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Oxidation of nitrobenzene by ozone in the presence of faujasite zeolite in a continuous flow gas–liquid–solid reactor

J. Reungoat, J. S. Pic, M. H. Manéro and H. Debellefontaine

ABSTRACT

This work investigates the oxidation of nitrobenzene (NB) by ozone in the presence of faujasite zeolite. Experiments were carried out in a gas–liquid–solid reactor where ozone transfer and NB oxidation took place at the same time. Three configurations of the reactor were compared: empty, filled with inert glass beads and filled with faujasite pellets. First, ozone transfer coefficient ($k_L a$) and decomposition rate constant (k_C) were determined for each configuration. In presence of solid, $k_L a$ was 2.0 to 2.6 times higher and k_C was 5.0 to 6.4 times higher compared to the empty reactor. Then, the various configurations were evaluated in terms of NB removal and chemical oxygen demand (COD) decrease. The faujasite reactor showed higher removal of NB and decrease of COD compared to other configurations under the same conditions suggesting that the faujasite increases the oxidation rate of NB. Oxidation of NB in presence of faujasite also proved to be limited by the transfer of ozone from the gas to the liquid phase.

Key words | adsorption, decomposition, ozonation, transfer, wastewater, zeolite

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INTRODUCTION

Processes based on biological degradation are often used for the treatment of industrial wastewaters containing organic pollution because they can economically degrade a wide range of compounds. However, some compounds can be toxic to the bacteria and inhibit their action or even kill them; therefore, biological degradation of organic pollution is not always possible. For example, the complete degradation of nitrobenzene (NB) by activated sludge has been reported to take 7 to 10 days (ATSDR 1990), a value incompatible with most of the wastewater treatment plants. For concentrations above 50 mg L^{-1} , NB can be very resistant to biodegradation and inhibit the degradation of other compounds (ATSDR 1990). Nitrobenzene and its derivatives have adverse effects on numerous organs (IARC 1996) and the evidence of carcinogenicity of NB in experimental animals has been established by the IARC (1996).

Cattley *et al.* (1994) recommended that the occupational exposure limit to NB should be as low as 0.2 ppm. Finally, the European Union Directive 2001/59/EC states that NB is “toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.” It is therefore crucial that non biological treatments, such as adsorption or chemical oxidation, are used to reliably remove NB or similar molecules from industrial wastewaters.

Activated carbon is widely used in adsorption processes because of its great adsorption capacity and its affinity for a large range of organic molecules. When activated carbon is saturated, it has to be regenerated or renewed, which is an expensive operation. The adsorbed molecules are then released and still have to be degraded by an additional treatment. Moreover, this thermal treatment also degrades the activated carbon adsorption properties in the long term.

Another way to remove non-biodegradable molecules is via in situ chemical oxidation. The most commonly used oxidant is ozone because it has a high oxidation potential, it does not remain in water, and ozonation processes can be run continuously. Oxidation by ozone proceeds either by a molecular mechanism or by a radical one. With regard to the molecular mechanism, ozone is a selective oxidant and its direct reaction with some molecules can be very slow. It is the case with NB; indeed, Hoigné & Bader (1983) reported the value of $0.09 \pm 0.02 \text{ L mol}^{-1} \text{ s}^{-1}$ for the second order rate constant of the reaction of NB with molecular ozone. On the other hand, ozone can self-decompose in water into non-selective hydroxyl radicals HO \cdot , known as some of the most powerful oxidizing agents. Oxidation by hydroxyl radicals in ozonation processes is known as indirect reaction. Beltrán (2004) obtained a value of $2.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ for the second order rate constant of the reaction of NB with hydroxyl radicals. But, in practice, hydroxyl radicals' concentration in ozonated water is very low (in the range of 10^{-14} to $10^{-13} \text{ mol L}^{-1}$) and oxidation via the indirect reaction is limited.

