Kinetics of phenol oxidation in a trickle bed reactor over active carbon catalyst

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Abstract: The wet air oxidation of phenol over a commercial active carbon catalyst was studied in a trickle bed reactor (TBR) in the temperature and oxygen partial pressure ranges of 120–160 °C and 0.1–0.2 MPa, respectively. The performance of the active carbon was compared in terms of phenol and COD destruction. The weight change of active carbon due to reaction was also measured. Finally, oxic phenol adsorption isotherms were assessed in batch conditions at 25, 125 and 160 °C. In order to use the conversion data obtained from the TBR for a kinetic study, special care was taken to check the kinetic control in the TBR experiments. Several kinetic models including power law or Langmuir–Hinshelwood expressions were considered to describe the catalytic oxidation of phenol over active carbon. The simple power law model with first order dependence on both phenol and oxygen concentration predicted satisfactorily the experimental data not only over the entire range of operating conditions studied, but also outside its validity range.

Keywords: phenol; active carbon; catalytic wet air oxidation; trickle bed reactor; kinetics

INTRODUCTION

Phenol and substituted phenols are bio-toxic priority pollutants that are often contained in aqueous effluents from the petrochemical, chemical, pharmaceutical and coal industries. These effluents require specific chemical remediation prior to their discharge to conventional sewage plants. Wet air oxidation (WAO) at 120–320 °C and 2–20 MPa is a well-established, but relatively expensive, treatment for moderately concentrated, toxic and non-biodegradable organic wastewater.1 Incorporating a solid catalyst in WAO (becoming CWAO) can enhance treatment performance at even milder operating conditions, thus making process economics more attractive. Supported transition metal oxides or noble metals are mainly used as solid catalysts.2 The first generation of these catalysts has been found to deactivate during CWAO due to leaching of the active phase3,4 and/or carbonaceous surface deposits,5 thus being unsuitable for continuous CWAO.1 More recently, catalysts with improved stability for (phenol) CWAO, either based on noble metals6,7 or mixed oxides,8,9 have been developed. Novel pillared-clay catalysts have also received attention for the catalytic wet oxidation of phenol.10

On the other hand, active carbon (AC) as catalyst is a potential alternative given its low price and proven high oxidation activity for phenol and various substituted phenols.11,12 With this catalyst, leaching of the active phase is completely eliminated and deactivation by carbonaceous surface deposits can be substantially reduced when a trickle bed reactor (TBR)13 is used. AC, therefore, showed stable catalytic activity in a TBR during 10-day runs of phenol oxidation at 140 °C and 0.2 MPa of oxygen partial pressure.11

However, kinetic studies of phenol CWAO over AC are very scarce in the literature.1,13,14 Some oxidation tests have been carried out in batch reactors with its characteristically high liquid-to-solid (catalyst) ratio. In the case of phenol and phenolic compounds that exhibit a high polymerisation potential, fast catalyst deactivation occurred in batch oxidation. This was most likely due to the formation of condensation products in the liquid phase and their...
subsequent deposition on the AC surface.\textsuperscript{5,11} Fixed bed reactors (FBR), and particularly trickle bed reactors, providing a low liquid-to-solid ratio have therefore been adopted as a suitable solution.\textsuperscript{7,11–13} However, kinetics obtained in batch systems cannot be successfully used for TBR design and almost no information is available for the latter operation regime.

Hence, to properly design and operate industrial CWAO units, the kinetics and catalytic performance of AC need to be found in continuous reactor systems. In the present study, the CWAO of phenol over a commercial active carbon catalyst is thoroughly examined in a small-scale TBR at 120, 140 and 160 °C and low oxygen partial pressures of 0.1 and 0.2 MPa. The aims are both to determine the catalytic performance of AC in the TBR and test the ability of TBRs to develop reliable kinetics for phenol and COD degradation, and to furnish a kinetic model for phenol oxidation in TBR that matches the experimental results.

**EXPERIMENTAL**

**Materials**

Deionised water and analytical grade phenol (Aldrich, Barcelona, Spain) were used to prepare phenol solutions of 5 g dm\(^{-3}\) (53 mmol dm\(^{-3}\)). The gaseous oxidant was compressed high purity synthetic air (Ceburos Metalicos, Barcelona, Spain). Commercial Activated Carbon (2.5 mm pellets) was purchased from Merck (Barcelona, Spain, Ref 2514). This AC is manufactured from wood and possesses a low ash content of 3.75%. The nitrogen Brunauer–Emmett–Teller (BET) method (Micromeritics ASAP 2000, Norcross, GA, USA) gives a specific surface area of 990 m\(^2\) g\(^{-1}\), a pore volume of 0.55 cm\(^3\) g\(^{-1}\) and an average pore diameter of 1.4 nm. Phenol adsorption tests showed a maximum capacity of 370 mg\(_{\text{Ph}}\) g\(_{\text{AC}}\)^{-1}, at 20 °C in oxic conditions. The term ‘oxic’ means ‘in the presence of (dissolved) molecular oxygen and is commonly used in the context of adsorption and oxidative coupling of phenolic compounds. Prior to use, the AC pellets were crushed and sieved to obtain the 0.3–0.7 mm fraction. Each sample was washed, dried at 110 °C for 12 h and stored under an inert atmosphere at room temperature.

