Catalytic wet air oxidation of phenol over active carbon catalyst
Global kinetic modelling using simulated annealing

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Received 23 February 2006; received in revised form 5 April 2006; accepted 8 April 2006
Available online 18 May 2006

Abstract

The catalytic wet air oxidation of phenol has been studied in an integral trickle bed reactor using active carbon as catalyst. Temperature, oxygen partial pressure and liquid space time have been varied from 120 to 160 °C, 1–2 bar and 0.05–0.55 kgcat kgL −1 h, respectively. The active carbon catalyst employed is stable and performs phenol and COD conversions over 99% and 85% with a low residual content of bio-toxic aromatic compounds. The distribution of the main intermediates has been quantitatively assessed by means of HPLC analysis to develop a global kinetic model for the phenol oxidation over active carbon. Several rate models and reaction pathways have been tested in the kinetic modelling. The involved model parameters have been optimised with the stochastical simulated annealing algorithm leading to a very satisfactory fit of the whole experimental data. On cost of a higher, but still reasonable, computational time demand, this easy to implement algorithm proves to be a robust alternative to the classical gradient-based Levenberg–Marquardt algorithm for multi-parameter identification.

Keywords: Phenol; Active carbon; Catalytic wet air oxidation; Trickle bed reactor; Reaction pathway; Kinetics; Simulated annealing

1. Introduction

Over the last decade, it has been shown that some active carbons alone can act as efficient catalysts in catalytic wet air oxidation (CWAO) of non-biodegradable pollutants, such as phenol and phenolic compounds [1–4]. Compared to most of the recently developed noble metal or metal oxide based catalysts, a commercial AC (Merck) tested in a laboratory trickle bed reactor (TBR) has demonstrated a similar or even better [5] and stable [6] activity for the CWAO of phenol. CWAO of bio-toxic pollutants over AC becomes especially attractive for sequential adsorption–oxidation cycles [7] or biological end-treatments [8]. These combined processes generally perform a superior cleaning effectiveness compared to single step oxidation and avoid the need of complete organic pollutant mineralisation in the CWAO step. However, the knowledge of the intermediate distribution and its related biodegradability, which can be obtained from respirometry tests [9] or ISO-standard No. 9888, is of relevance for the correct set-up of such combined chemical–biological treatment.

Because of the importance of CWAO and AC for the remediation of bio-toxic pollutants, the assessment of reliable kinetics (including intermediates) is required for the proper design, scale up and operation of CWAO units. Batch oxidation studies of phenol over AC are very scarce [10,11] and only phenol degradation has been considered. In case of phenolic compounds that show a high polymerisation potential, liquid phase condensation reactions become important and fast deactivation of catalysts has been observed in batch oxidation [11,12], most likely due to the irreversible deposition of condensation products on the catalyst surface. Alternatively, a liquid full fixed-bed reactor with oxygen pre-saturated liquid feed [13] has been operated at conversions smaller than 10% to avoid oxygen depletion. For phenol conversions of this magnitude, the progress of intermediate oxidation, however, cannot be satisfactorily monitored. To overcome this drawback, phenol oxidation over AC has been studied in an integral fixed-bed reactor under reaction control and stable catalyst activity...
phenol oxidation over AC [4,5] or Fe/AC [15] has been studied. The main difficulty in complex reaction systems is to obtain with confidence the numerous kinetic parameters involved. Usually, gradient-based methods are employed in non-linear parameter identification. These methods are very sensitive to starting values and frequently converge to local minima or fail to reach convergence, if only a poor guess is available for a complex model [17]. Global (deterministic or stochastic) optimisation techniques are better adapted to find the global minimum of the objective function, on cost of a higher programming and computational time. Nowadays, personal computers with high speed are available and such global strategies are becoming more competitive, especially for complex reaction systems. While deterministic methods generally require advanced programming skills, stochastic methods are much simpler to implement from a programming point of view. Goffe et al. [18] have pointed out that one of the most promising stochastic methods is the simulated annealing (SA) algorithm.

The aim of this study is thus to experimentally obtain a set of TBR data and develop a kinetic model for the CWAO of phenol over AC, which accounts for the disappearance of both phenol and main intermediates. The performance of the alternative stochastic simulated annealing algorithm is evaluated in the multi-kinetic parameter optimisation.

2. Experimental

2.1. Materials

Analytical grade phenol has been purchased from Aldrich and used without further purification for the preparation of 5 g/L feed solution with deionised water. The gaseous oxidant is high purity compressed air. The active carbon has been supplied by Merck (Ref. 102518) as 2.5 mm pellets. This AC is manufactured from wood and has a mineral ash content of 3.75 wt.%. The nitrogen BET method gives a specific surface area of 990 m²/g, a pore volume of 0.55 cm³/g and a mean pore diameter of 1.4 nm. Phenol adsorption tests performed at 20 °C under oxic conditions showed a capacity of 370 mg Ph/gAC at a phenol equilibrium concentration of 5 g/L. Prior to use, the AC pellets have been crushed and sieved to obtain the 25–50 mesh fraction (0.3–0.7 mm) for the oxidation experiments. The samples have been washed to remove all fines, dried at 110 °C overnight and then stored under inert atmosphere.