Zeolites are porous crystalline aluminosilicates with various frameworks formed by SiO $_4$ and AlO $_4$ tetrahedrons connected by oxygen atoms. This crystalline structure gives the zeolites a uniform pore size, making zeolites different from other microporous adsorbents. Pore sizes are in the range of a few Å, allowing small molecules to enter the solid frame and excluding large molecules, thus making zeolites selective adsorbents. Moreover the mineral composition of zeolites makes them highly resistant to chemical agents such as acids and bases or to oxidants such as ozone. Zeolites are basically hydrophilic, but they turn hydrophobic when the Si/Al ratio reaches 8 or 10 (Ruthven 1984). Zeolites with high Si/Al ratios are called high silica zeolites and are known to have good adsorption properties for organic molecules (Shu *et al.* 1997; Khalid *et al.* 2004).

High silica zeolites can catalyze ozone decomposition into radical species in the gas phase (Monneyron *et al.* 2003) but apparently not in water (Lin *et al.* 2002; Fujita *et al.* 2004a,b; Reungoat *et al.* 2007). However, previous studies have shown that some organic compounds could be oxidized faster by aqueous ozone when they were adsorbed onto zeolites than when not adsorbed, because of a micropore concentration effect (Fujita *et al.* 2004b, 2005;

Sagehashi *et al.* 2005). For example, Sagehashi *et al.* (2005) reported that 2methylisoborneol (MIB) was adsorbed onto USY high silica zeolite and determined that the concentration within the pores was about 10^7 fold greater than in the bulk liquid. In these studies, oxidation took place in a reactor containing zeolites where two water streams, one containing the target compound and another containing ozone, were mixed. Ozone was transferred from the gaseous to the aqueous phase in a separate vessel. The present study investigates the performance of a gas–liquid–solid reactor filled with zeolite pellets (faujasite) where the water stream containing the target compound (NB) and the ozonated gas stream are injected simultaneously. Nitrobenzene was chosen as a model pollutant because of its toxicity, its low biodegradability, and because it is highly refractory to ozone oxidation. Early work (Reungoat *et al.* 2007) has shown that faujasite has the highest adsorption capacity among several hydrophobic zeolites and that adsorbed NB could be oxidized by ozone. Ozone transfer and decomposition rates in the reactor were also characterized.

MATERIALS AND METHODS

Faujasite

The faujasite (385HUD3C) was supplied by Tosoh in cylinder-shaped pellets of 3.0 mm in diameter and 7.5 mm mean length. Pellets are made of microcrystals bound with clay; the binder represents 25% of the total weight. The SiO $_2$ /Al $_2$ O $_3$ ratio is 95. Its adsorption equilibrium properties for nitrobenzene were formerly determined (Reungoat *et al.* 2007): a Langmuir model fits the adsorption isotherm with a maximum adsorption capacity of 204 mg g^{-1} and a Langmuir constant of 0.13 L mg^{-1} . The faujasite was dried overnight in an oven at 105°C before use, no other treatment was applied.

Continuous flow gas–liquid–solid reactor

Experiments were carried out in a 20 cm length and 6 cm diameter double walled glass column (Figure 1). Temperature was set at 25°C. The column was fed with gas and liquid through a porous plate located at the bottom and they were

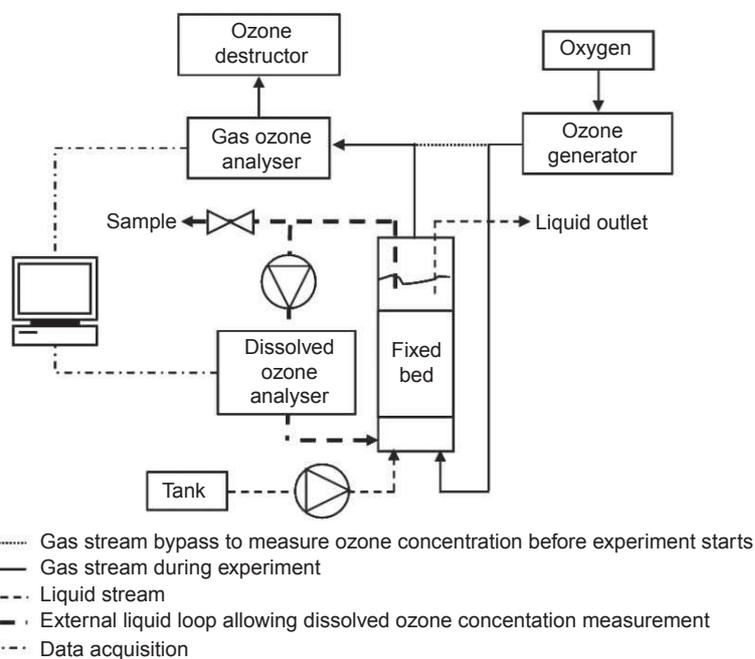


Figure 1 | Sketch diagram of the continuous gas-liquid-solid reactor.

