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**Catalytic Wet Air Oxidation of Aqueous
Organic Mixtures**

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Catalytic Wet Air Oxidation of Aqueous Organic Mixtures

Carmen Creanga Manole, Catherine Ayrat, Carine Julcour Lebigue, Anne-Marie Wilhelm, and Henri Delmas

Abstract

Catalytic Wet Air Oxidation (CWAO) has been investigated for the treatment of water contaminated by 4-hydroxybenzoic acid (4HBA) and equimolar mixture of phenol-4HBA. Both batch measurements for kinetics determination and continuous fixed bed operation have been performed on the same Activated Carbon (AC). After a fast initial deactivation AC was proved stable and efficient at moderate temperature and oxygen pressure, like for phenol degradation.

The kinetic study in the case of highly adsorbing material as AC may require complex approach to account for the variation of adsorbed reactants during batch oxidation. Adsorption isotherms at reaction temperature and with aged AC have been obtained according to Langmuir equation and used in 4HBA mass balance to derive more significant kinetic parameters. At high catalyst loading and relatively low pollutant concentration, the variation of 4HBA during the batch may be even higher on the solid than in the aqueous phase.

KEYWORDS: catalytic oxidation, adsorption, activated carbon

1. INTRODUCTION

A new sequential process (AD-OX) has been developed involving in the same reactor, first adsorption on activated carbon, then catalytic air oxidation, acting also as activated carbon (AC) regeneration (Polaert et al., 2002). The two successive steps, adsorption at room temperature and wet catalytic oxidation on AC at higher temperature and pressure have been investigated separately: the oxidation step is presented here.

Catalytic wet air oxidation (CWAO) on AC has already been successfully tested for the remediation of phenol and some other substituted phenols (Eftaxias, 2003, Fortuny et al., 1998). Recently oxidation on AC in three phase fixed bed was investigated with detailed comparison up-flow vs. down flow for aqueous solution of phenol (Suwanprasop et al., 2005). Same work was also successfully performed with 4-hydroxybenzoic acid (4HBA) (Creanga Manole et al., 2007), a phenolic compound, typically found in CWAO of olive oil industry wastes (Beltran-Heredia et al., 2001) and considered as toxic and refractory to usual wastewater biological treatment (Gonzalez et al., 1990).

Most often waste waters are mixtures of several pollutants. To investigate the feasibility of the AD-OX process with complex mixtures, a model mixture of phenol and 4HBA has been treated in this work. It aims to investigate the catalytic oxidation of this mixture in both batch autoclave - to calculate kinetic rate constants, and in fixed bed reactor to examine the performance of the continuous process. Unusual procedure is required for the batch kinetic investigation of this reaction, due to both important initial deactivation before steady behavior of AC and non negligible amounts of organic compounds adsorbed on AC. This last point involves taking into account time variations of adsorbed amounts during reaction - using adsorption isotherms on aged catalyst at reaction temperature - in addition to the time variations of the organic compounds in liquid phase.

2. KINETICS IN BATCH AUTOCLAVE

2.1 Experimental procedure

For the determination of intrinsic kinetic parameters, batch oxidation (of 4HBA and 4HBA-phenol mixtures) has been performed in a 300 ml-stirred autoclave (Parr Instruments) described in details by Suwanprasop, 2005. Operating conditions are: temperature between 130 and 160°C and 1 to 3.5 bar of oxygen partial pressure (total pressure ranging from 10 to 20 bar).

Kinetic experiments are carried out batchwise for the liquid and continuous for air at a flow rate of 60 L/h (Normal conditions of Temperature and Pressure - NTP) -more than fifty fold the maximum consumption - to ensure a constant oxygen partial pressure despite CO₂ formation. Water vaporization due to this gas stream is limited by a condenser. The stirrer speed has been set at 800 rpm such as to avoid on the one hand catalyst attrition and on the other hand eventual external mass transfer limitations of reactants.

Uncrushed Merck 2514 AC particles have been sieved to obtain a 1.25-1.6 mm sample of large particles. The reactor is loaded with 5.3 g of AC particles maintained in a fixed basket and 200 ml of pollutant solution which concentration is calculated so as to start oxidation - after preliminary adsorption at reaction temperature - with either 2-3 g/l 4HBA or approximately 6 g/l equimolar mixture solution (2.43 g/l phenol and 3.57 g/l 4HBA). During the course of reaction, liquid samples have been periodically taken, filtered, and immediately analyzed by HPLC to get the evolution of initial compounds and reaction intermediates. Physical damage of the catalyst due to attrition is not detected.