2.2. Experimental set-up

The laboratory TBR set-up available for the kinetic experiments as well as the experimental procedures have been described in detail elsewhere [19]. The reactor dimensions and the operating window are given in Table 1. In a typical series of oxidation experiments, the phenol solution and compressed air is mixed, preheated and then fed at the highest liquid flow rate to the reactor to saturate the AC fixed bed under oxic conditions. When the bed saturation is achieved (after 8–10 h), the phenol conversion slowly decreases to a plateau value depending on the selected temperature and air pressure. Normally, the system reaches this first steady state

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within 15–20 h. Then, the liquid flow rate is decreased to obtain a new steady state of reaction that corresponds to both higher space time and phenol conversion. By repeating this procedure for consecutively decreased liquid flow rates (at constant gas flow rate), the desired conversion-space time profiles could be established for 120, 140 and 160 °C and 1–2 bar of oxygen partial pressure.

2.3. Analysis

 Phenol and intermediate concentrations in the reactor outlet effluent have been regularly analysed by means of HPLC (Beckman System Gold) using a C18 reverse phase column (Spherisob ODS-2). The separation was achieved with a mobile phase of variable composition programmed at a 1 mL/min 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 [20]. Calibration was done with standard solutions of potassium hydrogen phthalate for COD ranging from 200 to 1000 mg/L.

3. Kinetic modelling

3.1. Reactor model

The laboratory TBR used for the experiments has been mathematically described assuming:

- Ideal plug flow of gas and liquid.
- Absence of mass transfer limitations (low reaction rates due to dilution).
- Constant catalyst activity (negligible AC combustion at the operating conditions employed).

The resulting isothermal one-dimensional model for the $j$ compound concentration can then be written in terms of space time:

$$\frac{dC_j}{d\tau} = \frac{R_j}{\rho_L}$$  \hspace{1cm} (1)

where $C_j$ is the compound concentration (mmol/L), $\tau$ the space time ($\tau = \text{catalyst mass/liquid mass flow rate} \ (\text{kg cat kgL}^{-1} \text{h}^{-1})$), $R_j$ (mmol kgcat$^{-1}$ h$^{-1}$) the net reaction rate of compound $j$ and $\rho_L$ (kg/L) is the constant liquid density. Each component, $R_j$, corresponds to the net destruction or production rates of the respective species as defined by the reaction pathway and kinetic model proposed. The reactor model is numerically solved with a fourth-order Runge–Kutta method. The precision of the numerical integration has been checked by repeating the calculations with an increasing number of iteration steps. The integration of Eq. (1) for space time as used in the experiments provides the model outlet concentrations, which are compared with the measured outlet concentrations to calculate the objective function value of the optimisation algorithm (Eq. (4)).

3.2. Rate models

A simple power law approach with first order of reaction for phenol and oxygen accurately predicted the entire range of experimental phenol conversions [5]:

$$r_{Ph} = k_0 \exp\left(-\frac{E_a}{RT}\right)x_{O_2}^x C_{Ph}$$  \hspace{1cm} (2)

The equilibrium molar fraction of dissolved oxygen ($x_{O_2}$) is calculated at each temperature and pressure according to the Henry’s law and coefficients as given by Himmelblau [21]. Similar power law equations have been established for all intermediates in the Rate Model 1 studied.

As phenol adsorsbs on AC [1], Langmuir–Hinshelwood (L–H) expressions should be also considered. Thus, in the Rate Model 2, simplest L–H type equations are chosen to account for adsorption–desorption phenomena of phenol and intermediate compounds. More mechanistic kinetics including dissociated or non-dissociated adsorption of oxygen on same or different active sites have not been tested because they increase the number of kinetic parameters, without significantly improving the data fit [14,22].

$$r_i = k_0 \exp\left(-\frac{E_a}{RT}\right)x_{O_2}^x \frac{K_{0i} \exp(-\Delta H_i/RT)C_i}{1 + \sum_j K_{0j} \exp(-\Delta H_j/RT)C_j}$$  \hspace{1cm} (3)

Rate Model 3 still proposes adsorption of phenol on AC, but the phenol attack occurs in the liquid phase close to the catalyst surface. This leads to power and L–H laws for phenol (Eq. (2)) and intermediates (Eq. (3)), respectively. Finally in Rate Model
4, the term corresponding to phenol adsorption in the denominator of Eq. (3) has been eliminated.

