

The objective of acid treatment was to remove minerals (particularly iron) that, as previously suggested, could have some impact on the catalytic activities of carbon. The iron and oxygen surface functionalities contents of the set HD are listed in Table 4.1.11.

Table 4.1.11. Chemical characteristics of HD samples.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH _{pzc}	Iron content (% wt)
HD	0.000	0.102	0.407	5.22	0.06
HDD	0.000	0.356	0.260	4.01	0.03
HDDH	0.061	0.000	0.051	9.41	n.m. ^a
HDDS	0.000	0.928	0.074	7.55	0.03
HDDSH	0.000	0.081	0.005	10.17	n.m. ^a

^a Iron content of HDDH and HDDSH is about that of the HDD (i.e., 0.03% wt).

Values of pH_{pzc} and surface oxygen content from Boehm titrations from Table 4.1.11 reveal that HD has a slight acidic to neutral surface. Demineralisation, i.e. HDD, had a moderate impact on the surface acidity, in spite of increasing up to 3.5 times the original content of lactonic functionalities. High temperature steam treatment, HDDS, drove the surface to the basic zone. In this case, despite the drastic increase of lactonic groups, the almost complete elimination of carboxylic functionalities renders an slightly basic surface, as its pH_{pzc} indicates. In all cases, hydrogen treatment produced a highly basic surface. However, the highest elimination of acidic functionalities, reflected in the higher pH_{pzc}, was achieved in sample HDDSH. High temperature hydrogen treatment dissociates the majority of the surface oxygen groups and significantly decreases surface polarity. The iron content of these demineralised samples was approximately half of the original value for all them.

The characterisation of the surface was also assessed by TGA. For instance, the weight loss of samples HDDS and HDDSH are drawn in Figure 4.1.16. The absence of the carboxylic groups that decomposes below 400°C can be clearly appreciated in sample HDDSH. The lower content of lactonic functionalities that decomposes below 700°C is also observed in the profile of sample HDDSH. Both samples showed weight losses above 700°C, where carbonyls and quinones decomposed according to the literature. These groups were not directly measured by Boehm titrations, but rather they are considered included in the phenolic type of groups. However, their presence again demonstrates that, as previously observed for ME samples (Figures 4.1.3 and 4.1.4), the treatment up to 900°C did not actually eliminate all the surface oxygen functionalities.

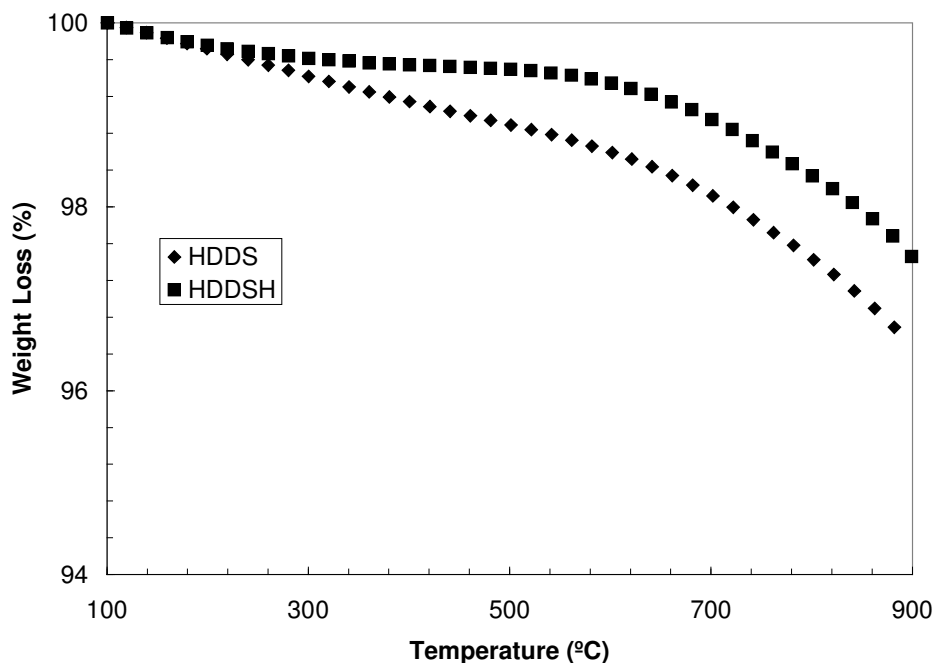


Figure 4.1.16. TGA profiles of the original HDDS and thermally modified sample HDDSH.

4.1.2.2. Adsorption isotherms

Phenol adsorption isotherms for the set HD of activated carbons are shown in Figure 4.1.17. Overall, the highest phenol removal was found for HDDSH, primarily due to its higher micropore volume compared with the other carbons of the group (nearly 45% higher than for the parent HD), and also due to the lower presence of oxygen functionalities. As already commented, oxygen functional groups impart hydrophilicity to the surface that could form water clusters and block the access of phenol molecules to pores. The highest phenol adsorption capacity of samples HD, HDD and HDDH is generally around the same value, 280 mg/g AC. The lowest adsorption capacity is shown by carbon HDDS, which also shows the highest surface oxygen content resulting from the steam treatment. In this case, the improvement of the microporosity, which should favour the phenol adsorption, is largely offset by the higher hydrophilicity of its carbon surface, on the whole decreasing the adsorption capacity down to 96 mg/g AC.

Table 4.1.12 collects the Freundlich parameters after fitting of the adsorption isotherms. As discussed in the subsection 4.1.1.3, the $1/n$ Freundlich parameter reflects the affinity of the surface adsorbent towards the adsorbate. For all samples, except HDDS, the $1/n$ values are relatively low, indicating a favoured interaction between phenol molecules and carbon surface. Sample HDDS, shows the lowest $1/n$, which could suggest a better interaction phenol-AC surface than with the rest of carbons from this set, but the value of R^2 from the adjustment indicates that in this case the Freundlich model did not fitted very well the experimental data, so that this statement must be cautiously taken.

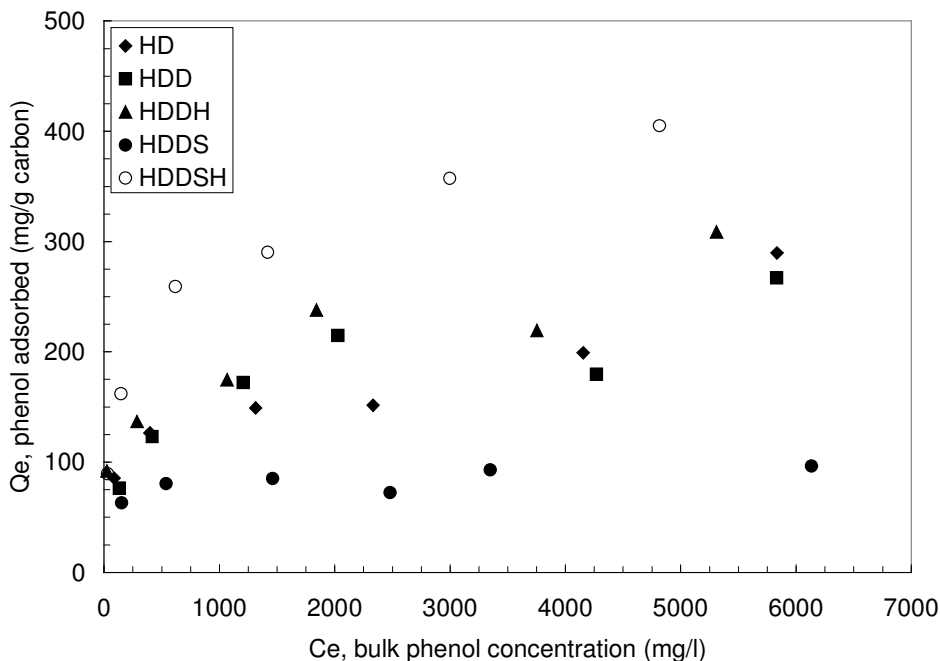


Figure 4.1.17. Adsorption isotherms of phenol by HD activated carbons at 20°C.

Table 4.1.12. Freundlich parameters for phenol adsorption of HD and heat treated samples.

Sample	K (mg/g AC)(l/mg) ^{1/n}	1/n	R ²
HD	36	0.20	0.95
HDD	20	0.29	0.89
HDDH	46	0.22	0.96
HDDS	40	0.10	0.66
HDDSH	36	0.29	0.98

4.1.2.3. Catalytic performance of HD's carbons in the TBR system.

The results of CWAO of phenol in the TBR system are shown in Figure 4.1.18. Similarly than for ME carbons, phenol disappearance during the first 10 hours of operation must be primarily imputed to the adsorption due to the progressive equilibration of the activated carbon bed, while later phenol removal, beyond 20 hours when a steady state is reached, can be mostly attributed to catalytic oxidation. It must be first commented that, in spite of the high mesoporosity of these samples, the phenol conversion achieved are roughly below that given by ME. Therefore, mesoporosity did not appear to be a critical factor for the catalytic performance in CWAO applications, although some impact does have.

Samples HD and HDD approximately show the same phenol conversion at steady state, between 25 and 30%. High temperature thermal treatment of HDD under hydrogen (HDDH) did not improve the performance of the activated carbon, since the phenol conversion achieved was about 22%, even lower than 25% given by the parent HD. Also, Figure 4.1.18 proves that steam treatment over HDD did not considerably improve the phenol conversion despite the considerable increase of the micropore volume already commented. The results indicate that the most significant change in catalytic activity is observed after the hydrogen thermal treatment performed over the HDDS sample, then giving HDDSH. The conversion obtained with HDDSH increased up to 40%, well above of that obtained with HDDS, 23%. This increase in phenol conversion could be explained by the oxidative coupling phenomena explained in the subsection 4.1.1.5 for carbon ME) According to Terzyk (2003), the presence of acidic surface functional groups inhibits phenolic compounds adsorption under oxic conditions by reducing its effectiveness in promoting adsorption via oxidative coupling reactions. It was demonstrated, through the characterisation of carbons ME after use as catalyst, that the carbon surface after a thermal treatment actually is re-oxidised inside the reactor. Considering that carbon HDDSH has a high mesopore volume free of oxygen functionalities, oxidative coupling reactions could be enhanced and the polymeric chains adsorbed and deposited on the HDDSH mesoporosity, resulting on a higher phenol conversion. As this phenol conversion is maintained over the period 20-50 hours, these phenolic chains should undergo further oxidation, then giving the classical partial oxidation products.

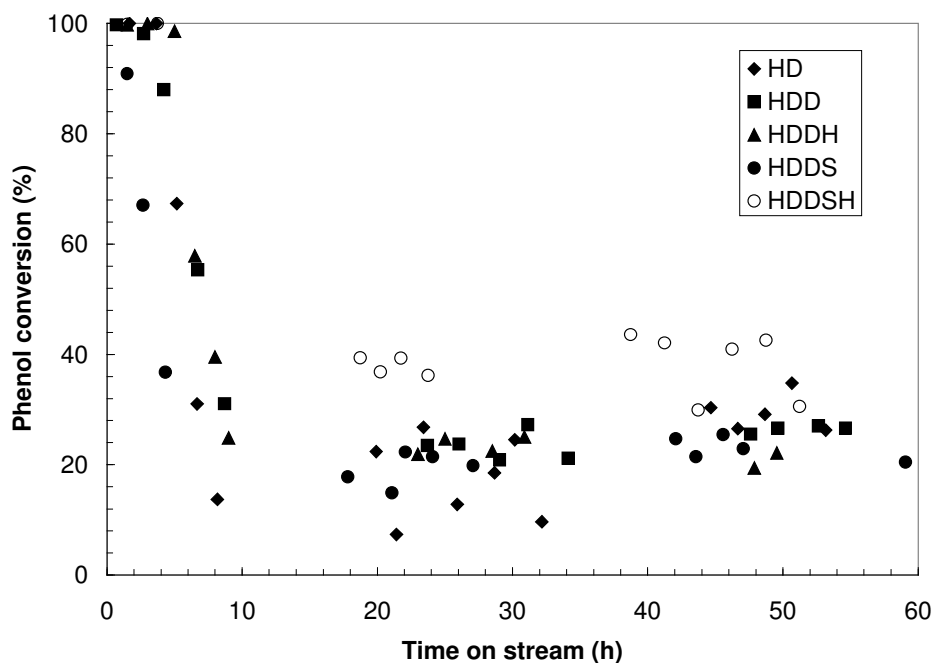


Figure 4.1.18. Phenol conversion in TBR reactor using commercial HD and thermal modified samples, at 140°C and 2 bar of oxygen partial pressure.

When analysing the TOC conversions obtained with HD's carbons, depicted in Figure 4.1.19, and its difference with the corresponding phenol conversions, several asseverations can be made. In general terms, only sample HDDSH shows a different behaviour in comparison with those obtained from the rest of carbons. Whereas the

TOC conversion for HDDSH is about 25%, the other samples achieved an average of 20%. However, as aforementioned, the difference between phenol conversion and TOC conversion is an indicator of the CO_2 selectivity of the oxidation, so this difference is the factor what should be compared. Despite the highest phenol conversion achieved by HDDSH, the lowest difference, i.e. the higher CO_2 selectivity, was found for HDDH, being these differences 20% and 1%, respectively. The higher difference between phenol and TOC conversions obtained for HDDSH agrees with a different oxidation pathway, as the phenolic chains are expected to be subsequently broken down by oxidation in fragments of still considerably TOC, which then can progress towards complete mineralisation.

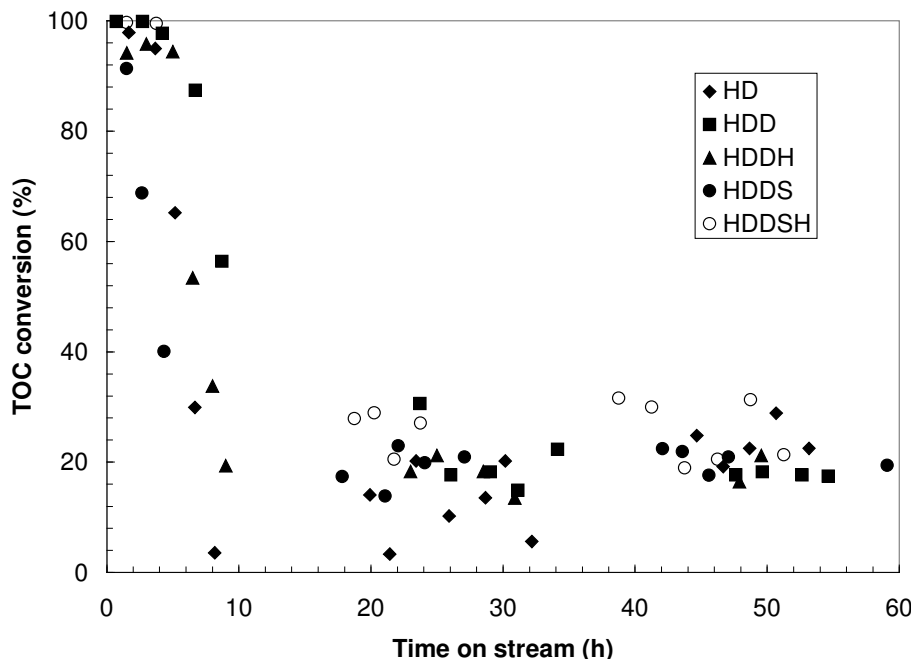


Figure 4.1.19. TOC conversion in TBR reactor using commercial HD and thermal modified samples, at 140°C and 2 bar of oxygen partial pressure.

Finally, the ΔW of all HD's samples and the final pH of the exited effluent are collected in Table 4.1.13. Low values of pH demonstrate the formation of highly acidic intermediates from phenol oxidation, whereas the positive values of ΔW suggest that there is actually deposition of compounds onto the activated carbon, which turn out in an increase of the final weight. The increase of weight is more relevant for the two hydrogenated samples, HDDH and HDDSH. For this latter, this matches well with the proposed oxidation pathway through the formation of phenolic polymers attached to the activated carbon. The correspondence of the weight gain and the occurrence of attached phenolic chains is supported by the TGA data shown in Figure 4.1.20, where most of desorbed species appear around 500°C, which could be assigned to cracking of hydrocarbons.

Table 4.1.13 Weight difference in HD's samples after operation in TBR and final pH of liquid stream.

Sample	ΔW (g)	Final pH on stream
HD	1.34	2.32
HDD	1.26	2.45
HDDH	1.56	2.46
HDSD	1.38	2.40
HDDSH	1.47	2.48

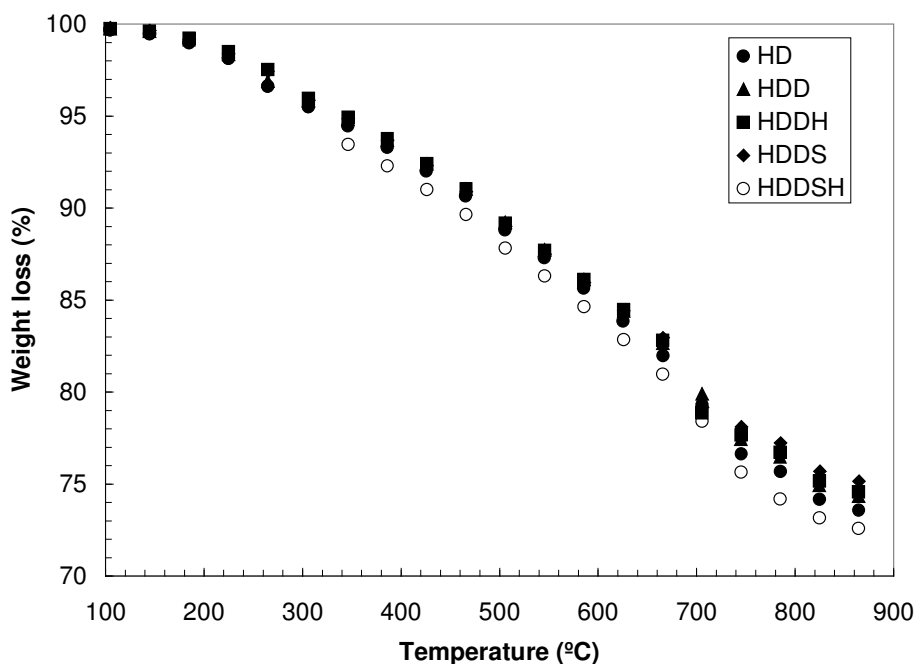


Figure 4.1.20. Weight loss for original and modified HD's after being used as catalyst.