**Apparatus**

Most of the continuous oxidation experiments of phenol were conducted in a downflow TBR (SS-316, 20 cm long and 1.1 cm id) placed in a temperature-controlled oven (±1 °C). The liquid feed was stored in a 5 dm\(^3\) stirred glass tank, which was connected to a high-pressure metering pump (Eldex AA-100-S2, Napa, CA, USA). The air was delivered from a high-pressure cylinder equipped with a pressure regulator to adjust the operating pressure. A needle valve coupled with a flow meter enabled the gas flow rate to be set and measured. The liquid and gas streams were mixed and preheated in the oven before entering the catalytic bed. Typically, the reactor was loaded with 6.6 g of AC retained between two sintered metal disks. The exited effluent was directed to a gas–liquid separator for liquid sampling. In some experiments, the reactor inlet and outlet sections were inverted to feed the gas and liquid mixture in upflow mode. A detailed scheme of the experimental arrangement is available in the literature.\textsuperscript{15}

**CWAO experiments**

The oxidation tests were performed in downflow and upflow mode at three temperatures (120, 140, 160 °C) and two oxygen partial pressures (0.1, 0.2 MPa). The air flow rate was set at 2.4 cm\(^3\) s\(^{-1}\) (STP) to ensure 100–250% oxygen excess in the gas phase based on the stoichiometric demand for complete phenol oxidation. The liquid flow rates selected (10–150 cm\(^3\) h\(^{-1}\)) corresponded to space-times of 0.04–0.6 h. At a fixed liquid flow rate, the reactor was rapidly heated up to the reaction temperature while saturation of the AC bed with phenol and oxidation reactions required approximately 20 h to reach steady state. After changes of liquid space-time, the evolution of phenol concentration was monitored to detect the new steady state of reaction, which, depending on the liquid flow rate, was achieved within 2–4 h. The liquid phase composition was immediately analysed by taking three samples at steady state conditions of reactions. The experimental error in the measured phenol and COD concentrations was evaluated to be in the range of ±5%. After each experimental series of approximately 5 days, the AC was dried for 24 h at 400 °C under nitrogen flow and subsequently weighed to detect any irreversible change of carbon mass that may have occurred during the experiments.

Following the same experimental procedure, additional phenol oxidation tests were conducted at 160–170 °C and 2–3.4 bar of oxygen partial pressure but using a smaller reactor size (10 cm long and 0.61 cm id). The AC load was 0.7 g, which led to a substantial reduction in the total experimental run time. In these experiments, the inlet phenol concentration was also varied from 0.5 to 10 g dm\(^{-3}\).\textsuperscript{15}

**Phenol adsorption**

Phenol adsorption isotherms were assessed in a batch reactor (0.3 dm\(^3\)) at 20, 120 and 160 °C under oxic conditions. Solutions of 200 cm\(^3\) with a given phenol concentration and 1 g of finely powdered AC (\(d_p < 0.1\) mm) were first thoroughly contacted under mechanical stirring (250–500 rpm) at ambient temperature and pressure to reach adsorption equilibrium rapidly. The slurry AC–phenol solution was then heated and kept under stirring at 120 °C until the new adsorption equilibrium was achieved. In the last step, the temperature was further increased to obtain the AC adsorption capacity for phenol at 160 °C before cooling to ambient temperature. Overall, the experimental series lasted about 7–8 h during which time liquid samples were regularly...
withdrawn to monitor, via HPLC analysis, the evolution of phenol concentration in the liquid phase. By repeating experiments with different initial phenol concentrations (0.5–5 g dm\(^{-3}\)), phenol adsorption isotherms were determined for 20, 120 and 160 °C under oxic conditions.

**Analysis**

Liquid samples were analysed with an HPLC (Beckman System Gold, San Ramon, CA, USA) using a C\(_{18}\) reverse phase column (Spherisob ODS-2) to obtain the concentrations of phenol and intermediates. The separation was achieved with a mobile phase of variable composition programmed at a 1 cm\(^3\) min\(^{-1}\) flow rate starting from 100% deionised water and ending at a 40/60% mixture of methanol and deionised water. Intermediates were detected with UV absorbance at a wavelength of 210 nm during the first 20 min. The wavelength was then switched to 254 nm for phenol detection. Single compounds were identified by injecting pure samples of the expected partial oxidation products. Calibration curves were established for each intermediate using aqueous samples of known composition. A standard mixture of phenol and oxidation products was periodically tested to correct deviations in retention time or peak area due to possible variations in flow rates and column performance. The liquid stream was also analysed for the remaining COD according to the closed-type reflux colorimetric method using potassium dichromate as oxidant. Calibration was done with standard solutions of potassium hydrogen phthalate for chemical oxygen demand (COD) ranging from 200 to 1000 mg dm\(^{-3}\).

