Exploring the effects of heat treatment and demineralisation on the catalytic activity of activated carbon for wet air oxidation of phenol

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Introduction

Activated carbon (AC) is an inexpensive and highly porous material that has a tremendous diversity in its structure and properties. It has been widely used as adsorbent or catalyst support for different environmental and chemical applications. AC can be produced from various carbonaceous precursors (e.g.; wood, coal, coconut shells, petroleum coke) by using a stream of activating gas (steam or carbon dioxide) or a chemical agent such as phosphoric acid. Both physical (surface area, pore volume, and pore size distribution) and chemical (surface chemistry) characteristics of activated carbons are important in their performance for different applications. Surface area, pore size distribution, and surface chemistry of activated carbons depend on the type of precursor and the utilized activation process. A large number of research papers can be found that deal with the modification of activated carbons for different applications. For example, high temperature heat treatment under an inert atmosphere or hydrogen has been employed to remove the surface oxygen functionalities and enhance the adsorption of a synthetic organic compound (Trichloroethylene) or natural organic matter (NOM) on various types of activated carbons [1, 2].

In recent years carbon researchers have explored the new uses of activated carbons not only as catalyst supports but as the catalysts. A summary of the historical applications of AC as catalyst support/catalyst can be found in a recent review paper by Stüber et al. [3]. As explained in details in this review, one of the promising catalytic applications of activated carbons is for the Catalytic Wet Air Oxidation (CWAO) of phenol in the wastewater treatment. Stüber et al. [4] have achieved up to 99% of phenol removal in a slurry reactor, at 160 ºC and 0.7 MPa of oxygen partial pressure, whereas Fortuny et al. [5] obtained 68 % of phenol removal in a fixed bed reactor, at 140ºC and 0.9 MPa of oxygen partial pressure, operating as a trickle bed reactor (TBR), both using a commercial AC as catalyst. More recently, Suarez-Ojeda et al. [6] used continuous CWAO of some phenolic compounds (phenol, o-cresol, 2-chlorophenol and p-nitrophenol), in a TBR system, as a suitable pre-treatment process for the biological treatment of industrial wastewater using a commercial activated carbon.

Although it has been demonstrated that activated carbons can be promising materials for the CWAO of phenolic compounds, it is not yet known which specific physico-chemical properties are responsible for their catalytic activities. In other words, it is not clear how textural porosity and surface chemistry of AC can impact the phenol conversion or how activated carbons can be produced or modified to have optimal properties for a maximum phenol conversion with desired selectivity for minimizing the production of toxic intermediates. To address these fundamental issues, a systematic study is performing in our laboratories to particularly understand the importance of surface area and pore size distribution, mineral content (especially iron), and various surface functionalities including oxygen-, nitrogen-, and phosphorous-containing groups.
for the catalytic properties of activated carbons. A part of this on-going investigation is presented in this paper.

The goal of this work is to study the significance of: (1) surface oxygen functionalities, and (2) mineral content (more specifically iron) on the CWAO of phenol. A commercially available activated carbon has been subjected to a mild demineralisation to reduce the mineral content specifically iron, while minimizing changes in other physico-chemical properties. Heat treatment under nitrogen or hydrogen was employed to remove the surface functionalities particularly acidic oxygen-containing groups. Phenol removal by different modified carbons has been studied by conducting batch isotherms as well as CWAO experiments using a TBR system.

Experimental

Materials. A commercial coal-based activated carbon, obtained from Merck (Ref. # 2514) was used as starting material. Obtained carbon was crushed and the 25–50 mesh size was separated, then repeatedly washed with deionised water to remove all the fines, and finally oven-dried overnight at 105 ºC. The 25-50 mesh size, washed carbon is referred to as “ME” in this paper. High-purity (99.9 %) crystallized phenol was purchased from Panreac. Analytical grade HCl was bought from Scharlab. Air, hydrogen and nitrogen were supplied by Carburos Metálicos, with a purity of 99.995%. Modified carbons were prepared according to the experimental protocols described in the following sections.

