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Urban Wastewater Treatment by Catalytic Ozonation

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ABSTRACT

This study focuses on the catalytic ozonation of organic matter recalcitrant to usual water treatment technologies. Experiments aimed to investigate the efficiency of the process TOCCATA[®], which uses a granular catalyst coupled with ozonation. Comparison was made between single ozonation, single adsorption onto the catalyst and catalytic ozonation. Adsorption was proven to contribute to decreased dissolved organic carbon. Catalytic ozonation enhanced organic matter removal and ozone transfer compared to single ozonation. Catalytic ozonation was modeled with global apparent first-order kinetics and single adsorption with pseudo-second-order sorption kinetics.

KEYWORDS

Ozone; Adsorption; Advanced Oxidation Process; Catalytic Ozonation; Kinetic Modeling; Organic Matter; Tertiary Treatment; Wastewater Treatment

Introduction

Part of organic matter including micropollutants of concern persists at the outlet of usual wastewater treatment plants (WWTPs) (Ternes 1998; Martin Ruel et al. 2011, 2012; Soulier et al. 2011). Conventional tertiary wastewater treatments such as oxidation processes, including ozonation which is known to be a powerful oxidation, are indeed quite selective, leading to limited removal yields in organics and can be responsible for the emission of some undesired by-products depending on the application conditions (Ikehata, Naghashkar, and El-Din 2006).

The application of advanced oxidation processes can consequently be necessary to improve oxidation yields of resistant organic matter (Bailey 1978; Jans and Hoigné 1998). Catalytic ozonation appears to be an interesting solution as a tertiary treatment to create less selective and more oxidant species thanks to solid catalysts (Baig and Mouchet 2010; Merle et al. 2009), among them the TOCCATA[®] catalytic process (Fontanier et al. 2006). Like any surface catalysis phenomenon in a three-phase medium, catalytic ozonation undergoes five main physicochemical phenomena: ozone transfer from the gaseous phase to the liquid phase, diffusion of dissolved molecules (ozone and organic matter) towards the active sites of the catalyst surface, followed by adsorption of both dissolved ozone and organic species, chemical reaction(s) onto the

catalyst surface and finally desorption of reaction products. This reaction induces substrate mineralization with the cleavage of covalent bonds and the formation of CO₂ and heteroatoms oxidized forms, as nitrate, phosphate or sulphate.

The applicability of heterogeneous catalytic ozonation has mostly been studied in industrial wastewaters or synthetic waters containing model compounds (Ma et al. 2005; Alvarez et al. 2009; Faria, Orfao, and Pereira 2009; Li et al. 2010; Aboussaoud et al. 2014). Few studies have, however, focused on natural waters or on domestic-like water matrices, as fulvic acids and humic substances, with different heterogeneous catalysts: titanium dioxide supported on alumina, nano-TiO₂ supported on zeolite and metals deposited on different supports as alumina, titanium dioxide and clay (Allemann et al. 1993; Volk et al. 1997; Karpel Vel Leitner et al. 1999; Gracia et al. 2000; Kasprzyk-Hordern et al. 2006; Wang et al. 2011). Their results are promising because of their high effectiveness in the conversion of refractory compounds.

Therefore, the present work deals with organic matter mineralization using the TOCCATA[®] catalytic ozonation process (Degremont 1999). The process is compared to single ozonation in order to evaluate its possible application to urban wastewaters. One should refer to the past results published on the mineralization of model compounds or organic matter in industrial

wastewaters using the same catalytic system (Fontanier et al. 2005; Baig and Petitpain 2003). The heterogeneous catalyst involved in this process is made with supported-type metal oxides. Experiments were carried out on treated wastewater issued from biological treatment to determine the performances, and the global kinetics of this process. As adsorption is an essential step for catalytic ozonation, a focus was made on its kinetics, and the experimental results were confronted to the most common models described in literature.

Materials and methods

Urban wastewater effluents were collected at the outlet of the secondary clarifier in two French biological treatment plants (WW1, WW2). Their characteristics are described in Table 1. TOCCATA catalyst is of type-

Table 1. Urban wastewaters' characteristics.

		WW1	WW2
pH		7.4	8.3
Conductivity	$\mu\text{s}\cdot\text{cm}^{-1}$	982	656
COD*	$\text{mgO}_2\cdot\text{L}^{-1}$	23	32
DOC**	$\text{mgC}\cdot\text{L}^{-1}$	6.59	9.15
DIC***	$\text{mgC}\cdot\text{L}^{-1}$	53.71	45.59

(*Chemical Oxygen Demand, ** Dissolved Organic Carbon, *** Dissolved Inorganic Carbon)

supported metal of granular shape characterized by 2-mm average diameter and $300\text{ m}^2\cdot\text{g}^{-1}$ surface area. The same load was used for all experiments without any regeneration treatment except washing to complete the recovery of inorganic carbon.