2.2 Properties of AC

Large particles of AC are used to minimize fast and continuous deactivation as reported previously during phenol oxidation when using powder (Stüber et al, 2001). A steep decrease of activity is however observed between the first two oxidation runs, but afterwards the time-concentration profiles in the liquid phase are found to be stable for a large number of further runs, as verified with final ones at standard conditions ($p_T=20$ bar, $T=150^\circ\text{C}$).

The properties of the catalyst are listed in Table 1.

Table 1. Physical properties of fresh and aged Merck Activated Carbon

	Fresh AC (Merck 2514)	Aged AC -1 (oxidation of 4HBA- phenol mixture)	Aged AC -2 (oxidation of 4HBA)
Volume weighted mean diameter, $D[4,3]$ (mm)	1.25	1.25	1.25
Apparent density (g/l)	1032	1459	1623
Pore volume (cm ³ /g)	0.57	0.17	0.30
BET surface area (m ² /g)	980	140	380
Average pore diameter (Å)	22	48	32

The apparent density for Aged AC-2 is higher than that of Aged AC-1 due to a higher true density (measured with Helium pycnometer). Table 1 shows that after a few oxidation runs, the BET surface area of AC has decreased from 980 m²/g (for fresh catalyst) to 380 m²/g for 4HBA oxidations (2.1 g of 4HBA treated per gram of AC) and 140 m²/g for mixture oxidations (6.3 g of pollutants treated per gram of AC). Pore volume has decreased from 0.57 cm³/g to 0.3 cm³/g for 4HBA and 0.17 cm³/g for mixture. Such a change in AC structure has already been reported during the Catalytic Wet Air Oxidation of phenol and some of its derivatives, attributed to the deposit of high molecular weight organic compounds (Suarez-Ojeda et al., 2005, Santos et al., 2006, Suwanprasop, 2005). In the case of phenol oxidation, the BET surface area dramatically dropped to 65 m²/g during similar experimental series (1.7 g of phenol treated per gram of AC) (Suwanprasop, 2005).

Modifications of AC properties seem to be more related to the nature of pollutant than to the amount treated, as catalyst activity is found stable after catalyst conditioning (first two runs).

In order to calculate the evolution of the adsorbed concentration of pollutant during a kinetics experiment, adsorption isotherms are required, at the reaction temperature and with aged AC. After the oxidation runs, aged AC particles have been disposed in a fixed bed and washed with bidistilled water during a week so that to eliminate all reversibly-adsorbed components. A batch desorption equilibrium of this washed AC has shown that the amount of 4HBA (and phenol) remaining on the solid ($q_0 < 5 \cdot 10^{-5}$ mol/g_{AC}) is then negligible when compared to the saturation value for fresh AC. After drying, adsorption experiments have been carried out on this aged AC to get the isotherms at 150°C.

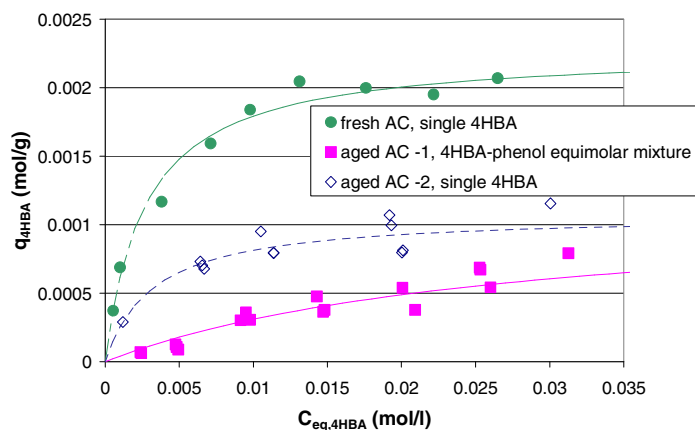


Figure 1. Adsorption isotherms of single 4HBA and 4HBA in a 4HBA-phenol mixture on fresh and aged AC

In Figure 1, the corresponding results are plotted for 4HBA, single and in the mixture. In the mixture, phenol concentration on AC was found to be negligible.