separated at the top of the column. Three configurations of the reactor were used: empty (equivalent to a bubble column), filled with glass beads and filled with faujasite pellets (Table 1). The NB solution was prepared in a 200 L tank by adding pure NB (VWR International, 99.5%, Rectapur) in demineralised water to obtain a final concentration around 60 mg L^{-1} . The solution was introduced in the column thanks to a peristaltic pump of which the flow rate could be set between 0 and 6 L h^{-1} . Ozone was produced from pure oxygen by an Ozone Technology OT 40 ozone generator. Before an ozonation experiment started, the gas flow rate was set at 36 L h^{-1} and ozone concentration was fixed around 30 g Nm^{-3} thanks to a UV analyzer (Trailigaz UVOZON TLG 200). The exhaust gas was collected at the top of the reactor for ozone

concentration measurement and destruction before venting out. An external liquid loop allowed dissolved ozone concentration measurement by a polarographic probe (Orbisphere model 410/probe 31330.15xx). The liquid flow in the *external* loop had to be set at 28.5 L h^{-1} to ensure accuracy of the dissolved ozone measurement; this is several times higher than the feeding flow rate, therefore the liquid phase in the reactor (fixed bed) is assumed to be perfectly mixed. The UV analyzer and polarographic probes were connected to a computer for data acquisition. Liquid samples collected from the reactor were filtered through Rotilabo® $0.45 \mu\text{m}$ PTFE membranes resistant to ozone (Roth Sochiel, France) and the residual ozone was rapidly stripped out by bubbling nitrogen in the sample.

Table 1 | Details of the three configurations of the gas-liquid-solid reactor

Configuration	Bubble column	Glass beads	Faujasite
Mass of material (g)	None	1,084	320
Solid shape		Sphere	Cylinder
Dimensions (mm)		5	3×7.5
Porosity of the bed		0.39	0.39
Total liquid volume (L)	0.86	0.45	0.45

Analytical methods

High Performance Liquid Chromatography (HPLC) was performed to measure the NB concentration in the samples collected during the experiments. Samples were filtered through a $0.45 \mu\text{m}$ membrane to remove solid particles and $20 \mu\text{L}$ were injected in a C18 Equisorb ODS2 column ($5 \mu\text{m}$, $250 \times 4.6 \text{ mm}$). Samples were eluted with a 35% acetonitrile/65% acidified water (H_3PO_4 , $\text{pH} = 2$) (v/v)

solvent at a 1 mL min^{-1} flow rate. Retention time of NB was 15 minutes and detection was assured by a UV diode array at $\lambda = 267 \text{ nm}$. A linear calibration curve was obtained in the range $0\text{--}250 \text{ mg L}^{-1}$ ($\pm 1 \text{ mg L}^{-1}$).

The chemical oxygen demand (COD) was determined by adding 2 mL of filtered sample in specific tubes containing the reagents necessary for organic matter oxidation (*Hach, Subra, France*). The tubes were then placed in an oven at 150°C for 2 hours. The COD was quantified by measuring the absorbance of the tubes at $\lambda = 600 \text{ nm}$ with a spectrophotometer. The COD range of these tubes is 0 to 1,500 ppm with an error of $\pm 15 \text{ mg L}^{-1}$.