4.1.3. Thermal treatment on carbon WV1 and WV2

4.1.3.1. Physical and chemical characterisation

Samples WV1 and WV2, as mentioned in section 3.1, are activated carbons made from wood. Their textural properties are listed in Table 4.1.14. Since it was not possible to make the characterisation by nitrogen adsorption isotherms, the data of surface area and iodine number provided by the manufacturer are included in Table 4.1.14. According to this information, both carbons have a high surface area, higher than the carbons used in the previous sections dedicated to ME and HD, however most of the porosity falls on the range of microporosity. Despite the iodine number cannot be numerically related to the microporosity, it is known that the adsorption of iodine preferentially occurs in the micropores, following a pore filling mechanism, and by capillary condensation when

adsorption happens in mesopores (Marsh and Rodríguez-Reinoso, 2006). Then, it is possible to assume that a high value of iodine number is indicative of high microporosity. Consequently, WV1 and WV2 can be considered as highly microporous carbons. Despite being made of the same raw material (wood), they present a very different distribution of surface oxygen groups. Since sample WV2 was treated to decrease its phosphorous content, a high concentration of carboxylic groups was detected, whereas practically neither lactones nor phenolics were encountered by Boehm titration. Hydrogen treatment effectively removed surface oxygen functionalities from carbons, as Boehm titrations and also TGAs (Figure 4.1.21) indicate. However, carboxyls were more efficiently removed as they vanish for WV1 and are lowered from 1.317 to 0.184 meq/g, over 85%, for WV2. Instead, lactones in WV1 were more reluctant but they were still halved. It is surprising that the pH_{pzc} of the parent WV2 was basic given the high concentration of carboxyls.

Table 4.1.14 Physical and chemical properties of parent and modified WV1 and WV2.

Sample	S_{ABET} (m^2/g)	Iodine number ($\text{mg}/\text{g AC}$)	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH_{pzc}
WV1	1400-1600 ^a	900 ^a	0.000	0.690	0.165	6.20
WV2	1400-1800 ^a	1200 ^a	0.000	0.000	1.317	8.35
WV1H	na	na	0.000	0.349	0.000	9.09
WV2H	na	na	0.000	0.000	0.184	9.93

^a Information provided by manufacturer.

The increase of the pH in the hydrogenated samples WV1H and WV2H also reflect the successful removal of acidic functionalities from carbon surface since it increased from 6.20 to 9.09 for WV1 and a more moderate 8.35 to 9.93 for WV2. The huge weight loss observed for WV1 is suspected to be related to the presence of residual activation agent, but this speculation cannot be checked as the manufacture process is not known. TGA profile for WV1H supports the reduction of lactonic groups after hydrogen treatment. These groups mainly decomposed between 400 and 700°C, which are actually the temperatures of higher weight loss in sample WV1. The difference between WV2 and WV2H is not easily perceived in the TGA profile, since carboxylic groups are mainly present in those carbons (Table 4.1.14) and these groups decomposed below 400°C.

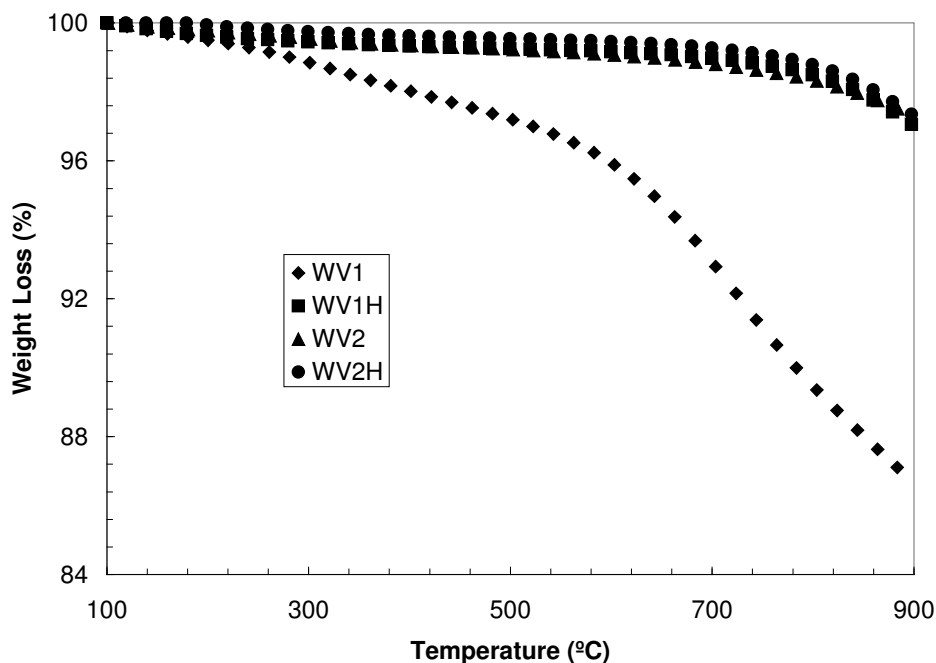


Figure 4.1.21. TG profiles of the original WV1 and WV2 and thermally modified samples.

4.1.3.2. Adsorption isotherms

Figure 4.1.22 depicts the phenol adsorption isotherms obtained for the WV's set of carbons. Adsorption isotherm of ME is included for comparative purposes. The maximum adsorption capacity of original WV1 and WV2 is almost identical, 336 and 340 mg/g AC, respectively. Both parent WV1 and WV2 have phenol adsorption capacity 28% higher than ME. This fact agrees with the higher surface area assumed for WVs.

In both cases, the adsorption capacity significantly increases after hydrogen treatment, 37% for WV1H and a lesser 11% for WV2H. This difference could be attributed to the fact that WV2H still has carboxyls in the surface. These groups are highly hydrophilic, attracting water molecules forming water clusters, thus decreasing the availability of adsorption sites for phenol. On the contrary, WV1 also had carboxylic groups, but they were totally eliminated after hydrogen treatment, so that WV1H possesses a more hydrophobic surface than that of WV2H.

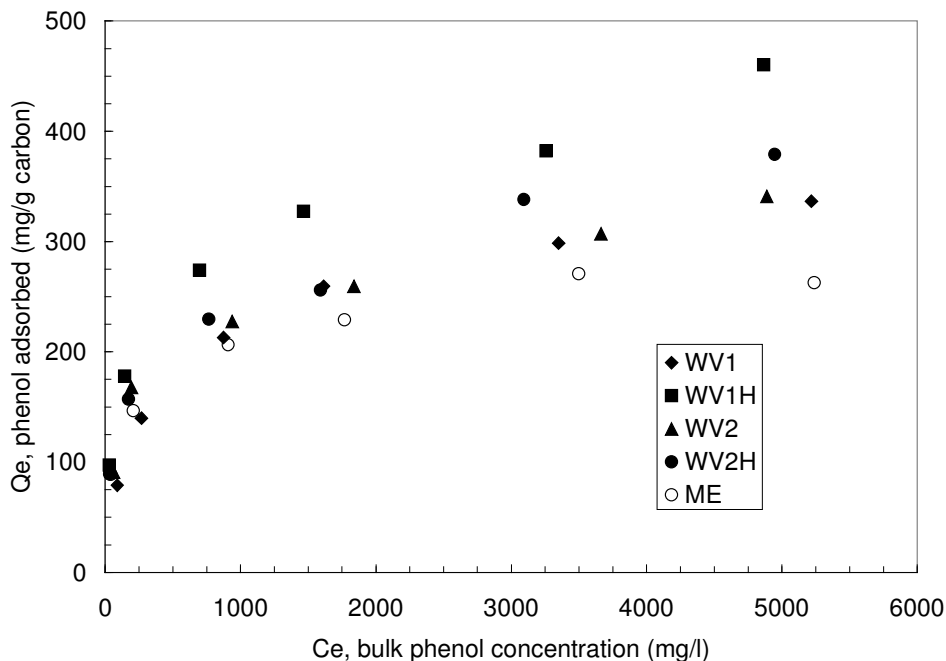


Figure 4.1.22. Adsorption isotherms of phenol by using commercial WV's and thermal modified samples at 20°C

Table 4.1.15 summarises the Freundlich parameters after fitting of the adsorption data. R^2 values are higher than 0.96 in all the cases, which demonstrates a good adjustment to the model. As for ME, the very low $1/n$ values indicate a high affinity between the phenol and the carbons surface.

Table 4.1.15. Freundlich parameters for phenol adsorption of the WV's set of carbons.

Sample	K (mg/g AC)(l/mg) ^{1/n}	1/n	R^2
WV1	19	0.35	0.97
WV2	33	0.28	0.96
WV1H	38	0.29	0.99
WV2H	35	0.28	0.99

4.1.3.3. Catalytic performance of WV's carbons in the TBR system.

Phenol conversion profiles for the WV's set of carbons are plotted in Figure 4.1.23. It is noteworthy that during the first 10 hours of operation, WV's carbons were not able to retain phenol from the liquid stream. As it can be seen in Figure 4.1.23, phenol concentration just after 5 hours of operation already reached 2500 mg/L, i.e. 50% of conversion when using WV1 and WV1H. This trend was not so evident for WV2 and WV2H, but still the equilibration time of the activated carbon bed was lower than expected if the time needed to reach equilibrium is estimated using the maximum adsorption capacity given in Figure 4.1.22 and the TBR operation conditions. This predicted time is 8.5 h, that is indeed higher than the experimentally observed. Given the intrinsic adsorption capacity, maybe kinetic considerations in the adsorption

process, due to their high microporosity, can explain the short time during which no phenol exited the reactor. In any case, the conversion obtained with both WV1 and WV1H at steady state is very low, 9 and 11% respectively. The phenol conversion was slightly better, 16%, for both WV2 and WV2H. It must be noted that, since these carbons are made from wood, no iron content was detected for both WV1 and WV2. This is a distinctive trend in comparison with the previously ME's and HD's and suggested that iron presence was a critical factor in their catalytic performance in CWAO.

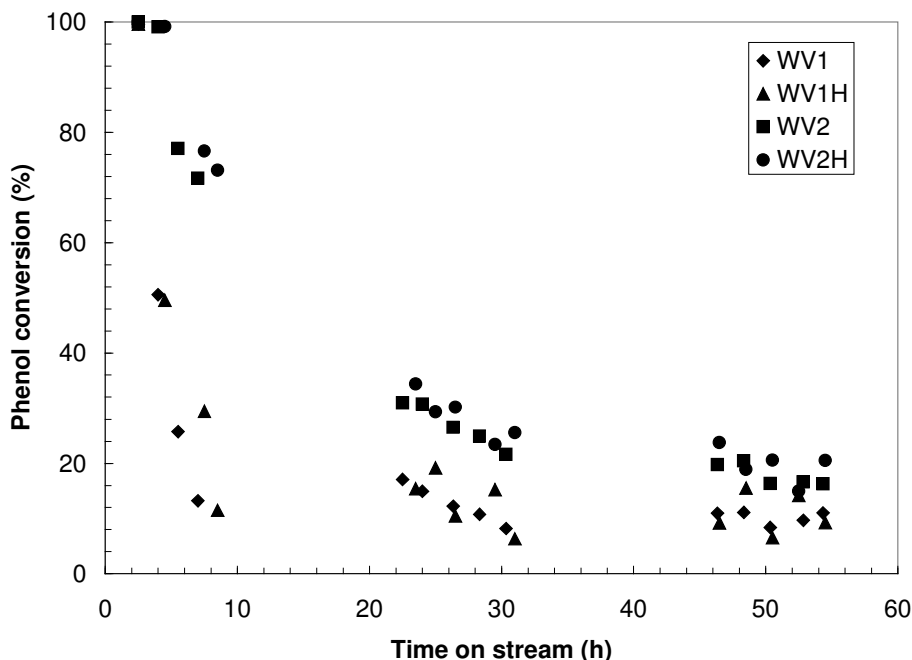


Figure 4.1.23. Phenol conversion in TBR reactor using commercial WV's and thermal modified samples, at 140°C and 2 bar of oxygen partial pressure

The acidic pH of the exited effluent, listed in Table 4.1.16, indicates the presence of acidic partial oxidation products from the phenol, as expected. Also, the positive ΔW in all the cases suggests the deposition of condensation phenolic compounds over the carbon surface. The increase is comparable to those obtained for ME's carbons and almost twofold those measured for HD's.

Table 4.1.16. Weight difference in HD's samples after operation in TBR and final pH of liquid stream.

Sample	ΔW (g)	Final pH on stream
WV1	2.433	2.52
WV2	2.727	2.32
WV1H	2.563	2.43
WV2H	2.836	2.29

TOC conversion evolution in front of the time on stream for WV's carbons is shown in Figure 4.1.24. The difference between phenol and TOC conversion is almost nil in all the cases. This indicates a high mineralisation. However in all cases, the presence of intermediates, although low, was in the four cases favoured towards aromatics, 73% and 76% for WV1 and WV2 respectively and 74% and 75% for WV1H and WV2H. This indicates that the catalytic activity of these carbons do not promote the formation of acids from the oxidation of the aromatic compounds form.

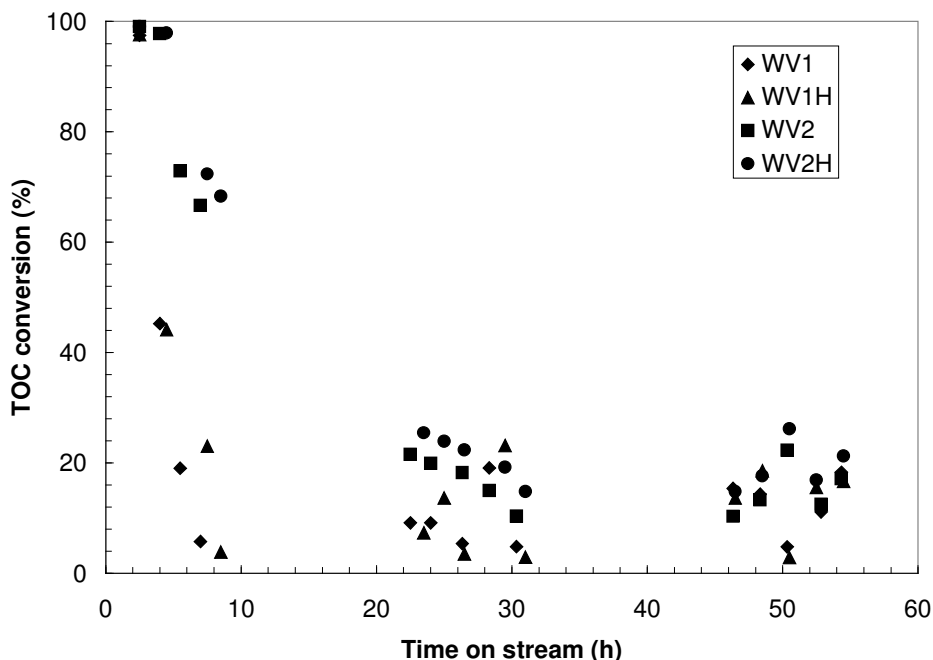


Figure 4.1.24. TOC conversion in TBR reactor using commercial WV's and thermal modified samples, at 140°C and 2 bar of oxygen partial pressure.

4.2. Commercial activated carbons

4.2.1. Physical and chemical characterisation

The textural properties of all commercial activated carbons are collected in Table 4.2.1. Surface areas are quite comparable, being in the range 800-1200 m²/g. An exception must be noted for GT with a remarkable low surface area of 681 m²/g. Although pore volumes are not available for all the samples, available information let to assume that these carbons are mostly microporous.. In the case of ME and F400, microporosity represents more than 75% of the total porosity.

Table 4.2.1. Physical properties of commercial activated carbons.

Sample	S_{ABET} (m^2/g)	$V_{\text{mic D-R}}$ (cm^3/g)	$V_{\text{mes+mac}}$ (cm^3/g)	V_{tot} (cm^3/g)	Iodine number (mg/g AC)
ME	1261	0.473	0.137	0.610	n.m.
CN	800 ^a	n.m.	n.m.	n.m.	800 ^a
F400	1035 ^b	0.404 ^b	0.149 ^b	0.553 ^b	1050 ^a
IR	900 ^a	n.m.	n.m.	n.m.	900 ^a
GT	602 ^c	n.m.	n.m.	n.m.	n.m.

^a Information given by manufacturer.

^b Data from Dastgheib et al., 2004.

^c Data from Santiago et al., 2005.

The chemistry of the surface is illustrated in Table 4.2.2, including iron content. All these commercial carbons are rather few functionalised, then giving a basic pH. Only CN has a noticeable acidic character due to its higher content of carboxylic groups. F400 and IR exhibit a more basic character than ME despite their higher content of carboxyls. This probably could be explained by their lower content of phenolics and lactones, compared to ME. In all the samples from mineral origin, iron have been measured at substantial concentrations, between 0.2 and 0.4% wt. In contrast, no iron was detected for GT, which is made from coconut shells.