It is clearly confirmed that the adsorption capacity of aged AC is highly reduced: the saturation value for fresh AC being 0.0023 mol/g_{AC}, it means that the saturation value is nearly divided by a factor 2. The effect of ageing on reducing the initial slope is even much greater.

Those isotherms are fitted using a Langmuir-type model, and the parameters are given in Table 2.

$$q_{4HBA} = q_{max} \frac{K_{4HBA} C_{4HBA}}{1 + K_{4HBA} C_{4HBA}} \quad (1)$$

Table 2. Langmuir isotherms parameters for 4HBA on fresh and aged AC (single / in the mixture)

Fresh AC, single 4HBA	$q_{max} = 2.27 \text{ mol/kg}_{AC}$	$K_{4HBA} = 0.3732 \text{ m}^3/\text{mol}$
Aged AC -1, 4HBA-phenol mixture	$q_{max} = 1.15 \text{ mol/kg}_{AC}$	$K_{4HBA} = 0.0367 \text{ m}^3/\text{mol}$
Aged AC -2, single 4HBA	$q_{max} = 1.08 \text{ mol/kg}_{AC}$	$K_{4HBA} = 0.3075 \text{ m}^3/\text{mol}$

2.3 Apparent kinetics results

Normalized 4HBA and phenol concentrations have been plotted versus time for the oxidation of 4HBA and 4HBA-phenol mixtures at 150°C (figure 2) and for different temperatures (figure 3). In the mixture, the observed degradation of phenol is always faster than the one of 4HBA.

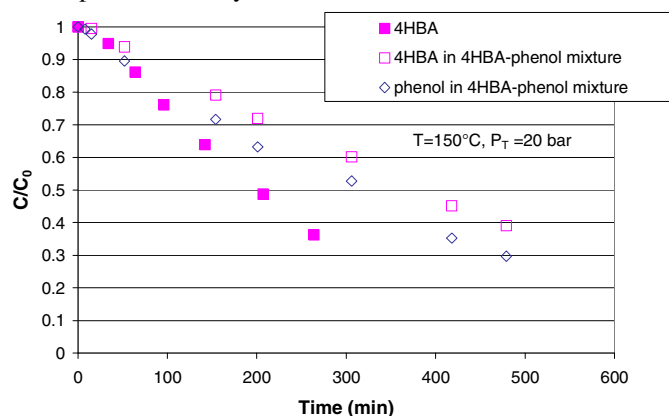


Figure 2. Evolution of reactant concentration in liquid phase

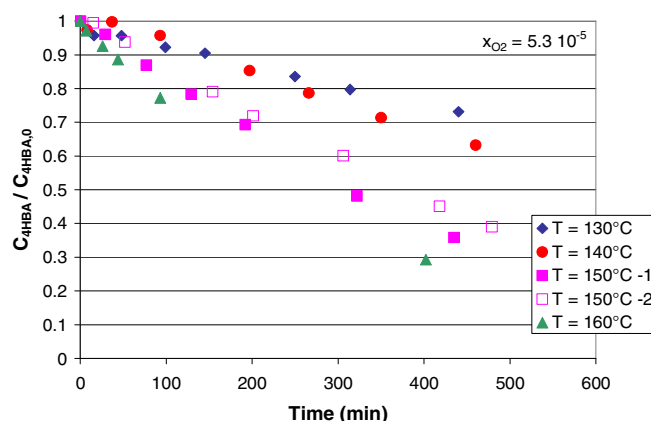


Figure 3. Effect of temperature on the kinetics (mixture of pollutants)

A first order is suggested when plotting the logarithm of pollutant concentration in the liquid phase as a function of time (not shown here) and at a fixed value of P_{O_2} , resulting in following apparent reaction rate: $R_{app} = k_{app} C_{pollutant}$. The values of the apparent kinetic constants are given in table 3.

Table 3. Values of the apparent kinetics constants in the mixture and for single 4HBA ($x_{O_2} = 5.3 \cdot 10^{-5}$)

Temperature (K)	$k_{4HBA,app}$ ($m^3_L \cdot (m^3_{AC} \cdot s)^{-1}$) apparent (mixture, 1)	$k_{Ph,app}$ ($m^3_L \cdot (m^3_{AC} \cdot s)^{-1}$) apparent (mixture, 2)	$k_{4HBA,app}$ ($m^3_L \cdot (m^3_{AC} \cdot s)^{-1}$) apparent (single)
413.15	$5.81 \cdot 10^{-4}$	$8.66 \cdot 10^{-4}$	$1.29 \cdot 10^{-3}$
423.15	$1.12 \cdot 10^{-3}$	$1.43 \cdot 10^{-3}$	$2.07 \cdot 10^{-3}$
433.15	$1.81 \cdot 10^{-3}$	$1.95 \cdot 10^{-3}$	$3.38 \cdot 10^{-3}$

Apparent activation energies can also be calculated:

$E_{1,app} = 84\,517$ J/mol and $E_{2,app} = 60\,546$ J/mol, respectively for 4HBA and phenol in the mixture.