### 3.3. Parameter estimation

The development of global kinetic models inevitably leads to a high number of kinetic parameters, in our case more than 30, transforming the task of parameter estimation into a critical feature in kinetic modelling. In general, multi-parameter optimisation methods are very sensitive to initial guess values and frequently converge to local minima. Multiple solutions with similar data fit arise and the model discrimination and physical interpretation of the optimised parameters become very difficult. In this study, the unknown parameters have been optimised by a non-linear regression technique. As stated before, the reactor equation (Eq. (1)) has been numerically solved with a fourth-order Runge–Kutta method to calculate the theoretical outlet phenol and intermediate concentrations ($C_{cal}$) of the objective function. Testing of different objective functions has shown that the best balanced criterion is to compare experimental and calculated concentrations in terms of absolute errors as given below in Eq. (4):

$$\Phi = \sum_{i,n,k} |C_{exp}^{i,n,k} - C_{cal}^{i,n,k}|$$

where the indexes $i$, $n$, $k$ run over the component, the experiment and the space time, respectively.

The application of absolute squared errors or relative squared errors inevitably resulted in significant deviations for the high concentration compounds or the low concentration compounds, respectively. The objective function has been minimised either by using the classical gradient-based Levenberg–Marquardt (L–M) algorithm or by stochastically varying the model parameter via the SA algorithm. A related CWAO kinetic study has demonstrated that SA greatly reduces the problems of initial guess values and local convergence [17]. The starting values used for the kinetic model parameters are taken from a previous study of phenol oxidation over AC [5]. Preliminary tests have shown that a simple kinetic and adsorption constants reparameterisation to rescale the pre-exponential factors as log($k_0$) and log($K_0$) is sufficient for achieving convergence of the SA algorithm.

It should be pointed out that the initial parameter space has been restricted to positive values, except for the heats of adsorption (only negative values) to exclude slightly better mathematical solutions that otherwise may contain meaningless model parameter values. The optimisation runs have been all carried out on a personal computer with a data processing frequency of 700 MHz.

### 4. Results and discussion

#### 4.1. Preliminary results

The kinetic control in the TBR experiments at the given conditions has been carefully verified in previous works [5,16]. In addition, a heterogeneous transport-reaction model, accounting for all the above mentioned mass transfer and hydrodynamic phenomena, has been developed and tested on the laboratory reactor data [16]. Using the phenol kinetics assessed previously [5], the heterogeneous model predictions have been found to be in very close agreement with both the experimental phenol conversions and the predictions of the homogeneous model assuming kinetic control (Fig. 1). Thus, it can be convincingly concluded that, at the operating conditions employed, the trickle bed reactor allows conducting the CWAO of phenol over AC in the kinetically controlled regime.

Homogeneous contribution to the oxidation of phenol has been neglected in the kinetic study. Preliminary experiments conducted in our laboratory at 140 °C, 0.9 MPa of oxygen partial pressure and using inert particles have indicated less than 2% of phenol conversion. Furthermore, related studies [4,14,15,23] reported negligible homogeneous conversion of phenol and intermediates at 140–160 °C and 16 bar of oxygen pressure (about 10 higher than in our study). This is also in agreement with non-catalytic wet air oxidation of carboxylic acids resulting in high activation energies of 132, 149 and 178 kJ/mol for maleic acid [24], formic acid [25] and acetic acid [25], respectively.

#### 4.2. Catalytic TBR performance of active carbon

The phenol and COD outlet concentration profiles obtained at different temperatures (120, 140, 160 °C) and oxygen partial...
pressures (1 and 2 bar) are plotted in Figs. 1 and 2. The increase of both temperature and pressure is seen to have a strong positive effect on phenol and COD destruction. The same trend holds for increasing space times, indicating that no significant liquid maldistribution should have occurred at the lowest liquid flow rates tested. At 160°C and low oxygen partial pressure of 2 bar, almost complete phenol destruction (>99%) and 85% of COD abatement have been performed for space times greater than 0.4 h. The remaining COD is mainly due to the accumulation of refractory acetic acid.

HPLC analysis of the liquid samples withdrawn from the reactor outlet reveals the presence of 15–60 peaks. A typical HPLC chromatogram is shown in Fig. 3b for a phenol conversion of 50%. Most of these peaks have insignificant areas and aromatic-like retention times, probably indicating the slow release of phenol condensation products initially formed and deposit on the AC surface [1]. A group of 20 different possible phenol oxidation products has been tested with standard solution (Fig. 3a) to obtain the intermediate distribution. Among them, six principal intermediates have been identified, i.e. ring compounds namely 4-hydroxybenzoic acid (4-HBA), p-benzoquinone as well as short chain carboxylic acids, such as maleic acid, its isomer fumaric acid, acetic acid and formic acid. Trace amounts of hydroquinone, catechol and oxalic acid have been also detected in the liquid samples. However, these intermediates could not be considered in the kinetic modelling because it has been impossible to accurately follow the evolution of their concentrations with space time. It must be pointed out that essentially the same intermediate distribution has been reported in the CWAO of phenol over a different AC catalyst [4] or a supported Fe/AC catalyst [15]. Comparing HPLC based COD and measured COD in a parity plot (Fig. 4) indicates that the HPLC analysis is mostly above 95% representative of the liquid phase composition. On the whole, the quality of the experimental data is satisfactory with a larger scattering for the runs at 140°C and 2 bar of oxygen partial pressure.