Experimental tools

Figure 1 schematizes the experimental setup that was used for semicontinuous single ozonation and catalytic ozonation runs. It consisted in two glass column reactors in parallel (6-cm inner diameter, 50-cm height), one was empty and the other was packed with 50 cm catalyst supported by a PTFE grid. Ozone was produced from pure oxygen (alpha grade) using an ozone generator (Ozonia OZAT CFS-1/3 2G). A set of valves and a flow controller ensured a constant $20\text{ L}\cdot\text{h}^{-1}$ (flowmeter value) inlet gaseous O_3 flow ($Q_{G,IN}$) into the reactor, with 1.2 bar absolute pressure and ambient temperature conditions, equivalent to $19.7\text{ L}\cdot\text{h}^{-1} (\pm 4\%)$ NTP. The work was carried out with an upflow co-current of ozonized oxygen gas (continuous intake) and polluted liquid solution (batch mode). A pump ensured total liquid recirculation ($40\text{ L}\cdot\text{h}^{-1}$) inside the contactor through a 1-L buffer tank.

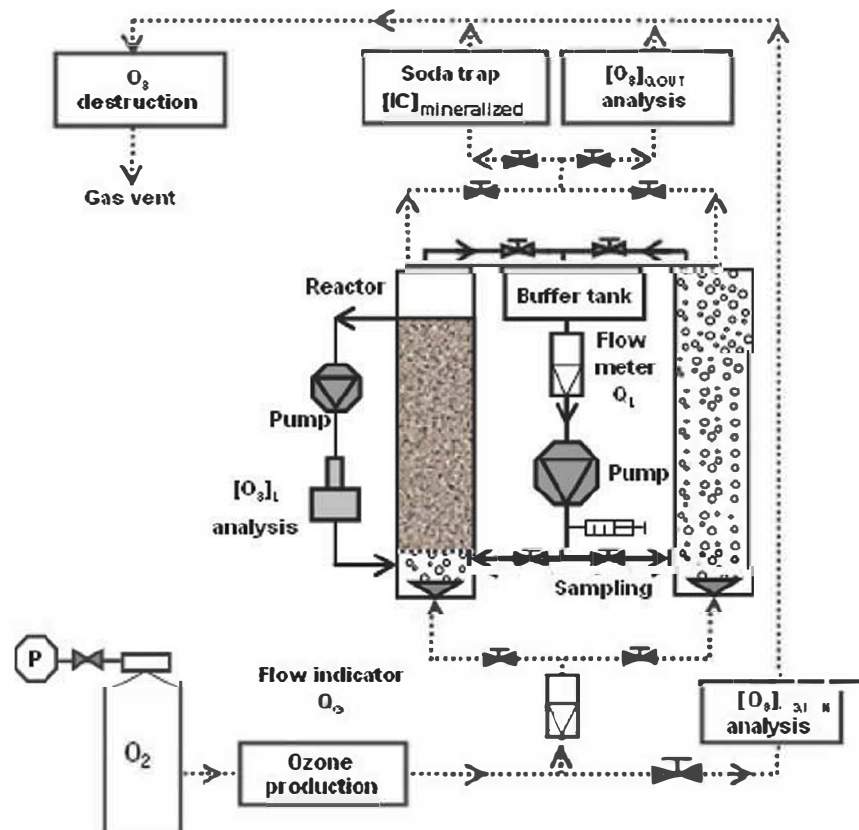


Figure 1. Experimental setup.

Table 2. Experimental operating conditions.

		Single ozonation WW1	Single adsorption WW1	Catalytic ozonation WW1	Catalytic ozonation WW2
Q_G	L.h ⁻¹ NTP	19.7		19.7	19.7
Q_L	L.h ⁻¹	40	40	40	40
$[O_3]_{G,IN}$	mg.L ⁻¹	100		100	100
Contact time t_c	min	231	133	144	144
V_{tot}	L	2.2	1.3	1.25	1.25

(Q_G : gaseous volumetric flow, Q_L : liquid recirculation volumetric flow)

Gaseous ozone was continuously analyzed at the inlet and the outlet of the column with two UV ozone analyzers (BMT 964 model) and dissolved ozone was measured at the half height of the catalytic bed with a polarographic dissolved ozone analyzer (410 Orbisphere model) equipped with an ozone sensor (31330 Orbisphere sensor). Carbon dioxide at the gaseous output was continuously trapped under Inorganic Carbon species (IC), representing the mineralized carbon, by circulating the contactor off-gas in a sodium hydroxide solution. The off-gas flow then went through an ozone thermal destructor (450 °C) before atmospheric release.

