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Catalytic Wet Air Oxidation of Phenolic Compounds and Mixtures over Activated Carbon: Conversion, Mineralization, and Catalyst Stability

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Catalytic wet air oxidation (CWAO) of phenolic compounds over three activated carbons (ACs) has been investigated in a semibatch autoclave to better understand the influence of AC properties on the efficiency and stability of CWAO. Phenol, 4-nitrophenol, 4-chlorophenol, and 4-hydroxybenzoic acid, as well as synthetic mixtures comprising two to four of the aforementioned molecules, have been chosen as model pollutants to evaluate synergy or competition effects. To this end, the amount of pollutant(s) (re)adsorbed on AC during a preliminary adsorption step, the pollutant conversion, and the mineralization yield obtained during CWAO as well as the AC stability upon recycling are compared for each case.

1. Introduction

Phenol and phenolic compounds are among the most prevalent organic pollutants found in industrial wastewaters because of their extensive use in petrochemical units, oil refineries, and polymer, pesticide, and pharmaceutical industries. In 2005, the global production of phenol was 8.8 million tons,[1] and its demand increased at about 5% per year over the 2001−2008 period.[2] Inhibitory effects of phenol on microbial activity have been reported for concentrations larger than 500 ppm,[3,4] and chlorinated phenols exhibit an even larger biotoxicity at similar concentrations.[5] Thus, medium to highly loaded phenolic effluents require additional solutions that should be combined with conventional biological treatment.

Catalytic wet air oxidation (CWAO) over activated carbon (AC) has been successfully tested for the remediation of phenol and some substituted phenols.[6–12] However, the mechanism responsible for this activity is far from being fully understood. The high adsorption capacity of the carbon, which would concentrate the pollutant in the vicinity of active species, and its ability to generate oxygenated free radicals from adsorbed oxygen have been pointed out as the most likely hypotheses.[7,13] The inorganic part of the carbon could also play a role if the ashes contained an active metal such as iron, which was proven to enhance the catalytic activity of the carbons.[10,12]

As both the specific surface area and the chemical surface composition of carbon are known to determine its behavior as adsorbent,[14] several authors specifically modified these properties of the AC in an attempt to better understand their role in the CWAO. Santiago et al.[7] applied oxidative liquid treatments with HNO_3, $(NH_4)_2S_2O_8$, and H_2O_2 and demineralization with HCl on two carbons from different sources (wood and coconut shell). The resulting modifications mainly affected the acidity of the carbons and thereby their phenol adsorption capacity. However, the treatments induced no major change in the AC performances in the CWAO of phenol in comparison to the existing differences between the original carbons. In fact none of the modified carbons showed a better catalytic activity. Conversely, Quintanilla et al.[8] observed a significant enhancement of phenol conversion when using a carbon previously oxidized with HNO_3. These two studies were performed in a fixed bed reactor, and the measured steady state performance also resulted from the transformations, both chemical and morphological, that the carbons underwent during the catalytic oxidation itself.[6–12] After oxidation runs of more than 50 h, Santiago et al. measured a lower BET surface area for all the modified carbons as compared to that of the parent carbons, while Quintanilla et al. found a protective effect of their acid treatment. This might explain the different activity of the modified carbons observed in these works. Therefore it is important to measure both the initial carbon activity and its evolution along with the AC physicochemical properties to discriminate the different effects.

Moreover, the presence of additional ring substituents was found to modify the phenol reactivity toward CWAO, but the ranking order of the different substituted phenols showed some discrepancies among the different studies.[8,9,15] Despite the fact that real wastewaters generally contain a range of different pollutants, to our knowledge only the study of Creanga et al.[11] reported the CWAO of a model (binary) mixture over AC. There is a clear need to study the behavior of different synthetic mixtures in order to evaluate possible synergy and/or competition effects between the pollutants.

In this work, the oxidation of phenol, 4-nitrophenol, 4-chlorophenol, 4-hydroxybenzoic acid, and corresponding two to four compounds mixtures was investigated in a stirred batch reactor. The aim was to compare the amount of pollutant(s) (re)adsorbed on the AC during the preliminary adsorption step, the pollutant conversion, and the mineralization yield achieved during oxidation and the AC stability upon recycling. ACs obtained from different precursor materials were first tested as catalysts for phenol oxidation. Subsequently, one of these carbons was selected to investigate the destruction of other phenolic compounds.

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Table 1. Precursor Materials and Textural Properties of the Activated Carbons

activated carbon	precursor material	BET surface area ($m^2 \cdot g^{-1}$)	microporous volume ($cm^3 \cdot g^{-1}$)	mesoporous volume ($cm^3 \cdot g^{-1}$)	mean pore diameter (Å)
S23	coconut	1230	0.49	0.04	17
L27	wood	1860	0.77	0.48	25
F22	coal	985	0.41	0.11	20

2. Experimental Section

2.1. Activated Carbons Tested. The three commercial carbons investigated were provided by PICA in the form of 1.5−2 mm pellets. They were crushed and sieved to get the 0.8−1 mm fraction. These carbons were issued from different precursor materials: F22 from coal, S23 from coconut shell, and L27 from wood.

