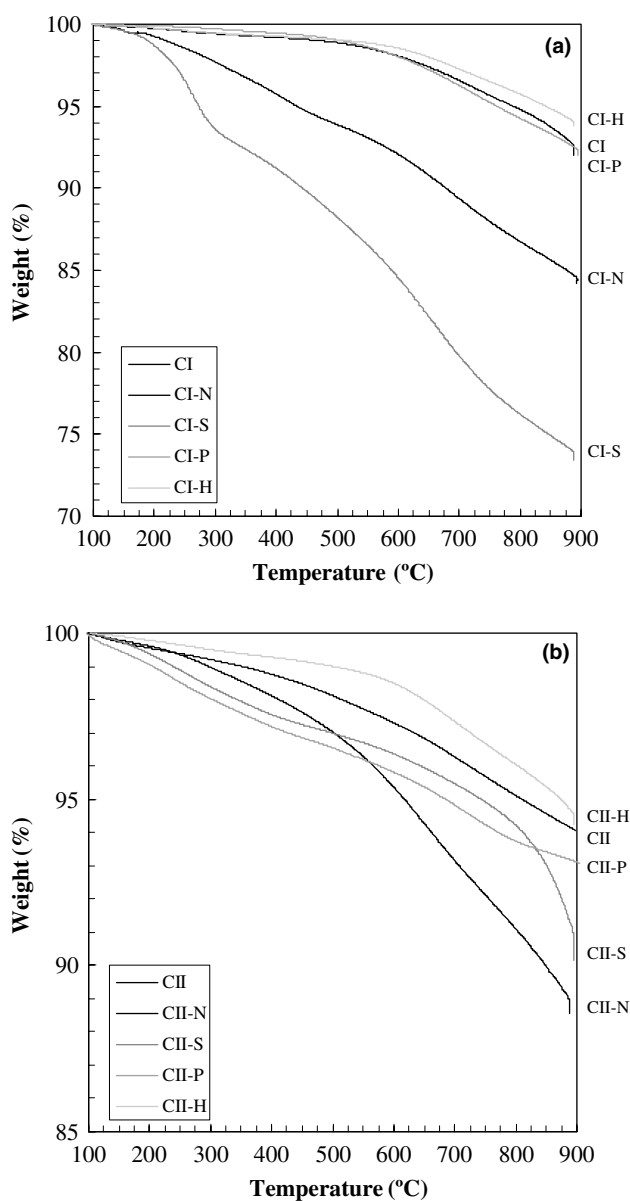
Table 4
Weight loss[a] during the TGA of the parent and treated activated carbons CI and CII

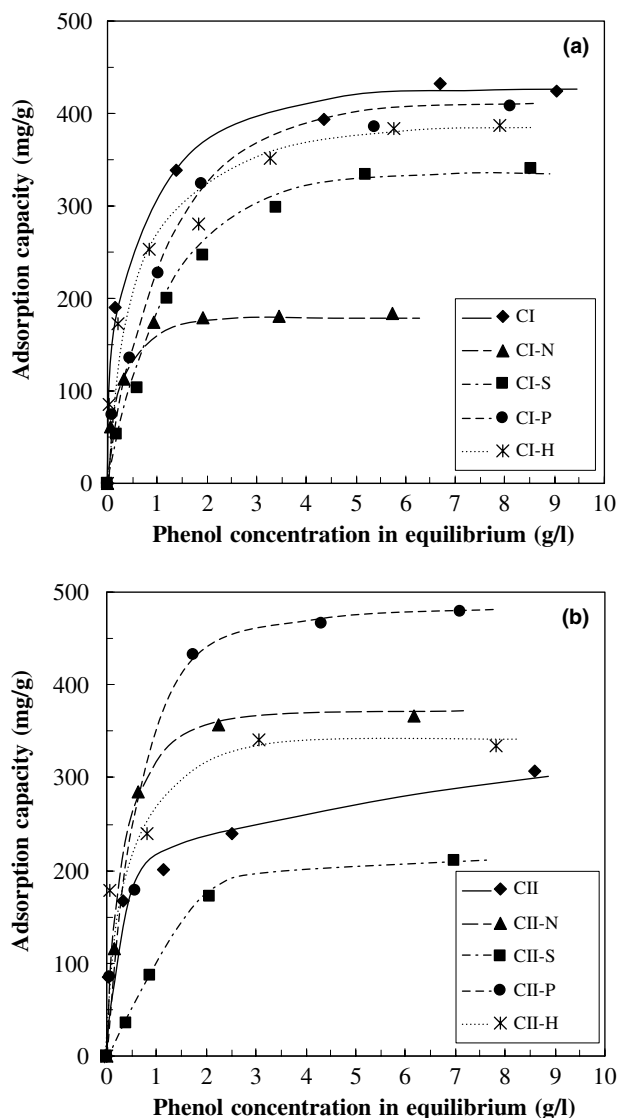| CI	CI–N	CI–S	CI–P	CI–H	CII	CII–N	CII–S	CII–P	CII–H
7.5	16.0	26.5	8.0	6.0	6.0	11.0	9.0	7.0	5.5