Experiments have been run on WW1 to compare single ozonation, catalytic ozonation and single adsorption onto the catalyst. Inlet conditions were gaseous superficial velocity $U_G = 7.1 \text{ m.h}^{-1}$ (empty bed), ozone inlet concentration $[O_3]_{G,IN} = 100 \text{ mg.L}^{-1} \pm 7\%$, and liquid recirculation superficial velocity $U_L = 14.1 \text{ m.h}^{-1}$ (empty bed) for each experiment. Experimental operating conditions are summarized in Table 2.

Catalytic ozonation experiments have been run according to a fixed bed operation as follows: 15-min single adsorption at startup followed by 6-h simultaneous ozone and wastewater circulation through the catalyst bed. The experiment has been repeated on WW2 to compare the evolution of the parameters under study for two different wastewaters.

Analytical methods

First, 12-mL samples were regularly collected at the bottom of the column and were filtered at $0.45 \mu\text{m}$ before analysis.

Dissolved Organic Carbon (DOC), Dissolved Inorganic Carbon (DIC), and Inorganic oxidized Carbon (IC) were determined using a TOC analyzer (TOC-Vcsh, Shimadzu) that involves catalytic oxidation at 720 °C prior to infrared detection of CO_2 (Standard method NFT 90.102). pH was measured with a pH meter (pH 538 WTW) and a pH electrode (Sentix 41 WTW).

COD (Chemical Oxygen Demand) was controlled with the NF T90-101 micromethod (2001), through a reaction with an acidic solution of potassium dichromate in the

presence of a silver catalyst and digested for 2 h at 150 °C: oxidizable organic compounds reduce the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) to the chromic ion (Cr^{3+}), and the decrease in dichromate ion is measured with a spectrophotometer at 420 nm. Initial and final solutions were analyzed with a spectrophotometer (Jasco 630) for UV-Vis absorbance.

Contact time

Contact time was calculated from the passage time and the number of passages according to the circulating liquid flowrate and the volumes of contactor and solution, which lead to Equation [1].

$$t_c = t \cdot \frac{V_L}{V_{tot}} \quad (1)$$

With t_c the contact time (min), t the reaction time (min), V_L the volume of liquid in the gas liquid contactor and V_{tot} the total liquid volume (L).

Carbon mass balance

Carbon mass balances were calculated after each experiment by considering the amount of inorganic carbon trapped from the off gas and the dissolved inorganic and organic carbon concentrations remaining in the treated liquid solution.

Ozone mass balances

The different terms of the ozone mass balances were calculated considering experimental inlet and outlet gaseous ozone and dissolved ozone concentration as follows:

$$O_{3_applied} = \int_0^t [O_3]_{G,IN} \cdot Q_G \cdot dt \quad (2)$$

$$O_{3_transferred} = \int_0^t [O_3]_{G,IN} \cdot Q_G \cdot dt - \int_0^t [O_3]_{G,OUT} \cdot Q_G \cdot dt \quad (3)$$

$$O_{3_consumed} = \int_0^t [O_3]_{G,IN} \cdot Q_G \cdot dt - \int_0^t [O_3]_{G,OUT} \cdot Q_G \cdot dt - [O_3]_{L(t)} \cdot V_{tot} - [O_3]_{G,OUT(t)} \cdot V_d \quad (4)$$

$$\eta_{O_3} = \frac{O_{3_applied} - O_{3_transferred}}{O_{3_applied}} \times 100 \quad (5)$$

With O_3 applied, O_3 consumed, and O_3 transferred the ozone weights that were respectively applied, consumed, and transferred during reaction (g), η_{O_3} the ozone transfer yield, $[O_3]_{G,IN}$ the inlet ozone concentration (mg.L^{-1}), $[O_3]_{G,OUT}$ the outlet ozone concentration (mg.L^{-1}), $[O_3]$ the dissolved ozone concentration (mg.L^{-1}), V_{tot} the total liquid volume, V_d the reactor dead volume (L) and t the reaction time (min). The ozone doses are calculated from the related ozone weight divided by the liquid volume corrected by the sample volumes withdrawn.