Data in table 3 confirm that in the mixture, observed phenol degradation is faster than 4HBA (the ratio of kinetic constants is 1.5 at 413K and 1.15 at 433K). It can be also noticed that the apparent kinetic constant for single 4HBA is about twice its value in the mixture.

2.4 Interpretation of kinetic data

As mentioned earlier the intrinsic kinetics determination from batch oxidation on activated carbon requires unusual complex procedure due to both large particles and relatively high loading of highly adsorbing catalyst, thus undergoing pore diffusion and strong adsorption.

The proposed model includes transient diffusion of both oxygen and pollutant inside the catalyst pores, as well as the simultaneous adsorption-desorption equilibrium on activated carbon.

Model hypothesis

The assumptions are the following ones:

- spherical geometry of particles, isothermal particles,
- complete mineralization of reacted pollutant to CO_2 and H_2O , so that $R_{O_2} = 7 \times R_{4HBA} + 7 \times R_{Ph}$,
- negligible external mass-transfer limitation,
- instantaneous adsorption equilibrium, no adsorption competition of oxidation intermediates.

Liquid volume variations due to sampling and water vaporization (even limited by the condenser) have been quantified experimentally from the final volume and taken into account in the model.

Intrinsic kinetic model

Following previous studies of phenol oxidation (Eftaxias, 2003, Fortuny et al., 1999), a simple power law is then used to describe the pollutant destruction over AC assuming a first order of pollutant, while the oxygen order has to be determined by the optimization algorithm.

The following rate equations have thus been used:

$$R_{4HBA} = k'_{4HBA,0} \exp\left(\frac{-E_1}{RT}\right) C_{4HBA} x_{O_2}^{\alpha_1} \text{ and } R_{Ph} = k'_{Ph,0} \exp\left(\frac{-E_2}{RT}\right) C_{Ph} x_{O_2}^{\alpha_2} \quad (2)$$

Model equations

In these conditions, the mass balances lead to the following equations inside the particle:

$$\varepsilon'_p \frac{\partial C_{4HBA}}{\partial t} + \rho'_p \frac{\partial q_{4HBA}}{\partial t} = \frac{D'_{e,4HBA}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{4HBA}}{\partial r} \right) - R_{4HBA} \quad (3)$$

$$\varepsilon'_p \frac{\partial C_{Ph}}{\partial t} + \rho'_p \frac{\partial q_{Ph}}{\partial t} = \frac{D'_{e,Ph}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{Ph}}{\partial r} \right) - R_{Ph} \quad (4)$$

$$\varepsilon'_p \frac{\partial C_{O_2}}{\partial t} = \frac{D'_{e,O_2}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{O_2}}{\partial r} \right) - (7 \times R_{4HBA} + 7 \times R_{Ph}) \quad (5)$$

$$q_{Ph} = 0, \quad q_{4HBA} = q_{max} \frac{K_{4HBA} C_{4HBA}}{1 + K_{4HBA} C_{4HBA}} \quad (1)$$

with constants given in Table 2 for aged AC at 150°C.

Boundary conditions:

$$\bullet \forall t, r = 0 \quad \frac{\partial C_j}{\partial r} = 0 \quad (\text{symmetry}) \quad (6)$$

$$\bullet \forall t, r = r_p \quad C_j = C_{L,j} \quad (\text{negligible external mass-transfer resistance}) \quad (7)$$

$$\frac{d(V_L \times C_{L,4HBA})}{dt} = -D'_{e,4HBA} \left(\frac{\partial C_{4HBA}}{\partial r} \right)_{r=dp/2} \frac{W_{AC}}{\rho_p} \frac{6}{d_p} \quad (8)$$