[a] In % w/w.

Fig. 2. Phenol adsorption isotherms of the parent and modified activated carbons: (a) CI and (b) CII. Lines show trends.

donor–acceptor complexes between phenol and basic oxygen groups or graphitic structures.

For CI, the liquid oxidation treatments (except with HNO₃) do not greatly affect the phenol adsorption capacity, which decreased by 10% at most. On the other hand, after HNO₃ treatment phenol adsorption capacity falls dramatically from 425 mg/g AC to 190 mg/g AC i.e. by 55%. Probably, besides changes in surface area and surface groups, the nitration detected could alter the adsorption mechanism in an unknown way or simply

hinders the entrance to otherwise available pores. Surprisingly, the behaviour of CII is different since phenol adsorption capacity increased after HNO₃ treatment.

Unexpectedly, the adsorption capacity for CII increases after all treatments except CII–S. Usually, a lower adsorption capacity should be expected due to the direct destruction of adsorption sites, the negative effect of the groups inserted and the micropore unavailability resulting from the presence of new surface groups at the entrance of the pores. This trend is well stated for dilute phenol solutions. However, at high phenol concentrations, several authors have observed the opposite behaviour. Terzyk et al. [43] (and references therein), for instance, observed an increase in phenol adsorption at high phenol concentrations after treatment with HNO₃. This effect was ascribed to the predominance of adsorbate-adsorbate interactions in the high phenol concentration zone, which could even be enhanced by the presence of oxygen groups. As Fig. 2a and b show, adsorption tests were carried out at equilibrated phenol concentrations up to 100 mmol/l, which is well beyond those of other studies. Here, no emphasis was put in the low phenol concentration zone, since, given the conditions of the CWAO tests, this zone is meaningless. Phenol–phenol interactions should therefore prevail in the reported range, since the tests were conducted close to saturation, given the lower surface area of CII.

3.2. Catalytic activity tests

The activated carbons were checked as catalytic matter for the CWAO of phenol for 50 h operation periods. The performance of the activated carbons will be discussed in terms of phenol conversion, X_{Ph}, as a measure of the phenol destruction ability as defined by Eq. (1),

$$X_{Ph} = 100 \frac{C_{Ph}^0 - C_{Ph}}{C_{Ph}^0} \qquad (1)$$

where C_{Ph} is the actual measured phenol concentration in the sample and C_{Ph}^0 is the initial phenol concentration. To discuss the depth of oxidation, COD measurements will also be used in terms of COD reduction described as in Eq. (1).