Table 4.2.2. Chemical properties of commercial activated carbons.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH_{pzc}	Iron content (% wt)
ME	0.097	0.123	0.031	7.36	0.40
CN	0.030	0.000	1.116	6.67	0.38
F400	0.013	0.058	0.190	8.49	0.21
IR	0.015	0.075	0.206	9.00	0.20
GT	0.000	0.021	0.193	9.19	0.00

4.2.2. Adsorption isotherms.

Figure 4.2.1 shows the phenol adsorption isotherms for these commercial activated carbons. F400 shows the highest maximum capacity, 340 mg/g AC . The lowest was obtained with sample ME, 260 mg/g AC . However, the difference is only around 30%. The other three activated carbons, CN, IR and GT, showed intermediate adsorption capacities. In general, it is possible to attribute their rather high adsorption capacity to the high values of surface area and elevated microporosity. In addition, the low amount of acidic functional groups, and the so related high pH_{pzc} could be favouring the phenol adsorption. Due to the low surface affinity for water, the solvent effect is less pronounced and the interactions responsible for the phenol adsorption over the AC are enhanced. Sample GT, in despite of having the lowest value of surface area, shows a

considerable phenol adsorption capacity, 20% higher than that found for ME (taken at about 5000 mg/L of equilibrium bulk concentration). Even without knowing the actual pore volume and distribution, this suggests that GT is actually highly microporous, as exhibits an adsorption capacity comparable to that of ME, which surface area is over two times greater.

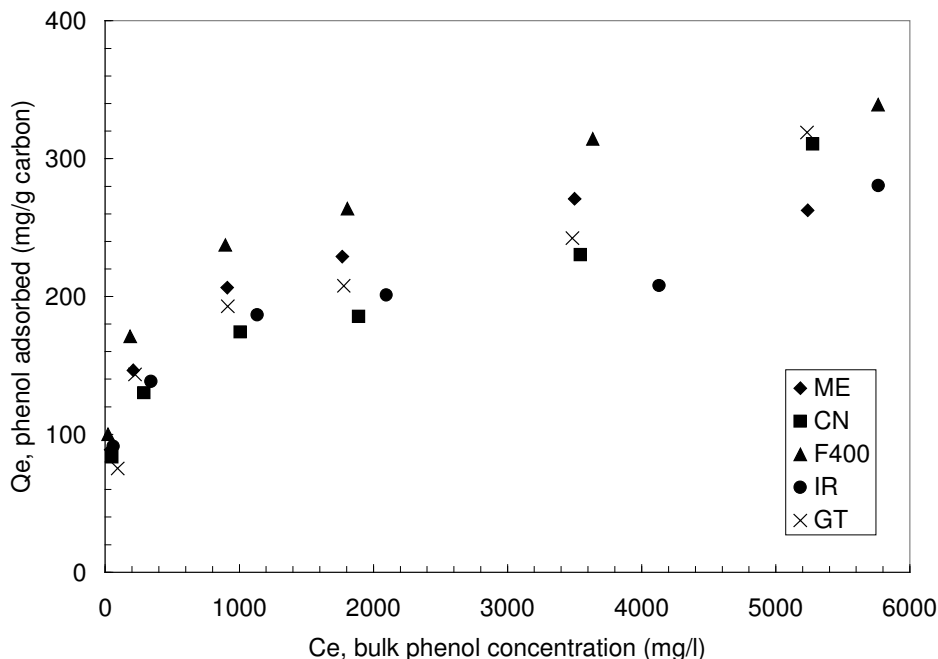


Figure 4.2.1. Adsorption isotherms of phenol by several commercial activated carbons at 20°C.

Table 4.2.3 summarises the Freundlich parameters for all the adsorption isotherms. As in the previous cases, the very low $1/n$ values reveal a very high affinity between the phenol and the activated carbon surface.

Table 4.2.3. Freundlich parameters for phenol adsorption of the commercial set of carbons.

Sample	K (mg/g AC)(l/mg) ^{1/n}	1/n	R ²
ME	40	0.23	0.98
CN	30	0.26	0.96
F400	53	0.22	0.99
IR	37	0.22	0.96
GT	22	0.30	0.92

4.2.3. Catalytic performance of the commercial carbons in the TBR system.

Phenol conversion evolution over time on stream for the TBR tests using these commercial AC is displayed in Figure 4.2.2. An inspection to Figure 4.2.2 shows that ME gave the highest phenol conversion at steady state, around 45%. The corresponding

phenol conversion achieved for IR, F400 and CN are between 20, 36 and 32%, approximately. It must be noted that GT rendered practically negligible catalytic activity for CWAO. These differences hardly can be ascribed to the textural properties or the surface chemistry. As it can be seen in Tables 4.2.1 and 4.2.2, all the samples have very similar textural properties, and there are no considerable differences regarding to the chemical characteristics, i.e. surface oxygen groups.

Neither, the phenol adsorption capacity appears to be correlated with the phenol conversion achievable, since all they provide good adsorption capacities. As stated, Figure 4.2.1 makes evident that the adsorption capacity of all these carbons is really similar, being the highest difference, between F400 and ME, of only 30%, 340 mg/g AC and 262 mg/g AC, respectively. However, ME giving the best phenol conversion is not the activated carbon with the highest phenol adsorption capacity. The lack of correlation is even more manifest when GT is concerned it yields negligible conversion although its adsorption capacity is of the same order.

Adsorption capacity no even completely governs the transition period after start-up, i.e. more or less during the first 10 hours of operation in the TBR. In this period, the apparent 100% phenol conversion is due to the adsorption that takes place on AC simultaneously with the oxidation reactions. Obviously, not all the commercial activated carbons behave the same way. Figure 4.2.2 evidences that only ME is capable of completely removing phenol from the effluent after 6 hours of operation, i.e. the activated carbon bed has not been yet equilibrated. By hour 10, all carbons except ME, were already equilibrated, so that this compound starts to appear in the exited effluent. Assuming that the activated carbon equilibrates with a 5000 mg/L phenol solution (which is not actually true as the simultaneous disappearance of phenol by oxidation results in a decreasing phenol concentration profile inside the reactor) the time needed to saturate the AC can be estimated taking into account the feed flow rate and the mass of the activated carbon bed. If so, ME retained phenol for a longer time than that predicted, which indicates that many phenol is destroyed meanwhile. The opposite behaviour can be observed for GT. According to its adsorption capacity, which is similar to ME, GT should be saturated after 8 hours of operation, but after just 4 hours it becomes incapable of retaining more phenol. Since GT provides nil destruction of phenol, this indicates kinetic limitations for adsorption in a bed, so probably the microporosity is not fully used for adsorption. In conclusion the adsorption capacities could not be related with the catalytic activity.

The main distinction between all the five samples lies at the iron content. It can be seen that, activated carbons giving significant phenol conversion have a remarkable iron content. However, there is not direct correlation between the iron content and the phenol conversion. For instance, ME and CN, practically have the same iron content (0.4%wt), but the final conversions at steady state are different one from each other, 45% and 30% respectively. Concerning to F400, which has the half the iron content than ME, gave a conversion of 38% at steady state. In turn, IR has the same iron content than F400, but a lower conversion was obtained, only 17%. Irrespective of the different phenol conversion achieved, this suggests that only if iron is present in the activated carbon, it is able to effectively perform as catalyst for wet oxidation. It is known that the mineral matter of the carbon is constituted mainly by inorganic salts of a diversity of metals, among them iron. However, the different behaviour also indicates that the location and/or the state of the iron play a key role in its performance.

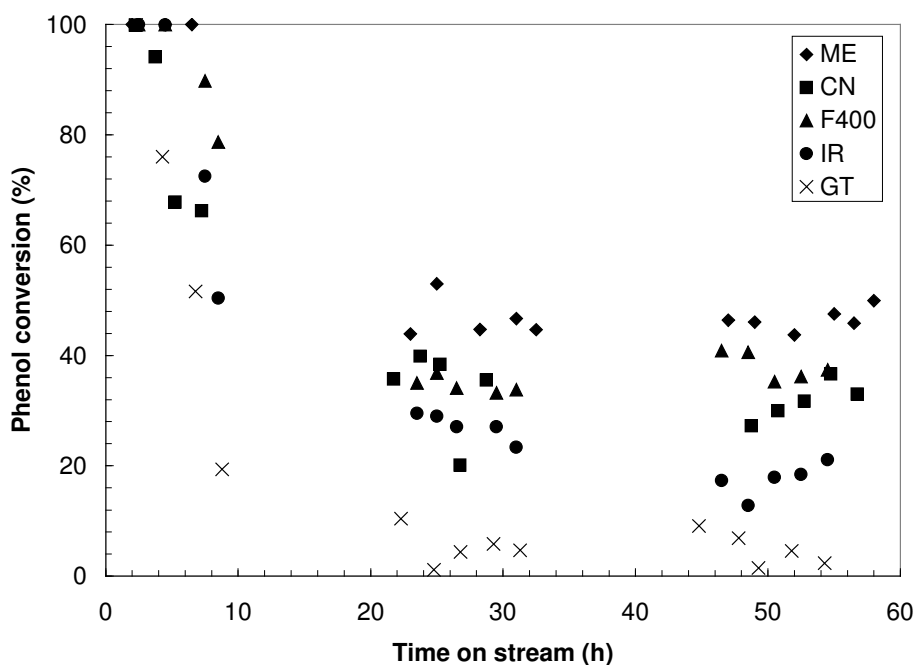


Figure 4.2.2. Phenol conversion in TBR reactor using commercial activated carbons, at 140°C and 2 bar of oxygen partial pressure.

A wide literature dealing with iron fixed on zeolites has proven that the position of the iron in the frame of the zeolites is determinant for the type of product obtained in applications of these materials as catalyst for the oxidation of phenol in aqueous phase. Phu et al. (2001) observed that extra-framework Fe can catalyse the oxidation of phenol more selectively into CO_2 than the extra-framework Fe. Iron molecules in the AC's could be located deeply embedded in the carbonaceous matrix, or more superficially forming salts. Therefore, different iron location in the carbonaceous structure could explain the disparity in catalytic activity of the commercial carbons studied in this section, assuming that iron is responsible for the catalytic behaviour.

In all the cases, the ΔW at the end of the test was positive (Table 4.2.4), being the gain for GT the highest value. As GT is not able to oxidise phenol, oxidative coupling dominates and the extent of the formation of phenolic condensation products, which later remains attached to the activated carbon surface, is larger. This carbon also furnishes the higher pH in the exited liquid effluent, 3.65. This clearly is related to the low catalytic activity shown by GT. Since the acidity of the liquid stream is directly related with the amount of acid intermediates produced from the phenol oxidation, the low phenol conversion yields higher pH.

Table 4.2.4. Weight difference in commercial AC's samples after operation in TBR and final pH of liquid stream.

Sample	ΔW (g)	Final pH on stream
ME	2.519	2.13
CN	2.119	2.78
F400	2.496	2.18
IR	2.387	2.41
GT	2.829	3.65

Differences between phenol and TOC conversions obtained with these commercial carbons are very similar, 13%, 15% and 18% for samples ME, CN and F400, respectively (see Figure 4.2.3). The difference for IR is only 7%, which indicates a better selectivity towards CO₂. As described in section 4.1.2 for HD's carbons, despite the lower phenol conversion given by IR, the CO₂ selectivity is more favourable than those obtained from carbons exhibiting higher catalytic activity. Slightly negative differences calculated for GT could be explained by some possible desorption of phenolic polymeric compounds, which are not taken into account in the phenol quantification by HPLC, but that are indeed later measured in the TOC analysis increasing its value, therefore giving negative differences. Anyway, both phenol and TOC conversions for IR are very low and the difference fall into the range of experimental error.

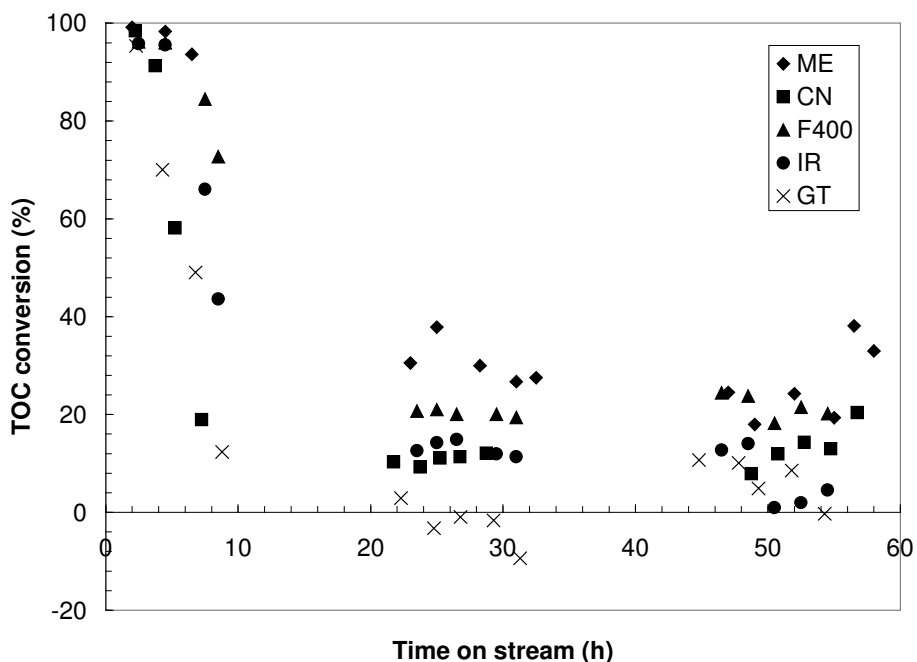


Figure 4.2.3. TOC conversion in TBR reactor using commercial activated carbons, at 140°C and 2 bar of oxygen partial pressure.

Concerning to the distribution of intermediates, it must be noticed that the commercial carbons giving lower phenol conversion also render low yield in acid compounds. Partial oxidation products from phenol oxidation using GT as catalyst were acid compounds in a 25%, and 29% for IR. Samples CN and F400 achieved 69% and 85%, respectively, of acids, whereas the higher formation of acids was obtained for ME, 94%. In summary, these results indicate that the higher the phenol conversion, the larger the formation of acidic compounds, as generally expected from a reaction pathway based in consecutive reactions (Eftaxias et al., 2006).

4.3. Preliminary remarks

Based on the results from the experiments completed using the different activated carbons described in sections 4.1 and 4.2, it is possible to make several preliminary assertions.

As discussed in the introduction chapter, the porosity of the activated carbons is determinant when evaluating its adsorption capacity towards any compound. For phenol, due to its molecular size the adsorption takes place mainly in the micropores. Because of this, highly microporous carbons are expected to exhibit high phenol adsorption capacities. Carbons ME, CN, F400, IR, GT, WV1 and WV2, which have a great percentage of its porosity in the micropore range show good adsorption capacities towards phenol (see Figures 4.1.10, 4.1.22 and 4.2.1). Samples derived from HD, which are more mesoporous, have a lower adsorption capacity when compared to ME (see Figure 4.1.17). Acid surface groups decrease the phenol adsorption capacity due to the formation of water clusters that hamper the access to phenol molecules. Moreover, they impede the formation of electron donor-acceptor complexes, one of the mechanism responsible for phenol adsorption. Thermal treatment under N₂ or H₂ demonstrated to be effective in removing most of the oxygen surface groups without affecting textural properties, thus enhancing the phenol adsorption mechanisms and increasing the adsorption capacity in all cases (see Figures 4.1.10, 4.1.17 and 4.1.22). Nevertheless, there is no correlation between the phenol conversion in CWAO and the adsorption capacity of the activated carbon used as catalyst.

Neither, a relationship between textural properties or surface oxygen functional group content and type with the catalytic activity can hardly be established. For instance, thermal treatment over ME did not improve its catalytic behaviour. But the increase in the microporosity of sample HDD by steam treatment (HHDS) with a latter thermal treatment un hydrogen to eliminate oxygen from surface (HDDSH) increased the conversion obtained from 20% to 40%. On the other hand, high microporosity of WV1 and WV2 did not furnish noticeable catalytic activity, even after thermal treatment under hydrogen in order to eliminate surface acid groups. Also, highly microporous commercial carbons show very different values of phenol conversion (see Figure 4.2.2).

On the contrary, when considering the mineral content, specifically iron content, two facts must be noted. Samples WV1, WV2 and GT containing marginal iron content, because its raw material originally had no iron content, showed very poor catalytic activity, only 11% for WV2 or even lower, 5%, for GT. However, activated carbons made from coals, with iron content ranging from 0.03 to 0.4% wt, offered higher phenol conversions, from 20% for IR and HDDS up to 45% for ME.

Based on these facts, in the next sections, the results from experiments designed to evaluate the impact of the iron content and the mesopore volume on the catalytic activity of activated carbon are presented. Carbon ME was chosen as base carbon for the modifications proposed, due to its high surface area and micropore volume, high iron content and because the high phenol conversion naturally achieved with this carbon. First, the effect of acid wash, i.e. demineralisation, on the properties of ME is studied in section 4.4, whilst the modification of the iron content and the mesopore volume impact on the performance of ME as catalyst are evaluated in section 4.5.

4.4 Demineralisation of ME activated carbon

4.4.1. Physical and chemical characterisation

As previously mentioned, demineralisation by HCl solution was applied to significantly reduce the mineral matter, i.e. metal content, of the ME. For the demineralised ME, MED, only a slight decrease in the meso- and macropore volumes were observed as shown in Table 4.4.1, while surface area and micropore volume remain almost unaltered. On the contrary, after treatment with an oxidant acid as HNO₃, MEN1, the modification of textural properties was severe. The surface area decreases 66%, and the overall porosity about 68%.