$$\frac{d(V_L \times C_{L,Ph})}{dt} = -D'_{e,Ph} \left(\frac{\partial C_{Ph}}{\partial r} \right)_{r=dp/2} \frac{W_{AC}}{\rho_p} \frac{6}{d_p} \quad (9)$$

$$C_{L,O_2} = \frac{p_{O_2}}{He} \quad (10)$$

$$\text{Initial conditions: } t=0 \quad C_{4HBA} = C_{L,4HBA0} \quad (\text{after preliminary adsorption}) \quad \forall r \quad (11)$$

$$C_{Ph} = C_{L,Ph0} \quad \forall r$$

$$C_{O_2} = 0 \quad \forall r$$

$$q_{Ph} = 0, \quad q_{4HBA} = q_{max} \frac{K_{4HBA} C_{4HBA}}{1 + K_{4HBA} C_{4HBA}} \quad (1)$$

ε'_p and ρ'_p are respectively the porosity and apparent density of the aged catalyst particles ($\varepsilon'_p = 0.49$ for single 4HBA and 0.25 for the mixture). ρ_p is the density of the fresh catalyst particles (it has been verified - see Table 1 - that the particle volume has not been modified by the carbonaceous deposit).

The effective diffusivity $D'_{e,j}$ is obtained from the molecular diffusivity $D_{m,j}$ (calculated from Wilke-Chang for 4HBA and phenol, and Diaz et al., 1987, for O_2):

$$D'_{e,j} = \frac{\varepsilon'_p}{\tau} D_{m,j} \quad (12)$$

with $\tau=3$ the tortuosity factor of the catalyst particles (value optimized from experiments carried out with two particle sizes: 1.25 mm and 0.63 mm).

Method of resolution

The model leads to a Partial Differential and Algebraic Equations system (PDAE). After normalization, it has been transformed using an orthogonal collocation method for the spatial derivatives (Villadsen et al., 1967) and the resulting DAE system has been solved using the Gear method (Hindmarsh, 1980, Sargousse et al., 1999). From the time-evolutions of 4HBA and phenol in the liquid phase, the oxygen orders at 150°C, 1.2 to 3.2 bar of oxygen partial pressure, and the rate constants at different temperatures have been optimized by a Gauss-Newton procedure.

Intrinsic kinetic parameters

A 0.5 oxygen order appears to best fit both the 4HBA and phenol time-concentration curves (Figure 4) and the rate constants optimized at the different temperatures are reported in Table 4.

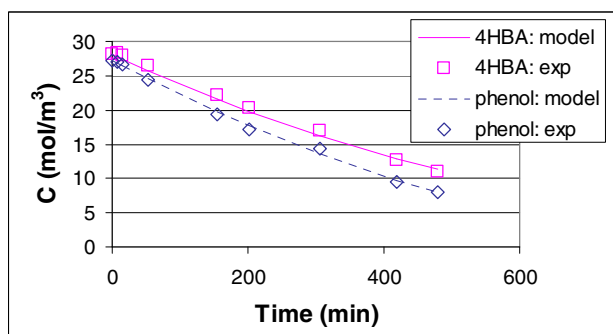


Figure 4. Evolution of pollutants concentrations in the mixture ($T=150^\circ\text{C}$, $p_{O_2} = 3.2$ bar)

The Arrhenius plot gives activation energies, 109012 J/mol and 78987 J/mol, respectively for 4HBA and phenol in the mixture.

Table 4. Values of the intrinsic kinetics constants for 4HBA and phenol

Temperature (K)	k'_{4HBA} ($m^3_L \cdot (m^3_{AC} \cdot s)^{-1}$) in the mixture	k'_{Ph} ($m^3_L \cdot (m^3_{AC} \cdot s)^{-1}$) in the mixture	k'_{4HBA} ($m^3_L \cdot (m^3_{AC} \cdot s)^{-1}$) single
413.15	0.32 (0.19)	0.32 (0.28)	0.33 (0.22)
423.15	0.74 (0.40)	0.60 (0.51)	0.81 (0.47)
433.15	1.37 (0.65)	0.92 (0.74)	1.85 (0.75)

When not accounting for the evolution of adsorbed 4HBA, the optimization leads to kinetic constants reported in brackets in Table 4.

Due to the significant adsorption capacity of AC (even reduced by polymeric deposit) and the operating conditions involving a ratio of liquid to solid volume of only 40, the contribution of the solid phase in 4HBA mass balance is clearly far from being negligible and should be accounted for kinetic optimization. However these results derived by a rather complex procedure should be even refined by more accurate adsorption isotherms and accounting for the possible competitive adsorption of oxidation intermediates.