**RESULTS AND DISCUSSION**

**Phenol adsorption on active carbon**

The amount of phenol adsorbed on the activated carbon (AC), \(q_e\) (mgPh gAC\(^{-1}\)), was calculated according to:

\[
q_e = \frac{V_L}{m_{AC}}(C_{Ph,0} - C_{Ph}(t))
\]

where \(V_L\) is the initial liquid volume (dm\(^3\)), \(m_{AC}\) is the quantity of AC loaded (gAC), \(C_{Ph,0}\) and \(C_{Ph}(t)\) are respectively the initial and running phenol concentrations (mgPh dm\(^{-3}\)) measured during an experiment. The ratio \(V_L/m_{AC}\) was considered to be constant during the experiments, since the total quantity of liquid withdrawn never exceeded 5% of the liquid volume initially loaded.

Oxic phenol adsorption isotherms were established for different temperatures (Fig 1(a)) and compared with the adsorption isotherms obtained in a nitrogen atmosphere (Fig 1(b)) at otherwise the same operating conditions.\(^{16}\) The presence of oxygen in the system has a marked influence on the phenol adsorption capacity, \(q_e\), of the AC. Under anoxic conditions, \(q_e\) decreased with an increase in temperature (Fig 1(b)). In the presence of dissolved oxygen, firstly, phenol adsorption capacities measured were larger than those obtained in anoxic conditions, and secondly, oxic phenol adsorption capacities at 160 °C were even slightly greater than those at 120 °C (Fig 1(a)). The most reliable explanation for these trends is the contribution of irreversible adsorption to the overall adsorption capacities. Basic surface groups of ACs can promote coupling reactions between phenol molecules to form dimers and higher size oligomers, which then strongly (chemically) adsorb on the AC.\(^{17}\) Both higher temperatures and oxygen partial pressures were found to enhance the rate of oxidative coupling.\(^{18}\) Therefore, if reversible adsorption on AC was the main mechanism for phenol adsorption under anoxic conditions, irreversible adsorption should become important at oxic conditions and account for approximately one-third (at 25 °C) to one-half (at 160 °C) of the total phenol adsorption capacity measured.

The apparent enhancement of phenol adsorption observed in an air atmosphere could also be attributed to the simultaneous oxidation of phenol over AC towards ring intermediates and carboxylic acids. However, only during adsorption at 160 °C did HPLC analysis of liquid samples detect two additional peaks with a very low area (see Fig 2). These peaks were not identified, but the retention time of the first peak (2.1 min) lay within the range of carboxylic

![Figure 1. Phenol adsorption isotherms for active carbon under (a) oxic (air) conditions and (b) anoxic (nitrogen) conditions.\(^{16}\)](image)
the carbon surface was even more complex because at the same time the AC itself was oxidised through direct oxygen attack.\textsuperscript{11} The smaller weight increase obtained at 0.2 MPa of oxygen partial pressure thus suggests that AC combustion is more sensitive than oxidative coupling to higher oxygen surface concentrations. Moreover, a related TBR study\textsuperscript{11} using the same AC reported an initial increase of 20\% in AC weight at 140 °C and 0.9 MPa of oxygen partial pressure. The AC weight (as well as phenol conversion) then decreased continuously with run time, leading to a 33\% loss in the initial weight after 10 days (Table 1). Along with the AC weight change, a progressive reduction of the initial AC surface area of about 63\% took place in the same run (Table 1). This was most probably due to pore blockage and destruction of the microporous carbon matrix.

It can be concluded that the CWAO of phenol over AC in a TBR is accompanied by the slowly developing phenomena of irreversible adsorption, partial AC combustion and changes in carbon surface properties that all play a role in the catalytic long-term performance of the active carbon. The same temporal evolution (in 3-day experiments) of conversion, AC weight and surface area was also observed during the gas phase oxydehydrogenation of ethylbenzene over AC.\textsuperscript{19} The detailed characterisation of the activated carbon suggested the formation of a surface coke layer that completely blocked the micropores of the ACs used. Elemental analysis of the carbon samples indicated a temporal change in elemental composition, i.e. a slow decrease in carbon content with a corresponding increase in oxygen and hydrogen at higher run times. Because of this composition change, the rate of gasification became progressively dominant, since the new oxygen surface groups formed were shown to be effective only in the gasification of coke but not in its formation. As for the CWAO of phenol, lower oxygen pressure and temperature delayed, but did not completely avoid, both the consumption of AC and the shift of ‘CWAO active’ surface groups to non-reactive groups.

**Catalytic performance of active carbon in TBR**

The phenol and COD conversion space-time profiles obtained at 120, 140 and 160 °C are given in Fig 3 for oxygen partial pressures of 0.1 and 0.2 MPa. Both phenol and COD destruction improved as temperature, pressure and liquid space-time increased. At low conversion of phenol, mineralisation of reacted phenol to CO\textsubscript{2} and H\textsubscript{2}O was almost complete, while the difference between phenol and COD conversion became larger as the phenol conversion increased. At 160 °C and 0.2 MPa, phenol and COD destruction beyond 99\% and 85\%, respectively, were accomplished for space-times greater than 0.4 h. The main intermediates detected were 4-hydroxybenzoic acid, benzoquinone, maleic, formic and acetic acids as well as traces of hydroquinone and oxalic acid. The AC catalyst exhibited accumulation of refractory

