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Experimental coupling and modelling of wet air oxidation and packed-bed biofilm reactor as an enhanced phenol removal technology

Marine Minière¹ · Olivier Boutin¹  · Audrey Soric¹

Abstract Experimental coupling of wet air oxidation process and aerobic packed-bed biofilm reactor is presented. It has been tested on phenol as a model refractory compound. At 30 MPa and 250 °C, wet air oxidation batch experiments led to a phenol degradation of 97% and a total organic carbon removal of 84%. This total organic carbon was mainly due to acetic acid. To study the interest of coupling processes, wet air oxidation effluent was treated in a biological treatment process. This step was made up of two packed-bed biofilm reactors in series: the first one acclimated to phenol and the second one to acetic acid. After biological treatment, phenol and total organic carbon removal was 99 and 97% respectively. Thanks to parameters from literature, previous studies (kinetic and thermodynamic) and experimental data from this work (hydrodynamic parameters and biomass characteristics), both treatment steps were modelled. This modelling allows the simulation of the coupling process. Experimental results were finally well reproduced by the continuous coupled process model: relative error on phenol removal efficiency was 1 and 5.5% for wet air oxidation process and packed-bed biofilm reactor respectively.

Keywords Coupled process · Advanced oxidation process · Wet air oxidation · Biological treatment · Biofilm packed bed · Process modelling · Phenol

Nomenclature

A_F	m^2	Total biofilm surface area
BOD	$g_{BOD} L^{-1}$	Biological oxygen demand
$C^{O_2(d)}$	$mol L^{-1}$	Dissolved oxygen concentration in WAO
C_{WAO}^{Hdq}	$mol L^{-1}$	Hydroquinone concentration in WAO
C_{WAO}^{AcAc}	$mol L^{-1}$	Acetic acid concentration in WAO
C_{WAO}^{PhOH}	$mol L^{-1}$	Phenol concentration in WAO
C_0^{PhOH}	$g m^{-3}$	Phenol concentration at the packing/biofilm interface
C_B^{PhOH}	$g m^{-3}$	Phenol concentration in bulk liquid
C_F^{PhOH}	$g m^{-3}$	Phenol concentration at the biofilm/boundary layer interface
C_{in}^{PhOH}	$g m^{-3}$	Phenol concentration in the influent
COD	$g_{COD} L^{-1}$	Chemical oxygen demand
D_F^{PhOH}	$m^2 s^{-1}$	Phenol diffusion coefficient in biofilm
D_L^{PhOH}	$m^2 s^{-1}$	Phenol diffusion coefficient in water
d_p	m	

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j_F^{PhOH}	Packing characteristic size $g_{\text{phenol}} \text{ m}^{-2} \text{ s}^{-1}$
k	Phenol flux $\text{L mol}^{-1} \text{ s}^{-1}$
k_{PhOH}	Phenol oxidation rate constant m s^{-1}
K_i	Phenol mass transfer coefficient g m^{-3}
K_{PhOH}	Phenol inhibition constant g m^{-3}
L_L	Phenol affinity constant m
Q	Boundary layer length $\text{m}^3 \text{ s}^{-1}$
R	Phenol flow rate Ratio of phenol diffusion coefficient in biofilm on phenol diffusion coefficient in water
r	Bacteria growth rate $g_{\text{COD-X}} \text{ m}^{-3} \text{ s}^{-1}$
r^{PhOH}	Phenol consumption rate $g_{\text{phenol}} \text{ m}^{-3} \text{ s}^{-1}$
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
X_H	Biofilm density $g_{\text{COD-X}} \text{ m}^{-3}$
X_V	Biofilm density used in R calculation $\text{kg}_{\text{VS}} \text{ m}^{-3}$
$Y_{X/H}$	Heterotrophic biomass yield $g_{\text{COD-X}} g_{\text{phenol}}^{-1}$
z	Distance from packing m
μ_{max}	Specific growth rate s^{-1}
ν_{water}	Water kinematic viscosity $\text{m}^2 \text{ s}^{-1}$

Introduction

Industrial wastewater treatment is a strong issue, as effluents could combine high organic waste concentration, refractory compounds at different concentrations and relatively low and intermittent flow rates. Chemical processes are known to be very efficient for the removal (oxidation) of many pollutants. They often involve chemical and/or energy consumption (Guieysse and Norvill 2014). On the contrary, biological processes are low-energy and maintenance consumers, but they are only efficient for biodegradable organic compounds. They cannot easily remove highly toxic pollutants or refractory compounds in normal operating conditions (Guieysse and Norvill 2014). Though a large range of processes are available, many pollutants, as for instance dyes, surfactants or

pharmaceuticals, are still refractory to conventional treatments. Moreover, environmental protection involves more and more stringent regulations on pollutant discharge in aquatic environment.

One way to improve pollutant removal with limiting extra costs is to combine different processes in order to benefit from their advantages and to overcome their drawbacks. This could create complementary and synergistic effects. An interesting coupled process is the combination of chemical and biological processes. During the last 40 years, more than 200 studies have been published about chemical–biological-coupled processes. Four literature reviews (Guieysse and Norvill 2014; Scott and Ollis 1995; Mantzavinos and Psillaki 2004; Oller et al. 2011) relate the evolution of this field from 1976 to 2013. Moreover, integrated processes have also gained more and more attention (Di laconi 2012). According to the effluent, one of the two following sequences is more relevant:

- Biological–chemical treatments aim at degrading biodegradable compounds and mineralizing remaining compounds which are refractory to biodegradation. These coupled processes are suitable for effluents with high concentration of biodegradable compounds and low concentration of hardly biodegradable compounds, such as pulp and paper mill effluents (Assalin et al. 2009) or landfill leachates (Lei et al. 2007). They are also suitable if the biological treatment of an effluent leads to specific metabolites inhibiting bacterial activity: a chemical post-treatment allows their oxidation.
- Chemical–biological treatments are the oxidation of hardly biodegradable or inhibitory compounds into more biodegradable ones and then a degradation of those compounds through a biological treatment. These coupled processes allow saving energy or chemicals due to partial oxidation in comparison with total chemical mineralisation. They are suitable for effluents containing a high fraction of hardly biodegradable compounds, such as petrochemical effluents (Ishak and Malakahmad 2013), as well as effluents containing toxic or inhibitory elements to micro-organism compounds, such as textile effluents with toxic dyes or pesticide effluents (Libra and Sosath 2003; Pariente et al. 2013).