Thermal treatments. Thermal modifications were performed using a quartz tube reactor placed inside a temperature-controlled oven. Temperature was controlled with an accuracy of ± 1ºC. For all heat treatments, 15 g of ME was placed in the quartz reactor. For heat treatment under either nitrogen or hydrogen, a 50cm³/min (under standard conditions) of the gas stream was used. For heat treatment under nitrogen, first the sample was heated with a heating rate of 20ºC/min from the room temperature to 100ºC, keeping the sample at this temperature for 10min. Then, the heating rate to reach the final treatment temperature was adjusted so the sample spent no more than 3 h inside the oven but at least 1.5 h at the maximum value of temperature. Three different temperatures were chosen to selectively remove different surface functional groups. After the treatment, modified ME was cooled under nitrogen atmosphere. Samples that were heat treated under nitrogen at 400 ºC, 700 ºC, and 900 ºC were identified as ME400, ME700 and ME900, respectively.

For heat treatment under hydrogen, first the sample was warmed up under nitrogen from room temperature to 90ºC with 10ºC/min rate, kept at this temperature for 15min, then heated to 900ºC with a heating rate of 20ºC/min. When 900ºC was reached, nitrogen was switched to hydrogen for 3 h. Finally the sample was cooled under nitrogen to the room temperature. ME carbon that was subjected to hydrogen treatment was labelled as “MEH”.

Demineralisation. ME sample was partially demineralised by using a HCl solution. One hundred grams of ME was placed in a glass flask containing 1 l of 1 N HCl and stirred for 24 h. Then the carbon was filtered, and the same washing procedure with the HCl solution was repeated. The acid-washed carbon was then extensively washed with deionised water and oven-dried overnight at 105ºC. This carbon was
labelled as “MED”. MED carbon that was further subjected to the heat treatment under hydrogen, according to the above protocol, was labelled as “MEDH”.

**CWAO experiments.** These experiments were carried out in a fixed bed reactor, operating in trickle flow regime to reduce polymerisation reactions, which are prevalent in slurry systems as previously demonstrated. The experimental set-up consisted of a 6 l stirred glass tank for the liquid feed solution, which was connected to a high precision metering pump (Eldex, Recipro HP Series model AA-100-S-2 CE) that could deliver up to 500 ml/h at a maximum pressure of 350 bar. This pump fed a trickle bed reactor which was a titanium tube (20 cm in length and 1.1 cm ID) filled with the activated carbon. A thermocouple was inserted axially into the reactor to measure the temperature inside the bed. The active carbon was retained by a stainless steel mesh at the bottom of the reactor. The reactor was placed in a temperature controlled air convection oven (± 1°C). The air used as oxidant in the reaction was supplied from a high pressure tank equipped with a pressure regulator. The gas and liquid streams were mixed and preheated before entering the reactor. There were two vessels to separate the outlet effluent, and a 2 ml tube for taking samples. A rotameter placed at the end of the line allowed measuring the air flow rate at the exit of the reactor. All the experiments were conducted for about 50 h. The air flow rate was held constant at 2.4 ml/s. The liquid space velocity was set to 8.2 h⁻¹ which is equivalent to a space time of 0.12 hr, according to the weight of the catalytic bed (~7 g). Phenol feed concentration was always 5 g/l. The experimental conditions were fixed at a temperature of 140°C and 2 bar of oxygen partial pressure, giving a total working pressure of 13.1 bar. Outlet liquid samples were periodically withdrawn and stored at ~4°C until they were analysed by HPLC (high pressure liquid chromatography). Also pH was measured for all samples.

**Adsorption isotherms.** Phenol adsorption isotherms were obtained at 20°C (± 2°C) in oxic conditions. Solutions with phenol concentrations ranging between 0.5 and 7.0 g/l were used to evaluate the adsorption capacity at high concentrations. In each case, 0.5 g of AC was allowed to equilibrate with 100 ml of phenol solution at different concentrations. They were stirred for 2 h, and left 0.5 h to let the AC to settle. The equilibrium time was determined based on the preliminary kinetics studies of selected samples. The final concentration of the samples was measured by HPLC.

**Characterization of activated carbons.** Selected physico-chemical characteristics of the virgin and modified ME carbons were determined according to the following methods.