The evolution of phenol conversion is shown in Fig. 3a and b for activated carbons CI and CII, respectively. As previously found [16], three different zones can be identified in all cases. In the first zone, from starting

Table 5
Maximum phenol adsorption capacity[a] of the parent and treated activated carbons CI and CII

CI	CI–N	CI–S	CI–P	CI–H	CII	CII–N	CII–S	CII–P	CII–H
425	190	350	410	380	310	370	220	475	340

[a] In mg phenol/g AC.

up to 4–8 h, adsorption predominates. This results in an apparent total phenol conversion. Note that for the given liquid flowrate and feed phenol concentration (5 g/L), the length of the adsorption zone at 140 °C is roughly in agreement with the adsorption capacities for CI and CII at 25 °C and 5 g phenol/L of bulk concentration. This is rather unexpected as the adsorption of phenol on activated carbon is known to be exothermic and the capacity should decrease as the temperature increases [25]. For CI, the room adsorption capacity in nitrogen atmosphere was found to drop about 40% at 140 °C [44]. However, further adsorption tests with CI carried out at oxic conditions and temperatures of 25, 120 and 160 °C reveal an initial, albeit small, decrease in adsorption capacity at 120 °C. Later, at 160 °C, the adsorption capacity is even restored to that at 25 °C.

Fig. 3. Evolution of phenol conversion during CWAO using the parent and modified activated carbons: (a) CI and (b) CII. Lines show trends.

Oxidation coupling of phenol can provide a satisfactory explanation of the enhanced adsorption exhibited by CI and CII in CWAO at 140 °C. It is known [20,22] that AC catalyses, albeit slowly at room temperature, the formation of phenol dimers that are subsequently irreversibly adsorbed on the AC surface, thus increasing the AC adsorption capacity. Higher temperature and partial oxygen pressure should significantly enhance the rate of oxidative coupling [22], which could result in an enlargement of the initial adsorption zone during CWAO experiments. Also, HPLC and COD analysis detected no oxidation intermediates during the adsorption period of apparent 100% conversion, which supports the oxidative coupling hypothesis. Interestingly, all the treated carbons show a shorter adsorption period, being only about 2 h for those contacted with strong oxidants.

The change in adsorption capacity due to the treatments cannot explain this behaviour because treated activated carbons mostly maintain their adsorption capacity. Grant et al. [22] also reported that carboxylic acid and ester groups do not promote irreversible adsorption, while there is some evidence that phenolic groups do. Hence, the smaller adsorption zone for CI–S, CI–N, CII–S and CII–N must therefore be related to the higher number of introduced carboxylic acid and lactone surface groups, which lowered the extent of irreversible adsorption.

Once the adsorption step has reached a pseudoequilibrium state, phenol conversion drops rapidly to achieve an almost constant phenol conversion, which is then maintained for hours. This drop in phenol conversion also marks the starting point for the occurrence of partial oxidation compounds, as detected by HPLC. As Fig. 3a and b shows, steady phenol conversion depends strongly on the activated carbon type rather than on the pretreatment applied. Comparing the performances of the parent activated carbons CI and CII, CI provides a high catalytic activity that leads to a steady phenol conversion of 50%. On the other hand, CII demonstrates to possess a low catalytic activity with a steady phenol conversion of roughly 8%. This proves that the surface oxidation treatments do not drastically change the original activated carbon trends when used in CWAO. Other specific origin properties, therefore, must play a critical role in their catalytic performance.