Chemical–biological processes are the most studied, as they can treat effluents with high toxicity. Among chemical and advanced oxidation processes, wet air oxidation (WAO)—an oxidation process in subcritical water at high temperature and pressure—is an efficient process with no chemical consumption (except oxygen or air). It can be optimised in terms of energy consumption (Lefevre et al. 2011). Verenich and Kallas (2002) showed that WAO as a pre-treatment could enhance biodegradability of pulp and paper mill effluents from 24 to 89%. Moreover, this process can

be economically viable for concentration of some relatively high wastes, due to its high efficiency and short residence time. However, an energy optimisation is needed in this case (Lefevre et al. 2011; Lefevre et al. 2012). Among biological processes, packed-bed biofilm reactors (PBBRs) are based on the biodegradation of pollutants by biomass attached on carriers (Warnoc et al. 2005; Ranade et al. 2011). They are very interesting since they need less space than suspended biomass reactors; they are easier to handle than fluidised bed bioreactors and also involve high sludge retention time leading to good efficiency. Zapata et al. (2010) successfully used a PBBR with a photo/Fenton pre-treatment for the decontamination of pesticide-containing wastewater, achieving 84% of mineralisation.

In many research studies, authors target model compounds. For instance, several studies on chemical–biological coupling use phenol, which is found in many industrial effluents (winery, olive mill, petrochemistry, coking, refinery, etc.) and which is dangerous for human health (Busca et al. 2008). Advanced oxidation process, coupled with biological process, is an interesting treatment for olive mill effluents containing high concentration of phenol (Mantzavinos and Kalogerakis 2005). For olive mill effluents, phenol concentrations can vary from 5.8 g L⁻¹ (Rivas et al. 2001) to 29 g L⁻¹ (Minh et al. 2008). Benitez et al. (1999) reached 84% of chemical oxygen demand (COD) removal from an olive mill wastewater by coupling ozonation with an aerobic biological treatment.

Although some studies give elements on the feasibility of coupling chemical–biological processes for the treatment of industrial effluents, they usually do not consider the whole and effective coupled process (Zapata et al. 2010; Wang et al. 2012). Most of them only analyse the chemically pre-treated effluent in terms of biological oxygen demand (BOD) and COD without implementing the experimental study of the biological step with the real effluent coming from the oxidation step. Moreover, in a review on chemical oxidation as a pre-treatment for biodegradability enhancement, Mantzavinos and Psillaki (2004) emphasised the lack of models for predicting the removal efficiency of the coupled process. Guieysse and Norvill (2014) concluded that researches should focus on a better assessment of this coupled technology in terms of sensitivity to operational parameters in order to optimise the whole process. This lack in process modelling and process assessment leads to a lack in economic estimation of some coupled processes (Oller et al. 2011).

Thus, this study aims at experimentally demonstrating the interest of coupling wet air oxidation with a packed-bed biofilm reactor on phenol degradation as a compound found in many industrial effluents. Even if some results are reported in literature (Assalin et al. 2009; Benitez et al. 1999; Lei et al. 2007), the originality and the interest of this work is the effective experimental coupling of the two processes and the inherent removal efficiency. Then, each process was modelled and

the whole process simulated in order to help the evaluation of this coupling approach.

Materials and methods

Materials

High-purity phenol (>99%) and acetic acid of analytical grade were bought from Sigma-Aldrich and Carlo Erba Reagents respectively. Pink dye Rhodamine WT (20 wt% rhodamine in water) for residence time distribution (RTD) experiments was bought from Acros Organics. Bioreactors were inoculated with samples of activated sludge from an urban wastewater treatment plant.

Experimental setup

The experimental coupling of wet air oxidation with packed-bed biofilm reactors was carried out on a phenolic solution. First, oxidation of a phenolic solution was carried out in a batch WAO reactor. Then, the resulting effluent was biodegraded by the means of two PBBRs in series.

Wet air oxidation step

Figure 1 shows the wet air oxidation batch reactor (Top Industrie, France). It was composed of a 152.8-mL stainless steel reactor equipped with a stirrer (Rushton propeller, maximum speed 2000 rpm). It was connected to a volumetric pump allowing injection of either phenolic solution, oxygen or nitrogen at a given volume or pressure. Maximum temperature and pressure were set at 350 °C and 30 MPa respectively. Temperature was regulated, thanks to a cooling jacket and an electric heating collar. Liquid samples were collected via a valve located at the bottom of the reactor.

A phenolic solution of 9.3 g L⁻¹ was prepared. This value is in the range of concentration in olive mill effluents and allowed decreasing the number of batch experiments. The operating conditions were chosen from previous experiments realised by our group to achieve a high removal rate of phenol with low concentration of residual phenol and high concentration of accumulated acetic acid (Lefevre et al. 2011). Temperature was set at 250 °C and pressure at 30 MPa, with a residence time of 15 min and an air factor (ratio between the oxygen really introduced to the oxygen needed at stoichiometry) of 1.7.