Using a CuO/Al2O3 catalyst very similar phenol and COD conversions have been achieved, although at 160°C, 12 bar of...
oxygen partial pressure and space times of 0.8 h [26]. The measured distribution of aromatic compounds and acetic acid as a function of phenol confirm that the AC is performing considerable less amounts of bio-toxic aromatic compounds, while the production of “biodegradable” acetic acid is strongly enhanced. These results clearly highlight the superior performance of the AC, which seems a particularly attractive catalyst for combined CWAO biological treatment of bio-toxic organic wastewater effluents.

4.3. Reaction pathway for phenol CWAO over active carbon

A hierarchical model building approach has been followed to develop a reaction sequence that accounts for all main intermediates detected. The oxidation routes of the compounds have been established with the help of the classical phenol oxidation pathway of Devlin and Harris [27] and related work on phenol CWAO over AC [4] or Fe/AC catalysts [15]. The former has been modified due to both the presence of 4-HBA (not observed by Devlin and Harris) and the trace formation of catechol, hydroquinone and oxalic acid. Firstly, the route of phenol degradation via catechol and o-benzoquinone had to be eliminated and hydroquinone has not been included as the primary intermediate in the formation of p-benzoquinone from phenol. Secondly, 4-HBA has not been detected in phenol CWAO over supported metal catalysts at acidic pH. At basic conditions (pH 8) it has been shown that phenol can react with \( \text{HCO}_3^- \) to give 4-HBA [28], but the formation of \( \text{HCO}_3^- \) from CO\(_2\) released in the phenol oxidation is thermodynamically hindered at acidic pH. From previous experiments (wet air oxidation of AC without phenol [6,15]), it can be concluded that phenol is necessary for the formation of 4-HBA. Eventually, phenol can interact with carboxylic acid surface groups to form 4-HBA. Further experiments are underway in our laboratory to elucidate this point. The appearance of both 4-HBA and p-benzoquinone in the liquid samples suggests that phenol undergoes two parallel reactions to yield 4-HBA (slow) and p-benzoquinone via hydroquinone (fast). This assumption has been tested in terms of kinetic modelling by comparing the prediction of the parallel phenol degradation route with two consecutive schemes as shown below:

\[
\text{Scheme 1 : } \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_4\text{O}_2 \rightarrow \text{C}_7\text{H}_6\text{O}_3 \\
\text{Scheme 2 : } \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_7\text{H}_6\text{O}_3 \rightarrow \text{C}_6\text{H}_2\text{O}_2 \\
\text{Scheme 3 : } \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_7\text{H}_6\text{O}_3 \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_4\text{O}_2
\]

The minimised objective function for Schemes 1–3 takes values of 67, 40 and 27 mmol/L, respectively, which confirms that two parallel phenol degradation reactions best match the experimental data. Maleic acid is then expected to form from both 4-HBA and p-benzoquinone and the destruction of maleic acid (including its isomer fumaric acid) yields acetic and formic acid. A direct oxidation of 4-HBA and p-benzoquinone to acetic acid and formic acid, respectively, is also allowed bypassing the formation of maleic acid. Finally, the accumulation of acetic acid observed during the experiments suggests that it is refractory to CWAO at the given conditions. The complete reaction pathway proposed consists of 9 possible reactions with 39 parameters (Rate Model 3) to be optimised. Obviously, the reaction sequence is complex, but in a first optimisation trial the aim was not to simplify the multi-parameter fitting.

In first place, it must be said that the L–M algorithm as available in its standard library version failed to converge in case of the proposed reaction pathway. The only way to reach convergence consisted in using the final values of SA algorithm as starting values for the L–M algorithm. Therefore, the L–M algorithm has not been further considered for parameter estimation. With the SA algorithm, the objective function value rapidly progresses to 100 mmol/L, although the final parameter tuning turns out to be relatively time consuming. After about 10–15 h, the run has been stopped with a criteria value of 81 mmol/L. The overall data fit is very satisfactory, although there exists a considerable mismatch in the prediction of the
maleic acid concentration profiles. The maleic acid molecule has a central position in the complete reaction pathway and it is surprising that the optimisation routine with four adjustable reactions is not able to match the maleic acid data. As a matter of fact, calculated rates from identified parameters show that the formation of maleic acid from benzoquinone (reaction (4)) and its destruction to formic acid (reaction (8)) are more than 20 times slower than the formation of maleic acid from 4-HBA (reaction (3)) and its destruction to acetic acid (reaction (7)). The same situation holds for reaction (9), i.e. the rate of direct formation of acetic acid from 4-HBA even resulted close to zero. It clearly appears that the proposed pathway with nine reactions is not adequate and has to be simplified.