**Surface area analysis.** Surface area and porosity of activated carbons were estimated from nitrogen isotherm at 77 K using a Micromeritics 2020ASAP instrument. Surface area was determined from BET equation, total pore volume from the near saturation uptake (at the relative pressure of 0.98), micropore volume from the Dubinin-Radushkevich equation, and volumes of meso plus macropores from subtracting the micropore volume from the total volume.

**pH of point of zero charge (pH_{pzc}).** Mass titration method was used to determine the point of zero charge of each sample. 5wt % carbon slurries in deionised water were prepared, then shaken for 24 h and the final pH of the slurry was measured and taken as the pH_{pzc}.

**Mineral content.** Samples were digested in concentrated nitric acid by a microwave digestion equipment. Diluted solutions were analyzed by Inductively
Coupled Plasma (ICP) atomic emission. No considerable amount of metals other than iron was detected.

**Boehm titration.** This method was used to determine the acidic surface functional group content of the samples. Solutions of NaHCO$_3$, Na$_2$CO$_3$ and NaOH (0.05 N) were prepared using DI water. 25 cm$^3$ of the base solution was added to 1 g of carbon in a 30 ml glass vial. Then, they were allowed to equilibrate for 1 day. At the end of the equilibration period, the carbon was separated from the solution, and the filtrate was titrated using standardized HCl solution. The number and type of acidic sites were calculated by considering that NaOH neutralizes carboxylic, lactonic and phenolic groups, Na$_2$CO$_3$ neutralizes carboxylic and lactonic groups, and that NaHCO$_3$ neutralizes only carboxylic groups. Carboxylic groups were therefore quantified by direct titration with NaHCO$_3$. The difference between the groups titrated with Na$_2$CO$_3$ and those titrated with NaHCO$_3$ was assumed to be lactones and the difference between the groups titrated with NaOH and those titrated with Na$_2$CO$_3$ was assumed to be phenols. Each determination was performed by duplicate.

**Results and Discussion**

**Characteristics of activated carbons.** Physical and chemical characteristics of activated carbons are tabulated in Tables 1 and 2, respectively. These results will be briefly discussed in the following paragraphs.

Surface area and pore volume values indicate that ME is a predominantly microporous carbon, having ~78% of its total pore volume in the micropore region. Overall, the heat treatment under the inert nitrogen atmosphere at different temperatures did not considerably change the textural properties of the materials. This is very important because in analyzing adsorption/reaction performance of these carbons only differences in their surface chemistry can be considered. For samples that were heat treated under hydrogen, an increase in the meso and macropore volume was observed while micropore volume and total surface area were not considerably changed. The increase in the meso and macropore volumes can be explained by the pore enlargement due to the gasification of the carbon surface by reacting with hydrogen. For demineralised carbon, a slight decrease in the meso and macropore volumes were observed while surface area and micropore volume appeared to be unchanged.

The objective of heat treatment under nitrogen at different temperatures was to remove different oxygen-containing surface groups and produce carbons with different surface chemistry. It has been reported that almost all of the oxygen surface functionalities can be decomposed at 900°C, while at 400°C mainly carboxylics can be removed, and at 700°C all of the oxygen functionalities except carbonyls and quinones expected to be separated from the activated carbon surface [7]. As evidenced by the increasing trend of pH$_{pzc}$ values, the carbon surface becomes more basic with increasing the heat treatment temperature, due to a higher removal of acidic oxygen-containing groups. This is also confirmed by the Boehm titration results that indicate an increasing trend in the reduction of strong (e.g., carboxylics), intermediate (e.g., lactones), and weak (e.g., phenolics) acidic groups (Table 2).

The goal of more severe heat treatment under hydrogen was to: (1) maximize the removal of all surface groups by using the reactive hydrogen atmosphere for a longer heat treatment period; and (2) stabilize the carbon surface for resistance to re-oxidation upon the exposure of the heat-treated carbon to the atmospheric air or during the TBR
experiments. It has been known that during the heat treatment under hydrogen atmosphere, hydrogen partially stabilizes the carbon surface by deactivation of the surface active sites (i.e., forming stable C-H bonds and/or gasification of unstable and reactive carbon atoms) found at the edges of the crystallites [8]. Very high pH\textsubscript{pzc} values of hydrogen treated carbons indicate the high basicity of the carbon surfaces due to almost complete removal of acidic oxygen functionalities. Boehm titration results show a complete removal of all strong and intermediate acidic groups and existence of only a small amount of weak phenolic groups on the surface of hydrogen treated carbons.