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**Table 1. Change of AC weight (DW\textsubscript{AC}) and AC surface area (DS\textsubscript{A})**

<table>
<thead>
<tr>
<th>P\textsubscript{O\textsubscript{2}} (MPa)</th>
<th>T (°C)</th>
<th>W\textsubscript{AC} (%)</th>
<th>S\textsubscript{A} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1\textsuperscript{a}</td>
<td>120–160</td>
<td>+33</td>
<td>−</td>
</tr>
<tr>
<td>0.2\textsuperscript{a}</td>
<td>120–160</td>
<td>+13</td>
<td>−</td>
</tr>
<tr>
<td>0.9\textsuperscript{a}</td>
<td>140</td>
<td>−33</td>
<td>−63</td>
</tr>
</tbody>
</table>

\textsuperscript{a} After 5 days on stream (this work).  

\textsuperscript{b} After 10 days on stream.\textsuperscript{11}
acetic acid, which accounts for the 15% of liquid phase COD remaining at the highest phenol conversions. The accumulation of acetic acid is not critical from an environmental point of view since it is easily biodegradable. However, it can cause pH values as low as 3, thus requiring reactor materials and catalysts that withstand the hot and corrosive reaction medium.

Compared with recently developed catalysts, the used active carbon displayed comparable or even better catalytic performance in phenol CWAO at 160°C and a significantly lower oxygen partial pressure of 0.2 MPa. For example, a composite black carbon tested at 160°C in a TBR yielded a similar performance, though this was achieved for a one order of magnitude higher space-time (2 h) and oxygen partial pressure (1.5 MPa). A 6% combustion of the composite was observed after 8 h of use, while our AC showed a stable activity over 10 days at milder conditions of 140°C and 0.2 MPa of oxygen partial pressure that was only surpassed by the Cu/Ni/Al-hydrotalcite catalyst. For supported catalysts, some deactivation is generally reported after a few hours of use and, in the case of copper-based catalysts, important leaching of the active phase cannot be avoided. Finally, it should be pointed out that in many studies, no attempt was made to monitor catalytic (long-term) stability.

**Kinetics of phenol CWAO over active carbon in TBR**

As outlined in the Introduction, because of the importance of oxidative coupling reactions, which mask the actual phenol oxidation, it does not seem appropriate to use batch reactors for kinetic studies of phenol CWAO. Integral fixed bed reactors with a high solid-to-liquid ratio can overcome this drawback of the batch reactor provided that kinetic reaction control is carefully verified in the range of operating conditions applied. CWAO of organic pollutants is generally characterised by low reactant concentrations (organic dilution, low oxygen solubility) that lead to low intrinsic reaction rates, which are helpful for achieving kinetic control in integral TBRs. However, the verification of kinetic regime must address the influence on reactor performance of gas–liquid hydrodynamics (partial catalyst wetting, liquid maldistribution at low liquid flow rates) and mass transfer between phases.

**Determination of kinetic regime in TBR**

Gas–liquid hydrodynamic and mass transfer parameters were evaluated from appropriate high-pressure literature correlations. Under the operating conditions tested, it was shown with the help of three-phase reactor flow maps that the TBR always operated in the trickle regime. Despite the large excess of oxygen in the gas phase, only the possibility of oxygen mass transfer limitation was considered, since the oxygen concentration in the liquid phase ranged from 0.9 to 1.8 mmol dm⁻³, which was 25–50 times smaller than the inlet phenol concentration of 53 mmol dm⁻³. The high values calculated from the γ reactant flux ratio (eqn (2)) of 17 and 34 further confirmed the condition of oxygen as the limiting reactant in our operating conditions:

\[
γ = \frac{D_{\text{eff}}^{\text{Ph},L} C_{\text{Ph},L}}{D_{\text{eff}}^{\text{O}_2,L} C_{\text{O}_2,L}}
\]  

where \(C_{\text{Ph},L}\) and \(C_{\text{O}_2,L}\) are the liquid phase concentrations of phenol and oxygen respectively, \(D_{\text{eff}}\) is the effective liquid diffusivity and \(v\) is the stochiometric coefficient of oxygen for complete phenol mineralisation. The extent of external and internal diffusion limitation was estimated at the highest temperature of 160°C through the common diagnostic criteria \(\alpha_{gl}\), \(\alpha_{ls}\) and Weisz–Prater \(\phi\). These quantities are defined as:

\[
\alpha_{gl} = \frac{r_{\text{o}_2} b \rho_b}{k_{\text{gl}} a C_{\text{Ph}} e} \leq 0.05–0.1
\]

\[
\alpha_{ls} = \frac{r_{\text{o}_2} b \rho_b}{k_{\text{ls}} a C_{\text{Ph}} e} \leq 0.05–0.1
\]

\[
\phi = \frac{r_{\text{o}_2} b \rho_b Q_f^2}{36 D_{\text{eff}}^{\text{O}_2}} \ll 2/(n + 1)
\]
Table 2. Performance of catalysts recently developed for CWAO of phenol