Accounting for the above results, reactions (4), (8) and (9) have been dropped off to establish the reaction pathway as proposed in Fig. 5. It postulates that maleic acid is mainly coming from the ring opening of 4-HBA, whereas p-benzoquinone break down to formic acid (reaction (4)) and acetic acid (reaction (5)) has to follow routes that bypass maleic acid formation. Experimental support comes from a close inspection of the intermediate profiles (Figs. 6–10). The profiles for 160 °C and 2 bar indicate that the maximum of p-benzoquinone occurs before that of formic acid at early space times compared to those of 4-HBA and maleic acid (in this order) appearing significantly later. Thus, the formation of formic acid and maleic acid must be mainly related to the destruction of p-benzoquinone and 4-HBA, respectively. At the reaction conditions tested, only 10% of phenol reacts towards 4-HBA. The remaining 90% disappears
through the fast production and degradation of \( p \)-benzoquinone (probably to oxalic acid and then) to formic acid, which readily decomposes over the AC. A direct path from \( p \)-benzoquinone to formic acid bypassing the formation of maleic acid is consistent with the Devlin and Harris mechanism. However, acetic acid formation via the decomposition route of maleic acid alone could not account for the high amounts of refractory acetic acid observed. The build-in of a (rather slow) reaction from \( p \)-benzoquinone to acetic acid has been necessary to improve the prediction of the acetic acid profiles. Alternatively, the oxidation route of phenol via catechol to \( o \)-benzoquinone and then to maleic acid could produce extra acetic acid, but it has been impossible to check this speculation with the available experimental data. Finally, data fitting with the more simple reaction scheme and SA algorithm led to a similar objective function value of 84 mmol/L. Despite the pathway simplification, the overall fit performed is very satisfactory and also provides significantly closer experimental and predicted maleic acid profiles. It is noteworthy that a similar oxidation sequence have been independently proposed for phenol oxidation from CWAO experiments of both phenol and intermediates over a different AC [4] and a supported Fe catalyst [15] using the same AC support as in our study. This is a convincing proof of the usefulness of our model building approach followed. The former works has also reported similar reactivity of phenolic ring compounds compound as observed in our study, i.e. a very fast destruction of hydroquinone and catechol, a fast destruction of \( p \)-benzoquinone and a slower degradation of 4-HBA. Contrary, it appears that, at least for the Fe/AC catalyst, both acetic and formic acid are refractory to CWAO [15].

The corresponding reaction equations of the reaction network developed here are listed below:

\[
\begin{align*}
C_6H_5OH + CO_2 & \rightarrow r_1 C_7H_6O_3 \quad (8) \\
C_6H_5OH + O_2 & \rightarrow r_2 C_6H_4O_2 + H_2O \quad (9) \\
C_7H_6O_3 + 4O_2 & \rightarrow r_3 C_4H_4O_4 + 3CO_2 + H_2O \quad (10) \\
C_6H_4O_2 + 5O_2 + H_2O & \rightarrow r_4 CH_2O_2 + C_2H_4O_2 + 3CO_2 \quad (11) \\
C_6H_4O_2 + 5O_2 + 2H_2O & \rightarrow r_5 4CH_2O_2 + 2CO_2 \quad (12) \\
CH_2O_2 + 0.5O_2 & \rightarrow r_6 CO_2 + H_2O \quad (13) \\
C_4H_4O_4 & \rightarrow r_7 C_2H_4O_2 + 2CO_2 \quad (14)
\end{align*}
\]

The net destruction or production rates \( R_j \) of the involved compounds can then be determined to:

\[
\begin{align*}
R_{\text{phenol}} &= -r_1 - r_2 \quad (15) \\
R_{\text{4-HBA}} &= r_1 - r_3 \quad (16) \\
R_{\text{p-benzo}} &= r_2 - r_4 - r_5 \quad (17) \\
R_{\text{maleic}} &= r_3 - r_7 \quad (18) \\
R_{\text{acetic}} &= r_4 + r_7 \quad (19) \\
R_{\text{formic}} &= r_4 + 4r_5 - r_6 \quad (20)
\end{align*}
\]
4.4. Rate model