Assuming a first order of reaction with respect to phenol concentration and a plug-flow model for the
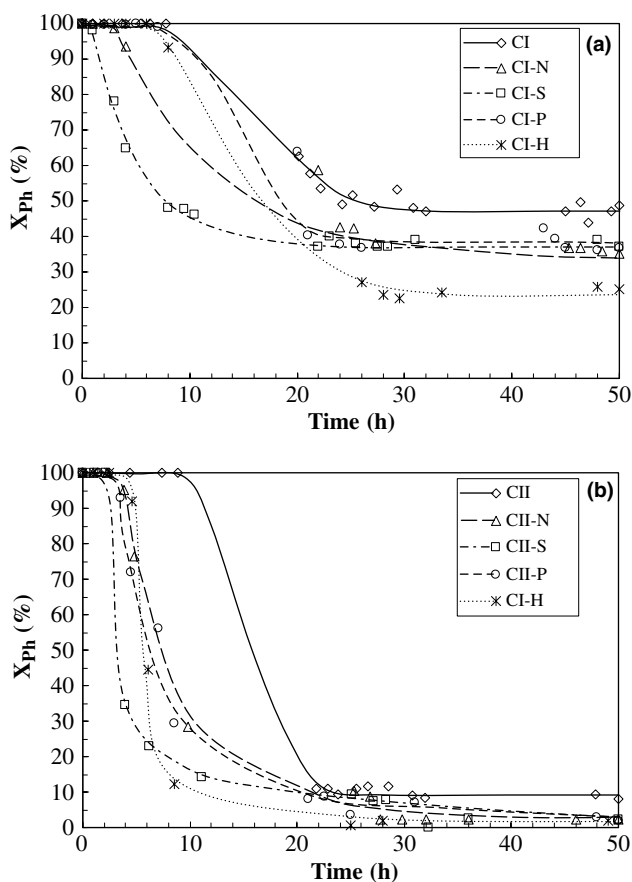
trickle bed reactor [13], the apparent kinetic constant, k_{ap}, for the phenol disappearance can be estimated from

$$k_{ap} = -\frac{Q_L}{W_{cat}} \ln\left(1 - \frac{X_{Ph}}{100}\right) \qquad (2)$$

where Q_L is the volumetric flowrate (L/h) and W_{cat} is the activated carbon mass (g) loaded in the reactor bed. The calculated kinetic constants are 5.6×10^{-3} L $g_{cat}^{-1} h^{-1}$ for CI and 6.8×10^{-4} L $g_{cat}^{-1} h^{-1}$ for CII, which means that the apparent kinetic constant is one order of magnitude higher for CI than for CII.

COD reduction profiles for the activated carbons were also obtained for CI and CII. These are not shown because COD reduction follows the same trends as phenol conversion. For CI, COD reduction at steady conditions is around 20% for all cases whereas for CII it is only about 1%. As expected, this reduction is obviously below that of phenol conversion. This indicates an incomplete mineralisation of the phenol because of the occurrence of intermediate compounds such as carboxylic acids, which are mostly resistant to further oxidation at these conditions.

The different performances of the two activated carbons are difficult to explain merely in terms of their respective surface area or content of functional groups and distribution, since no clear correlation is observed. Future research should therefore take into account other related differences that may interfere in the catalytic activity, such as the substantially lower ash content (4 times lower) and sulphur content (10 times lower) for CII and perhaps a different distribution of the basic sites on the carbon surface. Also, the various treatments conducted do not enable the nature of the carbon catalytic activity to be satisfactorily explained. It appears that the liquid phase treatments rather create unselective distinct surface groups, which makes it very difficult to correlate the measured catalytic activity with the multiple surface changes caused by the treatment. However, within a series of treated carbons, the activity seems to be related to the initial basicity or non-acidity of the carbon surface.

The modified activated carbons work less well in all cases for both CI and CII. In the case of CI, the steady phenol conversion for the modified carbons falls from 50% to 35–37% after treatment with oxidants. The overall kinetic constant for the modified activated carbons was approximately 3.5×10^{-3} L $g_{cat}^{-1} h^{-1}$, which means an almost 40% reduction in comparison with the original CI. For CII, the phenol conversion drops to an insignificant 2–3%, which in practice means null activity.

This decline could be connected to the destruction of basic groups or the generation of new lactone and carboxylic groups that could not be catalytically active.

Tables 2 and 3 clearly evicence that the lower activity is in agreement with a parallel increase in total oxygen content or surface acidity and a decrease in pH or total basicity. Behaviour was similar for the oxydehidrogenation (ODH) of ethylbenzene [45], where the catalytic activity was assigned only to surface phenolic groups and both lactones and carboxyls were ineffective for such a reaction. The drop in phenol conversion is even more severe for the activated carbons treated with HCl, for which the steady phenol conversions were 25% and 2%, respectively. It has been reported that the retention of chlorine chemisorbed on the activated carbon surface can decrease the pore size and can therefore influence the performance [27]. Also, while the elimination of the mineral matter may have an influence, the most striking result is that the HCl treatment produces the smallest surface area basicity, i.e. only 50% of that for the untreated parent carbons CI and CII.