First, the reactor was heated at 60 °C and pressurised at 2.6 MPa with nitrogen, the initial pressure being estimated from thermodynamic calculations using the Soave–Redlich–Kwong equation of state (Lefevre et al. 2011). Sixty millilitres of phenolic solution was injected, and the reactor was isolated and stirred. When the set temperature was reached, air was injected at the set pressure and the reaction began ($t = 0$).

Finally, after 15 min, the reactor was purged and the pre-oxidised solution was collected. This solution was kept at 4 °C, waiting for further biological treatment.

This procedure was done 15 times in order to recover 900 mL of pre-oxidised solution. This volume is necessary for biological operation conditions.

Packed-bed biofilm reactors

To enhance phenol biodegradation, a hardly biodegradable compound and a biological inhibitor, an acclimation phase is required. Two PBBRs were implemented in series: one acclimated to phenol and the other one fed with acetic acid. Then, the following series sequence was chosen: WAO effluent passed through the phenol-acclimated PBBR followed by acetic acid-fed PBBR. This allowed reducing phenol concentration and its inhibitory effect on the non-acclimated biofilm of the second reactor.

All experiments were conducted at ambient temperature (20 °C) in aerobic conditions. The bioreactors were made of a plastic cylinder of 4.6 cm of intern diameter schemed on Fig. 2. They were filled with Kaldnes K1® plastic packing till 25 cm height, supported by a stainless steel grid. Packing was 9.1 mm in diameter, 7.2 mm high with a porosity of 93% and a total specific area of 800 m² m⁻³ and protected surface area of 500 m² m⁻³. Total volume of the bed is 450 cm³. Feeding solution was brought thanks to a Masterflex pump, and the reactor was operated downflow with unsaturated conditions. Pebbles were placed at the top of the packing to allow good distribution of the feeding solution and to retain packing during backwashing. Aeration was done through air bubbling of the feeding tank and by natural draft.

Bacteria inoculum comes from an urban wastewater treatment plant located in Aix en Provence (France). The average concentration of suspended solids in the initial sample is 6.2 ± 1.9 g L⁻¹. In order to avoid any plugging problems, the sludge was diluted to reach a concentration of 350 mg L⁻¹. The inoculation phase consisted in a 2-day batch recirculation of the inoculum mixed with sucrose and nutrients. After the inoculation, the acclimation was carried out by feeding the PBBRs with increasing concentrations of acclimation substrate: phenol PBBR was acclimated for 43 days to a maximal phenol concentration of 800 mg L⁻¹, whereas acetic acid PBBR was fed for 23 days with a maximal acetic acid concentration of 944 mg L⁻¹. These durations allowed sufficient biomass growth. The feeding solution was recirculated continuously in the biofilter at a flow of 0.3 L h⁻¹. It was renewed every day. NH₄Cl and KH₂PO₄ were added as nutrients to the substrate solution at a C/N/P mass ratio of 100:5:1. For the treatment of the effluent coming from the WAO process, the PBBRs were feeding at a flow rate of 0.3 L h⁻¹.

Methods and analysis

Effluent analysis

Phenol, hydroquinone and acetic acid concentrations in the liquid samples are determined with gas chromatography. A Varian 3800 GC equipped with a CP-Sil 5 CB column and a flame ionisation detector was used with the following analytical method: injection temperature of 250 °C, column pressure of 0.079 MPa, detector temperature of 320 °C, helium flow (vector gas) of 17 mL min⁻¹ and inlet pressure of 0.275 MPa for hydrogen, 0.41 MPa for air and 0.55 MPa for helium. The temperature program started with a rise from 95 to 150 °C for 5.5 min, followed by 4 min at 150 °C and a final rise from 150 to 300 °C during 7.5 min. Using results from total organic carbon measurements and mass balances, the compounds detected through this GC analysis represent between 90 and 95% of the mass of carbon in each sample, in the conditions tested. An example of chromatogram evolutions is given in Sect. 2 of [supplementary materials section](#).

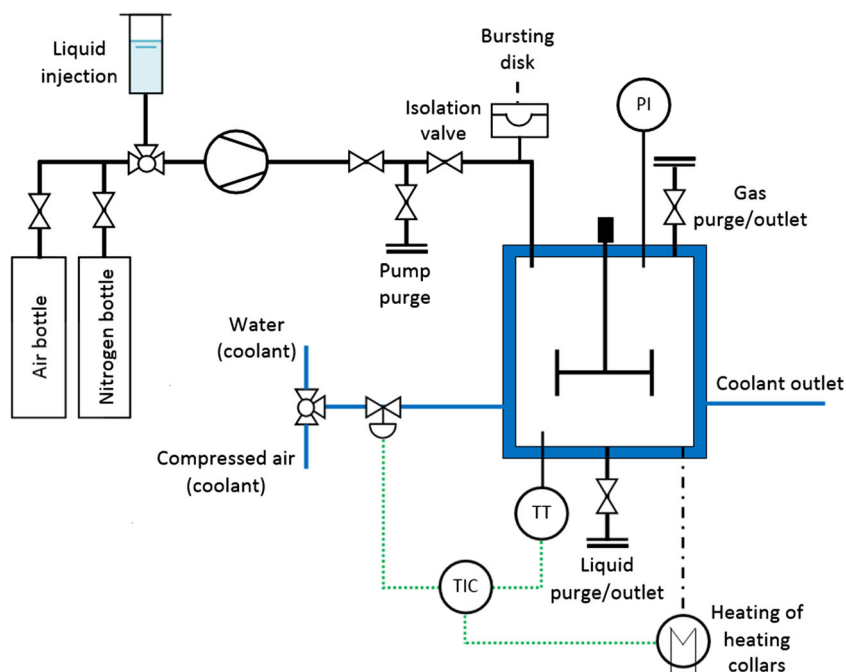
Characterisation of the phenol-acclimated PBBR

Experimental data on the phenol-acclimated PBBR was necessary for modelling: hydrodynamic behaviour, biomass analysis and performances of the bioreactor.