2.2. Physico-Chemical Characterization of Carbons.
2.2.1. Textural Properties. The surface area and pore volume of the carbons were measured from nitrogen adsorption isotherms at 77 K, using an ASAP 2010 analyzer (Micromeritics). The specific surface area was calculated from a BET plot for relative pressures between 0.01 and 0.2.[16] The mesoporous and microporous volumes were estimated according to Barrett−Joyner−Halenda[17] and Horvath−Kawazoe[18] methods, respectively. The mean pore diameter was deduced from the total porous volume at $p/p_0 = 0.98$ and the BET surface area.

2.2.2. Chemical Properties. The acid/base properties of the carbons were evaluated from the pH at the point of zero charge (pH_{PZC}) and the Boehm method.[19]

The pH_{PZC} was measured by the pH drift method.[20] A 0.1 g portion of carbon was added to 20 mL of 0.1 $mol \cdot L^{-1}$ NaCl solution, whose initial pH was adjusted with NaOH or HCl. The suspension was bubbled with nitrogen to eliminate the influence of atmospheric CO_2 and stirred for 3 days to reach equilibrium. After filtration the new pH of the solution was measured. The PZC occurred when there was no change in the pH after contact with the carbon.

For the measurement of surface functions, solutions of $NaHCO_3$, Na_2CO_3, NaOH, and HCl (0.1 N) were prepared using deionized water. A carbon sample of 1 g was suspended in 20 mL of each solution. When a high amount of acidic or basic surface groups was measured, the solution volume was increased to 40 mL for a better precision. The aliquots were degassed under N_2 and allowed to equilibrate for 3 days in a rotatory shaker thermostatted at 25 °C. Then, the carbon was separated from the solution and 10 mL of each filtrate were titrated (DL 50, Mettler Toledo) using HCl or NaOH (0.1 N), as required. As the strongest base, NaOH was assumed to neutralize all acidic surface groups, while Na_2CO_3 neutralized carboxyl and lactone groups and $NaHCO_3$ neutralized carboxylic acids only. The number of basic sites was calculated from the amount of HCl that reacted with the carbon. Titrations were triplicated in each case.

Since surface oxygen groups decompose upon heating at different temperature ranges,[21] thermogravimetry analysis (TGA) of the carbons was also performed on a SDT Q600 thermobalance (TA Instruments) under controlled atmosphere (nitrogen) to avoid AC burning. The samples (10 to 15 mg) were heated at 10 °C·min^{-1} from room temperature to 700 °C. This analysis was performed on both fresh and spent carbons.

Metal contents of the ACs were determined from ICP/AES analysis (Jobin Yvon, Ultima 2R) of acidic leachates, obtained after contacting 4−5 days with raw carbons or combustion residues. Full dissolution of the solid could be only achieved in the latter case. Metals whose oxides could act as oxidation catalysts were sought.

Finally, elemental analysis (CHNSO) was carried out using a Thermo Finnigan Flash EA111 analyzer.

2.3. Batch Reaction Experiment. In a standard experiment, 2 g of carbon (0.8−1 mm sieved fraction maintained in a fixed basket) and 200 mL of aqueous solution containing 1 g·L^{-1} of each phenolic compound (separate or in mixture) were mixed and left overnight to achieve adsorption equilibrium at 150 °C under nitrogen atmosphere. Subsequently a liquid sample was taken to measure the initial concentration(s). Then oxygen was provided, with a partial pressure of 3.5 bar (total pressure of 20 bar). All experiments were performed batchwise for the liquid phase stirred at 800 rpm, whereas air was continuously fed at a flow rate of 60 L·h^{-1}. These conditions guaranteed the absence of external mass transfer limitation.

2.4. Analysis of Liquid Solutions. All liquid samples were analyzed on a high performance liquid phase chromatograph with UV detection (UV 6000 diode array detector, Thermo Finnigan). The separation was achieved using a C18 reverse phase column (ProntoSIL C18 ace EPS) with a mobile phase composed of acidified water (pH = 2.2) and acetonitrile, fed at 1 mL·min^{-1}. The wavelength was set to 254 nm for phenol and 4-hydroxybenzoic acid (4HBA) detection, 275 nm for 4-chlorophenol (4ClP), and 317 nm for 4-nitrophenol (4NP). Quantification was made from a calibration curve periodically updated with fresh standard solutions. For single pollutant, binary, and ternary solutions an isocratic elution mode was used, whereas a gradient was applied for the four-compound mixture.

Withdrawn samples were further analyzed on the remaining chemical oxygen demand (COD) according to the closed-type reflux colorimetric method using potassium dichromate as oxidant (HACH method for 0−150 and 0−1500 mg·L^{-1} ranges). Precision of the method was assessed with standard solutions confirming deviations of less than 5%.

3. Results and Discussion

3.1. AC Screening for CWAO of Phenol. Catalyst activity performed in the first run as well as stability upon recycling, were examined for all the carbons. At each stage a characterization of the carbons was done to better understand the influence of their intrinsic properties on their long-term performances.