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor type</th>
<th>Operating conditions</th>
<th>$X$ (%)</th>
<th>$X_{\text{TOC}}$ (%)</th>
<th>Catalyst stability</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Ni/Al-hydrotalcite</td>
<td>Slurry</td>
<td>5 g dm$^{-3}$ Phenol 423 K, 0.9 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>$&gt;$99</td>
<td>Stable at 413K, 0.9 MPa in TBR</td>
<td>8</td>
</tr>
<tr>
<td>Active carbon</td>
<td>Trickle bed</td>
<td>5 g dm$^{-3}$ Phenol 433 K, 0.2 MPa O$_2$</td>
<td>$&gt;$75</td>
<td>$&gt;$67</td>
<td>runs over 15 days on stream</td>
<td>11</td>
</tr>
<tr>
<td>Pt/CBC</td>
<td>Trickle bed reactor</td>
<td>5 g dm$^{-3}$ Phenol 433 K, 1.5 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>$&gt;$90</td>
<td>Stable at 413K and 0.2 MPa for 10 days on stream</td>
<td>20</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>Semibatch-slurry</td>
<td>5 g dm$^{-3}$ Phenol 453 K, 1.5 MPa O$_2$</td>
<td>$&gt;$95</td>
<td>$&gt;$75</td>
<td>Authors state deactivation, but do not quantify it</td>
<td>21</td>
</tr>
<tr>
<td>CuO/C</td>
<td>Spinning basket</td>
<td>2.4 g dm$^{-3}$ Phenol 453 K, 3.6 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>$&gt;$70</td>
<td>Deactivation after six runs: 60% of copper leaching, X drops from 99% to 80%</td>
<td>4</td>
</tr>
<tr>
<td>Ru–CeO$_2$/C</td>
<td>Slurry</td>
<td>2.2 g dm$^{-3}$ Phenol 433 K, 2.0 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>57</td>
<td>Deactivation of catalyst was not tested</td>
<td>22</td>
</tr>
<tr>
<td>K–Mn–Ce–O</td>
<td>Slurry</td>
<td>1 g dm$^{-3}$ Phenol 383 K, 0.5 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>$&gt;$99</td>
<td>$-$2% after three consecutive runs (1 h of total run time)</td>
<td>9</td>
</tr>
<tr>
<td>Pt/TiO$_2$</td>
<td>Slurry</td>
<td>1.1 g dm$^{-3}$ Phenol 473 K, 0.8 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>$&gt;$95</td>
<td>Deactivation in TBR: X drops from 80 to 60% after 140 g of phenol passed</td>
<td>7</td>
</tr>
<tr>
<td>CuO/MCM-41</td>
<td>Slurry</td>
<td>1.3 g dm$^{-3}$ Phenol 473 K, 3.4 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>$&gt;$90</td>
<td>Deactivation of catalyst was not tested, important Cu leaching was observed</td>
<td>23</td>
</tr>
<tr>
<td>CuO–CeO$_2$</td>
<td>Semibatch-slurry</td>
<td>1 g dm$^{-3}$ Phenol 432 K, 0.73 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>$&gt;$90</td>
<td>Deactivation of catalyst was not tested, but Cu leaching was observed</td>
<td>24</td>
</tr>
<tr>
<td>CuO–2(CuO)–Cr$_2$O$_3$</td>
<td>Fixed bed</td>
<td>1.2 g dm$^{-3}$ Phenol 433 K, 1.6 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>$&gt;$70</td>
<td>No deactivation reported, but 10% Cu leaching after 160 h of operation</td>
<td>25</td>
</tr>
<tr>
<td>Al–Fe pillared clay</td>
<td>Batch-basket</td>
<td>0.5 g dm$^{-3}$ Phenol 423 K, 0.2 MPa O$_2$</td>
<td>$&gt;$99</td>
<td>—</td>
<td>Deactivation was not tested</td>
<td>10</td>
</tr>
</tbody>
</table>

From the previous calculations, it can be deduced that oxygen should be uniformly available at its solubility value both over the external liquid–solid surface and within the liquid-filled pore. However, the external liquid hold-up takes small values in our TBR of around 0.1 and the catalyst wetting efficiency is estimated to be between 0.25 and 0.5 for the liquid flow rates used. This means that a large section of the external particle surface is either covered only by an extremely thin liquid layer or is directly exposed to the gas phase. Since gas–solid mass transfer is generally one order of magnitude higher than that at the liquid–solid interface, the pores that connect to the ‘dry’ particle surface are also always saturated with oxygen. Also, considering that the external ‘dry’ catalyst surface not available for the reaction is much smaller compared with the internally wetted

Table 3. Estimation of oxygen mass transfer limitation and partial catalyst wetting for phenol CWAO over active carbon ($T = 160^\circ$C, $C_{\text{Ph,ref}} = 5$ g dm$^{-3}$)

<table>
<thead>
<tr>
<th>$P_{O_2}$ (bar)</th>
<th>$C_{O_2}^c$ (mm)</th>
<th>$k_{sp}a_0$ (s$^{-1}$)</th>
<th>$k_{sp}a_0$ (s$^{-1}$)</th>
<th>$a_{gl}$</th>
<th>$a_{ls}$</th>
<th>$\phi_{WP}$</th>
<th>$f_{w,c}$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>1.2</td>
<td>0.5–3</td>
<td>0.15</td>
<td>0.05–0.3</td>
<td>0.19</td>
<td>0.25–0.5</td>
<td>34</td>
</tr>
<tr>
<td>0.2</td>
<td>1.8</td>
<td>1.0</td>
<td>0.5–3</td>
<td>0.13</td>
<td>0.05–0.3</td>
<td>0.38</td>
<td>0.25–0.5</td>
<td>17</td>
</tr>
</tbody>
</table>

$a$ from Ref 27; $b$ from Refs 28, 29; $c$ Wetting efficiency ($f_w$) from Refs 27, 30.