Table 4 shows a few trends:

- the intrinsic kinetic constants for 4HBA single or in the mixture are very close;
- the intrinsic kinetic constants for phenol and 4HBA are of same magnitude.

Thus the observed faster degradation of single 4HBA compared to that in mixture (table 3) is mainly due to the stronger diffusion limitations of oxygen in the mixture (its consumption being double that for the 2-3 g/l 4HBA solution and the AC porosity being twice less).

The faster degradation of phenol is not so clear when taking into account the consumption of adsorbed pollutants, due to the differences in adsorption capacities for phenol (negligible) and 4HBA.

3. FIXED BED REACTOR

3.1 Experimental set-up and operating conditions

The experimental set-up, yet detailed in Suwanprasop et al. (2005), consists of a jacketed column of 120 cm high and 2.5 cm internal diameter. The reactor is packed with about 320 g of uncrushed and sieved activated carbon particles, same as in section 2.

The pollutant solution is fed to the column by a dosing pump and the liquid flow rate is checked by measurement of the mass of the feeding tank. Gas is supplied by two mass flow-controllers allowing different gas mixtures.

Temperature and flow rates are monitored on-line using a data acquisition system implemented in a microcomputer. The wall temperature is set to 140°C and the total operating pressure to 6 bar. Gas flow rate is 100 L/h (NTP), corresponding to an inlet gas velocity of about 10^{-2} m/s.

Liquid space time (τ_s) varies from 0.1 to 0.7 h (liquid velocities of 0.25 to 1.2 mm/s).

These conditions correspond to the bubble flow regime or transition to pulsed flow regime in up flow mode, and to the trickle flow regime in down flow mode.

After packing, the catalyst bed has first been saturated with the selected pollutant solution at reaction temperature (under nitrogen flow) until breakthrough was observed at the outlet.

Typical operation of continuous CWAO proceeds then by replacing nitrogen by the O_2/N_2 mixture corresponding to the desired oxygen partial pressure value and setting the selected operating conditions. Pollutant concentration at the reactor outlet has been measured each 30 minutes until steady state of reaction is reached (after 5 to 8 h depending on the operating conditions).

The same fixed bed has been used to treat successively: 2 g/l 4HBA, 6 g/l 4HBA-phenol mixture, 2.4 g/l phenol solutions.

3.2 Catalytic Wet Air Oxidation of 4HBA, phenol and mixture

Figure 5 shows conversion space-time profiles obtained in up flow operation for $p_{O_2}=2$ bar.

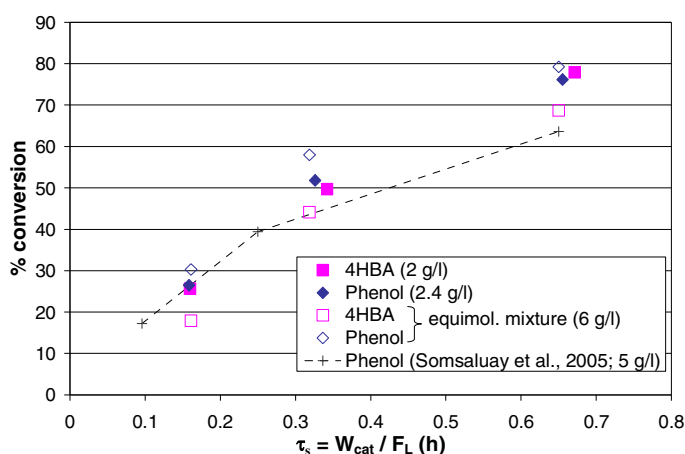


Figure 5. 4HBA and phenol conversions as functions of liquid space-time

As expected, pollutant oxidation improves when liquid space-time increases.

The differences in conversions obtained for a reactant alone or in the mixture can be explained by a possible evolution of AC porosity as observed in batch experiments (table 1): phenol is better converted in the mixture ($\varepsilon'_p = 0.25$) than alone ($\varepsilon'_p = 0.16$), whereas 4HBA conversion is higher for 4HBA alone ($\varepsilon'_p = 0.49$) than in the mixture ($\varepsilon'_p = 0.25$). Nevertheless these differences in conversions stay surprisingly low, especially in the case of 4HBA, whereas the O_2 consumption is much larger for the mixture. It should be mentioned that this fixed bed has worked successively with different effluents (about 3.5 g of pollutant treated per gram of AC) yielding a reduced change in porosity compared to the case of separate batch treatments of 4HBA-phenol mixture (or phenol): $\varepsilon'_p = 0.31$.