The different rate models have been tested on the simplified scheme with seven reactions. As expected, the use of power law equations for all compounds (Rate Model 1) is not sufficient (final objective function value of 125 mmol/L) to accurately describe the underlying kinetic phenomena. Surprisingly, with L–H expressions for all reactions (Rate Model 2), the optimisation rapidly reaches a high value of the objective function of 675 mmol/L without further progressing. The L–H model implies 33 adjustable parameters and its failure in fitting the data is probably due to the assumption that the phenol molecule is oxidised in its adsorbed state. There exists experimental evidence for a radical attack of the phenol molecule in the liquid phase. A first order with respect to phenol concentration has been observed in the CWAO over our AC for a large inlet phenol concentration range of 0.5–5 g/L. At the same temperature phenol adsorption on the same AC showed hyperbolic behaviour the adsorption capacity only increasing by 50% for phenol equilibrium concentrations from 1 to 4 g/L [5]. Furthermore, a recent study on the oxidation of organic contaminants (MTBE, TCE and TCP) with hydrogen peroxide catalysed by activated carbon [29] has concluded that the predominant oxidation pathway is a radical attack of the freely dissolved organic contaminant, while the sorbed organic fraction is nearly unreactive. According to the authors and our own work [30], the catalytic role of the AC is to generate the active radicals on its surface and strongly adsorbed compounds are not easily oxidised or may result in a decrease of the active sites for radical formation. However, a related study with a different AC conducted in an upflow fixed-bed reactor reported somewhat higher phenol conversions at smaller phenol inlet concentrations, which in the absence of mass transfer limitations cannot be explained by a first-order kinetics [14]. It seems that more experimental work is needed to clarify this interesting point.

A direct phenol attack has been tested with Rate Model 3, which still accounts for phenol adsorption but power law equations for reactions (1) and (2) instead of L–H expressions. As stated before, the SA algorithm converges to an objective function value of 84 mmol/L with a good match of experimental and predicted compound concentration profiles. The remarkable improvement in the data fit from Model 2 to Model 3 gives support to the hypothesis of a direct phenol attack in the liquid phase. Moreover, the calculation of phenol adsorption constants from the optimised parameters results in very small values of about 10⁻⁶ L/mmol. This indicates that phenol adsorption, although taking place may not play a direct role in the kinetic mechanism of phenol CWAO over AC. To test the influence of phenol adsorption in the model, a series of optimisation runs has been done with Rate Model 4, cancelling the contribution of phenol adsorption in the denominator of L–H equations for reactions (3)–(7). With this model, the best data fit has been performed, the objective function progressing significantly from 84 to 76 mmol/L. Finally, the block adsorption of either only aromatic intermediates or carboxylic acids has been checked, but in both cases the fit quality deteriorates to that obtained with the simple power law model. Thus, only the best results obtained with the simplified reaction network (Fig. 5) and Rate Model 4 are presented in the following section.

4.5. Model prediction and model parameters

Figs. 1, 2 and 6–10 also compare the model predictions and the experimental phenol, COD and intermediate concentrations. As can be seen in Figs. 1 and 2, calculated phenol and COD profiles show excellent agreement with experimental data leading to a very small mean error of only 4.5%. The prediction of intermediates, in particular for 140 °C and 2 bar, is less accurate (Figs. 6–10), but still very satisfactory given the complexity of the reaction system studied. Overall, the proposed model matches all data with a small global error of about 8% and it can be safely used for design and optimisation studies of CWAO units.

The parameters optimised with Rate Model 4 are listed in Tables 2 and 3. The oxidation reactions of phenol to 4-HBA and p-benzoquinone have activation energies of 82.4 and 72 kJ/mol, which lie in the range (65–85 kJ/mol [5]) observed for kinetically controlled CWAO of phenol over different supported catalysts. For the ring opening reactions of 4-HBA to maleic acid and p-benzoquinone to formic acid, respective values of 81 and 55 kJ/mol have been obtained. Few specific CWAO data is available to compare, but for oxidation of p-coumaric acid over CuOZnO/Al₂O₃ close activation energy of 72 kJ/mol has been reported [31]. Also, in the CWAO of phenol using 10%CuO/Al₂O₃ a similar value of 45 kJ/mol has been

| Table 2 | Frequency factors, activation energies and reaction orders obtained with Rate Model 4 and reaction scheme as proposed in Fig. 5 |
|-----------------|-----------------|-----------------|
| log $k_0$ (L/kg cat/h) | $E_a$ (kJ/mol) | $\alpha$ |
| 14.37 ± 0.02 | 82.4 ± 0.6 | 1.02 ± 0.02 |
| 13.67 ± 0.01 | 72.0 ± 0.4 | 0.92 ± 0.01 |
| 17.4 ± 0.6 | 81.0 ± 1 | 0.90 ± 0.1 |
| 19.9 ± 0.9 | 118 ± 4 | 0.60 ± 0.1 |
| 13.5 ± 0.4 | 55.4 ± 3 | 0.75 ± 0.06 |
| 14.7 ± 0.5 | 66.8 ± 3 | 0.77 ± 0.06 |
| 14.4 ± 0.1 | 55.6 ± 2 | 0.62 ± 0.03 |

* For reactions (1) and (2), frequency factor is in (L/kg cat/h), for the rest of reactions it is in (mmol/kg cat/h).

| Table 3 | Adsorption parameters for intermediates obtained with Rate Model 4 and reaction scheme as proposed in Fig. 5 |
|-----------------|-----------------|-----------------|
| Compound adsorbed | $K_0$ (L/mmol) | $\Delta H$ (kJ/mol) | $\Delta S$ (kJ/mol/K) |
| 4-HBA | 0.17 ± 0.04 | −1.9 ± 0.5 | 3.2 |
| p-Benzoquinone | 1.5 ± 0.05 | −1.9 ± 0.3 | 28.6 |
| Maleic acid | −1.7 ± 0.1 | −2.7 ± 0.5 | −32.6 |
| Acetic acid | 1.5 ± 0.2 | −0.6 ± 0.7 | 28.6 |
| Formic acid | 0.81 ± 0.07 | −3.4 ± 0.3 | 15.2 |
identified for the fast degradation of p-benzoquinone to formic and oxalic acid [17].