3.1.1. Properties of the (Fresh) Carbons. The three investigated carbons, issued from different precursor materials, differed from both their textural and chemical properties, given in Tables 1−3.

The main characteristics of the carbons can be thus summarized as follows: (i) L27 has the highest surface area of the three carbons and is both a micro- and meso-porous carbon. It is an acidic carbon, owing to its high amount of acidic surface groups, leading to a pH value of 6 at the point of zero charge. Its high oxygen content is also consistent with these results, as the oxygen surface groups of the carbons are reported as mainly acidic ones.[20,22] The value that takes the pH_{PZC} further depends on the nature of the acidic groups[23] which are weakly acid (phenolic groups) in this case. (ii) S23 is an essentially microporous and basic carbon with very low amount of inorganic matter (3%). (iii) F22 has a 20% lower surface area than S23, but a 3 times higher mesoporosity. It is also a basic

Table 2. Elementary Analysis of the Activated Carbons[a]

activated carbon	wt %					ppm					wt %
	C	H	N	S	O	Zn	Ni	Mn	Fe	Cu	ashes
S23	92.28	0.59	0.30		2.34	<1 (13)	<1 (3)	10 (5)	50 (116)	15 (74)	3.2
L27	71.10	2.53	0.34		19.30	20 (31)	30 (25)	90 (57)	70 (84)	90 (111)	8.3
F22	84.37	0.53	0.50	0.73	1.10	10 (13)	35 (24)	10 (6)	700 (578)	6 (28)	12

[a] Metal contents were estimated from analysis of acidic leachates on the basis of original AC weight; in brackets are given the values measured without pre-combustion of the carbons. Ash content was given by the provider.

Table 3. Surface Chemical Properties of the Activated Carbons

activated carbon	acidic groups (mmol·g^{-1})				basic groups (mmol·g^{-1})	
	phenolic	lactone	carboxyl	total	total	pH_{PZC}
S23	0.21	0.09	0.00	0.30	0.98	9.7
L27	1.51	0.24	0.10	1.85	0.59	6.2
F22	0.18	0.01	0.05	0.24	0.51	9.0

Table 4. Adsorbed Amounts of Phenol (q_e) Measured at 150 °C, at Equilibrium with Solution Concentration C_e (C_{ini} = 1 g·L^{-1})

activated carbon	C_e (mol·L^{-1})	q_e (mol·kg$_{AC}^{-1}$)
S23	0.0025	0.808
L27	0.0059	0.444
F22	0.0051	0.557

carbon with a lower amount of surface groups but with the highest percentage of ashes (12%).

The elemental analysis also shows that all ACs have low metal contents, except for a larger amount of iron (that could act as oxidation catalyst) in the case of F22. Results obtained from simple lixiviation of the carbons or dissolution of the combustion residues are in a good agreement, indicating that metals should be accessible to liquid reactants. Nitrogen and sulfur which could contribute to the carbon basicity[22] are only present in low amounts in the carbons, as oxygen for the basic ones. In fact, basic properties are usually associated with Lewis sites located at the π electron-rich regions within the basal planes rather than to pyrone-like structures.[20,22]

3.1.2. Initial Performance of the Carbons. The three carbons were compared for CWAO of phenol. As a possible step of the oxidation mechanism, adsorption of the pollutant was first studied. For this purpose, carbons were saturated at reaction temperature (150 °C) and under nitrogen atmosphere, before starting the oxidation. Such a procedure also allowed quantifying separately the contributions of adsorption and oxidation to the concentration variation of the pollutant in the liquid phase as the reactor operated with low solid content. The corresponding equilibrium concentrations and respective amounts of adsorbed pollutant are given in Table 4.

In the investigated concentration range, phenol is best adsorbed on the microporous and basic S23 carbon. Conversely, the adsorption of phenol is clearly hindered by the presence of acidic groups, as the lowest phenol uptake is obtained with acidic L27 despite its higher surface area (cf. Table 1). It should be noted that same experimental trends were found when using a higher initial phenol concentration (C_{ini} = 5 g·L^{-1}).[24]

Figure 1a illustrates the time evolution of normalized phenol concentration during the first oxidation cycle with the investigated carbons. Clearly phenol conversion was enhanced by the presence of the carbons. It increased according to the following order: L27 < F22 < S23, suggesting a possible relation between the initial activity of the carbons and their adsorption capacity.

3.1.3. Recycling of the Carbons. When recycling the ACs, a steep decrease of phenol conversion was observed between the first two runs, before the concentration−time profiles in the liquid phase became stable after three or four cycles, as shown for F22 in Figure 1b.