$r_{O_2}^{obs}$ was graphically obtained from experimental concentration–space–time profiles at $\tau = 0$ h for 160 $^\circ$C and 0.1–0.2 MPa of O$_2$. $\rho_b$ is the bed density, $C_{O_2}^c$ is the equilibrium concentration of oxygen in the liquid phase, $k_{sp}a_0$, is the gas–liquid volumetric mass transfer coefficient, $k_{sp}$ is the liquid–solid oxygen mass transfer coefficient, $a_0$ is the specific packing area, $d_p$ (0.5 mm) is the particle diameter and $n$ (1) is the reaction order with respect to oxygen. The resulting criteria values given in Table 3 are close to the respective limits established for the absence of a mass transfer contribution to the overall reaction rate. Additional support provided with the results of batch phenol oxidation tests over the same AC using different particle sizes. The results showed that pore diffusion only became significant for catalyst particles over 0.5 mm.13

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Pore surface area, partial wetting in downflow mode should positively affect the catalyst’s performance. This trend is clearly shown in Fig 4, which compares the reactor’s performance of phenol oxidation over AC for both fully wetted upflow mode and partially wetted downflow mode at 0.2 MPa of oxygen partial pressure and reactor temperatures of 120 and 160 °C. The downflow mode yields substantially lower phenol outlet concentrations (ie higher phenol conversions) in all conditions tested. The fully wetted upflow mode is therefore limited to a certain extent by the presence of gas–liquid mass transfer limitations of oxygen and should not be used to obtain kinetic data. For example, due to mass transfer limitations in upflow mode a 20% lower activation energy for phenol oxidation would result.

Another concern is axial dispersion and liquid maldistribution (channelling, wall flow) that can negatively influence the reactor conversion. Such effects were greatly reduced by the correct choice of particle and reactor geometry (\(L_R = 20 \text{ cm}, D_R = 1.1 \text{ cm} \) and \(d_P = 0.5 \text{ mm}\)). The relevant criteria of \(L_R/d_P\) and \(D_R/d_P\) take values of 400 and 20, respectively, which match the critical value of 20 established for safe operation. The calculated axial dispersion coefficient\(^{11}\) therefore has a very small value in the order of \(10^{-6} - 10^{-7} \text{ m}^2 \text{ s}^{-1}\), which ensures the absence of axial dispersion in our study. Finally, in our study no decrease was observed in experimental phenol conversion due to possible liquid maldistribution at the lowest liquid flow rates, as reported by Tukac and Hanika.\(^{12}\)

In conclusion, the comparison of our experimental reaction rates with mass transfer rates calculated from literature correlations clearly suggests that phenol oxidation was kinetically controlled in the TBR used for this study. Moreover, as the limiting reactant is in the gas phase, the low and varying catalyst wetting prevailing in this flow regime positively affected the reactor performance. Hence, our TBR is suitable for providing reliable data for the kinetic study of phenol CWAO. As shown in the following sections, the Arrhenius behaviour of reaction rate and the successful application of the kinetics outside its validity range further confirmed the reaction control during the experiments in the TBR.

**Effect of operating conditions**

**Inlet phenol concentration.** The effect of the inlet phenol concentration was investigated in the range of 0.5–10 g dm\(^{-3}\) at 170 °C and 0.34 MPa of oxygen partial pressure using the small reactor apparatus (0.7 g of AC). The raw conversion data were further analysed to obtain an apparent kinetic rate constant by assuming first order of reaction with respect to phenol concentration and ideal plug flow in the reactor:

\[
k_{app} = -\frac{1}{\tau} \ln(1 - X_{Ph})
\]

where \(k_{app}\) (gL gAC\(^{-1}\) h\(^{-1}\)) is the apparent kinetic rate constant, \(\tau\) (h) is the liquid space-time and \(X_{Ph}\) is the measured phenol conversion.

If the first order assumption was valid, the values of \(k_{app}\) should be independent of inlet phenol concentrations, ie the same \(k_{app}\) should result for all conversions obtained (at different inlet phenol concentrations). The calculated apparent rate constants plotted in Fig 5 show a certain scattering (13.2–19.3 gL gAC\(^{-1}\) h\(^{-1}\)). A linear regression analysis yields an almost parallel line to the inlet phenol concentration axis with a mean value of 15.8 gL gAC\(^{-1}\) h\(^{-1}\) and a regression coefficient close to 0 (\(R^2 = 0.0012\)). This means that \(k_{app}\) is not correlated to the inlet phenol concentration.