In agreement with other studies [4,15], the AC catalyst is not able to oxidise acetic acid, which is completely refractory at the given conditions. On the other hand, formic and maleic acid are much more easily converted over the AC and consistent low activation energies of 67 and 56 kJ/mol have resulted for formic and maleic acid destruction, respectively. Almost the same value (70 kJ/mol) has been determined for formic destruction over 10%CuO/Al2O3 [17], but there exists certain dispersion depending on the catalyst used. Formic acid oxidation over 1%Pt/C conducted at low temperatures (9–20 °C) has resulted in lower activation energy of 47 kJ/mol [32], while homogeneous CuSO4 catalyst has given a higher one of 94 kJ/mol [33]. Nevertheless, the positive action of catalysts in formic oxidation is clearly confirmed by the high activation energies of 121 kJ/mol [33] and 149 kJ/mol [25] obtained for homogeneous non-catalytic oxidation of formic acid. The scattering in activation energy for maleic acid oxidation is similar. For maleic acid wet air oxidation, values of 99 kJ/mol [34] and 132 kJ/mol [24] have been evaluated from kinetic experiments. The use of supported catalysts seems to accelerate the oxidation yielding lower activation energies of 116 kJ/mol for 0.5%Pt/Al2O3 [24] and 27 kJ/mol for 10%CuO/Al2O3 [17]. The latter value seems too low, although maleic acid has been detected in very low amounts (less than 0.1 mmol/L) indicating that it is readily oxidised over the catalyst employed [17]. It can be thus concluded that the AC employed in our study shows a particular high potential for the degradation of rather refractory maleic and formic acid as confirmed by its low activation energy.

Within the small pressure range considered in this study (to avoid burning-off of AC), the phenol disappearance and ring opening reactions except for p-benzoquinone break down (r4 and r5) are almost linearly proportional to the oxygen mole fraction. Generally, a 0.5 order is obtained in phenol CWAO, when higher pressures and wider intervals are employed. Contrary, the formation of acetic acid from maleic acid has a 0.6 order, and the formation and destruction of formic acid shows a 0.75 order. The observed oxygen orders suggest that, in the absence of significant non-catalytic homogeneous oxidation, the destruction of these carboxylic acids occur both through catalytic oxidation and (to a smaller extend) through decarboxylation. In formic acid oxidation over different catalysts, 0.5 [32] or first order [33,35] have been proposed for oxygen, although a smaller value of 0.23 has been also estimated for this reaction in the global kinetic modelling of phenol oxidation over 10%CuO/Al2O3 [17]. The same kinetic study has reported an oxygen order of 0.5 for maleic acid oxidation, which is close to the 0.6 order obtained for our AC catalyst. For (catalytic or non-catalytic) decarboxylation reactions, a zero dependence on oxygen is to be expected, as confirmed by several kinetic studies dealing with the oxidation of maleic acid over 0.5%Pt/Al2O3 [24] and malonic acid over 10%CuO/Al2O3 [17] or 5%/graphite [36].

It is more difficult to discuss the adsorption parameters because on one hand only few adsorption data is available from CWAO kinetic studies and on the other the data shows significant discrepancies. In the case of phenol oxidation, negative adsorption enthalpies have been obtained differing widely from −33 kJ/mol (CuO/AC [37]), −62 kJ/mol (CuOZnOCoO [13]) to −109 kJ/mol (MnO2/CeO2 [38]). Carboxylic acids (butyric, propionic, acetic, maleic, oxalic and formic acid) are reported to be strongly bounded to the metal surface and only weakly to the support, when the metal is noble (Pt, Ru) and the support is carbon [39–41]. Finally, for our AC used, kinetic modelling of phenol CWAO has indicated a rather small adsorption enthalpy of −7.4 kJ/mol and adsorption experiments has revealed a rather weak dependence of adsorption on temperature within 120–160 °C and air atmosphere [5]. A positive value of 76.7 kJ/mol is also reported for phenol adsorption on a different AC [14], but this is in clear contradiction to the (generally accepted) exothermic nature of phenol adsorption on AC [5,7]. In our optimisation study imposing a negative starting guess for the organic compounds (−6 kJ/mol), all heats of adsorption (Table 3) converge without any further restriction to small negative values (between −0.6 and −3.4 kJ/mol). At a first glance, these values seem to have physical meaning, confirming that adsorption phenomena either depend weakly on temperature or are not directly influential in the reaction mechanism within the range of temperatures studied.