Hydrodynamic characterisation Hydrodynamic behaviour of the PBBR was analysed by residence time distribution measurements using Rhodamine as a tracer. This tracer was recovered at the exit between 96 and 100% and hence not degraded by bacteria, confirming it is a hardly biodegradable compound. A tracer solution made of both substrate (phenol at acclimation concentration) and Rhodamine WT (at 0.06 mg L⁻¹) was injected under a step injection form. Finally, the effluent was regularly sampled for 3 h and analysed. A calibration curve of the absorbance at 555 nm of a Rhodamine WT solution, as a function of its concentration, was obtained. Presence of phenol had no influence on the absorbance of the Rhodamine solution at 555 nm.

Biomass analysis A local mass balance in biofilm is also necessary to implement a PBBR model. This mass balance requires the knowledge of some biomass characteristics. Biomass density in biofilm is the quantity of active biomass per volume of biofilm. Biofilm volume was calculated assuming a biofilm density of 1.0 g L⁻¹ since it is mainly constituted of water. Active biomass is the fraction of biomass which really degrades the substrate; the other fraction is the dead biomass which degraded over time in the deep layer of the biofilm. It was obtained from the volatile solid weight converted in chemical oxygen demand by considering the following factor value 1.42g_{DCO-X} g_{VS}⁻¹ (IWA Publishing 2006).

Fig. 1 Wet air oxidation batch reactor



The weights of the wet biofilm and solids were determined as follows: few packings were sampled, weighted and sonicated for 20 min in 30 mL of deionised water for biomass detachment. Centrifugation at 13500 rpm for 15 min allowed removing supernatant water. Then, the solid phase was recovered, dried at 105 °C for 24 h and weighted to determine the total solid fraction. Finally, the sample was heated at 550 °C for 5 h (until mass stabilised) and weighted to calculate the total volatile solid fraction.

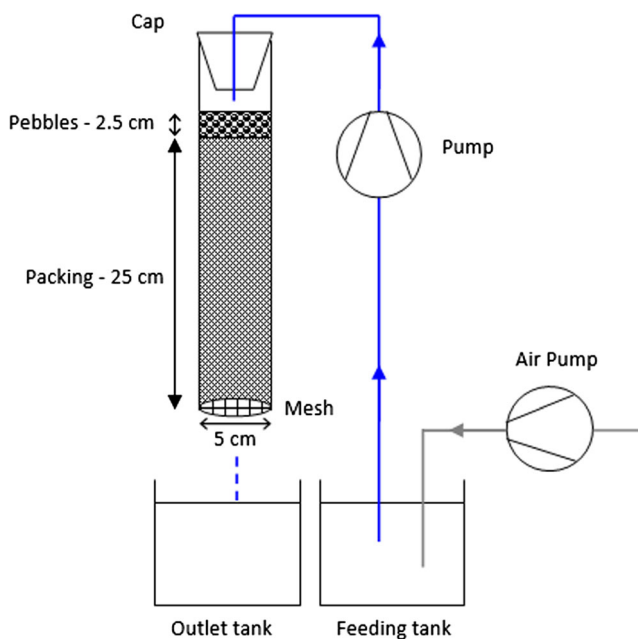


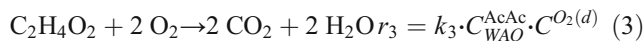
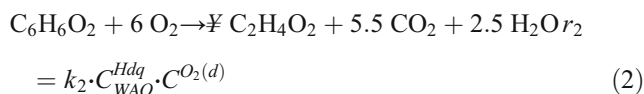
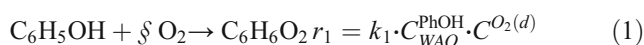
Fig. 2 Packed-bed biofilm reactor

Coupled-process modelling

Wet air oxidation modelling

Wet air oxidation was simulated using the software ProsimPlus® (Prosim, France). Predictive Soave–Redlich–Kwong thermodynamic model was chosen (Lefevre et al. 2011).

A model with two intermediate compounds (acetic acid and hydroquinone which are the two main degradation compounds identified through GC analysis) and three reactions was considered, with their associated reaction rates r_i :



The kinetic parameter was taken from a previous study (Lefevre et al. 2011).

A simulation was developed considering the continuous co-current bubble column, as in many industrial plants (Debelfontaine et al. 1999). The experimental conditions previously given are the same, but here a bubble column is simulated, different from the batch reactor used to obtain degradation rates and molecular composition. Hydrodynamics of this kind of reactors can be quite complex since it depends on many parameters as axial dispersion, gas hold-up and gas–liquid interfacial area (Kantarci et al. 2005). However, a hydrodynamic model with five isothermal continuously stirred tank reactors

(CSTRs) in series can be assumed (Lefevre et al. 2011). Oxygen and nitrogen input flow rates were automatically calculated using an air factor of 1.7. Pressure is set to 25 MPa and temperature to 250 °C. Vapour and liquid outputs were finally cooled at 20 °C and relaxed at atmospheric pressure.

Phenol-acclimated PBBR modelling

The phenol-acclimated PBBR was modelled with three compartments as shown in Fig. 3. Two components were used: biomass as particulate compound and phenol as dissolved compound. It was assumed that phenol was the limiting substrate. Steady state was also assumed, which implied that biomass concentration and biofilm thickness were constant over time. Thanks to RTD experiments, it has been proven that the bulk liquid was completely mixed (see “Phenol-acclimated PBBR” section), so that the concentrations were homogeneous all along this compartment. This result has been yet obtained for a more general case of packed columns under trickle-flow conditions, also through RTD experiments (Van Swaaij et al. 1969). A boundary layer involved phenol mass transfer resistance between bulk liquid and biofilm. Diffusion and reaction processes both occurred inside the biofilm. Phenol consumption was only considered inside the biofilm: degradation occurring in the bulk liquid due to small quantities of suspended biomass was neglected.