Determination of ozone transfer and decomposition parameters

The first order kinetic rate constant of ozone decomposition (k_C), the solubility parameter (m) and the overall mass transfer coefficient ($k_L a$) were determined for the three reactor configurations according to the method described in López-López *et al.* (2007) adapted for a continuous flow reactor. Ozone was bubbled in the reactor fed with water free of NB and the evolutions of the ozone concentrations in the outlet gas and in the liquid phase were observed. Typical concentration profiles are shown in Figure 2 where the unsteady and steady state periods have been separated. Once the steady state has been reached, the mass balance for ozone dissolution in the liquid phase of the reactor reduces to Equation (1), where Q_G and Q_L are the volume gas and liquid flow rates respectively and V_L is the liquid volume in the reactor. The mass balance for ozone

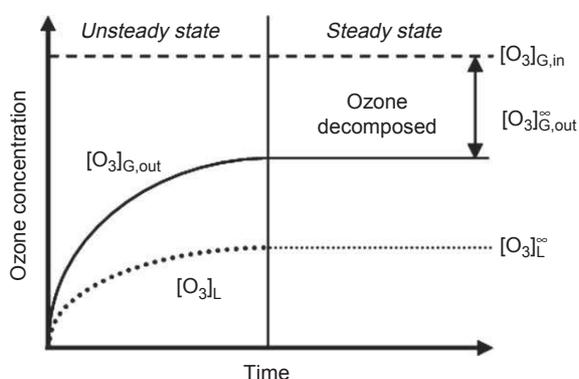


Figure 2 | Typical ozone concentration profiles in the liquid and gas phases $[\text{O}_3]$.

dissolution in the liquid phase is presented in Equation (2); $[\text{O}_3]_L^*$ is the equilibrium concentration in the liquid. Note that $[\text{O}_3]_L^*$ is always higher than $[\text{O}_3]_L$, the ozone concentration in bulk liquid, because of the ozone auto-decomposition in water. Integration of Equation (2) over the unsteady state period provides the expression of $k_L a$ (Equation (3)). Moreover, the solution for the steady state period allows the writing of m according to Equation (4) where an average concentration for the gas phase was used. This parameter is defined as the ratio between ozone concentrations in the liquid phase and in the gas phase at equilibrium. Considering that the gas phase behaves like in a plug flow reactor, this average value is obtained by Equation (5).

$$k_C = \frac{Q_G \times ([\text{O}_3]_{\text{G,in}} - [\text{O}_3]_{\text{G,out}}^\infty)}{[\text{O}_3]_L^\infty \times V_L} - \frac{Q_L}{V_L} \quad (1)$$

$$\frac{d[\text{O}_3]_L}{dt} = k_L a \times [\text{O}_3]_L^* - \left(k_L a + k_C + \frac{Q_L}{V_L} \right) \times [\text{O}_3]_L \quad (2)$$

$$\text{Ln}([\text{O}_3]_L^\infty - [\text{O}_3]_L) = \text{Ln}[\text{O}_3]_L^\infty - (k_L a + k_C) \times t \quad (3)$$

$$m = \frac{k_L a + k_C + \frac{Q_L}{V_L}}{k_L a} \times \frac{[\text{O}_3]_L^\infty}{[\text{O}_3]_G^\infty} \quad (4)$$

$$\overline{[\text{O}_3]_G} = \frac{([\text{O}_3]_{\text{G,in}} - [\text{O}_3]_{\text{G,out}})}{\text{Ln}\left(\frac{[\text{O}_3]_{\text{G,in}}}{[\text{O}_3]_{\text{G,out}}}\right)} \quad (5)$$

RESULTS AND DISCUSSION

Ozone transfer and decomposition parameters

Ozone decomposition first order rate constant k_C

For a given configuration, all the values of k_C are in the same range regardless of the liquid flow rate, indicating that ozone decomposition rate does not depend on hydrodynamic (Table 2). Values measured in the bubble column configuration are consistent with the literature. In other configurations, k_C is 5.0 and 6.4 times higher in presence of glass beads and faujasite respectively. This increase in the value of k_C indicates the presence of active sites capable of catalyzing ozone decomposition. In the case of faujasite,

Table 2 | First order ozone decomposition rate constant k_c in the three reactor configurations for various liquid flow rates and comparison with literature data

Configuration	Inlet liquid flow rate (L h ⁻¹)	pH	$k_c \times 10^3$ (s ⁻¹)		
			Measured	Mean	Literature
Bubble column	0	4.4	1.0	0.93	0.70–0.90*
	0.8	4.2	1.3		0.25–0.71†
	3.4	4.6	0.7		2.36–2.62‡
	6.0	5.1	0.7		0.27–0.47§
Glass beads	0	6.1	4.8	4.63	
	0	6.3	3.5		
	0.8	5.6	5.7		
	3.4	5.9	3.6		
	6.0	5.7	4.4		
	6.0	5.7	5.8		
	6.0	5.7	5.8		
Faujasite	0	5.5	7.0	5.93	
	0.8	6.0	6.3		
	3.4	6.1	4.2		
	6.0	6.0	6.2		

*Roth & Sullivan (1983).