Results and discussion

Experiments were carried out for single ozonation, catalytic ozonation and single adsorption. The investigations focused on ozone consumption, variations of dissolved organic and inorganic carbon and oxidation rate. Figure 2 describes DOC evolution with contact time, Figure 3 shows DOC evolution with the transferred ozone dose, Figure 4 is DIC evolution with contact time and Figure 5 is pH evolution with contact time. All experiments lasted 6 h, corresponding to a contact time of 130 min in the presence of solid and of 230 min in the case of exclusive liquid feed, because the introduced liquid volume amounts were different to fill the column with and without catalyst (1.25 L and 2.2 L, respectively). Each experiment was carried out twice with a satisfactory repeatability.

Single ozonation resulted in partly reducing DOC (39% degradation) and DIC (15% degradation), and ozone transfer was very low (recovering 70% inlet ozone at the gaseous output). DOC decreased slowly during the first 20-min contact time until a stable value due to by-compounds resistant to ozone. Further addition of ozone did not achieve reduction of any of the remaining organic matter. pH was stable during the experiment (Figure 5).

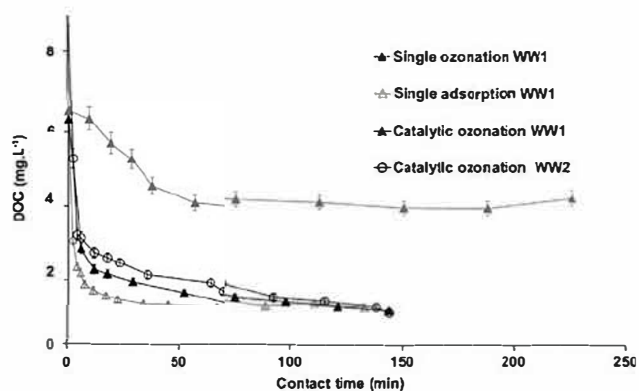


Figure 2. DOC evolution with contact time.

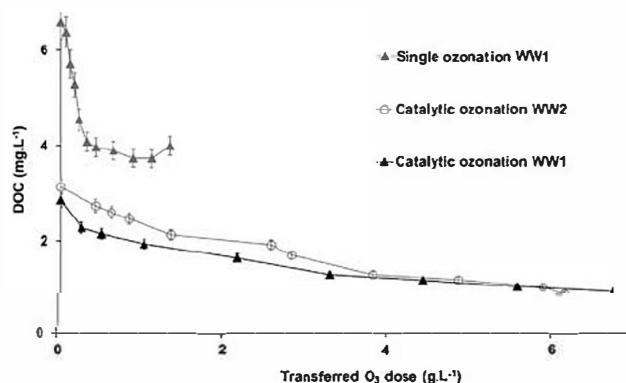


Figure 3. DOC evolution with transferred ozone dose.

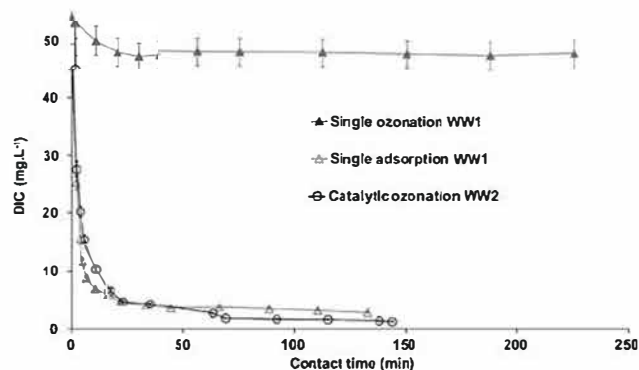


Figure 4. DIC evolution with contact time.

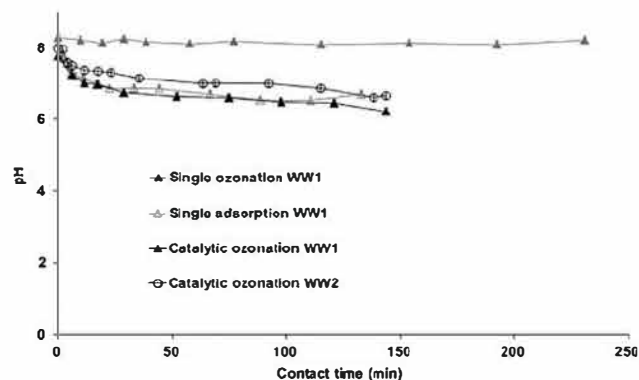


Figure 5. pH evolution with contact time.