Chemical properties of the acid wash ME samples are collected in Table 4.4.2. The iron content of the parent ME carbon was about 0.4% and no considerable amount of other metals was found on it. Demineralisation procedure decreases the iron content about 60%, while small change was observed in the overall surface acidity, as indicated from the pH_{pzc} value, although some carboxylic groups were generated, thus decreasing somewhat the pH_{pzc}. In contrast, treatment done with HNO₃ drastically decreases the pH_{pzc}, mainly due to the formation of apparently more carboxyls. The content of carboxylic groups increased in sample MEN1 by a factor of 45 with respect to the parent ME, whereas the increase in MED was just 3.5 times. However, it must be pointed out that treatment with HNO₃ also can result in the creation of nitrogen containing surface groups at some extent, and strongly adsorbed nitric acid, which imparts additional acid character to the material (Salame and Bandosz, 1999). As predicted, iron content was also affected by the acid wash, which was reduced a 60% by HCl treatment and a 70% by HNO₃ treatment. However, it must be noted that an even noticeable amount of remaining iron amount was present in both MED and MEN1 activated carbons, which is expected to provide significant catalytic activity for CWAO.

Table 4.4.1. Physical properties of parent and modified ME.

Sample	S _{BET} (m ² /g)	V _{mic} D-R (cm ³ /g)	V _{mes+mac} (cm ³ /g)	V _{tot} (cm ³ /g)
ME	1261	0.473	0.137	0.610
MED	1272	0.484	0.108	0.592
MEDH	1275	0.490	0.195	0.685
MEN1	430	0.176	0.020	0.196

Table 4.4.2. Chemical properties of parent and modified ME.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH _{pzc}	Fe content (% wt)
ME	0.097	0.123	0.031	7.36	0.40
MED	0.010	0.117	0.113	6.90	0.16
MEDH	0.061	0.000	0.000	10.33	n.m. ^a
MEN1	0.019	0.068	1.393	3.02	0.12

^a It is expected that iron content of MEDH is about that of MED, i.e., 0.16%.

4.4.2. Adsorption isotherms.

The results displayed in Figure 4.4.1 show that demineralisation increased the phenol uptake 20% for MED, probably due to a reduction in the overall surface polarity and hydrophilicity. As previously mentioned, the mineral content of the MED was below half of that present in ME, although the overall concentration of oxygen containing groups was similar. By demineralisation and the subsequent elimination of metal-oxygen complexes that could be located at the edges of the carbon pores, phenol adsorption is enhanced because of the higher hydrophobicity also avoiding the formation of water clusters as already mentioned several times. However, there is no important modification on the adsorption capacity of MED after hydrogen treatment. Instead, nitric acid wash, MEN1, strongly decreases the adsorption capacity of ME down to 148 mg/g AC, 45% lower than that of the parent ME, 262 mg/g AC. This worsening could be attributed to the evident loss of microporosity and surface area, and to the much higher content of acidic groups on MEN1 surface.

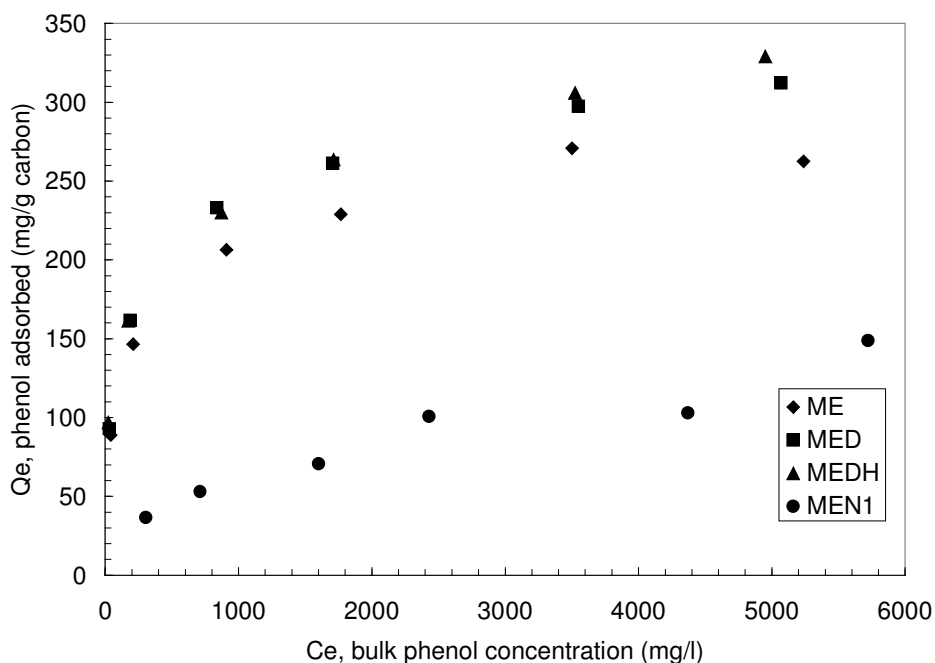


Figure 4.4.1. Phenol adsorption isotherms over activated carbon at 20°C.

The low $1/n$ values of Freundlich parameters shown in Table 4.4.3 indicates that the adsorption is still favoured by good interactions between phenol and the carbon surface. In sample MEN1, this value increases to 0.45, indicating that in this case the adsorption capacity was clearly less favourable after modification by HNO_3 wash.

Table 4.4.3. Freundlich parameters for phenol adsorption of the demineralised ME's set of carbons.

Sample	K (mg/g AC)(l/mg) ^{1/n}	1/n	R ²
ME	40	0.23	0.98
MED	43	0.24	0.98
MEDH	49	0.23	0.99
MEN1	3	0.45	0.96

4.4.3. Catalytic performance of carbons in the TBR system.

Figure 4.4.3 depicts the phenol conversion profiles for the different demineralised samples. It can be seen that demineralisation causes a considerable reduction in the phenol conversion. This value decreases from 45% for the parent ME down to 25% for the demineralised carbons, regardless the treatment applied. Micropore volumes of all carbons are similar (in the case of MED is even higher), therefore it cannot be the reason for the different phenol conversion. On the other hand, the slightly lower overall porosity of MED (only 3% lower) contrasts with the much lower porosity of MEN1, but both gave a lower phenol conversion. Neither, stabilisation by hydrogen treatment and an almost complete elimination of oxygen containing groups, MEDH, prevents this demineralised sample from rendering worse phenol conversion. The lower adsorption capacity of sample MEN1 clearly affects the adsorption controlling initial period of reaction, i.e. first hours of operation, as phenol was detected in the outlet effluent just two hours after start-up. Nonetheless, this lower adsorption capacity has no impact on the phenol conversion at steady state, thus being comparable to the rest of the demineralised samples. Therefore it can be concluded that the catalytic activity shown by ME carbon must indeed be ascribed to the iron present on its mineral matter.

Difference between phenol and TOC conversions, the latter presented in Figure 4.4.4, is about 5% for samples MED and MEDH. In this case, the thermal treatment under hydrogen did not modify the selectivity towards CO_2 as discussed in the subsection 4.1.1 where the effect of hydrogen thermal treatment on carbon ME was discussed. In any case, some detrimental effect was observed for carbon MED, since the difference of conversions is 13%, which means a lower selectivity towards CO_2 .

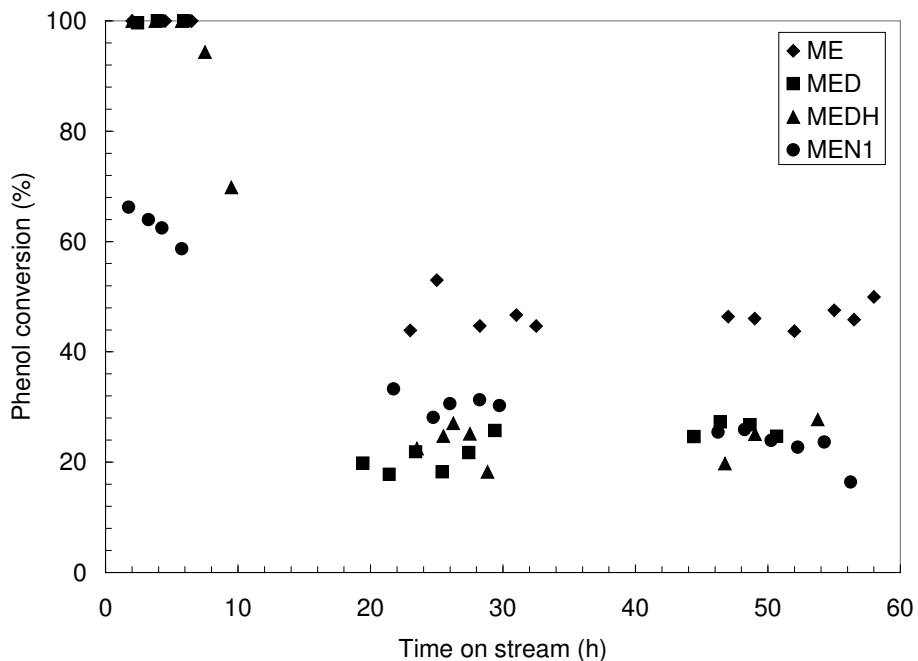


Figure 4.4.2. Phenol conversion in TBR reactor using ME and acid wash modified samples, at 140°C and 2 bar of oxygen partial pressure.

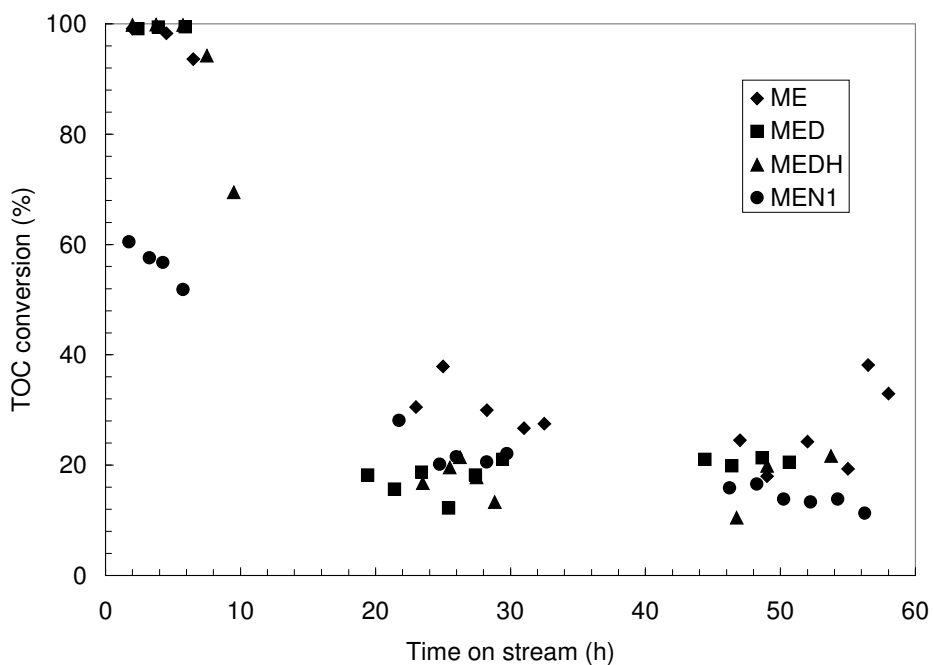


Figure 4.4.3. TOC conversion in TBR reactor using ME and acid wash modified samples, at 140°C and 2 bar of oxygen partial pressure.

All samples except MEN1 have similar ΔW after 55 hours of operation inside the reactor. In all the cases, the weight increased, which indicated that phenolic chains were irreversible adsorbed onto the activated carbon after operation. It must be noticed that ME, MED and MEDH show similar behaviour, whilst the lower value observed for MEN1 could be related to the initial presence of more carboxylic surface groups, which prevent the formation of phenol condensation compounds by oxidative coupling as previously commented.

Table 4.4.4. Weight difference in ME and acid wash modified samples after operation in TBR and final pH of liquid stream.

Sample	ΔW (g)	Final pH on stream
ME	2.519	2.13
MED	2.496	2.35
MEDH	2.400	2.49
MEN1	1.067	2.33

4.5. Metal impregnation of ME activated carbons

4.5.1. Physical and chemical characterisation

In this section, the results obtained for a set of activated carbons derived from the parent ME are presented. The ME activated carbon was subjected to different procedures in order to enhance its mesoporosity and then to deposit iron by impregnation. First, acid treatment with HNO_3 or H_2SO_4 was carried out with the double objective of demineralising and mainly generating acid sites for enhanced iron impregnation.

Table 4.5.1 shows that the acid treatment did not significantly modify the surface area and micropore volume of ME, as seen for samples MES and MES. However, an important increase of the mesopore volume can be observed, mainly in the sample washed with H_2SO_4 , which increased three folds, while HNO_3 only doubles the micropore volume. After impregnation with iron or calcium and subsequent carbonisation at 1000°C , the mesopore volume was even enhanced, but the other textural properties did not undergo major changes. The mesopore volume was at least increased by a factor of 2.5 for all the impregnated samples. It must be pointed out that the mesopore volume enlarges up to $0.108 \text{ cm}^3/\text{g}$ for MESCa. There are evidences that sulphuric acid widens the existing porosity of activated carbons (Jiang et al., 2003). Also, calcium has been used before as a promoter of mesoporosity in the production of activated carbon from sewage sludge (Rio et al., 2005a). It has been proposed (Zheng and Kozinski, 2000) that above 800°C calcium carbonate decomposes releasing CaO and CO_2 . The release of CO_2 can enlarge the existing pores but can even form new pores. Since all samples were heated at 1000°C , the calcium carbonate decomposition can explain the increase in the porosity of all samples containing Ca. In fact, MESCa owns the highest overall pore volume ($0.631 \text{ cm}^3/\text{g}$). In this case, the two effects, i.e. sulphuric acid wash and CaCO_3 decomposition, contributed to the observed increase. In all the samples impregnated with iron, an increase in the mesopore volume can also be

generally observed, yet it is more moderate. This can be explained by the catalytic effect of iron in the carbonisation of activated carbon also releasing CO₂, with the same enlarging pore effect already described. The microporosity of all samples remain practically unchanged, although generally a slight decrease can be noted. The highest decrease was observed for MENCaFe being about 13%. However, the loss of total pore volume in that sample is just 5%, keeping practically the total volume from the parent ME, yet that with a different distribution. In general, all samples are still highly microporous, since the micropore volume means around 80% of the total porosity.

Table 4.5.1. Physical properties of parent and modified ME.

Sample	S _{ABET} (m ² /g)	V _{mic} (cm ³ /g)	V _{mes} (cm ³ /g)	V _{tot} (cm ³ /g)
ME	1206	0.483	0.029	0.569
MEN	1149	0.459	0.068	0.577
MES	1261	0.499	0.092	0.653
MEFe	1119	0.448	0.072	0.567
MENFe	1085	0.431	0.082	0.562
MESFe	1147	0.453	0.087	0.599
MECa	1111	0.444	0.074	0.566
MENCa	1117	0.442	0.075	0.573
MESCa	1175	0.461	0.108	0.631
MECaFe	1126	0.451	0.072	0.572
MENCaFe	1052	0.417	0.072	0.541
MESCaFe	1158	0.456	0.085	0.608

Table 4.5.2 proves that the carbonisation step at 1000°C under N₂ was effective for removing carboxylic and phenolic groups from surfaces of samples MEFe, MECa and MECaFe. However, it is noteworthy that samples that were acid treated show an increase in the carboxyl and lactone content. This latter apparently increased over four times for MESCa. A total elimination of phenolics was nearly achieved in all cases. An explanation for these results could be that some residual sulphuric or nitric acid could remain trapped in the pores, thus reacting with the bases used in the Boehm titrations, resulting in a higher consumption and false surface oxygen content, higher than that actual. Also, iron imparts acid character and contributes to the acidity of the carbon.

Table 4.5.2. Chemical properties of parent and modified ME.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH _{pzc}
ME	0.097	0.123	0.031	7.36
MEFe	0.033	0.075	0.000	8.55
MENFe	0.119	0.202	0.049	7.99
MESFe	0.021	0.074	0.048	8.27
MECa	0.000	0.128	0.000	8.84
MENCa	0.002	0.142	0.035	9.36
MESCa	0.000	0.531	0.011	10.77
MECaFe	0.000	0.359	0.000	8.57
MENCaFe	0.000	0.441	0.006	8.63
MESCaFe	0.000	0.352	0.030	7.66

In Table 4.5.3, Fe and Ca content of all samples is collected. In general terms, acid wash was an effective pre-treatment for creating groups with ion-exchange ability, since the higher metal contents are found for the samples previously washed with acid, particularly those treated with H₂SO₄. The increase of metal content, yet rather small, in sample ME not treated with acid, MEFe could be explained by the originally already notable amount of surface oxygen groups that this activated carbon exhibits. Obviously, the creation of new ion-exchange sites by acid wash promotes an increase in the amount of metal that is later fixed in the carbonaceous structure during the carbonisation. Combined metal impregnation was effective, because the content of both metals increases in all the cases. However, the amount of calcium impregnated in these combined samples was lower than when using single calcium impregnation. This could be explained by the fact that calcium carboxylates formed on ME surface undergo dissociation, releasing calcium ions thus lowering the content fixed if compared with the sample only impregnated with calcium acetate. These carboxylic groups releasing calcium ions can later fix iron. This explains why MECaFe gave a higher iron content than MEFe, specially when considering that none of them were treated with acid. MENCaFe showed the same calcium content than MECaFe, but the iron content is practically two times higher, this suggests that the carboxylic groups created by the acid wash help the fixation of iron rather than calcium. MESCaFe showed a slight increase in calcium content compared to MECaFe and MENCaFe, but lower iron content than MENCaFe, which indicates that H₂SO₄ is not so suitable for fixing iron.

Table 4.5.3. Iron and calcium content of ME and modified samples.