†Qiu (1999).

‡Ledakowicz *et al.* (2001).

§López-López *et al.* (2007).

these sites may be silanol groups (SiOH) created during the dealumination treatment and that are supposed to be responsible for the catalytic activity of faujasite towards ozone decomposition in the gas phase (Monneyron *et al.* 2003). Clay, the binder used to create the faujasite pellets, could also provide silanol groups. As glass is mainly made of silica (SiO₂), defects could also lead to the formation of silanol groups. The catalytic activity of faujasite is in contradiction with what has been previously reported (Lin *et al.* 2002; Fujita *et al.* 2004a,b; Reungoat *et al.* 2007). However, given the mass of material used here, this catalytic activity is low and might not have been detected in previous experiments using lower quantities.

Table 3 | Ozone transfer coefficient k_{La} and solubility parameter m in the three reactor configurations

	Bubble column				Glass beads				Faujasite			
	0	0.8	3.4	6.0	0	0.8	3.4	6.0	0	0.8	3.4	6.0
Liquid flow rate (L h ⁻¹)	0	0.8	3.4	6.0	0	0.8	3.4	6.0	0	0.8	3.4	6.0
$k_{La} \times 10^3$ (s ⁻¹)	9.8	4.6	7.5	8.8	16.1	17.2	18.5	25.7	12.9	16.7	11.4	18.2
Mean value of $k_{La} \times 10^3$ (s ⁻¹)	7.6					19.9				15.0		
m	0.230	0.268	0.271	0.284								

Ozone transfer coefficient k_{La} and solubility parameter m

In the bubble column, the values of k_{La} are in the same range whatever the flow rate is; the mean value is $7.6 \times 10^{-3} \text{ s}^{-1}$ (Table 3). Roustan *et al.* (1996) studied ozone transfer in up-flow co-current bubble column and showed that the value of k_{La} depends only on the superficial gas velocity and on the hydrodynamic of the liquid flow determined by the Reynolds number. In our case the gas flow rate is constant and the liquid flow is laminar whatever the liquid flow rate is and k_{La} can be calculated by Equation (6) given by Roustan *et al.* (1996) where U_G is the superficial gas velocity. The obtained value of $5.7 \times 10^{-3} \text{ s}^{-1}$ is consistent with the experimental values. The values of the solubility parameter do not depend on the flow rate (Table 3) and they are consistent with data from the literature (Table 4).

$$k_{La} = 0.092 \times U_G^{0.516} \quad (6)$$

Thermodynamics imposes that there is a single value of m for a given temperature but the determination of k_c , k_{La} and m , carried out for each experiment, can lead to dispersed results due to the experimental errors. For this reason the mean value of $m = 0.263$ determined with the bubble column was used in Equation (4) to evaluate k_{La} in other configurations. For all tested flows, k_{La} values are in the same range for a given configuration, and even if k_{La} appears to be higher at a flow rate of 6.0 L h^{-1} , no clear pattern could be evidenced. The mean values of k_{La} for both configurations are similar and 2.6 and 2.0 times higher than in the bubble column for the glass beads and the faujasite configurations respectively. Farines *et al.* (2003) studied ozone transfer in a co-current upflow reactor filled with silicagel pellets of 3.33 mm diameter which are similar to the glass beads and the faujasite pellets used in this study.