Catalytic ozonation enhanced DOC removal yield up to 90% and DIC removal accordingly (99%). Ozone transfer yield was close to 70%. Figure 10 indeed reveals that the presence of the catalyst ensures a virtually linear increase in the transferred ozone dose as a function of applied dose whatever the water used. Despite the high ozone transferred dose, dissolved ozone concentration was stable at low value around 0.4 mg.L^{-1} during catalytic ozonation experiments, because the catalyst highly decomposes O_3 . Then, 66% removal of

DOC was already recorded upon adsorption at startup, DOC then decreased slower during catalytic ozonation.

Regarding **single adsorption** onto the catalyst, DOC decreased sharply (70%) during the first 20 min and then slower. Removal yields reached 85% for DOC and 95% for DIC after 6-h treatment duration.

pH decreased until a stable value in both experiments with catalyst (Figure 5) with an acidification of the wastewater matrix due to the acidic surface of the catalyst and to the formation of acidic intermediates during ozonation.

Catalytic ozonation therefore enhances DOC and DIC decrease compared to single ozonation, and the presence of the catalyst improves ozone transfer and ozonation efficiency for reducing persistent compounds. Single adsorption is also responsible for a sharp decrease of DOC and DIC but only concentrates it at the surface of the catalyst.

A study of the kinetics can be useful to better understand the involved mechanisms. In particular, any surface catalysis phenomena is initiated by the adsorption of reactants onto the catalyst so that the apparent rate includes adsorption kinetics. A focus on single adsorption was, therefore, first carried out to evaluate adsorption kinetics versus the global ones by uncoupling the mechanisms.

Adsorption kinetics

Single adsorption onto the catalyst was performed during 6 h and reached 86% removal yield for DOC. During the first 20 min, DOC showed a sharp decrease (70%), which then becomes slower. The single adsorption process can usually be described by four main steps: molecule migration towards the catalyst (particle convection), diffusion through the boundary layer onto the catalyst surface, pore diffusion, and bonding with the surface active sites of the catalyst.

A kinetic modeling was therefore investigated to estimate sorption rates and to approach possible mechanisms controlling the adsorption process. Most common literature models used to describe adsorption kinetics were studied: Lagergren pseudo-first-order model (Lagergren 1898) based on solid capacity, Ho and McKay pseudo-second-order model (Ho and

McKay 1999, 1998) that assumes chemisorption as the controlling step, the Weber and Morris intraparticle diffusion model (Weber and Morris 1963) and the Elovich equations (Elovich 1939) based on multilayer adsorption.

These models are described in Table 3, Equations [6], [7], [8], [9] where t_c is contact time (min), q_e the amount of DOC adsorbed at equilibrium ($\text{mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1}$), q_t the amount of DOC adsorbed on the surface of the catalyst at any time t ($\text{mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1}$), k_1 the pseudo-first-order chemical sorption rate constant (min^{-1}), k_2 the pseudo-second-order chemical sorption rate constant ($\text{g}_{\text{catalyst}} \cdot \text{mg}_{\text{DOC}}^{-1} \cdot \text{min}^{-1}$), k_i the intraparticle diffusion rate constant ($\text{mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1} \cdot \text{min}^{1/2}$), c the intercept for the Weber and Morris model ($\text{mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1}$), α and β Elovich rate constants ($\text{g}_{\text{catalyst}} \cdot \text{mg}_{\text{DOC}}^{-1} \cdot \text{min}^{-1}$). Table 4 develops the different models linearization results (Equations [10], [11], and [12]); the correlation coefficient with experimental data and the kinetic constants were calculated for each model.

The reaction is not likely to be a pseudo-first-order reaction even if the Lagergren model linearization plot has a high correlation coefficient with the experimental data. Indeed, the experimental maximum adsorbed amount used for calculation ($q_{\text{exp}} = 0.01 \text{ mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1}$) differs highly from the intercept of the Lagergren model linearization ($q_e = 0.002 \text{ mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1}$). The Elovich model was also excluded because of a bad linearization correlation coefficient.

The model that best fits with the experiment data is, therefore, the Ho and McKay pseudo-second-order model, which gives a good value for the amount of adsorbed DOC at equilibrium and the best correlation coefficient with the experimental data. Figure 6 draws the pseudo-second-order linearization (Equation [11]), based on Ho and McKay theory, which assumes both a fast fixation of the pollutants onto the most reactive sites and a slow fixation onto the low energy sites. The following sorption parameters can then be calculated: $q_e = 0.01 \text{ mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1}$ and $k_2 = 59 \text{ g}_{\text{catalyst}} \cdot \text{mg}_{\text{DOC}}^{-1} \cdot \text{min}^{-1}$. According to the literature, this model supports the hypothesis that chemisorption is the rate-controlling step during adsorption, involving valency forces through

Table 3. Adsorption kinetic models' equations and linear equations.