Sample	Fe content (wt%)	Ca content (wt%)
ME	0.40	0.15
MEFe	0.51	n.m.
MENFe	1.43	n.m.
MESFe	2.08	n.m.
MECa	n.m.	0.40
MENCa	n.m.	0.79
MESCa	n.m.	0.90
MECaFe	0.75	0.20
MENCaFe	1.88	0.30
MESCaFe	1.15	0.20

n.m. Not measured

4.5.2. Adsorption isotherms.

Figure 4.5.1 shows the phenol adsorption isotherms for all these samples. In general, all samples impregnated with either Fe, Ca or both exhibit higher adsorption capacity than the parent ME. Also, MESCa shows a high adsorption capacity compared to the other Ca impregnated samples. This could be related to the high mesopore volume of this sample, which allows adsorbing a higher amount of phenol. An increase in the adsorption capacity in all samples was indeed expected, since it is well known that elimination of oxygen functionalities favours the adsorption of phenol on the activated carbon surface. In the case of samples that were impregnated with both metals, the adsorption capacity increases a quite high 58%, approximately.

Parameters of Freundlich equation for the adsorption isotherms are given in Table 4.5.4. In general terms, all samples have a low value of the $1/n$ parameter, again indicating favourable phenol-AC surface interactions. Also, all R^2 values are higher than 0.97, which means that all isotherms fit very well the model.

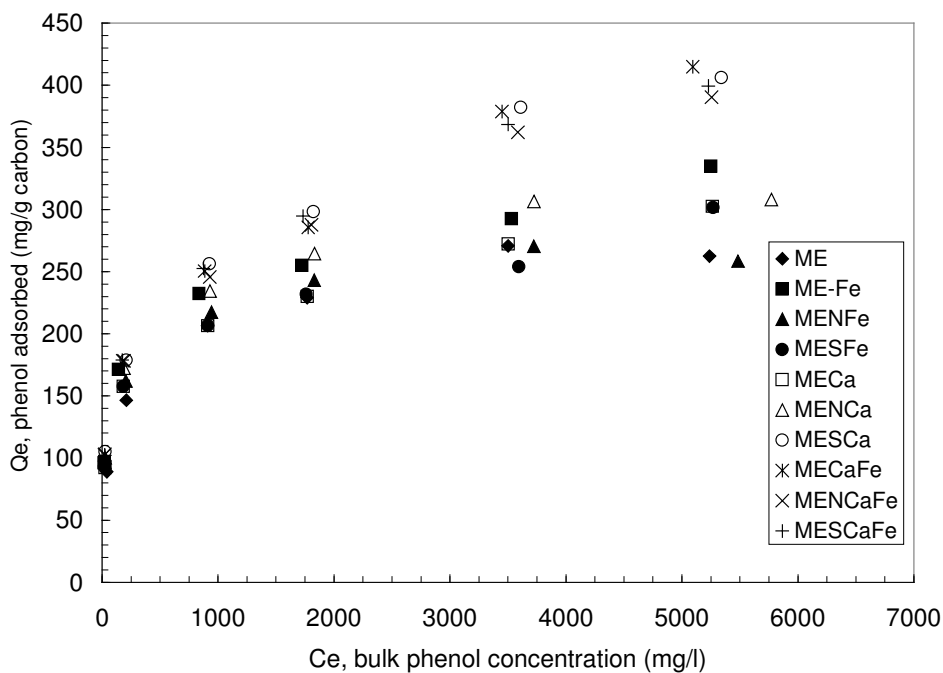


Figure 4.5.1. Phenol adsorption isotherms over activated carbon at 20°C.

Table 4.5.4. Freundlich parameters for phenol adsorption on ME and metal impregnated samples.

Sample	K (mg/g AC)(l/mg) ^{1/n}	1/n	R ²
ME	40	0.23	0.98
MEFe	55	0.21	0.98
MENFe	56	0.19	0.97
MESFe	52	0.20	0.99
MECa	48	0.21	0.99
MENCa	54	0.21	0.98
MESCa	45	0.26	0.99
MECaFe	47	0.25	0.99
MENCaFe	47	0.24	0.99
MESCaFe	47	0.25	0.99

4.5.3. Catalytic performance of carbons in the TBR system.

Regarding the catalytic activity, the phenol oxidation conversions as a function of time obtained in the TBR tests are represented in Figure 4.5.2. Considering the catalytic performance, two different behaviours can be distinguished. Samples with similar or lower catalytic activity than ME (MECa, MECaFe, MENCa, MESCa), and samples giving considerable higher conversion (MENFe, MESFe, MENCaFe, MESCaFe). MEFc shows intermediate trends. The results demonstrate that the addition of iron largely enhances the catalytic behaviour of the activated carbon. Thus, samples containing Fe, i.e. MENFe, MESFe, MENCaFe and MESCaFe render steady conversion around 75%, well above the 45% given by the parent ME. Sample MEFc, which has just 0.1% wt more Fe content than the parent ME shows an intermediate increase of 15% of conversion, demonstrating that even a small increase in the amount of iron available in the carbon could improve the catalytic performance.

The incorporation of calcium to the carbon did not modify the catalytic activity, since samples MECa, MENCa and MESCa did not furnish better performance than the parent ME. However, it must be noted that both MENCa and MESCa are acid washed samples, so that the actual iron content is expected to be lower. Therefore, the predicted phenol conversion should be poorer. Instead, the obtained conversion is comparable to that of the parent ME. This unexpected trend could be ascribed to the higher mesopore volume of these samples, which suggests that mesoporosity also plays a relevant role.

Albeit it must be also pointed out that MECa, which is not acid washed, should give better phenol conversion than that found, as it should contain the original Fe content but with enhanced mesoporosity. A possible explanation might relate this fact to the presence of Ca; iron could be hindered by calcium hydrated ions, then making original iron less available. In turn, MECaFe is not affected by this drawback as Fe was impregnated after Ca.

Due to the typically acidic reaction conditions in the TBR, leaching of iron (also Ca) is likely and therefore it was measured. Values of metal content at the end of the CWAO runs are collected in Table 4.5.6. It must be clarified that the metal content calculations of the spent carbons were done using the mass obtained after use. This mass includes also the products of the oxidative coupling occurring inside the reactor. This last value was used since it is difficult to ascertain the actual amount of the remaining activated carbon, since the possible loss of carbon mass could be largely offset by the increase due to the attached polymeric material. Figures 4.5.3, 4.5.4 and 4.5.5 compared the metal content before and after use. Regarding Ca, the leaching in samples MENCa and MESCa was about 70% in both cases. This means that, after 55 hours on stream, the Ca content was very close to that original. A different trend is found for Fe. Samples MENFe and MESFe show leaching of 15% and 53%, respectively, which clearly indicates that nitric acid wash before impregnation was more effective in order to incorporate iron to the activated carbon. However, even in the case of MESFe, which lost half of its initial iron content after 55 hours on stream. Anyway the final value is still threefold in comparison to that of the parent ME, allowing the phenol conversion to reach a value 30% above that given by the parent ME. Samples containing both Fe and Ca present high leaching of both metals, over 85% percent in all cases except for iron in sample MECaFe, which is only 47%.

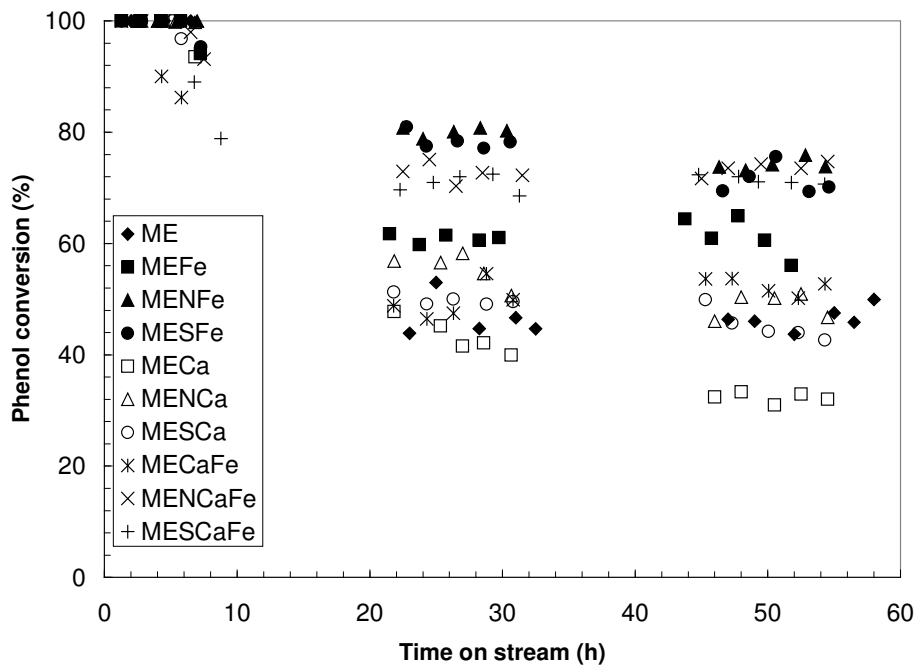


Figure 4.5.2. Phenol conversion in TBR reactor using ME and metal impregnated modified samples, at 140°C and 2 bar of oxygen partial pressure.

Table 4.5.5. Fe and Ca content after used in CWAO

Sample	Fe content (% wt)	Ca content (% wt)
ME	0.31	0.02
MEFe	0.61	n.m.
MENFe	1.22	n.m.
MESFe	0.98	n.m.
MECa	n.m.	0.33
MENCa	n.m.	0.23
MESCa	n.m.	0.27
MECaFe	0.40	0.02
MENCaFe	0.21	0.03
MESCaFe	0.17	0.02

n.m. Not measured

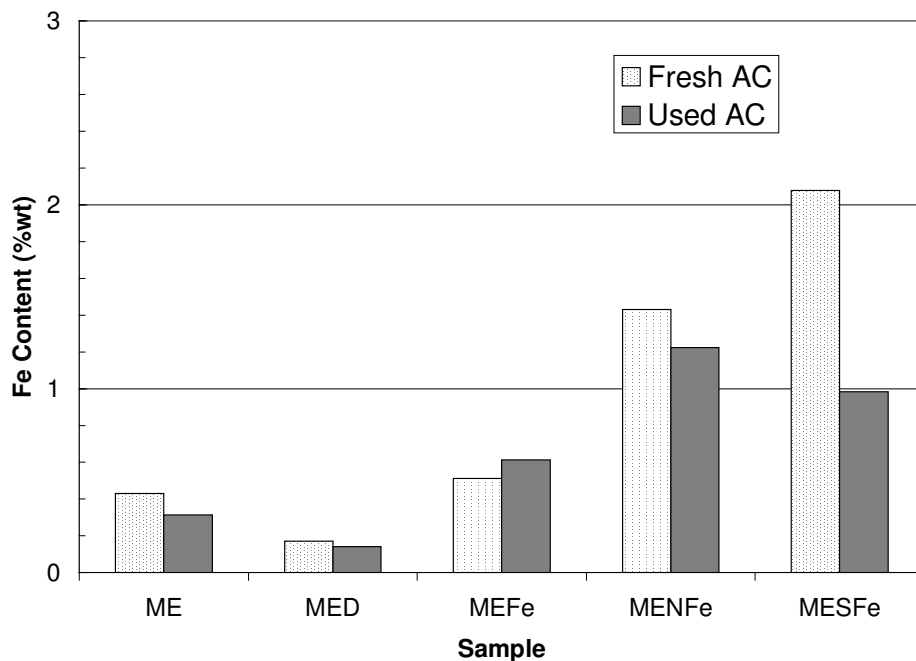


Figure 4.5.3. Iron content expressed in %wt of fresh and used in CWAO activated carbons.

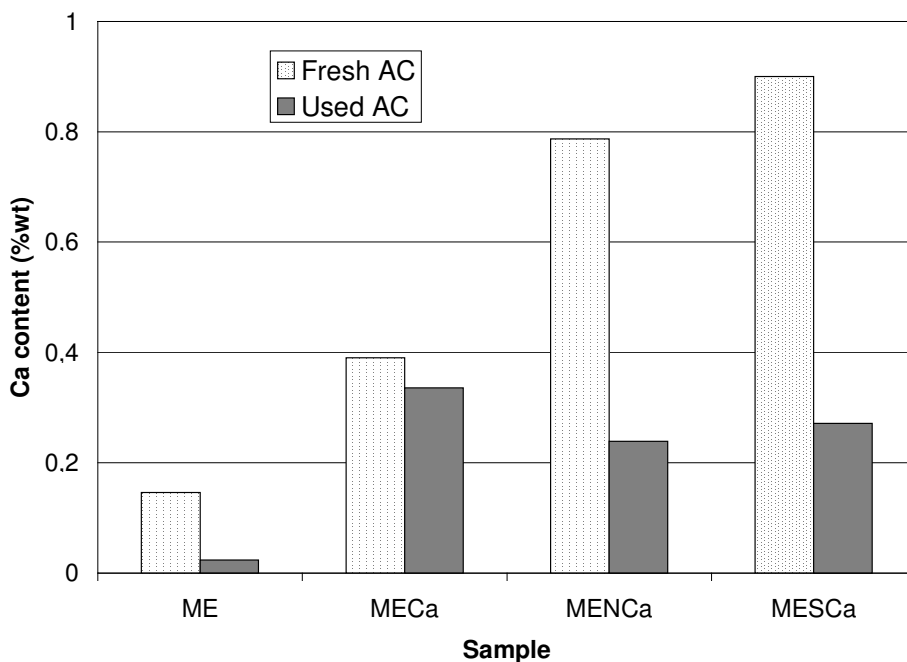


Figure 4.5.4. Calcium content expressed in %wt of fresh and used in CWAO activated carbons.

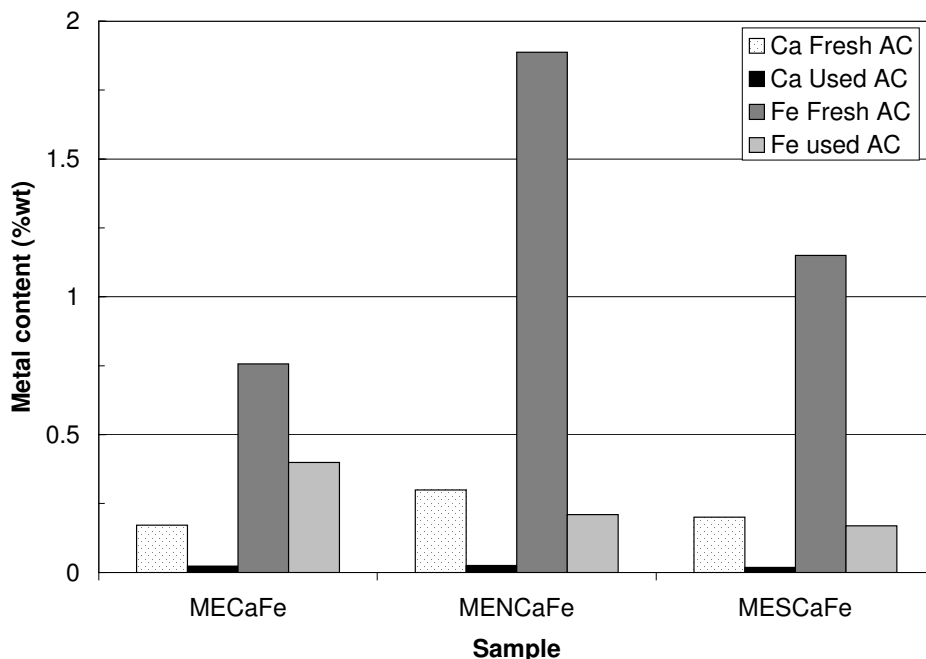


Figure 4.5.5. Iron and calcium content expressed in %wt of fresh and used in CWAO activated carbons.

TOC conversion in the effluent exiting the reactor during the run was measured and the results are presented in Figure 4.5.6. TOC behaviour shows similar trends than phenol conversion. Overall, the incorporation of iron improves the TOC conversion achieved at steady state. As before seen for phenol conversion, the presence of calcium and its derived enhanced mesopore volume did not improve the performance of MECa, MENCa or MESCa in comparison to ME.

Probably because of the leaching and the presence of iron in the liquid stream (Table 4.5.7), the different TOC conversion obtained with samples MENFe, MESFe, MENCaFe and MESCaFe, unlike what was observed for phenol conversion, where all these samples gave similar values, could be explained. These results suggest that homogeneous iron is promoting further degradation of the phenol partial oxidation products, e.g. quinone like compounds, carboxylic and condensation products.

Table 4.5.7 also summarises the weight of the activated carbon bed after use. All samples showed increase in the final weight, which reveals deposition of phenolic polymeric compounds as a product of the oxidative coupling occurring over the activated carbon.

In addition, all samples impregnated with iron showed an important fraction of the intermediates as acidic compounds, which agrees with the low pH values encountered in the exited effluent, also collected in Table 4.5.7. The amount of acid compounds was higher than 85% of the total partial oxidation compounds for all cases. This value is lower than the 94% obtained with ME, but it is important to highlight that both phenol and TOC conversions also increased for all the activated carbons impregnated with iron, except MECaFe, which gave approximately the same conversion than ME. Therefore,

even being lower the acid content, the performance of Fe impregnated carbons is more favourable as the phenol conversion is significantly higher.

A further inspection to Table 4.5.7 illustrates that the high values of Fe in the aqueous phase, because of the leaching, coincides with those cases achieving high phenol conversion. Therefore, it was mandatory to determine whether or not the phenol conversion reached was resulting from the iron impregnated over the activated carbon, or the homogeneous iron could be contributing to phenol disappearance.