To determine the validity of the model parameters, it is useful to evaluate the statistical significance of the optimised model parameters. A drawback of SA is its lack of statistical functions to calculate the uncertainty in the model parameters. Alternatively, the individual errors reported in Tables 2 and 3 have been approximated by assuming a linear behaviour close to the solution and choosing a 95% confidence interval. As can be seen in Table 2, the kinetic parameters are confident showing very small uncertainties, especially phenol disappearance reactions (1) and (2). Contrary, the compound adsorption enthalpies cannot be identified with precision, calculated errors being very important (Table 3). A similar trend has been observed in the kinetic modelling of phenol oxidation over 10%CuO/Al2O3 [17] and butyric, propionic and acetic acid oxidation over 1%Pt/C [41]. A weak (or different) dependence of compound adsorption on temperature at the different operating conditions and catalysts employed in the studies could thus explain the large discrepancies (and statistical uncertainties) in the available literature adsorption enthalpies as outlined before.

Moreover, most of the adsorption constants are not thermodynamically consistent with the Van’t Hoff relation ship (Eq. (21)), because the adsorption entropies (ΔS0) of organic compounds do not meet the Boudart–Mears–Vannice [42] chemical–kinetic criteria (Eq. (22)), as shown in Table 3:

\[
\ln K_i = \frac{\Delta S_i}{R} - \frac{\Delta H_i}{RT} \quad (21)
\]

\[
\Delta S_i < 0
\]

\[
10 < - \Delta S_i < 12.2 - 0.00014\Delta H_i \quad (22)
\]

Overall, it can be said that the kinetic model developed is capable to represent the whole experimental data set with
accurate precision. Due to the little influence of adsorption and the resulting inconsistency in adsorption parameters, the model should not be used for extrapolation purpose. However, this restriction is only a small inconvenient, because at lower temperatures (where adsorption can become more influent) the reaction proceeds at a very slow rate, while at higher temperature (and pressure) the combustion of AC is greatly enhanced. Thus, there is no interest in conducting the CWAO of phenol over AC outside the considered temperature and pressure range.

5. Conclusions

The CWAO of phenol over active carbon has been performed in a trickle bed reactor at 120–160 °C and 1–2 bar of oxygen partial pressure. The oxidation occurs under kinetic control and almost complete phenol conversion (>99%) has been obtained at 160 °C, 2 bar and liquid space time of 0.4 h with a COD conversion of 85%. The remaining COD can be mainly attributed to the accumulation of refractory, but biodegradable acetic acid. The active carbon catalyst can thus offer a particularly attractive solution for the integration of CWAO of organic pollutants as a pre-treatment step into a biological treatment plant.

Based on the main intermediates detected (4-HBA, p-benzoquinone, maleic acid including its isomer fumaric acid, acetic acid and formic acid), a consistent global reaction network has been proposed for the CWAO of phenol over AC (Fig. 5). Accordingly, phenol oxidation follows two distinct degradation routes through hydroxylation or carboxylation of phenol, both in para position, to yield either p-benzoquinone and then formic acid (fast route) or 4-HBA and then maleic and finally acetic acid (slow route). 4-HBA, which has not been detected in CWAO of phenol over supported catalysts at acidic pH, could be formed from phenol and carboxylic surface groups. The kinetic modelling of the data also indicates that phenol is rather attacked in the liquid phase, while the adsorbed fraction of phenol may not participate directly in the oxidation. Related studies support this assumption, but more experimental work is needed to elucidate both the mechanism of phenol attack and 4-HBA formation for the AC catalyst.

The global kinetic model proposed has been obtained by a hierarchical model approach and contains 31 parameters, which have been optimised by non-linear multi-parameter fitting. The numerical procedure has been performed in a reasonable computational time with a stochastic algorithm termed simulated annealing, whereas the classical Levenberg–Marquardt algorithm failed to reach convergence. The application of stochastic methods to non-linear multi-parameter optimisation is thus a competitive alternative to the classical gradient-based estimation techniques. The overall consistence of the kinetic model and network developed has been confirmed by the very satisfactory prediction of phenol, intermediates and COD data. However, an error and consistency analysis of the model parameter have revealed that the adsorption parameters can not be precisely obtained, due to the weak temperature dependence of adsorption between 120 and 160 °C employed in the kinetic experiments.

Acknowledgements

The funding for this work has been provided by the Spanish Ministerio de Educación y Ciencia and FEDER (grants REN2001/1589TECNO, REN2002/03565/TECNO) and the Departament d’Universitats, Recerca i Societat de la Informació de la Generalitat de Catalunya (project ITTO1-4). We are indebted to the Rovira i Virgili University for awarding a doctoral fellowship to one of the authors.

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