Such deactivation behavior was already reported in the literature for the CWAO of phenols and attributed to the chemisorption of condensation products, blocking the access to micropores.[6−12] In our study both porosity measurements and thermogravimetry analysis done on spent ACs confirmed the decrease in surface area. Thus, the BET surface area decreased to 175 and 222 m^2·g^{-1} for S23 and F22 respectively, due to a strong reduction of microporosity (by about 80%). A large increase of carbon weight loss between 350 and 700 °C was also observed when comparing fresh (3.9, 14.9, and 1.2% weight loss for S23, L27, and F22, respectively) and spent (9.7, 24.3, and 13.7%, respectively) ACs, corresponding to chemisorbed species which should include the phenol oligomers[8] (cf. section 3.2.2.).

Figure 1a points out that this deactivation was more significant for the basic and microporous carbons, F22 and S23, than for the acidic and more mesoporous one (L27). The oxidative coupling reactions which form the oligomers are known to be enhanced by surface basic groups on the carbon and hindered by acidic surface groups, which might explain this better stability of L27. Its lower adsorption capacity should also reduce such reactions. After stabilization of carbons, the reaction rate was found to be first order with respect to the pollutant concentration from plotting the logarithm of the concentration in the liquid phase as a function of time.

When using a higher initial concentration of phenol (5 g·L^{-1}) in all the experimental series (5 experiments), similar conclusions could be derived:[24] S23 gave a better phenol conversion than other carbons at first oxidation, but also underwent the largest deactivation upon recycling, with a final BET surface area of 15 m^2·g^{-1}. Conversely, L27 best maintained its original textural (final S_{BET} = 389 m^2·g^{-1}) and catalyst properties. After stabilization, activity order was then as follows: L27 > F22 > S23.

Despite its apparent better stability, L27 was found too friable for long-term recycling experiments, resulting in a sample weight decrease up to 25% after successive uses. For this reason, F22 was selected for further investigation of substituted phenols and their mixtures.

3.2. CWAO of Substituted Phenols and Mixtures. 3.2.1. Pollutant Solutions. Subsequently the batch oxidation of three para-substituted phenols, 4-nitrophenol (4NP), 4-chlo-

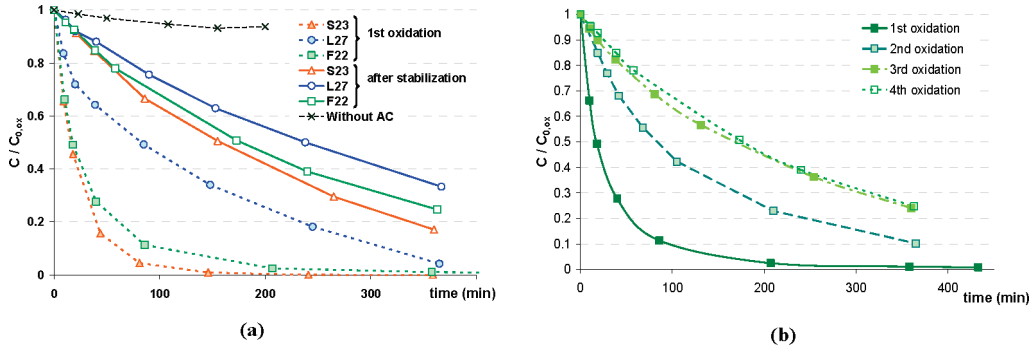


Figure 1. Normalized phenol concentration−time profiles during CWAO of phenol (p_{O2} = 3.5 bar, T = 150 °C, C_{ini} = 1 g·L^{-1}): (a) initial and stabilized performance of the investigated carbons, (b) successive oxidations with recycling F22. ($C_{0,ox} = C_e$ refers to the concentration after adsorption).

Table 5. Properties of Phenol and Substituted Phenols[25]

properties	phenol	4HBA	4NP	4ClP
pK_a at 25 °C	9.9	4.6 and 9.2	7.2	9.4
solubility at 25 °C (g·L^{-1})	93	5	17	27
octanol−water partition coefficient: log K_{ow}	1.5	1.37	1.91	2.39
COP (V)	1.089	1.36	1.433	1.094
Hammett constant	0.00	0.44	0.78	0.22

Table 6. Properties of Fresh and Spent F22 Used for CWAO of Phenols and Mixtures

	textural properties			TGA weight loss (%)		
solution	BET surface area (m^2·g^{-1})	microporous volume (cm^3·g^{-1})	mesoporous volume (cm^3·g^{-1})	25−200 °C	200−700 °C	1 h at 700 °C
fresh AC	985	0.41	0.11	4.4	1.2	9.7
phenol	222	0.09	0.08	3.9	16.8	11.2
4HBA	425	0.12	0.11	4.8	14.2	2.7
4NP	553	0.23	0.03	3.1	14.9	6.8
4ClP	424	0.17	0.07	2.5	5.4	2.8
Mix2_4HBA	341	0.10	0.06	4.5	13.3	2.8
Mix2_4ClP	206	0.06	0.03	2.5	12.3	2.5
Mix3	159	0.05	0.05	3.2	14.9	3.0
Mix4	189	0.05	0.04	1.5	13.6	2.6

rophenol (4ClP), and 4-hydroxybenzoic acid (4HBA) was studied over F22. The properties of these phenols are summarized in Table 5. These substituents are all electron withdrawing, increasing the critical oxidation potential (COP) of the aromatic ring with respect to phenol (particularly for 4HBA and 4NP). This should modify their oxidability and tendency to form oligomers on a carbon surface. Moreover, the molecules differ in their water solubility which might influence their relative adsorption on activated carbon.