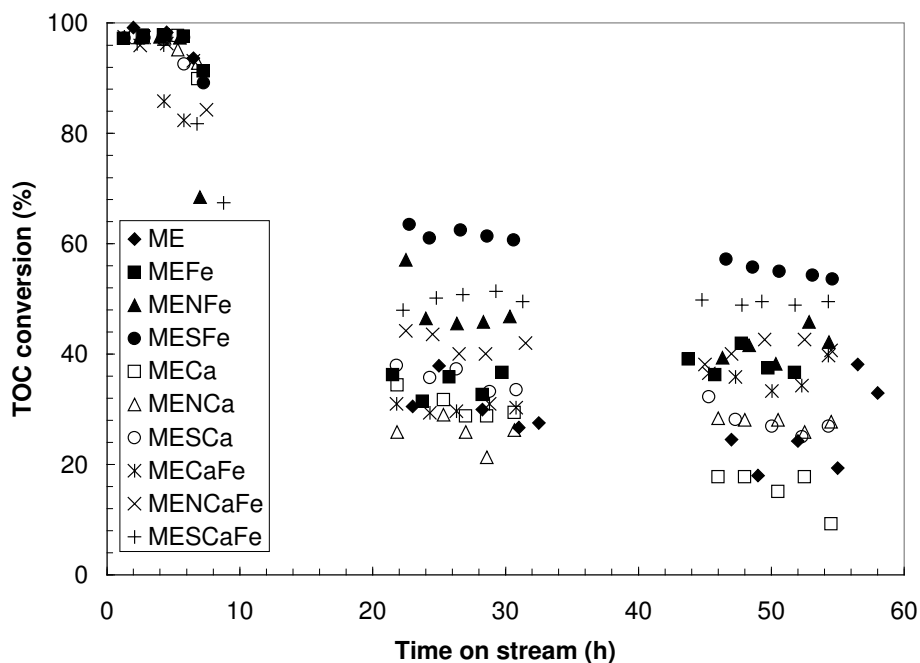


Figure 4.5.6. TOC conversion in TBR reactor using ME and metal impregnated modified samples, at 140°C and 2 bar of oxygen partial pressure.

Table 4.5.6. Weight difference in ME and acid wash modified samples after operation in TBR, final pH and iron content of liquid stream.

Sample	ΔW (g)	Final pH on stream	Fe in aqueous phase (mg/L)
ME	2.519	2.13	9.9
MEFc	2.407	2.41	13.5
MENFc	2.000	2.29	14.7
MESFc	1.687	2.27	19.6
MECa	2.466	2.50	0.5
MENCa	2.283	2.43	1.5
MESCa	2.126	2.34	0.5
MECaFe	2.592	2.33	5.5
MENCaFe	2.081	2.13	25.3
MESCaFe	1.866	2.39	17

Figure 4.5.7 assesses the phenol conversion obtained from several tests carried out with iron in homogeneous phase, using ME to fill the reactor and carborundum, which is an inert material. Using ME to fill the reactor and adding iron in the feed solution, 20 mg/L, no improvement in the final conversion is observed (test MEFHom). Actually the conversion after 50 hours of run is even 10% lower than that obtained with ME (45%). Adding iron in the feed solution using silicon carbide as bed (test InFeHom) barely reached a 10% of conversion. Although homogeneous Fe indeed provides some catalysis, this is not high enough as to explain the improved performance of the iron impregnated samples. Therefore, the enhanced catalytic performance must be mostly ascribed to the Fe supported over the modified activated carbons.

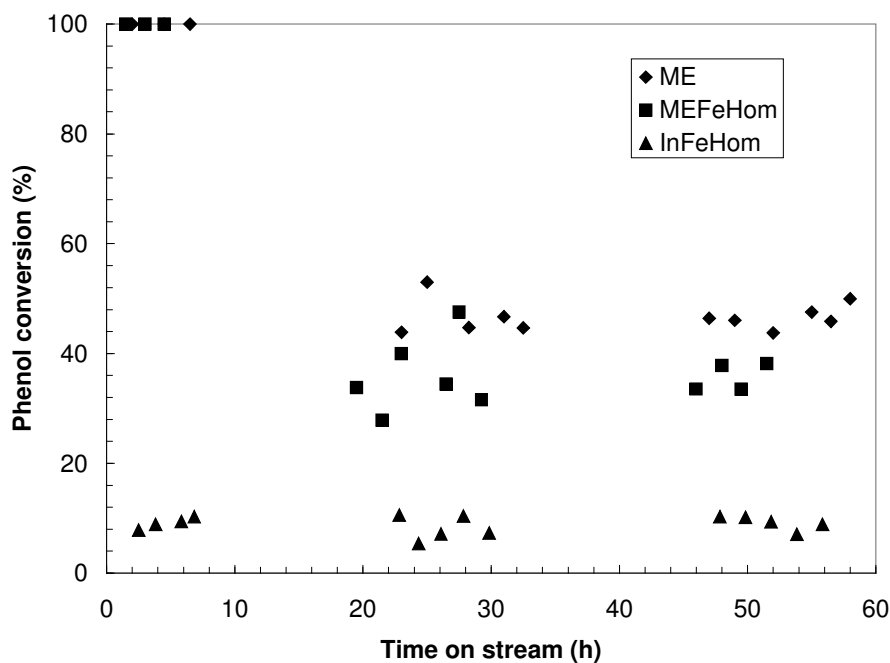


Figure 4.5.7. Phenol conversion in TBR reactor using ME and homogeneous iron, at 140°C and 2 bar of oxygen partial pressure.

4.6 Additional remarks

From results presented in subsections 4.4 and 4.5, it is possible to state that iron contained in ME is determinant in the catalytic activity shown by this commercial carbon for CWAO of phenol. The improvement of the mesopore volume, e.g. MECa (Table 4.5.1), did not modify the catalytic behaviour since the phenol conversion was practically the same than that obtained with the parent ME. Activated carbons impregnated with iron give much better catalytic performance than the parent ME. This additional catalytic activity can be ascribed to the impregnated iron, even occurring some iron leaching, as homogeneous iron cannot provide the additional phenol conversion encountered. Therefore, it is proposed that iron content is the main parameter responsible for the catalytic activity of activated carbon, which agrees with the known catalytic properties of this metal.

Because of this, the tailored manufactured activated carbons were intended to reproduce these conditions by means of designed experimental procedures.

4.7. Designed activated carbons

4.7.1. Physical and chemical characterisation

This part of the research work was developed at the laboratories of the Centre for Environmental Control and Waste Management (CECWM) of the Imperial College of London. The raw material for preparing the activated carbons were supplied by the laboratory and the temperature and time selected for the manufacturing of activated carbon from willow had been already optimised in a previous research owned by CECWM. The one-step pyrolysis procedure was chosen in order to obtain activated carbons comparable to the parent ME. This method allows making the carbonisation and activation of the raw material in practically just one single step. Steam chosen as activation agent since was selected because it promotes the development of microporosity during the activation stage (Ioannidou and Zabaniotou, 2007).

Table 4.7.1 summarises the liquid and solid products rendered during the manufacture of the activated carbons. Sample MW1, made from willow through one-step pyrolysis, gave higher liquid yield than when the same raw material was used but chemical activation applied, in sample MW2, where the highest yield was gaseous products, specially for MW2Fe. This is due to the catalysing effect that metals like potassium and iron have on the gasification reactions during the activation. In fact, gas formation during the manufacturing of MW2Fe gave the highest gas yield observed in all cases. Iron in this case is accelerating the formation of CO and CO₂, decreasing also the solid yield if compared with MW2 that was made from the same raw material through chemical activation but without previous iron impregnation. The liquid product yield in sample MCS, made from coconut shells and by one-step pyrolysis activation, was very similar to that obtained with sample MW2. However, this value for MCSFe was the lowest of all the carbon manufactured because the carbonisation was conducted before the iron impregnation step, and the values in Table 4.7.1 are calculated from products obtained after the activation. In the manufacturing of the chars that were later used in the iron impregnation, the liquid products yield was about 70%. For that reason, after the iron impregnation and the activation with steam, the liquid product yield was only about 10%, because most of the organic material that is later released as oils was already eliminated in the char production step.

However, due to the nature of its raw material, the activated carbons MW1, MW2 and MW2Fe did not have the strengthness needed to withstand the exigent operation conditions in the TBR. For that reason, only carbons MCS and MCSFe made from coconut shells were employed in the performance tests of phenol adsorption and catalytic activity.

Table 4.7.1. Yields obtained in the manufacturing of activated carbons.

Sample	Solid product (% wt)	Liquid product (% wt)	Gas + losses (% wt)
MW1	17.1	51.7	31.2
MW2	14.9	38.8	46.3
MW2Fe	11.8	16.5	71.7
MCS	19.0	35.4	45.6
MCSFe	56.4	10.4	33.2

The physical properties of samples MCS and MCSFe are listed in Table 4.7.2. ME has been included for comparative purposes. MCS is a highly microporous carbon since 96% of its total porosity is in the micropore range. The surface area is also relatively high, which indicates that steam was effective as activating agent promoting the formation of micropores. Sample MCSFe, on the contrary, showed a surface area 40% lower than MCS and also 47% lower micropore volume. Despite the iron is supposed to enhance the gasification of the carbon, thus promoting the porosity, in this case the iron impregnated on the char made from the coconut shells could have reduced the interaction of the water with char and their needed reaction. As a result, development of the surface area and microporosity were suppressed and only superficial reactions, typically producing mesoporosity, promoted. Actually, some increase in the mesopore volume, from 4% to 9%, was observed in sample MCSFe (Marsh and Rodríguez-Reinoso, 2006; Alcañiz-Monge et al., 2007).

Table 4.7.2. Physical properties of tailored activated carbons.

Sample	S_{ABET} (m^2/g)	$V_{\text{mic D-R}}$ (cm^3/g)	$V_{\text{mes+mac}}$ (cm^3/g)	V_{tot} (cm^3/g)
ME	1261	0.473	0.137	0.610
MCS	830	0.369	0.014	0.383
MCSFe	493	0.194	0.020	0.214

The nitrogen adsorption isotherms are shown in Figure 4.7.1. The shape of the isotherms for both activated carbons matches the Type I classification according to IUPAC, typical from highly microporous materials. The low adsorption capacity shown by MCSFe evidences the low value of surface area of this sample.

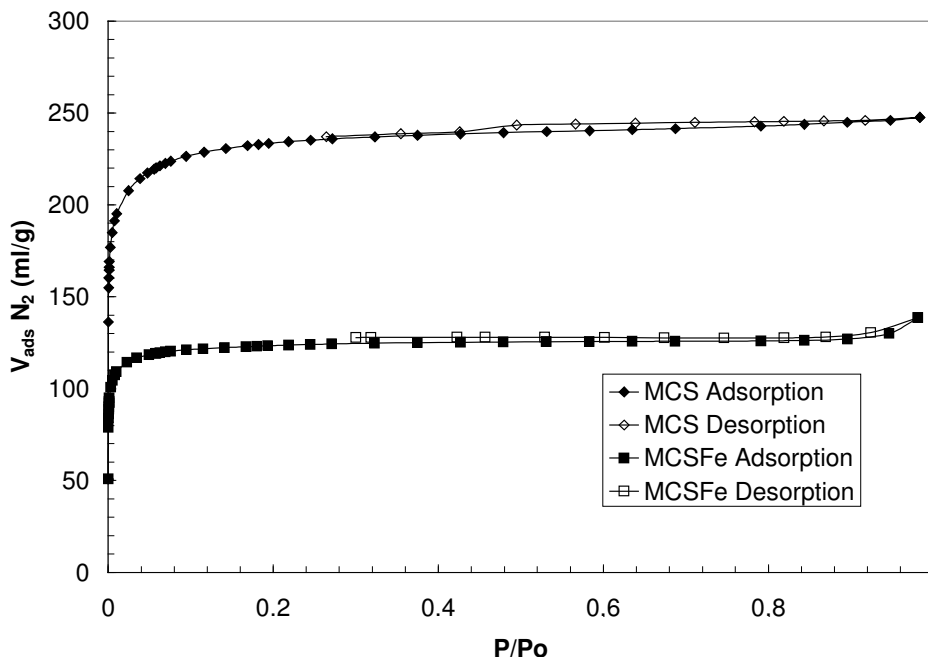


Figure 4.7.1. N₂ adsorption isotherms on tailored carbons.

Since one of the commercial carbons, GT, is also made from coconut shells, it was subjected to HNO₃ wash as previous pre-treatment to the iron impregnation later performed according to the procedure described in section 3.5. This sample, GTNFe, was prepared in order to compare the properties of the tailored activated carbon made from the same raw material and the adapted procedure.

Chemical properties of all samples are collected in Table 4.7.3. Samples MCS, MCSFe, MW1 and MW2 showed very high values of pH_{pzc}. This could be due to the elevated temperatures used for the activation step. Since, after the activation, the samples were left to freely cool from 1000°C until room temperature under just the nitrogen flow, most of the acidic surface functionalities were probably decomposed in CO and CO₂ during cooling. Samples with iron content showed a more acidic character. In case of sample GTNFe, the previous HNO₃ wash could be imparting acidic properties to this sample as some nitric acid trapped into the pores in hard to remove. Also, the iron content contributes to the acidity of the carbons this could explain the low value showed by carbon MW2Fe.

In all the home-made manufactured activated carbons, the iron impregnation method was effective for fixing iron in the carbonaceous matrix, specially in MW2Fe. Anyway, iron content is very low probably because the impregnation was directly performed over the raw material without any previous pre-treatment, so that probably there was no acidic oxygen surface groups with ion-exchange ability. Therefore, the iron content was resulting from just physical adsorption of iron salts and then a low content must be expected.

Table 4.7.3. Chemical properties of tailored activated carbons.

Sample	Phenolics (meq/g)	Lactones (meq/g)	Carboxyls (meq/g)	pH _{pzc}	Fe content (%wt)
ME	0.097	0.123	0.031	7.36	0.40
MCS	0.059	0.033	0.000	10.82	0.00
MCSFe	0.017	0.042	0.000	10.52	0.20
GT	0.000	0.021	0.193	9.19	0.00
GTNFe	0.093	0.313	0.026	6.92	0.30
MW1	0.069	0.063	0.000	11.82	0.00
MW2	0.087	0.041	0.003	11.63	0.00
MW2Fe	0.009	0.298	0.057	7.54	0.02

4.7.2. Adsorption isotherms.

The phenol adsorption isotherms of the tailored carbons are presented in Figure 4.7.2. Samples MCS and GT showed high adsorption capacity at 5000 mg/L of bulk concentration, in the same order of the parent ME. On the other hand, sample GTNFe showed a decrease of about 15% in its original adsorption capacity. The higher amount of oxygen surface groups present on this carbon and the presence of iron impart additional hydrophilic character to the carbon surface, which could be responsible for the reduction of the phenol adsorption capacity. As already commented, they could be promoting the formation of water clusters surrounding oxygen containing groups in the carbon surface. However, the strongest phenol adsorption capacity reduction belongs to MCSFe giving loss of 74% in its original adsorption capacity. All carbons studied in this research have demonstrated that surface chemistry is determinant in their performance as adsorbent for phenol. Since MCS and MCSFe have very similar oxygen content (see Table 4.7.3), the decrease of the adsorption capacity should be attributed to the difference in the surface area and micropore volume, which is indeed considerable as seen in Table 4.7.2.

In Table 4.7.4, Freundlich parameters from fitting of experimental data are shown. All $1/n$ values are relatively low, which indicates high affinities between these carbons surfaces and phenol. However, the R^2 value for the fitting of samples MCSFe and GTNFe is lower than that obtained for ME or MCS. The fact that correlations are rather low could be related to the low adsorption capacity of these samples

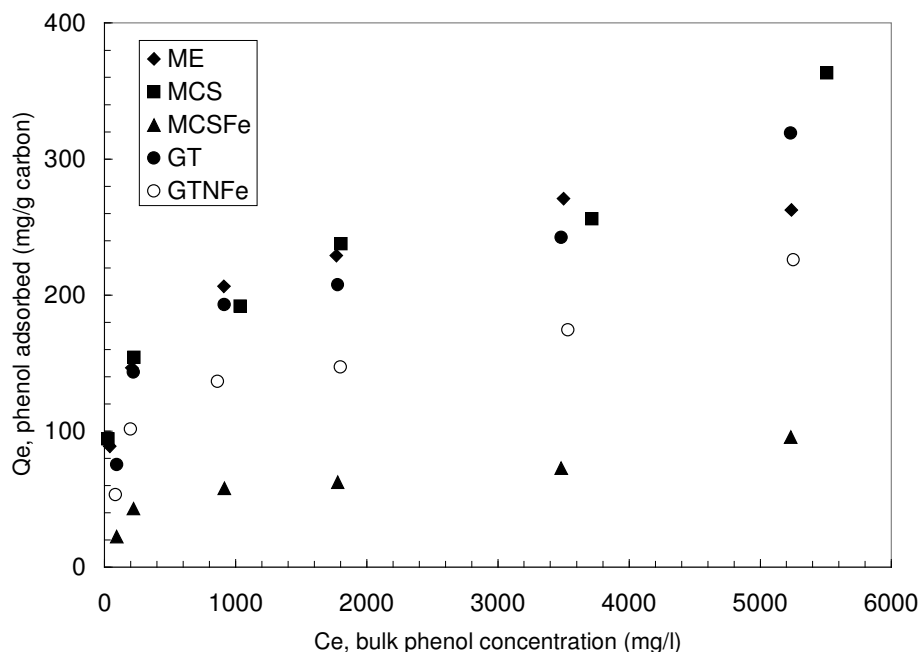


Figure 4.7.2. Phenol adsorption isotherms over tailored activated carbons at 20°C.

Table 4.7.4. Freundlich parameters for phenol adsorption of the tailored carbons.