	Equation		Linear equations	
Lagergren Pseudo first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	(6)	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$	(10)
Ho and McKay Pseudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	(7)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	(11)
Weber and Morris Intraparticle diffusion	$q_t = k_i t^{1/2} + c$	(8)		
Elovich Multilayer adsorption	$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$	(9)	$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{1}{\beta} \ln(t)$	(12)

Table 4. Comparison of different kinetic models for single adsorption.

	Lagergreen	Ho and McKay	Weber and Morris	Elovitch
R^2	0.83	1	Step 1: 0.95 Step 2: 0.82	0.89
q_e	$\text{mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1}$	0.002	0.01	
k_1	min^{-1}	0.0298		
k_2	$\text{g}_{\text{catalyst}} \cdot \text{mg}_{\text{DOC}}^{-1} \cdot \text{min}^{-1}$		59	
k_i	$\text{mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1} \cdot \text{min}^{-1/2}$		Step 1: 0.0038 Step 2: 0.0002	
c	$\text{mg}_{\text{DOC}} \cdot \text{g}_{\text{catalyst}}^{-1}$		Step 1: 0.001 Step 2: 0.009	
α	$\text{g}_{\text{catalyst}} \cdot \text{mg}_{\text{DOC}}^{-1} \cdot \text{min}^{-1}$			9.21
β				1329.79

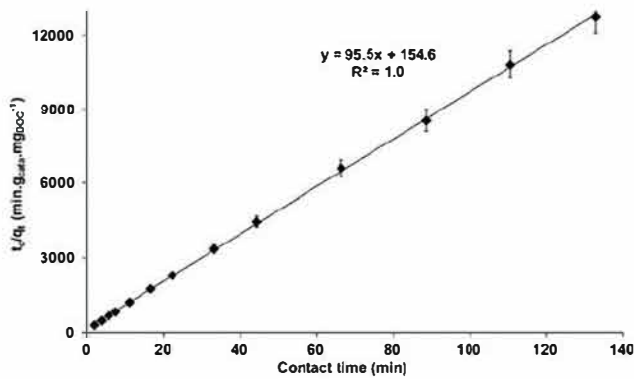


Figure 6. Ho and Mc Kay Pseudo-second-order adsorption kinetics applied to WW1 single adsorption.

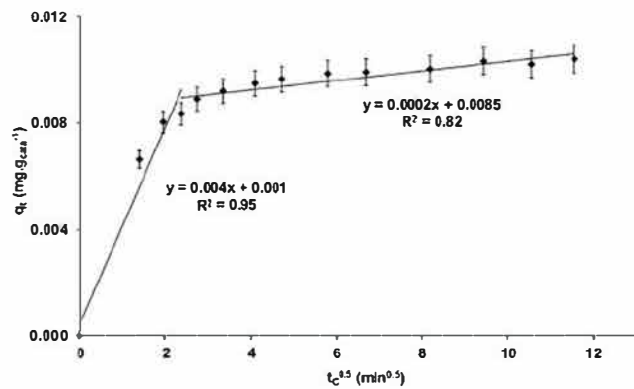


Figure 7. Weber and Morris intraparticle adsorption model correlated with WW1 single adsorption experimental data.

sharing or exchange of electrons between the adsorbent and the adsorbate.

To further understand the diffusion mechanism, the Weber and Morris model (Weber and Carell Morris 1963) has also been investigated. This model assumes negligible film diffusion and intraparticle diffusion as the rate controlling step. According to Equation [8], the plot of q_t versus $t_c^{0.5}$ in Figure 7 shows two different linear sections with different slopes because of different

successive steps occur during adsorption. This can be due to DOC adsorption onto the external surface of the catalyst (including macropores and micropores) that first takes place, followed then by DOC interaction with the micropores, causing diffusion resistance increase and the diffusion rate decrease (Crini and Badot 2010).

However, the Ho and McKay model limited by adsorption seems to be more consistent with the experimental data than the Weber and Morris model limited by diffusion. Indeed, the catalytic material is mesoporous, which is more consistent with the Ho and McKay model framework than the Weber and Morris model applicable to microporous materials. As a conclusion, single adsorption seems to be governed by pseudo-second-order kinetics as in the Ho and McKay model, which considers chemisorption as the rate-controlling step.