Equations

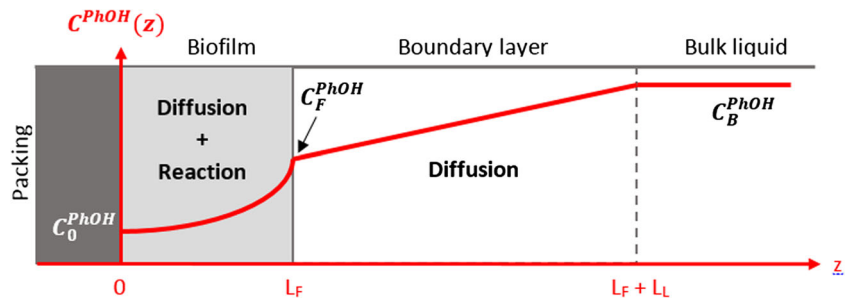
The following phenol mass balances result from the previous hypothesis: bulk liquid Eq. (4), boundary layer Eq. (5) and biofilm Eq. (6). These equations respect two conditions: flux continuity at the boundary layer/biofilm interface Eq. (7) and no flux at the biofilm/packing interface Eq. (8).

$$Q \cdot (C_{in}^{PhOH} - C_B^{PhOH}) + J_F^{PhOH} \cdot A_F = 0 \quad (4)$$

$$-D_L^{PhOH} \frac{d^2 C^{PhOH}}{dz^2} = 0 \quad (5)$$

$$-D_F^{PhOH} \frac{d^2 C^{PhOH}}{dz^2} + r^{PhOH} = 0 \quad (6)$$

Fig. 3 Biofilm model schematic representation—phenol concentration evolution along the three compartments: biofilm, boundary layer and bulk liquid



$$j_F^{PhOH} = -D_F^{PhOH} \frac{dC^{PhOH}}{dz} \Big|_{z=L_F} = -k_{PhOH} (C_F^{PhOH} - C_B^{PhOH}) \quad (7)$$

$$-D_F^{PhOH} \frac{dC^{PhOH}}{dz} \Big|_{z=0} = 0 \quad (8)$$

As phenol is an inhibitory compound, Haldane kinetics was used (see Eq. (9) and Eq. (10)).

$$r^{PhOH} = -\frac{1}{Y_{X/H}} \cdot r \quad (9)$$

$$r = \mu_{max} X_H \cdot \frac{C^{PhOH}}{C^{PhOH} + K_{PhOH} + \frac{C^{PhOH2}}{K_I}} \quad (10)$$

The problem was solved as a second-order non-linear differential equation with given initial conditions:

$$C_0^{PhOH} \text{ and } \frac{dC^{PhOH}}{dz} \Big|_{z=0} = 0 \quad (11)$$

The resolution consisted in finding the initial value C_0^{PhOH} respecting the condition presented in Eq. (4). The resolution of second-order non-linear differential equation was done using the 4th order Adams–Bashforth method initialised with the Runge–Kutta 4 method.

Parameters

Phenol diffusion coefficients in biofilm were calculated using Fan correlation (Fan et al. 1990); see Eq. (12). Even if biofilm is mainly constituted of water (intra- and extra-cellular water), the presence of bacteria (solid material) limits diffusion compared to pure water.

$$R = \frac{D_F^{PhOH}}{D_L^{PhOH}} = 1 - \frac{0.43 * X_V^{0.92}}{11.19 + 0.27 * X_V^{0.99}} \quad (12)$$

The phenol mass transfer coefficient was calculated using correlation (13) (Logan 2012). This correlation is valid for Reynolds between 10^{-3} and 5.8 (in this study, $Re = 0.35$). Boundary layer thickness was calculated as $L_L = D_L^{PhOH} / k_{PhOH}$.

Table 1 Physical and kinetic parameters used in the PBBR model

Parameters		Unit	Value	Reference
Physical parameters	D_L^{PhOH}	$m^2 s^{-1}$	$8.8 \cdot 10^{-10}$	Toxicity datasheet (INERIS)
	k_{PhOH}	$m s^{-1}$	$1.35 \cdot 10^{-6}$	Logan 2012
Kinetic parameters	μ_{max}	h^{-1}	0.308	Saravan et al. 2008
	K_{PhOH}	$mg L^{-1}$	44.9	
	K_i	$mg L^{-1}$	525	
	$Y_{X/H}$	$g_{SS} g_{phenol}^{-1}$	0.6	Nuhoglu and Yalcin 2005
			0	Pawlowksy and Howel 1973

$$Sh = \frac{k_{PhOH} d_p}{\nu_{water}} = 2 + 1.58 * Re^{0.4} * Sc^{1/3} \quad (13)$$

Kinetic parameters (Table 1) were taken from Saravanan's study since it has similar characteristics with the present study (Saravan et al. 2008). The yield factor $Y_{X/H}$ was taken from other studies reported in the literature (Nuhoglu and Yalcin 2005; Hsien and Lin 2005; Pawlowksy and Howell 1973).

Results and discussion

Experimental results

Wet air oxidation

Wet air oxidation of the initial phenolic solution led to a high phenol removal rate of 97%. Analysis revealed a high concentration of acetic acid ($2.4 g L^{-1}$). According to the GC chromatograms, only those two organic compounds were detected, so that 84% of total organic carbon (TOC) removal was calculated. Eighty-three percent of remaining TOC was due to acetic acid.