Mixtures were also prepared, comprising 1 g·L^{-1} of each phenolic compound involved. As reference compound, phenol was present in each solution. Two binary mixtures (4HBA-phenol and 4ClP-phenol, further labeled Mix2_4HBA and Mix2_4ClP, respectively), a ternary mixture (phenol-4ClP-4NP, Mix3) and a solution comprising the four pollutants (Mix4) were subjected to CWAO.

The pH of the solutions was initially acid (4−6) and not adjusted during the CWAO (forming acidic intermediates). Therefore electrostatic interactions are not believed to play a significant role as, with the exception of 4HBA, all molecules should have been in non-ionic forms.

As previously, successive oxidations were performed with the same carbon sample, and the following features were examined for both fresh and spent ACs: textural properties, thermogravimetry profile, adsorption capacity, and time-evolution of pollutant concentrations during oxidation.

3.2.2. Evolution of Carbon Properties. The textural properties of F22 after CWAO of the different pollutants are listed in Table 6, reflecting a smaller loss of surface area after the oxidation of substituted phenols as compared to phenol. This is due to the higher COP of these molecules resulting in reduced oxidative coupling reactions.[25] These trends are also consistent with the observations of Suarez-Ojeda et al.[8] (for phenol and chlorophenol) and Santos et al.[9] (for phenol and nitrophenol). The difference between the AC aging with 4HBA (COP = 1.36 V) and 4ClP (COP = 1.09 V) is however more obvious in the case of the binary mixture with phenol than for the single pollutant solution. It should be also mentioned that a series of 16 consecutive oxidations was carried out in the case of phenol (for kinetic investigation), and about 4 cycles for the remainder of the pollutants.

When treating mixtures, the surface area of the carbon was generally more reduced than in the case of treating pure pollutants owing to the concentration effect (as shown in section 3.1.3.), with the exception of the 4HBA−phenol mixture. In this latter case, a protective effect of 4HBA was observed (with respect to phenol solution). The microporosity of the carbon was the most affected (up to 90% decrease), except for the CWAO of 4NP.

Below 200 °C, the TGA weight loss was lower for the spent ACs which could be attributed to the loss of specific area reducing thereby the amount of physisorbed species. Then, the thermogravimetry profile showed a continuous and fast decrease for all the spent carbons as compared to what was observed for the fresh one. Conversely, during the temperature holding at 700 °C, the weight loss rate was surprisingly lower in most

Table 7. Adsorption Capacity of Fresh and Recycled F22 (Initial Concentration of 1 g·L^{-1} for Each Pollutant)[a]

solution	fresh AC					recycled AC
	$q_{e,phenol}$	$q_{e,4HBA}$	$q_{e,4NP}$ (mol·kg$_{AC}^{-1}$)	$q_{e,4ClP}$	$q_{e,total}$	$q'_{e,total}$ (mol·kg$_{AC}^{-1}$)
phenol	0.557				0.557	0.181
4HBA		0.614			0.614	0.371
4NP			0.662		0.662	0.157
4ClP				0.712	0.712	0.333
Mix2_4HBA	0.338	0.412			0.750	0.042
Mix2_4ClP	0.410			0.573	0.984	0.254
Mix3	0.277		0.408	0.512	1.198	0.460
Mix4	0.029	0.376	0.460	0.394	1.258	0.231

[a] q_e is the amount of pollutant adsorbed at 150°C on fresh AC. For recycled AC, q'_e was calculated by adding the adsorption at the end of the previous cycle when cooling the solution after oxidation and the subsequent preliminary adsorption at 150°C when contacting the AC with fresh solution. $q_{e,total} = \sum_i q_{e,i}$.

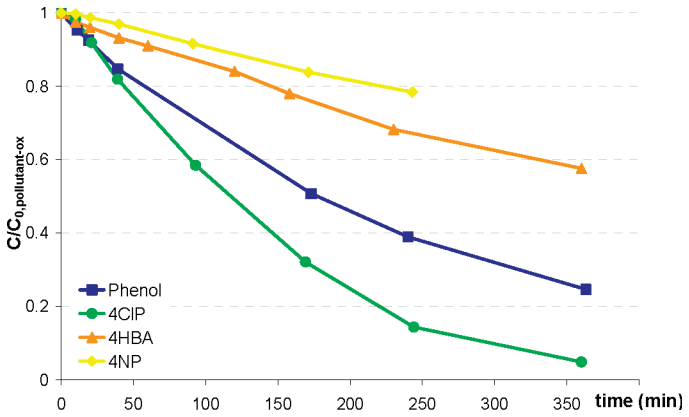


Figure 2. Normalized concentration−time profiles of the phenols during batch CWAO on F22, after stabilization of AC activity (p_{O_2} = 3.5 bar, T = 150 °C, initial concentration of 1 g·L^{-1} for each pollutant) ($C_{0,ox}$ refers to the concentration after adsorption).

cases, which could mean that some of the corresponding oxygen groups (possibly phenolic, carbonyl, and/or quinone) were transformed during CWAO. For 4HBA and 4NP, the TGA weight loss between 200 and 700 °C was rather high with respect to the lower loss of surface area. The corresponding profiles exhibited several marked inflection points which indicate that different species were chemisorbed, including new surface groups having low calcination temperature (like carboxyl ones).