Table 4 | Comparison of the value of the solubility parameter m obtained at 25°C in this study with data from the literature for temperatures of 20 and 30°C

	20°C	30°C
This study (mean)	0.263 (25°C)	
Perry & Chilton (1973)	0.354	0.230
Roth & Sullivan (1981) at pH = 7	0.241	0.189
Caprio <i>et al.</i> (1982)	0.25	0.18
Horváth <i>et al.</i> (1985)	0.344	0.286
Masschelein (1991)	0.24	0.15
Roustan <i>et al.</i> (1996)	0.240	
López-López <i>et al.</i> (2007)	0.311	

They showed that the value of $k_L a$ is mainly influenced by the superficial gas velocity. For a superficial gas velocity of $2.9 \times 10^{-3} \text{ m s}^{-1}$ and a superficial liquid velocity of $2.8 \times 10^{-3} \text{ m s}^{-1}$ they obtained the $k_L a$ value of $10.53 \times 10^{-3} \text{ s}^{-1}$ which is below the values obtained here but in the same range. The value of $k_L a$ is mainly directed by the interfacial area (Roustan *et al.* 1996) which represents the exchange surface between gaseous and liquid phases per unit of volume. This surface depends on the bubble size and the gas retention in the reactor. The same porous plate and gas flow rate were used in all the experiment so the bubbles' size at the bottom of the reactor is assumed to be constant. The increase in $k_L a$ can then be explained either by a higher gas retention in the reactor, by a fractionation of the bubbles inside the reactor or by a combination of these phenomena. Further investigations, outside of the scope of this study, would be necessary to conclude.

Nitrobenzene oxidation

Preliminary experiments in a batch reactor showed that, when a pure oxygen gas stream is bubbled in a NB solution, stripping of NB is negligible and oxidation does not occur (results not shown). Decrease of NB concentration and COD were determined for the three configurations of the reactor for three different liquid flow rates: 0.8, 3.4 and 6.0 L h^{-1} . For the bubble column and the glass beads configurations, a sample was collected from the outlet of the reactor once the ozone concentrations in the gas and the liquid phases had reached a steady state. The NB concentration and the COD were measured and compared with the inlet water to determine their decrease in the reactor for

each of the liquid flow rates. For the faujasite configuration, the zeolite was first loaded with NB to limit adsorption during oxidation experiments. To that purpose, the reactor was fed with a 60 mg L^{-1} NB solution at 1.4 L h^{-1} flow rate during 258 hours. There was no gas fed in the reactor but the pump of the external loop was working in order to obtain a uniform adsorbed quantity of NB over the whole reactor. Samples were collected regularly to determine the outlet NB concentration and a mass balance indicated that, at the end of this adsorption step, the amount of NB adsorbed was approximately 63 mg g^{-1} . This was confirmed by calculating the adsorbed quantity with the Langmuir model assuming equilibrium with a solution at 3.4 mg L^{-1} , the final NB outlet concentration. The Langmuir model lead to an adsorbed quantity of 62.5 mg g^{-1} confirming the mass balance and the fact that the equilibrium had been reached in the reactor. Following this initial step, inlet liquid flow rate was set at 0.8 L h^{-1} and ozonated gas was introduced in the reactor. Samples were collected regularly from the liquid outlet to measure NB concentration and COD during 15.5 hours. During this time, the decreases of NB concentration and COD were stable indicating that the reactor was on a steady state and average performances were calculated (Table 5). Then, the inlet liquid flow rate was increased to 3.4 L h^{-1} and samples were collected regularly during 22.6 hours. The decreases of NB concentration and COD also proved to be stable during this period. Finally, the flow rate was set to 6.0 L h^{-1} for 58.3 hours. During the first 40.4 hours, the NB and COD removal decreased from 90 to 75% and from 85 to 50% respectively. The high initial performances can be attributed to the combination of oxidation by ozone and adsorption. Then, adsorption diminished with time as the adsorbed quantity increased and eventually reached the equilibrium with the liquid concentration. After 40.4 hours, the observed removals stabilized and the reactor reached a steady state.

At a flow rate of 0.8 L h^{-1} the three configurations removed over 95% of NB. The residence time in the reactor is long enough to oxidize nearly all the NB. The glass beads and faujasite reactors both decreased the COD by around 80% compared to 59% only for the bubble column. Indeed, oxidation of NB leads to the formation of by-products that can be difficult to oxidize with ozone. In the glass beads and faujasite reactors, the higher ozone decomposition rate

Table 5 | Reduction of nitrobenzene concentration (NB) and chemical oxygen demand (COD) observed in the reactor at steady state and dissolved ozone concentrations