As previously mentioned, demineralization by HCl solution was used to significantly reduce the metal content of the ME. The iron content of ME carbon was ~0.3% and no considerable amount of other metals was found in the sample. Demineralization reduced the iron content to almost half of the original value, while a little change was observed in the overall surface acidity, as indicated from the pH\textsubscript{pzc} value.

Table 1. Physical characteristics of activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_A\text{BET} (m^2/g))</th>
<th>(V_{\text{mic}} (cm^3/g))</th>
<th>(V_{\text{tot}} (cm^3/g))</th>
<th>(V_{\text{mes+mac}} (cm^3/g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>1261</td>
<td>0.473</td>
<td>0.610</td>
<td>0.137</td>
</tr>
<tr>
<td>ME400</td>
<td>1225</td>
<td>0.487</td>
<td>0.623</td>
<td>0.136</td>
</tr>
<tr>
<td>ME700</td>
<td>1262</td>
<td>0.514</td>
<td>0.642</td>
<td>0.126</td>
</tr>
<tr>
<td>ME900</td>
<td>1185</td>
<td>0.468</td>
<td>0.599</td>
<td>0.131</td>
</tr>
<tr>
<td>MED</td>
<td>1272</td>
<td>0.484</td>
<td>0.592</td>
<td>0.108</td>
</tr>
<tr>
<td>MEH</td>
<td>1213</td>
<td>0.451</td>
<td>0.646</td>
<td>0.195</td>
</tr>
<tr>
<td>MEDH</td>
<td>1275</td>
<td>0.490</td>
<td>0.685</td>
<td>0.195</td>
</tr>
</tbody>
</table>

Table 2. Chemical characteristics of activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phenolics (meq/g)</th>
<th>Lactones (meq/g)</th>
<th>Carboxylics (meq/g)</th>
<th>Fe content (wt%)</th>
<th>pH\textsubscript{pzc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>0.097</td>
<td>0.123</td>
<td>0.031</td>
<td>0.30</td>
<td>7.36</td>
</tr>
<tr>
<td>ME400</td>
<td>0.031</td>
<td>0.220</td>
<td>0.018</td>
<td>a</td>
<td>7.44</td>
</tr>
<tr>
<td>ME700</td>
<td>0.039</td>
<td>0.092</td>
<td>0.008</td>
<td>a</td>
<td>7.70</td>
</tr>
<tr>
<td>ME900</td>
<td>0.011</td>
<td>0.039</td>
<td>0.005</td>
<td>a</td>
<td>8.10</td>
</tr>
<tr>
<td>MED</td>
<td>0.010</td>
<td>0.117</td>
<td>0.113</td>
<td>0.16</td>
<td>6.90</td>
</tr>
<tr>
<td>MEH</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>a</td>
<td>10.74</td>
</tr>
<tr>
<td>MEDH</td>
<td>0.061</td>
<td>0.000</td>
<td>0.000</td>
<td>b</td>
<td>10.33</td>
</tr>
</tbody>
</table>

Note: a- Iron content of heat treated carbons is about that of ME (i.e., 0.30%), b- Iron content of MEDH is about that of the MED (i.e., 0.16%).
**Adsorption isotherms.** Phenol adsorption isotherms of different activated carbons are shown in Figure 1. It should be noted that although the experiments were performed under oxic conditions but due to the short equilibrium time (~2 h) of experiments the phenol polymerization was not significant, as confirmed in earlier studies.

Overall, it is evident that heat treatment increases the phenol uptake. This is due to a reduction of surface acidic and polar groups. Surface polar and hydrophilic sites (including oxygen groups and metal species), particularly those located at the entrances to the carbon micropores, act as centers for formation of water clusters that hinder the access of the synthetic organic adsorbates to the adsorption sites [1]. Therefore, a reduction in the surface hydrophilicity expected to increase the adsorption of phenol.