This bed has only been characterised at the end of the experimental series, but it is believed that change in AC structure occurs mainly during the steady state establishment of first run with a new effluent, as the catalyst activity is then quite stable.

It can be also noticed that phenol conversion in this fixed bed is slightly improved compared to that obtained with another similar AC bed (Suwanprasop et al., 2005) treating only single phenol (5 g per gram of AC), confirming a protective effect of 4HBA.

Compared to the results of intrinsic kinetics, the better conversions of phenol than 4HBA may suggest an overestimation of the adsorption effect in the calculation of the kinetics parameters.

Finally no significant differences concerning intermediates are found when comparing batch autoclave and fixed bed experiments of 4HBA and 4HBA-phenol mixture oxidation: the evolutions of intermediate concentrations versus pollutant conversion are comparable and similar values of normalized liquid phase concentrations are also found in both reactors. As reported in the case of phenol oxidation (Eftaxias, 2003, Suwanprasop et al., 2005), formic and acetic acids are the major intermediates, obtained as final organic products. The concentrations of other aromatic compounds (mainly 1,4-benzoquinone and 2AHB) and other carboxylic acids remain very low.

It can be concluded that oxidation should proceed in the same way in the batch and continuous reactors, despite very different liquid to solid ratios.

4. CONCLUSION

The particular behavior of activated carbon as catalyst of phenol (and derivatives) oxidation (high initial reduction of activity and of adsorption capacity) implied an atypical batch procedure for kinetic identification: use of large AC particles which have to be recycled and calculation of the time variations of pollutant adsorbed amounts. Batch catalytic oxidation of 4HBA was found to obey nearly the same intrinsic kinetics, whenever single or mixed with phenol. Apparent rates were however rather different when varying the pollutant, due to a change in oxygen diffusion limitations (affected by the actual catalyst porosity as well as the initial concentration of pollutant(s)). The reduction of the catalyst porosity was remarkably less with single 4HBA than with a 4HBA-phenol mixture and less with the mixture than with phenol alone, confirming the trend of a protective effect of 4HBA.

When operated consecutively on the same fixed bed, the various pollutants: phenol, 4HBA and mixture, showed differences in conversions qualitatively similar to the apparent degradations in batch reactor, but of reduced importance. Full modeling of this continuous operation, taking into account external mass transfer limitations, axial dispersion, and including the actual mean properties of the AC bed during the successive operations, is then required to quantify those differences and is under progress.

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NOTATIONS

C_j	concentration of compound j (mol/m ³)
$D'_{e,j}$	effective diffusion coefficient of compound j in aged AC pores (m ² /s)
$D_{m,j}$	molecular diffusivity of compound j (m ² /s)
d_p	catalyst particle diameter (m)
E	activation energy (J/mol)
F_L	liquid flow rate (kg/h)
He	Henry constant of oxygen in water (bar (mol/m ³) ⁻¹)
k'_0	pre-exponential factor of rate constant in Eq.(2) (m ³ _L . (m ³ _{AC} . s) ⁻¹)
K_{4HBA}	isotherm constant of 4HBA on AC (m ³ /mol)
p	pressure (bar)
q	adsorbed amount on activated carbon (mol/kg _{AC})
r	particle radial coordinate (m)
R	universal gas constant (8.314 J kg ⁻¹ K ⁻¹)
R_j	consumption rate of j (mol s ⁻¹ m ⁻³ _{AC})
t	time (s)
T	temperature (K)
V_L	liquid volume (m ³)
W_{AC}	catalyst weight (kg)
x	liquid molar fraction

Greek Letters

ϵ_p	catalyst porosity
ϵ'_p	aged catalyst porosity
ρ_p	catalyst particle density (kg/m ³)
ρ'_p	aged catalyst particle density (kg/m ³)
τ	tortuosity factor
τ_s	liquid space time (W_{AC}/F_L) (h)

Subscripts

0	at initial time of oxidation
4HBA	4-hydroxybenzoic acid
AC	activated carbon
L	liquid
O ₂	oxygen
p	particle
Ph	phenol
T	total

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