Configuration	Bubble column			Glass beads			Faujasite		
	0.8	3.4	6.0	0.8	3.4	6.0	0.8	3.4	6.0
Liquid flow rate (L h^{-1})	0.8	3.4	6.0	0.8	3.4	6.0	0.8	3.4	6.0
NB removal (%)	99	66	45	99	71	54	97	94	75
Min-max							96-98	92-97	71-78
COD removal (%)	59	32	18	82	-	23	79	69	49
Min-max							66-87	49-83	45-55
$[\text{O}_3]_{\text{L}}$ (mg L^{-1})	2.40	0.02	0.00	2.82	0.03	0.00	0.00	0.00	0.00

and transfer coefficient possibly enhanced the oxidation of these products. In the bubble column and glass beads configurations, dissolved ozone was measured indicating that the reaction rate is not limited by the gas to liquid transfer of ozone. On the contrary, in the faujasite reactor, there was no dissolved ozone. This shows that the reaction was limited by the ozone transfer and that ozone consumption rate was higher in this configuration which could be due to the oxidation of adsorbed NB.

For the flow rate of 3.4 L h^{-1} , removal of NB by faujasite reactor remained high at 94% whereas it decreased to 71 and 66% for the glass beads reactor and the bubble column respectively. The higher removal of NB in the faujasite reactor compared to the bubble column could be due to higher ozone transfer and decomposition. But the k_C and $k_{L}a$ values in the faujasite reactor are similar to the glass beads reactor and its efficiency is higher by 20%; it is therefore suggested that the presence of faujasite enhanced NB oxidation kinetics. Compared to the 0.8 L h^{-1} experiment, the decrease of COD in the faujasite reactor dropped slightly down to 70% whereas it fell down to 30% in the bubble column (results obtained with the glass beads reactor were inconsistent). The dissolved ozone concentrations in the bubble columns and the glass beads reactor were very close to zero, the reaction rate was thus not limited by ozone transfer but close to it. No dissolved ozone was measured in the faujasite reactor indicating that performances were limited by the ozone transfer.

At 6.0 L h^{-1} , the NB removal in the faujasite reactor was lower (75%) compared to other flow rates but it was still higher than in the bubble column and the glass beads reactor, 45% and 54% respectively. The decrease of COD stabilized around 49% in the faujasite reactor whereas it

was only 18 and 23% in the bubble column and the glass beads reactor respectively. This seems to confirm that the presence of faujasite increases the oxidation rate of NB and suggests that it also enhances the oxidation of NB by-products. But in all configurations, no dissolved ozone could be measured indicating that the reaction was limited by the ozone transfer. The difference between the bubble column and the other configurations can then be explained by a higher ozone transfer rate in the latter but no explanation could be advanced for the better performance of the faujasite reactor compared to the glass beads reactor. Adsorption of NB and its oxidation byproducts onto faujasite could be a reason but this is in contradiction with the steady state observed.

The investigation of the mechanism and by-products of NB oxidation by ozone was out of the scope of this study. Merle *et al.* (2010) determined the oxidation mechanism and by-products formed during the ozonation of NB in presence and absence of activated carbon. They showed that, in both cases, NB oxidation leads to the formation of nitrophenols and small carboxylic acid which are less toxic than NB. It is assumed that oxidation mechanism is very similar in presence of faujasite and the same by-products are formed but this would have to be confirmed experimentally.

CONCLUSIONS

The study of ozone transfer and decomposition in three configurations of a continuous flow reactor showed that, in presence of glass beads or faujasite pellets, the ozone transfer coefficient $k_{L}a$ increased 2.6 and 2.0 fold respectively compared to the empty reactor equivalent to a bubble

column. The presence of solid also increased the ozone decomposition rate k_C 5.0 and 6.4 fold in the presence of glass beads and faujasite respectively. This confirmed previous findings that faujasite has no or poor catalytic effect on ozone decomposition. The faujasite reactor showed higher decrease of NB concentration and COD compared to the empty column and the glass beads configurations suggesting that the zeolite increases the oxidation rate of NB and its by-products. This could be possibly due to a micropore concentration effect as previously reported by Fujita *et al.* (2004b, 2005) and Sagehashi *et al.* (2005). Further investigations are needed to elucidate the oxidation mechanisms in the presence of faujasite. Results also showed that the oxidation of NB and its byproducts in the presence of faujasite was limited by the transfer of ozone from the gas to the liquid phase.

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