Sample	K (mg/g AC)(l/mg) ^{1/n}	1/n	R ²
ME	40	0.23	0.98
MCS	43	0.23	0.96
MCSFe	7	0.30	0.93
GT	22	0.30	0.92
GTNFe	17	0.30	0.93

4.7.3. Catalytic performance of tailored carbons in TBR tests.

The phenol conversions obtained with these tailored carbons in the TBR tests are shown in Figure 4.7.4. The phenol conversion obtained with MCS is practically twice that that obtained with the commercial GT also made from coconut shells, 8% vs. 3.5% respectively, although both are marginal for practical purposes. Regardless of the iron content of sample MCSFe, which is half that of ME (see Table 4.7.3), the conversion achieved with MCSFe is considerably lower, only 10% compared to 45% given by ME. Even when compared to the commercial F400 having similar iron content (see Table 2.2.2), the phenol conversion exhibited by MCSFe is too low, since F400 furnishes 38%. The low catalytic activity could be attributed to the very low value of surface area and low micropore volume developed during activation of this carbon. Actually the value of phenol conversion obtained with MCSFe is practically the same observed for MCS, which suggests that both MCS and MCSFe are affected by serious problems of surface availability.

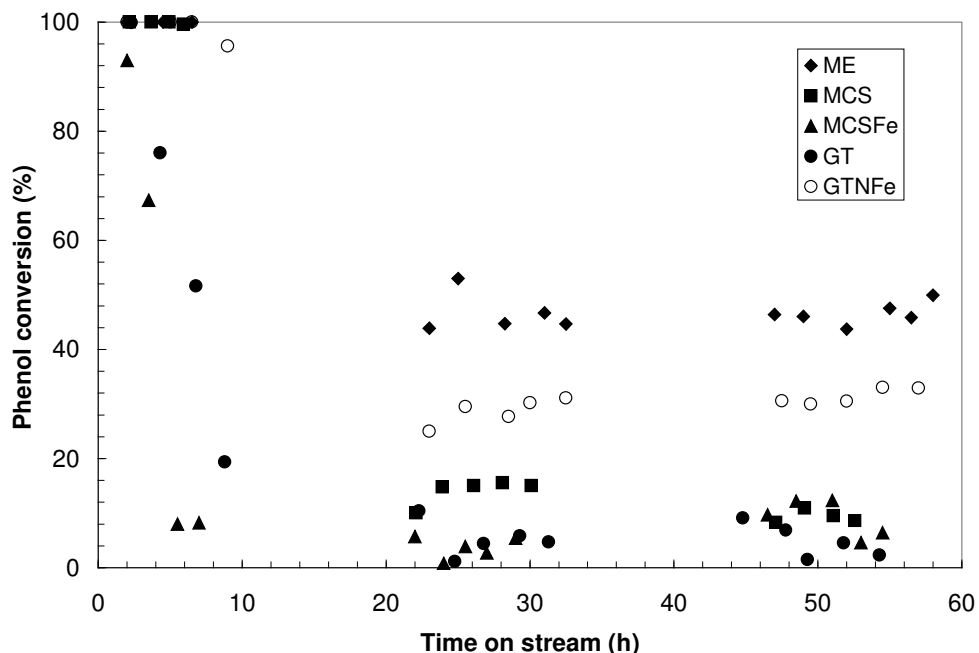


Figure 4.7.3. Phenol conversion in TBR reactor using tailored manufactured samples, at 140°C and 2 bar of oxygen partial pressure.

On the contrary, sample GTNFe showed a noticeable catalytic activity for phenol oxidation, being clearly superior than the original GT, 33% and 3.5%, respectively. Originally, GT shows no iron content since it is made from coconut shells that is not expected to contain significant amount of iron, unless coming from mineral impurities. Through the acid wash pre-treatment and iron impregnation modification, it was possible to provide this carbon with the same iron content than a commercial carbon made from coal (F400). Despite the surface area of this carbon is half of ME, for instance, its adsorption capacity is very similar (see Figure 4.2.1), which suggests that it has a high volume of micropores. This microporosity and the formation of carboxylic functionalities after acid wash could be responsible for the high amount of iron later fixed in GTNFe with the thermal treatment.

When analysing the amount of acidic compounds formed as intermediates with these carbons, some noticeable observations can be made. With carbon MCS, 33% of the intermediates formed where acids. This value is higher than the 25% observed with carbon GT. This is a low mineralisation that correlates with their poor catalytic performance. However, the amount of acids formed as intermediates of the phenol oxidation pathway considerably increased when iron was incorporated to the carbon, up to 88% and 89% respectively, even in the case of MCSFe, for which the increase of phenol conversion, compared to MCS, is only from 8% to 10%. For GNTFe, the increase of the phenol conversion also produces an improvement in the amount of acidic compounds formed, which reaches 89% in comparison to the 25% from GT.

Leaching of iron also occurred for MCSFe and GTNFe. The iron content in the used activated carbons after 55 hours on stream are listed in Table 4.7.4, as well as the ΔW of all carbons studied in this section, the pH and the iron concentration in the exited effluent at the end of the run. The leaching was about 80% for sample MCSFe and 57%

for GTNFe. Since the iron in the exited effluent is measured at the last sample taken from the reactor and the iron concentration obtained for MCSFe is very low compared to that measured for ME and GTNFe, it is possible to presume that most of the leaching could be occurring during the first hours of operation. Zhu et al. (1997) proposed that during the carbonisation step, iron atoms migrate from the outer surface to the inner part of the bulk of carbon particles. This migration depends on the temperature of the carbonisation. Also time could affect the iron migration in the carbon. However the actual impact of these parameters have not been reported. For MCSFe, the iron impregnation was done before the activation, but after carbonisation. The textural properties of the char could dominate the proposed iron migration, remaining most of it on the external surface, where probably it cannot be properly fixed into the carbonaceous matrix, resulting in faster leaching. The iron supported on GTNFe seems to be more resistant to the acidic operation conditions existing inside the reactor, since the leaching was considerably lower.

The leaching was about 80% for sample MCSFe and 57% for GTNFe. Since the iron in the liquid is measure in the last sample taken from the reactor, and the value measured in the case of MCSFe is very low compared with the one measure in the liquid when using ME and GTNFe, it is possible to think that most of the leaching could be occurring in the first hours of operation. Zhu et al. (1997) proposed that during carbonisation step, iron atoms migrate from the surface to the inner part of the bulk of carbon particles. This migration depends on the temperature of the carbonisation. Also time could be affecting the iron migration in the carbon, however the effect of this parameter has not been reported. In case of sample MCSFe, the iron impregnation was done before the activation, but after carbonisation. The textural properties of the char could be affecting the proposed iron migration, remaining most of it on the surface, where it probably can not be properly fixed in the carbonaceous matrix, with the consequent high percentage of leaching. The iron fixed in GTNFe seems to be more resistant to the acidic conditions of operation inside the reactor, since the leaching was considerably lower.

Table 4.7.5. Weight difference in ME and tailored manufactured samples after operation in TBR and final pH of liquid stream.

Sample	ΔW (g)	Final pH	Fe in the outlet effluent (mg/L)	Fe content after use (% wt)
ME	2.519	2.13	9.9	0.31
MCS	2.900	3.85	0.0	0.00
MCSFe	2.051	2.96	0.3	0.04
GT	2.829	3.65	0.0	0.00
GTNFe	3.244	2.49	7.3	0.13

Finally, TOC conversion evolutions in front of time on stream are presented in Figure 4.7.5. Alike for GT, MCSFe gives some negative TOC conversions. This negatives values of conversion, when so low phenol removal is achieved could be attributed to the later release of phenol polymers from the surface, which were attached during the first hours of operation but that are not measured as phenol by means of HPLC, albeit they are later counted when measuring the TOC of the sample.

Since negatives values of TOC conversion were obtained with samples GT and MCSFe, is difficult to calculate the difference with phenol conversion. In any case, samples MCS and GTNFe showed difference with phenol conversion, 2% and 18% respectively. This later value is even higher than the 13% of difference observed for ME. This indicates that the incorporation of iron in carbon GT increases not only the phenol conversion and the formation of acids as intermediates. It also improves the selectivity towards CO₂.

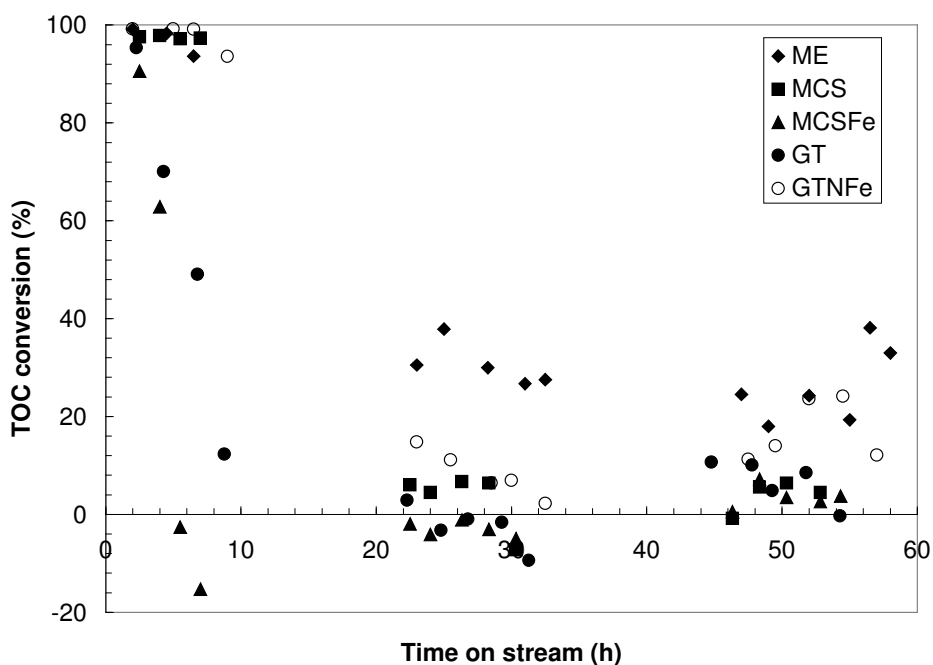


Figure 4.7.4. TOC conversion in TBR reactor using tailored manufactured samples, at 140°C and 2 bar of oxygen partial pressure.

In summary, coconut shells can be successfully used to produce activated carbons with mechanical stability to resist the operation conditions inside the TBR. Also, the one-step pyrolysis with steam produces highly microporous materials. However, in order to furnish catalytic activity for phenol oxidation, it is necessary to incorporate iron. The results demonstrate that in order to have iron catalytically active is desirable to incorporate it by impregnation after activation, since the oxidative environment during the activation step could give a non catalytically active iron phase.

Chapter V

Conclusions and future work

5.1. General conclusions

The main conclusions derived from this investigation are summarised as follows.

1. Thermal treatments under inert atmosphere are effective in eliminating oxygen surface functionalities present in the activated carbon, which are formed during activation. Thus, after treatment at 900°C, the predominant remaining groups are carbonyls and other oxygenated functionalities with basic character. The treatment under hydrogen was effective not only for removing these oxygen groups, but also for stabilising the carbon surface, as hydrogen reacts with the reactive sites remaining after the decomposition of the surface oxygen groups.
2. The removal of the more acidic surface oxygen groups improves the phenol adsorption capacity because it enhances the mechanisms proposed as responsible for the phenol adsorption on AC. On the one hand, it favours the formation of donor-acceptor complexes between the phenol aromatic ring acting as acceptor and the remaining carbonyls in the AC surface acting as electron donors. On the other hand, there is an increase of the π - π interactions between the π electrons of the carbon basal plane and the phenol aromatic ring.
3. Also, the reduction of the surface acidity by outgassing the surface oxygen groups reduces the hydrophilic character of the carbon surface, avoiding the formation of water clusters (i.e. the solvent effect) that block the active sites for the phenol adsorption. This acidity reduction was evidenced by the high pH_{pzc} values shown by all the activated carbons thermally treated either under nitrogen or hydrogen.
4. Thermal treatments did not modify the textural properties, i.e. surface area and pore volume of the activated carbons. This means that the phenol adsorption capacity of a carbonaceous material can be improved by a physical treatment that actually did not alter its porosity.
5. However, both the improvement of the adsorption capacity and the removal of surface oxygen groups did not substantially alter the catalytic performance in comparison with that shown by the parent activated carbon. This suggests that the chemical properties of the activated carbon surface and the improved adsorption capacity are not the key factor for its catalytic activity.
6. Neither mesopore volume did seem to decisively contribute to the catalytic activity shown by activated carbons. Samples derived from HD carbon, which are highly mesoporous, showed a poor catalytic activity. Only a slight increase in the conversion obtained with HDDSH was observed and it is rather attributed to the formation of phenolic polymeric compounds attached to the surface, which could be promoted by the enhanced meso and microporosity of this sample allowing a higher phenol adsorption during the first hours of operation in the reactor.

However, sample MESC_a, which also have a higher mesopore volume than its parent ME, did not show any improvement in its capacity to oxidise phenol, since the conversion obtained with these two carbons is practically identical, 42% and 45%, respectively.

7. The demineralisation of sample ME produces an important decrease in the phenol conversion, from 45% down to 25%. This result demonstrates that mineral matter, more specifically iron that is the metal found in higher amount in this carbon, has a great influence in the catalytic activity of this material. This is confirmed by the fact that, three commercial ACs with high surface area and high micropore volume, but with no mineral matter present due to its raw material, show no catalytic behaviour in the oxidation of phenol.
8. Iron content of the activated carbon has proven to correlate with the catalytic performance for CWAO of phenol in a TBR. By increasing 3.5 times the amount of iron in the parent carbon ME, it is possible to increase the phenol conversion up to 80% as for MENFe and MESC_aFe.
9. The location of the iron in the activated carbon matrix seems to be critical for the subsequent catalytic behaviour in phenol oxidation. Assays done with several commercial activated carbons demonstrate that despite having the same iron content, two carbons like ME and CN exhibit different catalytic behaviour, giving different conversions (45% and 30% respectively), although both remarkable. Different selectivity for the formation of partial oxidation compounds was found, too. This appears to indicate that not only the content of iron is necessary in order to show catalytic behaviour, but it is also needed that iron to be available in a suitable form to actually perform as catalyst.
10. One-step pyrolysis procedure was effective to manufacture activated carbon from coconut shells, achieving high values of surface area and well developed porosity, although most of the porous being in the range of microporosity. MCS carbon, despite having 34% lower surface area, shows the same adsorption capacity than commercial carbons like ME made from coal or GT which is also made of coconut shells. However, due to the absence of mineral matter in the sample made from coconut shells, carbon MCS did not show any catalytic performance. Sample MCSFe, made also from coconut shells with an iron impregnation step included before the activation, shows also lack of catalytic behaviour as MCS. This indicates that, despite having similar iron content than IR or F400, two commercial AC made from coal, the iron in sample MCSFe is not catalytically active. In conclusion, the iron in the carbonaceous materials does not always show catalytic activity, probably due to the position or even the crystalline phase in which it is present.
11. Iron impregnation is more effective when the carbonaceous materials have been previously treated with acid to form addition surface acidic groups. These acidic groups exhibit ion exchange properties enhancing the iron adsorption onto the surface, later fixed by the gasification under nitrogen.
12. It was possible to incorporate iron to a commercial activated carbon made from coconut shells, GT, that showed nil catalytic activity in the CWAO of phenol. The iron content, initially negligible, was increased up to 0.3% wt. This iron impregnated carbon, GTNFe, was capable of oxidising phenol and gave a conversion of 30% at steady state.

5.2. Future work

The most relevant finding of this research work is that the iron content of activated carbon is the main responsible for the catalytic activity shown by this material, despite other parameters probably affects the catalytic performance.

However, the location of iron in the carbonaceous structure and perhaps its crystalline phase seem to be determinant in the behaviour of this metal as catalyst. In this study, none of these two parameters were deeply studied. So, in order to design experimental procedures to manufacture activated carbons with appropriate catalytic properties it, is necessary to fully identify the suitable location of iron and its optimum state and optimising the protocols of preparation. Moreover, highly mesoporous activated carbons should be designed for this purpose.

It would be also necessary to evaluate the performance of the iron impregnated carbons and their stability-durability at different conditions in TBR. A complete screening of the temperature, oxygen partial pressure and space time effect is needed in order to assess the yielded product distribution, which should be suitable for posterior biotreatment. In addition, kinetics are needed for a subsequent design of scaled reactors.

As metal content is believed to be critical for wet oxidation applications of the activated carbons, other raw materials for their preparation like petroleum coke could be of interest because of its natural high metal content.

An interesting research opportunity is the development of hybrid materials, like zeolite/carbon composites that include iron in the zeolite. This material could show several advantages when compared to Fe supported over activated carbon. For instance, it would have both hydrophilic and hydrophobic character, since the presence of the zeolite will increase the hydrophilicity of the material. Also, due to the more organised structure of the zeolite, it could be easier to locate the iron in the structure in positions that favour the catalytic activity, whereas the activated carbon would serve for enhancing the generation of oxygen radicals form the molecular oxygen.

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Annex A

In this Annex are collected the pH profiles of the liquid samples from TBR experiments of all the carbons used in this work.