PBBRs in series

As TOC concentration of the pre-oxidised effluent is quite high, it was twice diluted to avoid stressing bacteria. This

obviously would not be done in an industrial process, but the phenol initial concentration has been chosen high in order to decrease the number of WAO experiments at the laboratory scale. Phenol-acclimated PBBR has led to 60, 51 and 53% of phenol, acetic acid and TOC removal respectively. Phenol removal efficiency has indicated that biomass was successfully acclimated to phenol. Acetic acid removal efficiency has also shown that, even if phenol-degrading biomass was selected during the acclimation step, acetic acid was easily biodegradable by this bacterial consortium. Moreover, acetate is a metabolic intermediate of many carbon sources, such as glucose and potentially phenol, so that the net removal efficiency might represent both production (due to phenol degradation) and consumption of acetic acid (Bajaj et al. 2008). After 34 days of phenol acclimation, removal efficiency of a synthetic phenolic solution of $800 mg L^{-1}$ was 35%. This rate was relatively low and much lower than in the coupling experiment (60%). This can be explained by two main reasons: phenol concentration was higher ($800 mg L^{-1}$ against $133 mg L^{-1}$) so the inhibitory nature of phenol had more impact, and high fraction of dead volume (according to RTD results) decreased the performance of the whole PBBR. Nevertheless, this result was consistent with those found in other studies (Zapata et al. 2010; Wang et al. 2012). Two results from literature are lower than the removal efficiency achieved in this study (Nuhoglu and Yalcin 2005; Marrot et al. 2006) (Table 2). In the Nuhoglu and Yalcin (2005) study, the lower biomass concentration probably explained this

Table 2 Comparison between this study and literature

Characteristic	Unit	Marrot et al. 2006	Nuhoglu and Yalcin 2005	This study
Acclimation process	/	Suspended biomass	Suspended biomass	Biofilm
Acclimation phenol concentration	$g L^{-1}$	3.0	1.45	0.8
Acclimation time	day	120	25	34
Tested phenol concentration	$g L^{-1}$	0.7	0.68	0.8
Residence time	min	15	30	16
Biomass concentration per void volume	$g L^{-1}$	9–10	1.8–2.0	14.3
Phenol removal efficiency	%	30	25	35

Table 3 Phenol, acetic acid and TOC concentrations at different stages of the coupled process

Concentration (mg L ⁻¹)	Phenol	Acetic acid	TOC
Initial influent	9320	/	7132
Pre-oxidised effluent	252	2366	1138
Diluted effluent	133	1252	602
Biologically treated effluent—1st PBBR	53	608	284
Biologically treated effluent—2nd PBBR	49	141	94
Final removal efficiencies	99%	/	97%

difference. On the contrary, in the Marrot et al. (2006) study, operating conditions were very close to this study but the acclimation time and concentration were higher, which should involve higher rates. Indeed, this lower performance might be explained by the acclimation process: acclimation of suspended biomass seems less efficient than acclimation of attached biomass in a biofilm. This phenomenon may be a consequence of the physical structure of biofilm: development of slow-growing organisms (able of degrading phenol in this case) is facilitated thanks to small biological niches where they are protected and cannot be washed out like in homogeneous systems (IWA Publishing 2006). The Pishga (2011) study on anaerobic phenol biodegradation confirmed this observation by comparing the performances of free and immobilised cells both acclimated to 1000 mg L⁻¹ of phenol. It was shown that, at high concentration of phenol (over 500 mg L⁻¹), phenol removal efficiencies were significantly higher in immobilised cell experiments.

Acetic acid-fed PBBR led to 7, 77 and 67% of phenol, acetic acid and TOC removal respectively. Phenol removal efficiency in the second PBBR was very low: bacteria consortium was clearly not adapted to phenol degradation which confirms that specific biomass or specific acclimation is necessary to ensure phenol degradation. The acetic acid removal efficiency is consistent with pilot-scale experiments conducted by Zeng et al. (2013) who achieved 69% of TOC removal

in an aerobic PBBR also packed with Kaldnes K1 and fed with a synthetic effluent made of easily biodegradable organic compounds.

Regarding the whole biological treatment, the removal efficiencies of phenol, acetic acid and TOC were finally 63, 89 and 84% respectively. It was also demonstrated that coupling two PBBRs with different bacteria consortia leads to better performances than using only one of them.

Overall experimental results

The results regarding the process coupling are summarised in Table 3. Phenol degradation was mainly due to pre-oxidising but was also slightly improved thanks to the biological treatment (from 97 to 99%). Besides, biological treatment clearly improved TOC removal (from 84 to 97%) since organic carbon was mainly due to accumulated acetic acid which is refractory to chemical oxidation but easily biodegradable. Finally, these results clearly demonstrated the feasibility and the interest of coupling wet air oxidation with PBBR as a treatment of a refractory compound.

Biomass analysis indicates that reactional volume changes with time, probably generated by biomass clogging some parts of the reactor (more details in supplementary material, Sect. 1).

Modelling results

The general scheme of the simulation of the whole coupled process is proposed in Fig. 4.