Other effects can negatively influence the performance of both the parent and modified activated carbons. What is often overlooked is that on their own the 50 h phenol CWAO experiments must be considered a soft liquid phase oxidation treatment of the carbons. This can lead to gradual changes in carbon surface area, progressive carbon consumption [13] as well as formation of a carbonaceous deposits on the carbon surface [46]. In the present study, the BET analyses of the used carbons also reveal that there is a strong reduction in surface area (see Table 6). For the activated carbons treated with oxidants, the surface area reduction after a 50 h period of operation ranges from 66% to 76% for CI. Surface area reduction was more marked (95%) for the CI–H and even more impressive for CII, for which the surface area fall from 600 m^2/g to less than 10 m^2/g. However, for the CI carbon, Fortuny et al. [13] found in a 10-day run of phenol CWAO that the surface area gradually fell by up to three times, whereas the phenol conversion remained constant. Thus, the BET surface area does not appear to be the only critical parameter, since total surface area (micro and meso) is certainly not an adequate measure of the active area available for the oxidation process.

The reduction in surface area could hypothetically be attributed to the carbon consumption detected when an activated carbon is subjected to CWAO conditions [13]. However, at the current temperature of 140 °C, 2 bar of

Table 6
Surface area[a] of parent and treated activated carbons CI and CII after use in CWAO

CI	CI–N	CI–S	CI–P	CI–H	CII	CII–N	CII–S	CII–P	CII–H
415	369	263	263	58	170	3	88	9	12

[a] In m^2/g.

oxygen partial pressure and the short time period considered, the destruction of surface area associated with carbon consumption should be limited. To support this hypothesis, the weight of the activated carbon bed was measured after each experiment and, compared to the initial weight, the change was always negligible. Overall, the change in mass is positive in most cases, i.e. after the reaction the mass is higher, fluctuating from −2% to 2%. This suggests that other mechanisms contributing to reductions in surface area e.g. pore blockage due to polymer formation must be taken into account. Indeed, the formation of a coke layer as part of the reaction mechanism has been proposed for the ODH of ethylbenzene [47]. To check this possibility, TGAs were conducted over the used ACs. The results are collected in Table 7.