The phenol conversion data are therefore in line with the postulated first order of reaction with respect to the inlet phenol concentration. This result may also suggest that the phenol concentration at the catalyst surface is directly proportional to its bulk liquid concentration. However, phenol isotherms measured for the same activated carbon at oxic conditions (see Fig 1(a)) showed almost constant phenol adsorption capacity for equilibrium liquid phenol concentrations.

**Figure 5.** Calculated apparent kinetic rate constant obtained at different phenol inlet concentrations using the small TBR: 0.7 gAC, 170 °C, 0.34 MPa of O\(_2\).
higher than 2 g dm\(^{-3}\). The phenol destruction over AC seems to follow a more complex reaction mechanism during CWAO involving a limiting step, which depends linearly on the phenol concentration in the liquid phase. A possible explanation for this may be the (proven) formation of free oxygenated radicals on the carbon surface that can attack both adsorbed and dissolved phenol molecules in the liquid phase close to the surface. Nevertheless, the surface characterisation of the active carbon used in this study showed the presence of different oxygenated surface groups. It could be also possible that oxidation and adsorption of phenol involves distinct surface groups.

**Oxygen partial pressure.** Only a small pressure range of 0.1–0.2 MPa has been considered in the study due to the accelerating effect of higher partial oxygen pressure on the AC combustion rate. Within this narrow interval and for all reaction temperatures studied, the TBR reaction rates approximated graphically at zero space-time exhibit clear first order behaviour with respect to oxygen partial pressure. For metal- or metal oxide-supported catalysts, a 0.5 order is generally obtained in CWAO \(^{10,11}\) and mechanistically interpreted as dissociated adsorption of oxygen on the active sites. For the AC catalyst and kinetic control in the TBR oxidation experiments, the first order dependence on oxygen pressure should indicate a different mechanism in which the oxygen molecule adsorbs and attacks the phenol molecule without previously undergoing dissociation.

**Reaction temperature.** As shown before in Fig 4, the performance of the AC catalyst in terms of phenol and COD conversion is seen to strongly depend on the reaction temperature. To determine the activation energy \(E_A\) of phenol oxidation, an Arrhenius plot (Fig 6) was constructed using the TBR conversion data for 0.1 and 0.2 MPa. Linear regression analysis of the data at the two pressures showed very close \(E_A\) values of 82.2 kJ mol\(^{-1}\) and 82.3 kJ mol\(^{-1}\) with regression coefficients of 0.995 and 0.9997, respectively. The \(E_A\) values are comparable to those in the literature for kinetically controlled phenol oxidation over metal oxide-supported catalysts (84–85 kJ mol\(^{-1}\) for CuO/Al\(_2\)O\(_3\) \(^{32}\) and CuO–ZnO/Al\(_2\)O\(_3\) \(^{13}\) 65 kJ mol\(^{-1}\) for MnO\(_2\)/CeO\(_2\) \(^{5}\)). We can therefore conclude that the oxidation of phenol in the TBR used proceeded in the kinetically controlled regime.

**Reaction kinetics**

Conversion of phenol and COD is a key aspect in wastewater treatment and knowledge of the rate law is mandatory for scale-up and process development studies. At the given operating conditions, our TBR operates in a kinetic regime. Although AC combustion and oxidative coupling accompany the oxidation of phenol, these reactions develop only over a large time scale and should not mask the fast reaction kinetics of phenol oxidation. In this situation, a kinetic analysis of the phenol and COD conversion data can be made assuming ideal plug flow and kinetic regime in the TBR. The resulting differential mass balance (eqn (7)), with a suitable kinetic model, was then solved to calculate the phenol and COD outlet concentrations:

\[
\frac{dC_i}{d\tau} = \rho_l r_i
\]

where \(C_i\) is the phenol or COD concentration (in mmol dm\(^{-3}\) or mg dm\(^{-3}\)), \(\tau\) is the space-time (h), \(\rho_l\) is the liquid density (kg dm\(^{-3}\)) and \(r_i\) is the respective reaction rate.

The kinetic model should be as simple as possible, but matching the physical mechanism and experimental observations. From the previous results, it can be deduced that a simple power law (eqn 8) with first orders for phenol and oxygen concentration should provide a reasonable fit of the data:

\[
r_i = k_{0i} \exp(-E_i/RT) \tau_{0i}^{\alpha} C_i
\]

where \(k_{0i}\) is the respective frequency factor (dm\(^3\) kg\(^{-1}\) h\(^{-1}\)), \(E_i\) is the respective activation energy (J mol\(^{-1}\)), \(R\) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \(x_{o2}\) is the dissolved molecular oxygen mole fraction and \(\alpha\) is the reaction order with respect to the oxygen concentration. The reaction orders of phenol and COD were fixed at 1, while \(\alpha\) was left free for optimisation to confirm the experimentally observed first order behaviour. Accurate values of \(x_{o2}\) were calculated at each temperature and pressure using Henry’s Law and coefficients given by Himmelblau. \(^{34}\) All \(x_{o2}\) values were taken to be constant throughout the reactor, since the highest oxygen consumption was below 5% of the available amount of oxygen in the gas phase. Also, changes of phenol concentration due to the temperature effect on liquid density and vaporisation pressure were accounted for in the model calculations.
More complex kinetic equations (Langmuir–Hinshelwood–Hougen–Watson, LHHW) including adsorption and desorption phenomena are also frequently proposed for CWAO. For phenol destruction, we tested thus the commonly used models, based on single or dual site mechanisms for the surface reaction as well as dissociated, non-dissociated or no oxygen adsorption. All the models predicted the experimental data indiscriminately well, so only the simplest law, which includes single site mechanism and no oxygen adsorption, is presented (eqn (9)):