Wet air oxidation process

Wet air oxidation simulation on ProsimPlus® was conducted considering a phenol solution input flow rate of 0.3 L h⁻¹ (see Fig. 5). CSTR volumes (and so on the residence time) were adjusted to obtain a similar phenol removal efficiency than in

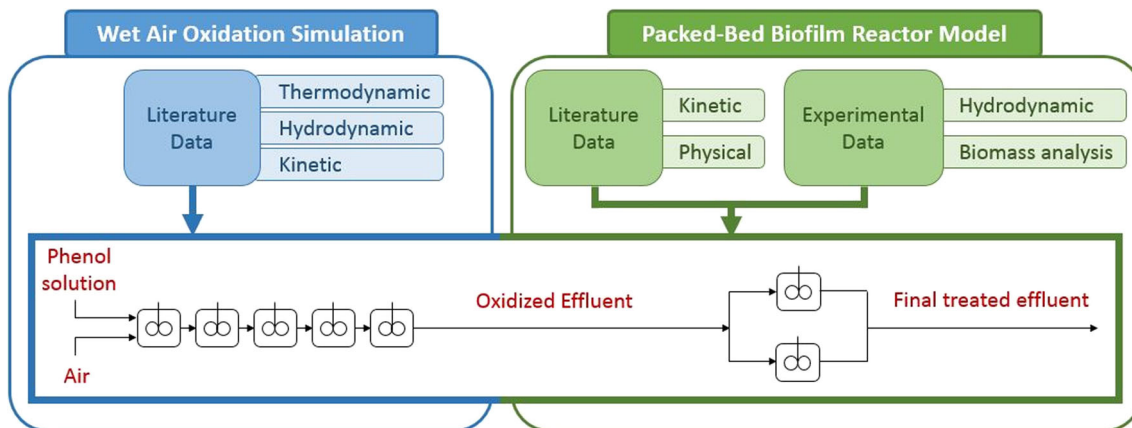


Fig. 4 Schematic diagram representing the coupled process modelling method

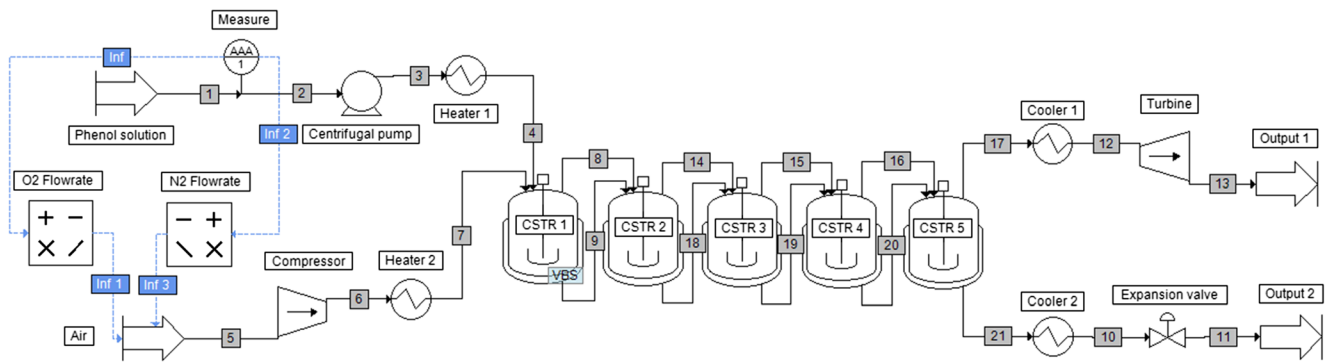


Fig. 5 Wet air oxidation simulation on ProsimPlus® software

the batch WAO experiment: with five CSTRs of 15 mL each—that is, a total residence time of 6.6 min—96% of removal was obtained. These five CSTRs simulate a real industrial bubble column usually used for wet air oxidation.

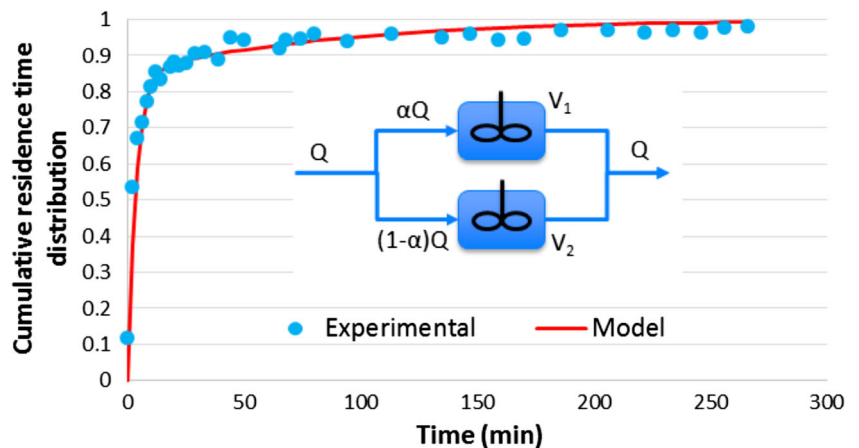
Phenol-acclimated PBBR

Hydrodynamic behaviour Cumulative residence time distribution was well represented by two parallel CSTRs (volume V_1 and V_2) with a different flow in each branch (flow ratio α) as shown in Fig. 6 and related (see more details in supplementary material, Sect. 3). RTDs were determined after 34 and 43 days of phenol acclimation.

According to RTD results, reactional volume—and so on the residence time—was very low on day 34. For this reason, the PBBR was backwashed on day 35 with water and air bubbles for 30 min. One week later, another RTD experiment was done (day 43). It showed that backwashing was efficient since the reactional volume was more than doubled.

Comparison between model and experiment Modelled and experimental removal efficiencies were very close: 32 and 35% respectively for the experiment on day 34 (relative error of 8%) and 56 and 60% respectively for the coupling experiment on day 43 (relative error of 7%).