Note that, except for CI–S, the weight loss during TGA is notably higher for the used activated carbons than for the fresh activated carbons. Although the species released were not identified in this study, it is believed that the difference lies in the presence of carbonaceous compounds chemically attached to the activated carbon surface. Fig. 4a and b display the change in weight during the TGA of the CI and CII (both original and modified) after use in CWAO. It is noteworthy that the difference in surface groups seems to vanish after the CWAO runs since the TGA curves are very similar for all carbons except for CII–S. This gradual homogenisation of the carbon surface has been also reported for the ODH of ethylbenzene [47]. On the other hand, weight loss is found to be much smaller in case of parent CI and CII. This suggests that these carbons are better able to conserve their original surface group distribution and probably, therefore, also their original catalytic activity. A more detailed inspection of Fig. 4a and b evidences that the greatest release of gaseous species takes place above 400 °C. As this is the temperature at which the cracking of hydrocarbon species occurs, this fact provide further evidence of the existence of the carbonaceous layer. Numerous studies have reported the formation of stable phenolic polymers through oxidative coupling [22–24,48,49]. There is also evidence that oxygen basic sites, such as chromene-type and pyrene-type, promote the oxidative coupling of phenolic compounds [14] but carboxylic acid-type groups do not [20]. To date, there is still no direct proof, however, that stable phenolic polymers form at temperatures in the range of CWAO conditions.
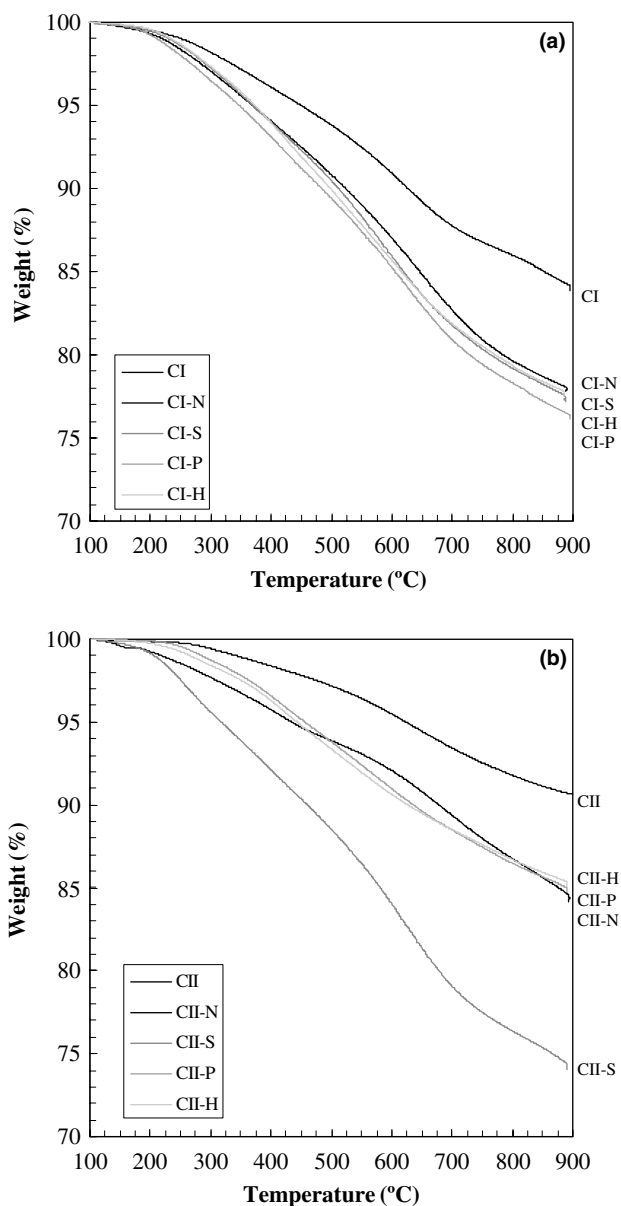

Fig. 4. TGA profiles of the parent and modified activated carbons after use for 50 h in CWAO: (a) CI and (b) CII.

However, the enhanced adsorption at 140 °C in the CWAO tests indicates that polymeric chains should already have formed during the adsorption-dominating period and later simultaneously with the oxidation of the phenol and its intermediates. In fact, the formation of polymeric substances has been indeed verified during the liquid-phase phenol oxidation over activated carbon

Table 7
Weight loss[a] during the TGA of the parent and treated activated carbons CI and CII after use in CWAO

CI	CI–N	CI–S	CI–P	CI–H	CII	CII–N	CII–S	CII–P	CII–H
16.0	22.0	23.0	24.0	22.5	9.0	16.0	26.0	15.0	15.0

[a] In % w/w.

[46] and metal-supported catalysts [50] in slurry systems. One can also speculate with a possible phenol degradation reaction pathway that combines the generation of phenolic polymers linked to the activated carbon surface with the simultaneous polymer destruction by oxidation reactions, as reported for the ODH of ethylbenzene over activated carbon.

These carbonaceous deposits formed from the phenol substrate could eventually block the access to the porous structure of the activated carbons, thus lowering the apparent surface area measured. As illustrated by Tables 4 and 7, the weight loss given by TGA after CWAO is always two to three times higher for the used HCl and H_2O_2 treated carbons, 40% in the case of the used HNO_3 treated carbons and, except for CI–S, still 13% lower for the used $(NH_4)_2S_2O_8$ treated carbons. This indicates that the formation of condensed carbonaceous species is indeed influenced by the treatments. Strong oxidants such as HNO_3 and $(NH_4)_2S_2O_8$ mainly introduce carboxylic and lactone groups that greatly suppress the oxidative coupling of phenol, while softer HCl and H_2O_2 treatments would favour the formation of carbonaceous species on the carbon surface. Also, the change in weight loss is in the same order of magnitude for both activated carbons, so the formation of these polymers does not seem to be the primary reason for the catalytic performance of phenol oxidation.