\[
\frac{r_{Ph}}{K_0 \exp(-\Delta H/RT)C_{Ph}} = k_0 \exp(-E_a/RT)x_{O2}
\]

where \(k_0\) is the frequency factor for the surface reaction rate, \(K_0\) is the adsorption pre-exponential factor and \(\Delta H\) is the enthalpy of adsorption for phenol, respectively.

The unknown model parameters of eqns (8) and (9) were optimised by a nonlinear regression technique. Equation (7) was numerically solved with a fourth order Runge–Kutta method to calculate the outlet phenol and COD concentrations. The objective function (sum of relative squares) was then minimised using a Simulated Annealing Algorithm to find the parameter values that best fit the experimental phenol and COD profiles. The initial estimated values for the involved kinetic parameters were taken from previous results or in the case of the adsorption parameters from the literature.

The good quality of the fit obtained by the power law model is also illustrated in Fig 3 for all temperatures and pressures studied. On average, the predicted phenol conversion (solid lines) deviated from the experimental phenol conversions by only 4%. The best parameter match is shown in Table 4 with a 95% confidence interval. The activation energy for phenol destruction over AC was 69.3 (±0.4) kJ mol\(^{-1}\). This was about 15% lower than the initial estimated value graphically obtained from an Arrhenius plot and reaction rates approximated at zero space-times. On average, the predicted results or in the case of the adsorption parameters from the literature.

In a last step, the power law model was tested against experimental conversion data obtained in two more CWAO experiments under operating conditions outside the validity range of the model (small TBR, 160–170°C and 0.2–0.34 MPa). Figure 7 illustrates the resulting parity plot that compares the experimental data points with those calculated from the power law model. The kinetic model adequately estimates phenol conversion as long as conversion is below 60–70%. For higher conversions that are achieved by lowering the liquid flow rate, the model clearly overpredicts the experimental conversion. This deviation from a kinetic regime may be related to the negative effect of liquid maldistribution reinforced by the smaller reactor configuration.

Overall, the power law model developed for the phenol CWAO over active carbon is proven to accurately calculate phenol and COD conversion,
The catalytic performance of a commercial active carbon and its reaction kinetics were assessed for the CWAO of phenol in a TBR operated under mild conditions of temperature and oxygen partial pressure. A temperature of 160 °C, 0.2 MPa of O₂ and space-times of 0.4 h resulted in phenol and COD destructions above 99% and 85%, respectively. The model, when tested against data obtained from a smaller TBR at higher temperature and oxygen partial pressure, also correctly reproduced the experimental phenol conversion as long as kinetic control of reaction is provided in the smaller TBR. The reliability of the kinetic model developed in this work will make it a useful tool for the scale-up and modelling of TBRs applied to CWAO technology.

**CONCLUSIONS**

The catalytic performance of a commercial active carbon and its reaction kinetics were assessed for the CWAO of phenol in a TBR operated under mild conditions of temperature and oxygen partial pressure. A temperature of 160 °C, 0.2 MPa of O₂ and space-times of 0.4 h resulted in phenol and COD destructions above 99% and 85%, respectively. The remaining 15% of COD was refractory acetic acid. The main intermediates detected were 4-hydrobenzoic acid, benzoquinone, maleic, formic and acetic acids as well as trace amounts of hydroquinone and oxalic acid. The active carbon showed a similar or even better catalytic performance at lower pressures and space-times than most of the noble metal or transition metal oxide-based catalysts recently developed for the CWAO of phenol.

The evaluation of the common multiphase reactor diagnostic criteria confirmed that in the operating conditions studied, the CWAO of phenol in the TBR is controlled by the chemical reaction. The results of the active carbon weight change due to reaction and the oxic adsorption isotherms of phenol on active carbon indicate that the CWAO of phenol in the TBR is accompanied by slowly developing reactions of AC combustion and oxidative coupling. Although the adsorption of phenol on the active carbon was seen to take place, kinetic analysis showed that both the simple power law model and more mechanistic Langmuir–Hinshelwood models can accurately predict the entire experimental results. For the power law model, activation energy was 69.3 kJ mol⁻¹ for phenol destruction with a first order dependence of the reaction rate on phenol and oxygen concentration. The model, when tested against data obtained from a smaller TBR at higher temperature and oxygen partial pressure, also correctly reproduced the experimental phenol conversion as long as kinetic control of reaction is provided in the smaller TBR. The reliability of the kinetic model developed in this work will make it a useful tool for the scale-up and modelling of TBRs applied to CWAO technology.

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