Single ozonation kinetics

Generally, a global second-order reaction rate is used in ozonation processes (first order with respect to organic matter and to dissolved ozone, Equation [13]). To obtain an estimation of the second-order rate constant, a rough “integration” of the rate law was done and $\frac{\text{DOC}_0 - \text{DOC}}{\text{DOC}}$ evolution versus $[\text{O}_3]_L \times t_c$ was plotted (Fontanier 2003). The correlation parameter was quite high ($R^2 = 0.89$) and the following second-order constant was calculated: $k_{\text{single O}_3} = 7.10^{-4} \text{ L.mg}^{-1}.\text{min}^{-1}$ i.e. $k_{\text{single O}_3} = 33.6 \text{ L.mol}^{-1}.\text{min}^{-1}$ for WW1 single ozonation, in relation with:

$$-\frac{d\text{DOC}}{dt} = k_{\text{single O}_3} \cdot \text{DOC} \cdot [\text{O}_3]_L \quad (13)$$

Catalytic ozonation kinetics

In the case of the catalytic ozonation experiment, dissolved ozone concentration remained quite low and constant (maximum dissolved ozone values: 0.87 mg.L^{-1} for WW1; 0.74 mg.L^{-1} for WW2, mean dissolved ozone values: 0.40 mg.L^{-1} for WW1; 0.21 mg.L^{-1} for WW2) along the experiments. Thus, kinetic order degenerates to pseudo-first-order kinetics as defined by Equation [14], which can be integrated and put in the linear form of Equation [15]. The corresponding linearization curve is plotted in Figure 8.

$$-\frac{d\text{DOC}}{dt_c} = k_{\text{co}} \cdot \text{DOC} \quad (14)$$

$$\ln\left(\frac{\text{DOC}}{\text{DOC}_0}\right) = -k_{\text{co}} \cdot t_c \quad (15)$$

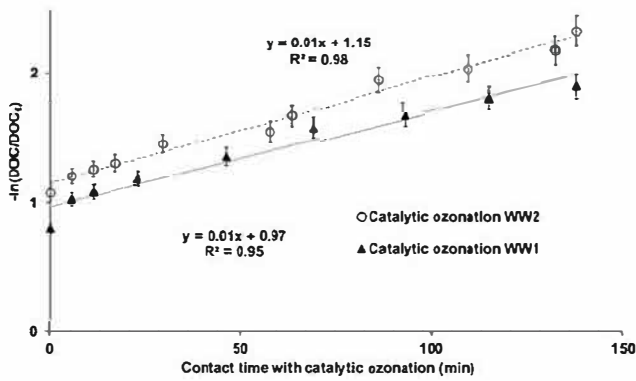


Figure 8. First-order kinetic model linearization for catalytic ozonation experiments.

With k_{CO} the apparent first-order kinetic constant for catalytic ozonation (min^{-1}), DOC and DOC_0 the current and initial Dissolved Organic Carbon (mgC.L^{-1}), and t contact time (min).

The linear regression gives quite good results, confirming that catalytic ozonation follows a pseudo-first-order kinetic model during the ozonation after the initial adsorption step (i.e., after 5-min contact time between liquid and catalyst at startup). The corresponding pseudo-first-order constant rate is $k_{CO} = 0.01 \text{ min}^{-1}$ for both wastewaters.

Mineralization extent

Concerning both single ozonation and catalytic ozonation experiments, carbon balances (Figure 9) showed that all organic carbon removed from the solution was mineralized into carbon dioxide further trapped at the gaseous output under inorganic carbon using soda solution. Mineralized IC and desorbed IC in Figure 9, respectively, stand for the inorganic carbon amount measured at the gaseous output directly during the experiment and after post-washing treatment. Figure 9 highlights that the balances are consistent since the amounts of DOC and DIC removed from wastewater correspond to the quantity of

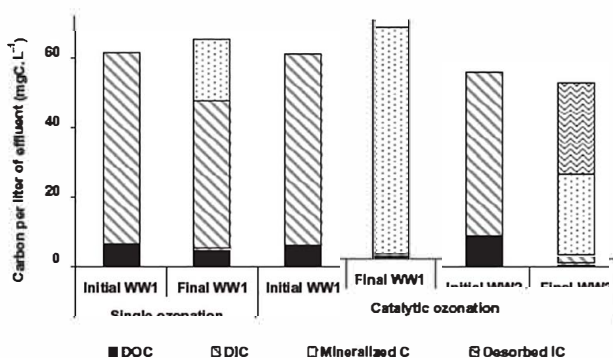


Figure 9. Carbon mass balances.

carbon dioxide recovered under carbonate ions, with an acceptable error with respect with measurement accuracy: 12.7%, 5.7%, and 6.4% for catalytic ozonation on WW1, WW2, and single ozonation on WW1, respectively.