Nonetheless, it is believed that the activated carbon plays a more dynamic role in the overall phenol oxidation mechanism i.e. it is more than a mere adsorbent. In fact, activated carbon could help to generate oxygen radicals, which subsequently attack the organic substrates (adsorbed or in solution) present in the medium. For instance, the capacity of some activated carbons to form hydrogen peroxide from molecular oxygen has been verified for the oxidation of Fe(II) to Fe(III) [51]. The importance of the basic functional surface groups, such as quinones and chromene-type compounds, was therefore proved.

The build-up, on the surface, of polymers that block access to the pores can also hinder the activated carbon's role as oxygen radical generator, which may happen for CII since, even with good adsorption capacity, its activity for phenol oxidation is marginal in all cases. This build-up could be due to the lower surface area for CII, but also to an insufficient oxidation rate of the polymers due to a low ability to generate oxygen radicals caused by its own chemical surface characteristics. The latter possibility was checked by measuring the equilibrated hydrogen peroxide production from an activated carbon suspension in acid water continuously saturated with oxygen. These tests were conducted for both parent and treated activated carbons. It is noticeable that CI generates hydrogen peroxide one order of magnitude higher than CII. In turn, there are no significant differences between parent and modified activated carbons.

One may therefore conclude that the treatments did not markedly change the factors that are mainly responsible for the CWAO performance observed. This is underlying proof that the poor performance of CII must be attributed to some original physico-chemical property that is responsible for the lower capacity to generate oxygen radicals, though the surface changes during pretreatment and during the CWAO test also play a role. There is still no satisfactory explanation for the opposite catalytic performance shown by both activated carbons since the characterisation does not reveal any clear differences. However, the results suggest that basic groups in the liquid phase oxidation of phenol are important. This is probably related to the ability of AC to generate oxygen radicals. Research is ongoing in order to verify this hypothesis by testing activated carbons with tailored basic sites.

4. Conclusions

Two commercial activated carbons were modified by oxidative liquid treatments with either HNO_3, $(NH_4)_2S_2O_8$ or H_2O_2 and demineralisation with HCl. They were then tested for CWAO of phenol at 140 °C and 2 bar of oxygen partial pressure in a trickle bed system.

Surface area was practically unaffected by the treatments. In all cases, the total number of acidic sites increased. Most of the new functional groups created were lactones or carboxylic groups, although the number of phenolic or carbonyl groups also increased. In general, there was a considerable destruction of basic sites. Phenol adsorption capacity was affected by these modifications. Exactly how this capacity was affected depended on the activated carbon and the treatment used.

The parent activated carbons showed opposite catalytic performances for the CWAO of phenol. While CI yielded significant catalytic activity, affording 50% phenol conversion at the operating conditions tested, CII exhibited poor catalytic activity yielding a meagre 8% under the same conditions i.e. one order of magnitude less than CI. The modified activated carbons performed similarly or slightly poorer in all cases. The small decrease in catalytic activity is believed to correlate with the destruction of basic surface groups.

The changes in textural and surface properties during CWAO may also affect the final performance. In all cases, there was a reduction in surface area after the CWAO experiments. Simultaneous oxidative coupling of phenol was also observed during CWAO. This led to the formation of stable phenolic polymers that could block the access to catalytic sites.

The main reason for the different performances is believed to be the capacity of the activated carbons for

generating oxygenated radicals from molecular oxygen in aqueous phase. This is much higher for CI than for CII. The basic sites are thought to play an essential role in this process, so their catalytic effect is being checked in ongoing research.

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