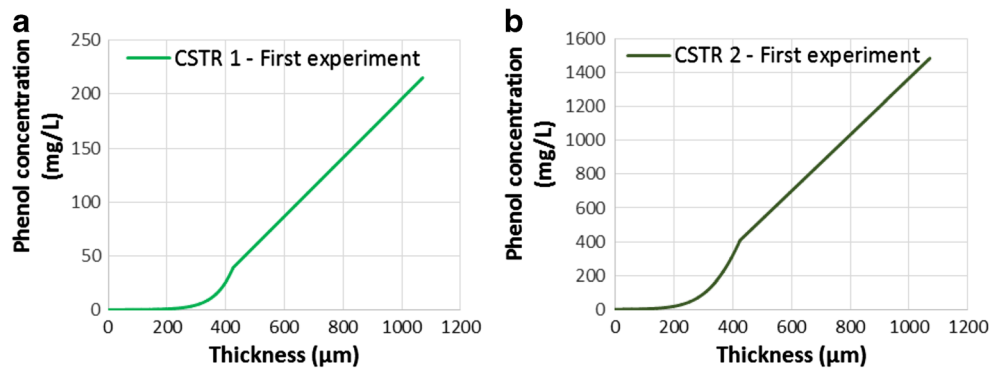
Fig. 6 Experimental and modelled cumulative residence time distribution in function of time (day 34) with schematic model representation (deviation is less than 15%)



The phenol concentration profiles (as a function of biofilm and boundary layer thicknesses) are shown in Fig. 7. It appears that the low phenol mass transfer coefficient involved a very thick boundary layer of 630 μm , which is higher than the biofilm itself (425 μm). Besides, most of phenol degradation occurred in the first half of the biofilm. This shows that a high fraction of biomass was not really active in the biofilm. Thus, it shows that a regular backwashing of the reactor is necessary in order to increase the reaction volume instead of growing a too thick and partly inactive biofilm. However, frequency of backwashing must also be low enough to allow a good development of slow-growing bacteria and to increase sludge retention time. Frequency and duration of backwashing are parameters that must be optimised.

Influence of operating parameters Since the model shows good accordance with experimental results, it is interesting to assess the influence of some operating parameters on the predicted phenol removal efficiency. Data from the coupling experiment (day 43) was used to obtain the results shown in Table 4. Phenol flow rate is one of the most important parameters to optimise phenol degradation. Indeed, if flow rate is twice decreased (i.e. residence time doubled), removal efficiency is improved from 56 to 65%. On the contrary, with

Fig. 7 Modelled phenol concentration profiles in CSTR 1 and CSTR 2 in the first experiment (day 34)



the tested conditions, phenol concentration and biomass density do not influence phenol removal efficiencies.

To conclude, this model, established from both experimental and literature data, fits well the experimental results and could be used in a global simulation integrating both WAO and PBBR.

Overall modelling results

Input flow rates in WAO simulation and in the PBBR model were 0.3 L h^{-1} , so that continuity was ensured. Besides, phenol WAO output concentration was used as input of the PBBR model. Results of this continuous coupled process modelling are very similar to experimental results (see Table 5): the relative difference between modelled and experimental phenol removal efficiencies was 1, 5 and 1% for the WAO, phenol-acclimated PBBR and global coupled process respectively.

As phenol flow rate (residence time) was an important parameter in PBBR modelling, its influence on the phenol removal efficiency of the whole coupled process has been assessed. If phenol flow rate is increased by 50% (4.4 min of residence time), removal efficiencies in the WAO, PBBR and global processes are 94.3, 46.7 and 97.0% respectively. In the other case where phenol flow rate is increased by 50% (9.9 min of residence time), removal efficiencies are 98.4, 62.3 and 99.4% respectively.

Table 4 Influence of different parameters on phenol removal efficiency

Parameter	Parameter variation	Removal efficiency variation
Phenol flow rate	-50%	+15.4%
	+50%	-8.8%
Phenol initial concentration	-50%	+0.2%
	+50%	-0.4%
Biomass density in biofilm	-50%	-1.9%
	+50%	+0.7%

Conclusion and prospects

Feasibility and interest of coupling wet air oxidation and packed-bed biofilm reactors have been demonstrated on phenol degradation. Biological treatment clearly enhances TOC removal and allows limiting wet air oxidation to phenol degradation. Moreover, PBBR is also able to slightly improve phenol degradation.

It has been demonstrated that two PBBRs in series with a phenol-acclimated PBBR followed by an acetic acid-fed PBBR is necessary to limit the phenol inhibitory effect and thus to improve performances. Optimisation of the first PBBR in terms of temperature, hydrodynamics, pH and aeration process seems very important to avoid residual phenol in the intermediate effluent and so to improve TOC removal efficiency in the second PBBR.

Furthermore, both processes were successfully modelled separately:

- For WAO, a continuous bubble was simulated from literature data. A simplified hydrodynamic model was assumed, so it would be interesting to further enhance this simulation by taking into account a more complex hydrodynamic behaviour.
- A PBBR model was implemented from experimental and literature data. Regarding the phenol-acclimated PBBR model, good accordance was found between modelled and experimental phenol removal efficiencies. It also

Table 5 Results of WAO and PBBR models as a coupled process

Phenol	Flow rate (mg h ⁻¹)	Modelled removal efficiency	Experimental removal efficiency
WAO influent	2790	/	/
WAO effluent/PBBR influent	109	96.1%	97%
PBBR effluent	47	57.1%	60%
Final removal efficiency		98.3%	99%

appeared that most of the reaction occurred in the first half part of the biofilm. This demonstrates that a fine compromise is to be found on backwashing frequency to increase both reactional volume (with less inactive biomass) and sludge retention time.

At the end, the continuous coupled process was modelled using WAO simulation effluent as influent of the PBBR model. Experimental results were well fitted by the simulation ones, and phenol flow rate influence was assessed. Other parameters as WAO operation temperature or phenol concentration would have to be assessed in the future.

A next stage would be to include potential recycling streams between biological treatment and chemical oxidation steps. This global simulation would allow optimising the coupled process design in order to improve its performances in terms of both removal efficiencies and energy consumption. The modelling and simulation parts are hence very important to further work on the economic positioning of this kind of coupling processes.

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