There are two suggested mechanism for the phenol adsorption: (1) $\pi-\pi$ interaction between the aromatic rings of phenol and activated carbon surface; and (2) electron donor-acceptor complexation mechanism primarily between the electron pairs of oxygen from carbonyl groups (donor) and activated carbon aromatic rings (acceptor) [9]. Heat treatment results in the removal of the surface oxygen groups that partially withdraw $\pi$ electrons from the aromatic sheets of AC and therefore have deactivating effects. Therefore, it is expected that removal of oxygen groups enhance the $\pi-\pi$ interaction and consequently phenol uptake. Regarding the second mechanism, it is expected that samples treated at 900°C under nitrogen or hydrogen have a lower number of carbonyl groups, comparing to others, and therefore a lower contribution from the complexation mechanism.

Results show that demineralisation increased the phenol uptake probably due to a reduction in the overall surface polarity and hydrophilicity. As previously mentioned, the mineral content of the MED was almost half of ME, and the overall concentration of oxygen groups were similar. It is expected that further heat treatment of MED carbon enhance the phenol uptake due to an additional decrease in the surface polarity.
Catalytic performance of carbons in the TBR system. The results of CWAO of phenol in TBR system is shown in Figure 2. It appears that removal of phenol during the first ~10 h is primarily from the adsorption, while later phenol removal (after ~20 h) that reaches a steady level can be attributed to mostly catalytic oxidation.

Results indicate that heat treatment of ME at 900°C increases its phenol conversion. This may be explained by almost complete removal of surface acidic groups, that can hinder the adsorption of phenol on the carbon surface and consequently lower the phenol conversion on the carbon surface. Furthermore, MEH is slightly more effective than ME900 (heat treated under an inert atmosphere) for the phenol removal. The better performance of MEH, comparing to ME900, might be attributed to the more stable surface of hydrogen treated carbon (as previously discussed) that makes it more resistive to re-oxidation during the TBR operation. Catalytic oxidation of other heat treated carbons, appears to be similar to that of the original ME. This is probably due to insufficient removal of surface acidic groups during the heat treatment process and/or re-oxidation of carbons during the TBR operation.

Some reports in the literature can be found that stress on the important catalytic activities of carbonyl and quinone groups for the oxidation reaction, as can be exemplified by the oxidative dehydrogenation of ethylbenzene on activated carbons [10]. We have an on-going research to properly characterise these functionalities on the surface of heat treated carbons and investigate their impact on the CWAO of phenol. This subject will be addressed in future publications.

Figure 2 also shows that demineralisation causes a considerable reduction in the phenol conversion. It also indicates that further high temperature heat treatment of MED under hydrogen does not improve the performance of the activated carbon. An inspection of physico-chemical characteristics of the demineralised carbons (MED and MEDH) shows that they have a lower iron content and higher meso and macropore volumes, comparing to other carbons. Micropore volumes of all carbons are similar and slightly higher mesoporosity of demineralised carbons should not have any detrimental impact on the phenol conversion, since it would facilitate internal diffusion. Therefore it can be concluded that the lower conversion is caused by a lower iron content, which is expected due to the known catalytic activity of iron for various reactions [11]. Currently we have an on-going study to further understand the impact of the carbon mesoporosity as well as iron content on the CWAO of phenol.

Conclusions

Based on the results of this study high temperature heat treatment at 900°C can considerably increase both phenol adsorption in the batch experiments and phenol conversion in the CWAO performed using a TBR system. Heat treatment under hydrogen atmosphere appears to be more effective than treatment under an inert atmosphere for CWAO. This might be attributed to the stabilization effect of hydrogen treatments against re-oxidation during the operation.

A comparison of the CWAO results of ME carbon, before and after demineralisation, suggests that a higher iron content will result in a higher phenol conversion.
Figure 2. Phenol removal/conversion by different activated carbons in the TBR at 140°C, 2 bar of oxygen partial pressure and 0.12 h of spatial time.

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References