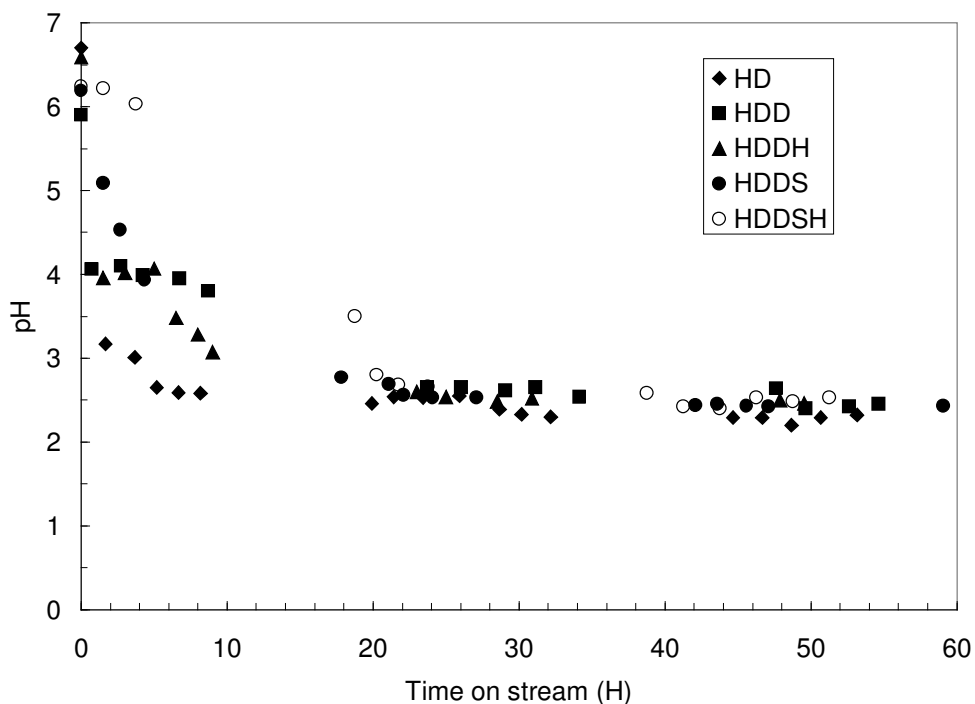


Figure A.1. pH profile of liquid samples from TBR for HD's carbons.

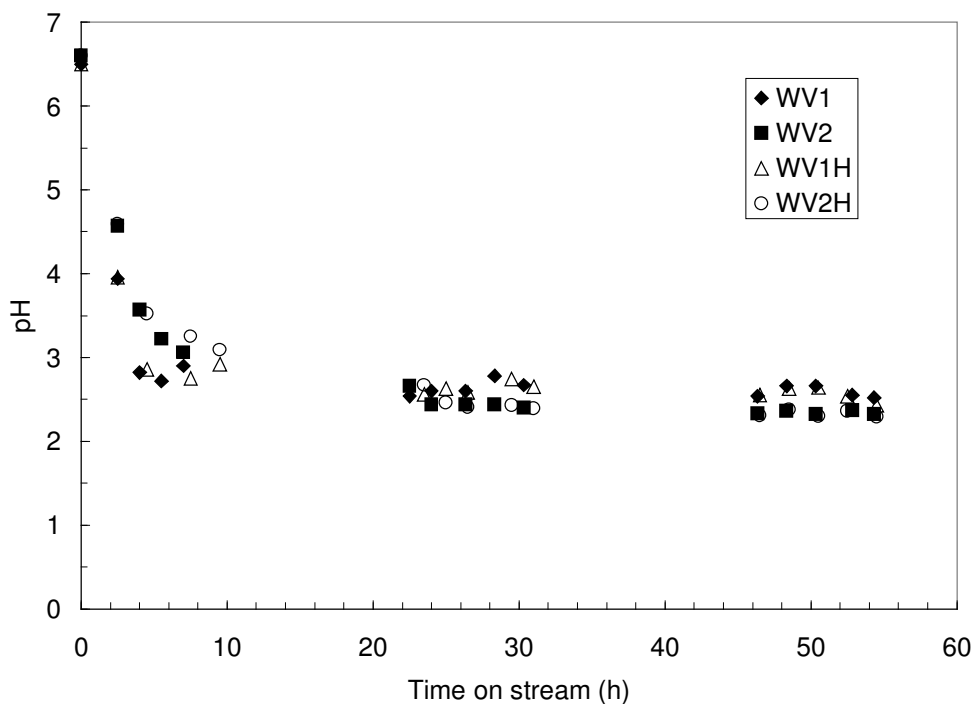


Figure A.2. pH profile of liquid samples from TBR for WV's carbons.

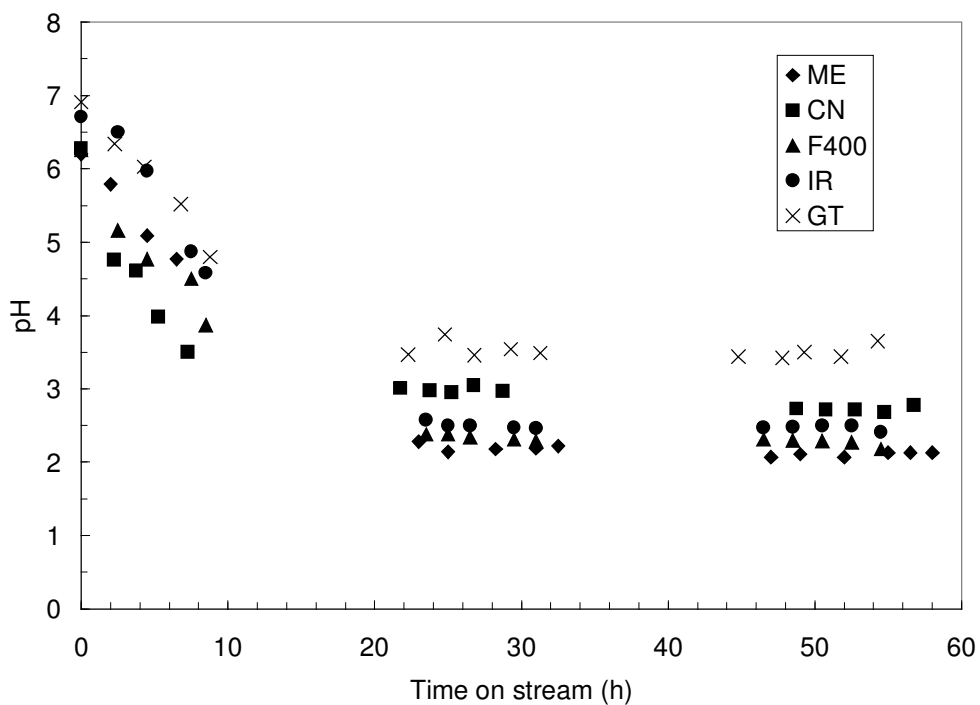


Figure A.3. pH profile of liquid samples from TBR for commercial ACs.

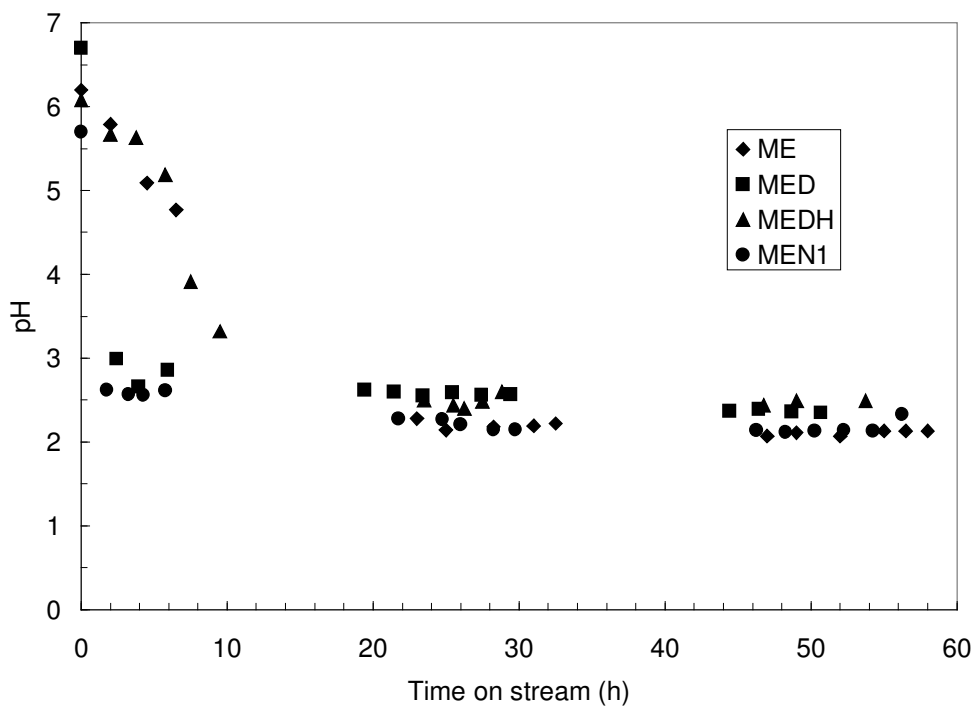


Figure A.4. pH profile of liquid samples from TBR for acid washed ACs.

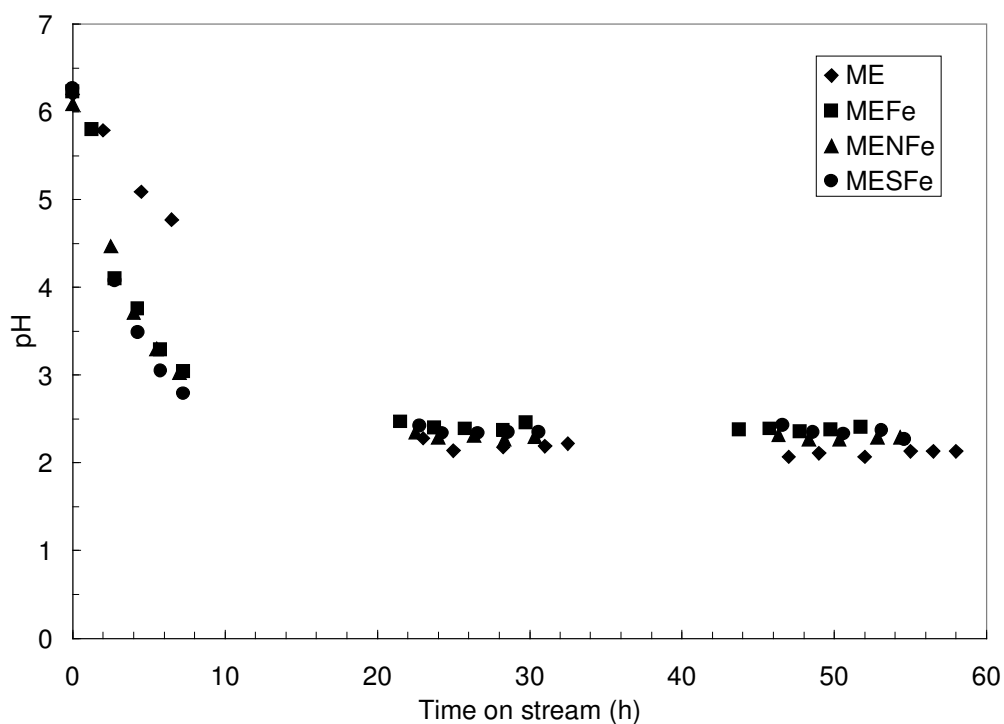


Figure A.5. pH profile of liquid samples from TBR for iron impregnated ACs.

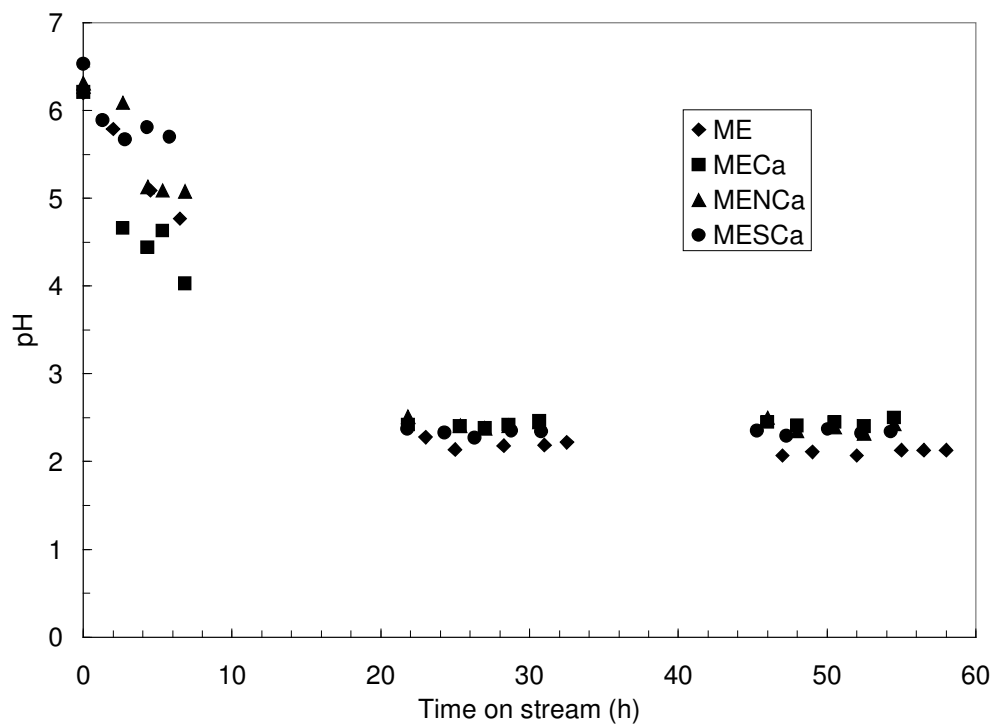


Figure A.6. pH profile of liquid samples from TBR for calcium impregnated ACs.

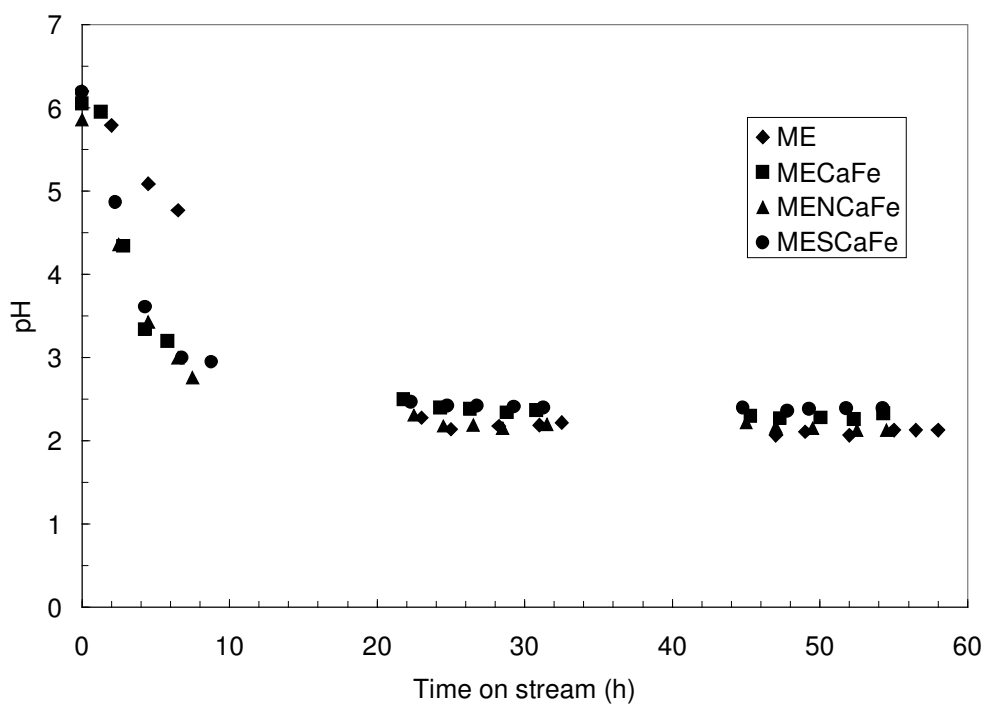


Figure A.7. pH profile of liquid samples from TBR for iron and calcium impregnated ACs.

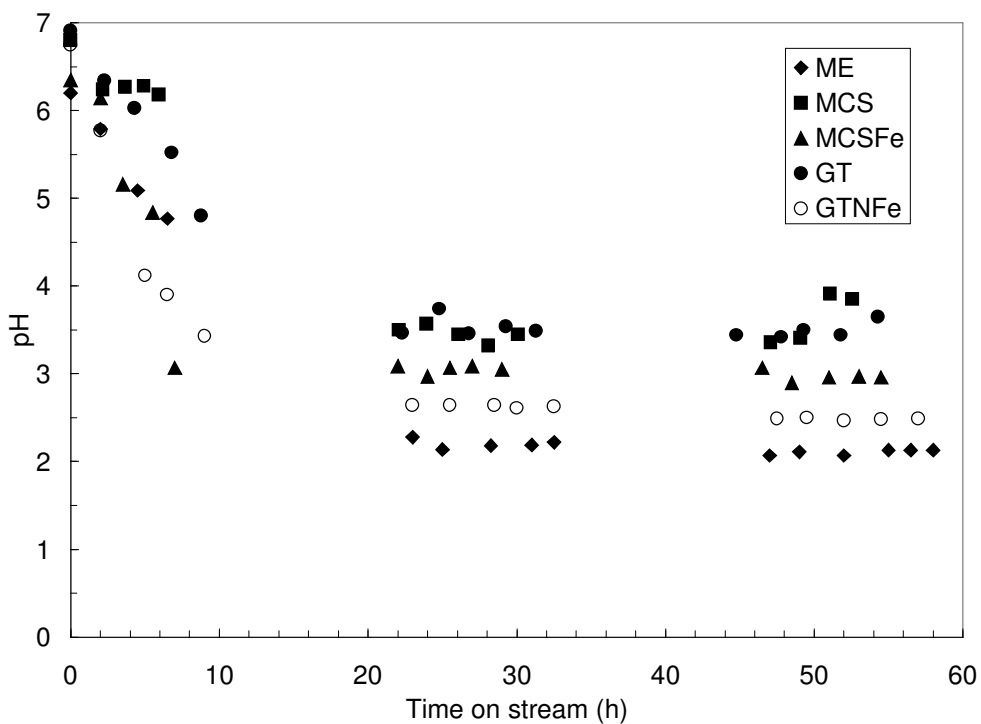


Figure A.8. pH profile of liquid samples from TBR for tailored ACs.