3.2.3. Adsorption Properties. Prior to their oxidation, the adsorption of the molecules on F22 was investigated (at reaction temperature) for both fresh and recycled carbons (Table 7). In the latter case, the amount readsorbed (q'_e) was calculated from the concentration decrease during the preliminary adsorption step when contacting used carbons with fresh solution at 150 °C, as well as that observed at the end of the previous oxidation when cooling the solution under nitrogen atmosphere. For mixtures, the corresponding total amount of pollutants adsorbed was also calculated ($q_{e,total}$ or $q'_{e,total}$).

The adsorption capacity of fresh carbon was similar for all investigated compounds, though slightly higher for substituted phenols due to the electron withdrawing character of the substituents and the enhanced dispersion interaction between the molecule and the carbon.[25] Water solubility of substituted phenols is also lower than that of phenol (cf. Table 5), further improving their affinity toward activated carbon.[26] The total amount of pollutants adsorbed increased with the total pollutant loading as maximum capacity of the carbon was not reached (>1.5 mol·kg$_{AC}^{-1}$ for phenol according to results obtained with 5 g·L^{-1} solution[24]).

After several cycles, the readsorbed amount was much less and varied more with respect to the nature of the pollutant, depending on both its oxidability (determinating AC regeneration efficiency) and the progressive modification of AC properties. For instance, 4NP which was found to be refractory to CWAO (cf. section 3.2.4.1.) was considerably less readsorbed, as a significant amount of pollutant was still present on the AC after oxidation. For phenol, the large loss of BET surface area could explain the weaker readsorption.

In mixtures the trends were even more complex, accounting also for competitive adsorption effects that clearly occurred to the detriment of phenol, as observed by Creanga[27] for a 4HBA−phenol mixture.

3.2.4. Catalytic Oxidation. Being more relevant to continuous CWAO, only the data obtained after stabilization of AC activity are displayed in the following sections.

3.2.4.1. Single Pollutants. Figure 2 shows that the oxidation behavior of the investigated phenols was very different, without any clear relation to their respective adsorption on the carbon. The reactivity order was as follows: 4ClP > phenol > 4HBA > 4NP both after stabilization of AC activity and during first oxidation.[24] This trend is in agreement with results of continuous CWAO regarding the relative oxidability of phenol: phenol > 4NP[8,9] and chlorophenol > phenol.[8] Some correspondence with the COP value of the susbstituents can be found, as the conversion was lower for 4NP and 4HBA (COP ≈ 1.4 V) than for phenol and chlorophenol (COP ≈ 1.1 V). Nevertheless this parameter cannot explain alone the differences between each individual pollutant, as for phenol and 4ClP.

COD conversion measured in the liquid phase (Table 8) confirmed the refractory nature of 4NP and 4HBA. The COD removal was also much higher for both 4ClP and phenol. However, it seems that the 4ClP oxidation intermediates were more refractory than the molecule itself, as suggested by the high proportion of intermediates in the final mixture.

3.2.4.2. Influence of the Solution Composition. The oxidation behavior of single phenol and 4-chlorophenol or mixed with

Table 8. COD Data during Batch CWAO of Single Pollutants, after Stabilization of AC Activity (p_{O_2} = 3.5 bar, T = 150°C, Initial Concentration of 1 g·L^{-1} for Each Pollutant, F22 Carbon)[a]

pollutant	COD of initial solution (mg·L^{-1})	measured COD (mg·L^{-1})		$COD_{f,ox}/COD_{0,ox}$ (%)	contribution of intermediates to remaining COD (%)
		oxidation t = 0	oxidation t = 360 min		
phenol	2380	2224	803	36.1	37.9
4HBA	1622	1035	796	76.9	31.4
4NP	1610	1479	1195	80.8	2.9
4ClP	1618	849	265	31.2	85.1

[a] $COD_{0,ox}$ is the COD value measured at the zero time of oxidation, that is, after preliminary adsorption; $COD_{f,ox}$ is the COD value measured at the end of oxidation.

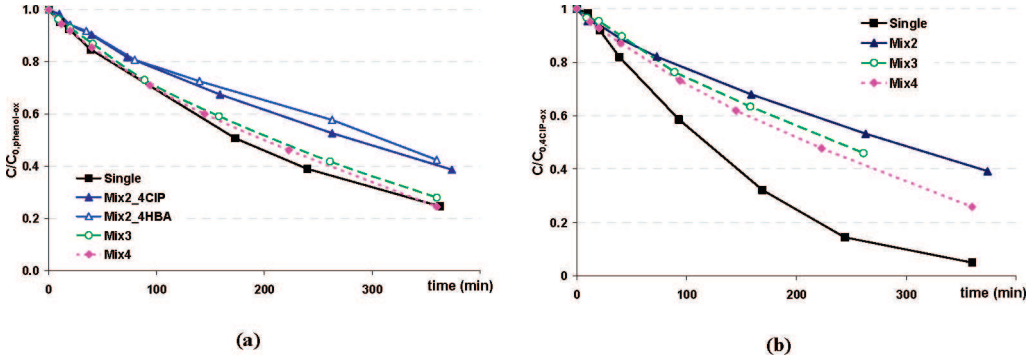


Figure 3. Normalized concentration−time profiles of the considered pollutant (single or in mixtures) during batch CWAO over F22, after stabilization of AC activity (p_{O2} = 3.5 bar, T = 150 °C, initial concentration of 1 g·L^{-1} for each pollutant): (a) phenol, (b) 4-chlorophenol (4ClP) ($C_{0,ox}$ refers to the concentration after adsorption).

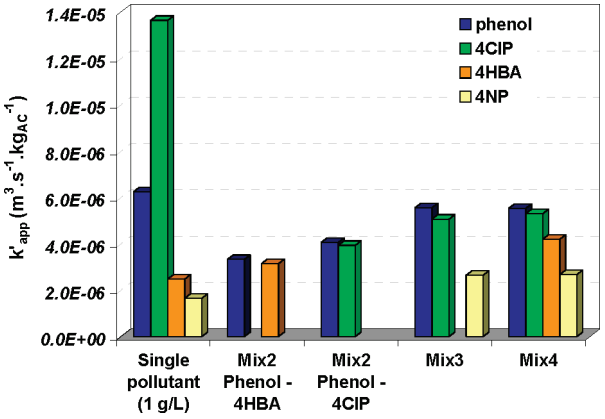


Figure 4. Apparent oxidation rate constants (k'_{app}) calculated after stabilization of AC activity according to $R_{pol,app} = k'_{app}C_{pol}$ for the different compound mixtures studied (p_{O_2} = 3.5 bar, T = 150 °C, initial concentration of 1 g·L^{-1} for each pollutant, F22 carbon).

other phenol(s) is compared in Figures 3a and 3b, respectively. It is seen there that these two molecules were less reactive in mixtures (especially 4ClP). Also phenol conversion in the binary mixture did not seem to depend much on the second compound.

According to the estimations of Weisz modules, oxygen diffusion limitations can play a role in the CWAO of mixtures, being higher for more concentrated solutions (the Weisz modulus of oxygen calculated at the beginning of oxidation varied between 0.2 and 5 for the studied systems). However, surprisingly the conversion of phenol and 4-chlorophenol did not follow a monotonous trend with respect to the number of pollutants in solution.

Figure 4 compares for all investigated single solutions or mixtures the apparent rate constants, which were calculated at stable AC activity from a logarithmic concentration−time plot. The plot shows that there is a ratio of 10 between the single oxidation rate constants of 4ClP and 4NP, but a leveling of individual reactivity takes place in the mixture: the oxidation of 4ClP was clearly penalized, whereas the degradation of the most refractory molecules (4NP and 4HBA) was enhanced. These trends can be thus only explained by a synergetic effect of the other pollutants.

The literature reported some examples of such promoting (or inhibiting) effect for the noncatalytic oxidation of aromatic molecules. Fu et al.[28] reported that the presence of phenol could greatly enhance the removal efficiency of nitrobenzene, by generating free radicals initiating its oxidation. On the other hand, nitrobenzene inhibited phenol oxidation at the lowest investigated temperatures by increasing the induction period corresponding to the formation of these radicals. Apolinario et al.[29] investigated the WAO of nitroaromatics in mono- and multicomponent systems. They observed that trinitrophenol, hardly oxidized individually, was much better degraded when mixed with more reactive dinitrophenol, while the co-oxidation was again detrimental to the latter compound.

On the whole, similar trends can be observed in the present study: the conversion of the most reactive molecules (phenol, 4ClP) usually decreased in mixtures, while more refractory pollutants (4NP, 4HBA) were more easily oxidized. Thus the large differences observed between the individual oxidation rate constants of these phenols almost vanished when they were oxidized in mixtures. A particular effect is observed for 4NP, whose presence promoted the oxidation of both phenol and 4ClP as compared to the corresponding binary mixture. This might be due to some chemical modification on the carbon surface as suggested by the thermogravimetry profiles (cf. 3.2.2.).

The COD conversion (Table 9) varied between 17 and 51% for the different mixtures, being higher for the ones containing 4NP. The COD of the solution after preliminary adsorption was comparable to that of the fresh solution, the difference coming from the balance between adsorption (due to pollutant addition)

Table 9. COD Data during Batch CWAO of Mixtures, after Stabilization of AC Activity (p_{O_2} = 3.5 bar, T = 150°C, Initial Concentration of 1 g·L^{-1} for Each Pollutant, F22 Carbon)[a]

solution	COD of initial solution (mg·L^{-1})	measured COD (mg·L^{-1})		$COD_{f,ox}/COD_{0,ox}$ (%)	calculated COD (mg·L^{-1})		contribution of intermediates to remaining COD (%)
		oxidation t = 0 ($COD_{0,ox}$)	oxidation t = 360 min ($COD_{f,ox}$)		oxidation t = 0	oxidation t = 360 min	
Mix2_4HBA	3937	4445	3187	71.7	4053	1899	40.4
Mix2_4ClP	4079	3955	3299	83.4	3688	1434	56.5
Mix3	5491	5550	2710	48.8	5325	2036	24.9
Mix4	6794	7642	4029	52.7	6630	2117	47.5

[a] Calculated COD was based on the concentrations of introduced pollutants only.

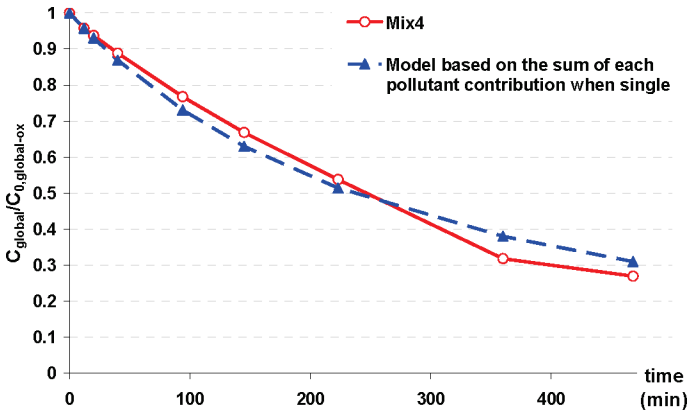


Figure 5. Time-evolution of the normalized global molar concentration of Mix4 during batch CWAO over F22, after stabilization of AC activity (p_{O_2} = 3.5 bar, T = 150 °C, 1 g·L^{-1}, initial concentration of 1 g·L^{-1} for each pollutant). $C_{0,ox}$ refers to the concentration after adsorption. Model: $C_{global} = \sum_{i \in mix4} C_{0,i-ox} \cdot \exp(-(k'_{app,i})_{single}(w_{AC}/V_L)t)$.

and desorption (due to temperature rise from 25 to 150 °C). This result reflects the very low efficiency of readsorption. Moreover this COD value was also close to that calculated from the concentrations of introduced pollutants, which indicates that desorption of intermediates was also low.

3.2.4.3. Case of the Four-Compound Mixture. Finally, Figure 5 compares the measured time-evolution of the normalized global molar concentration of the four-compound mixture with the prediction of a simple model based on the oxidation rate constant of each single pollutant:

$$C_{global} = \sum_{i \in mix4} C_{0,i\text{-ox}} \exp\left(-(k'_{app,i})_{single} \frac{w_{AC}}{V_L} t\right)$$

where $(k'_{app,i})_{single}$ represents the apparent oxidation rate constant measured from the concentration−time profiles of single pollutants (m^3·s^{-1}·kg$_{AC}^{-1}$), w_{AC} is the weight of AC (kg), V_L is the volume of solution (m^3), and t is the reaction time (s).

In terms of global molar concentration it can be said that this four-compound mixture behaves approximately as the sum of each pollutant taken separately, meaning that the overall oxidation kinetics has not been much affected by any mixture effects. However, additional experiments should be conducted with different mixtures and operating conditions to explore the validity range of the lumped global concentration model proposed.

4. Conclusion

A batch procedure was established for the CWAO of phenols including presaturation of the AC at reaction temperature as well as recycling of the carbon during successive experiments. This allowed assessing useful data on initial adsorption and readsorption of the molecules studied and deactivation upon cycling of three activated carbons used as oxidation catalysts.

The deactivation of carbons could be related to the evolution of their properties, which vary according to the nature of both the carbon (acido-basic character, micro/meso-porosity) and the solution to be treated (molecule COP, concentration). In all cases, BET surface area was decreasing, so that oxidation only resulted in a partial regeneration of AC adsorption capacity (less than 50%). Investigated phenols were similarly adsorbed on fresh AC, but their oxidability at stable AC activity was very different with apparent reaction rate constants ranging from 1 (4NP) to 10 (4ClP).

In mixtures, the removal of refractory pollutants (4NP in particular) was improved, while the conversion of the more reactive compounds (phenol, 4ClP) usually decreased, resulting in much closer oxidation rate constants of the molecules. On the other hand, the oxidation of the four-compound mixture was found to behave as the sum of each pollutant oxidized separately. Therefore, further experimental data should be obtained at different operating conditions to ascertain whether the leveling of individual oxidation in mixtures can be generalized. In this case, global magnitudes that are relatively easy to determine such as chemical oxygen demand or total organic carbon would then be suitable tools to evaluate the oxidation behavior of complex mixtures.

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