Regarding WW1 single ozonation, most DOC and DIC remained in the liquid solution and only 27% of the total recovered carbon was found in the soda trap as inorganic carbon. DOC was consequently not totally oxidized probably because of the formation of products more resistant to ozone molecular attack, which is known to be rather selective. Regarding WW1 catalytic ozonation, removed DOC and DIC were mostly recovered as carbon dioxide at the gaseous output (98%). Regarding WW2 catalytic ozonation experiments, 94% of initial DOC and DIC were recovered, mostly at the gaseous output. Only 47% was however recovered during the reaction, because the remaining 53% stayed adsorbed onto the catalyst. Inorganic carbon recovery was consequently achieved in WW2 experiment by implementing catalyst washing using ultra pure water circulation under oxygen purging as post-treatment. A higher DOC initial value in WW2 was probably responsible for this specific behavior. Regarding carbon balances, the addition of the catalyst therefore enhances oxidation efficiency for mineralizing organic matter by achieving less-selective reactions with faster kinetics than single ozonation.

Ozone transfer efficiency

Figure 10 focuses on ozone transfer. The transfer yield, η_{O_3} , was constant during each experiment. Catalytic ozonation experiments on wastewaters were also compared to experiments with ultrapure water under similar conditions. Catalytic ozonation experiments showed the same yield (η_{O_3} close to 65%) whether they were performed using different wastewaters or ultrapure water. The catalyst is therefore able to govern ozone transfer so that no influence of the water quality appears. The catalyst/ozone reaction was fast enough to produce a very low dissolved

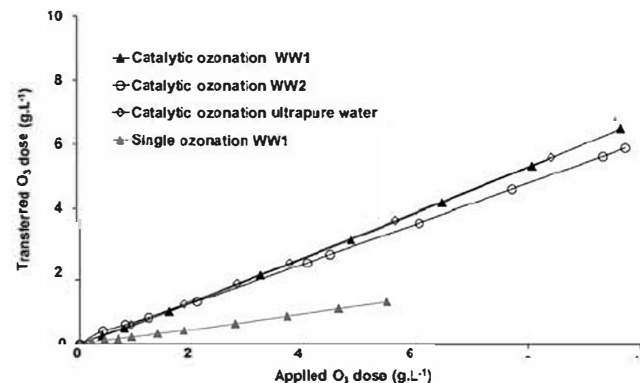


Figure 10. Transferred ozone dose versus applied ozone dose.

ozone concentration (0.4 mg.L^{-1}). All these observations are consistent with a reaction pathway based on two successive reactions as evoked by Fontanier (Fontanier et al. 2006). The first consists in the fast formation of highly reactive metal oxide from ozone and catalyst interaction. Single ozonation had a much lower transfer yield ($\eta_{\text{O}_3} = 24\%$ for WW1), due to lower kinetics for ozone reactions occurring in the wastewaters resulting in lower ozone demand. The measured dissolved ozone concentration was consequently much more important during single ozonation (26 mg.L^{-1} reached in the 20 first min of reaction time with WW1), compared to catalytic ozonation. Thus catalytic ozonation enhanced O_3 transfer compared to single ozonation because of fast ozone consumption by the catalyst. However, it is worth noting that hydrodynamic conditions were not strictly the same for single ozonation and catalytic ozonation experiments. The catalytic packing indeed accelerates water and gas velocities that favor mass transfer. A little improvement of ozone transfer rate can then be expected.

Impact on other wastewater characteristics

Other parameters have also been evaluated for initial and final solutions after experiment with ozone to better understand which compounds have been degraded, and to characterize treated wastewater after catalytic ozonation.

The control of Chemical Oxygen Demand has shown that the initial COD ($23 \text{ mgO}_2\text{.L}^{-1}$) has been reduced down to the detection limit equal to $10 \text{ mgO}_2\text{.L}^{-1}$ for both experiments related to single and catalytic ozonation applied to WW1 and WW2. This occurs when DOC removal rates highly differ, which highlights different oxidation pathways.

A focus on UV-Vis absorbance was realized for a better understanding of which kind of organic compounds have specifically been degraded. Figure 11 and

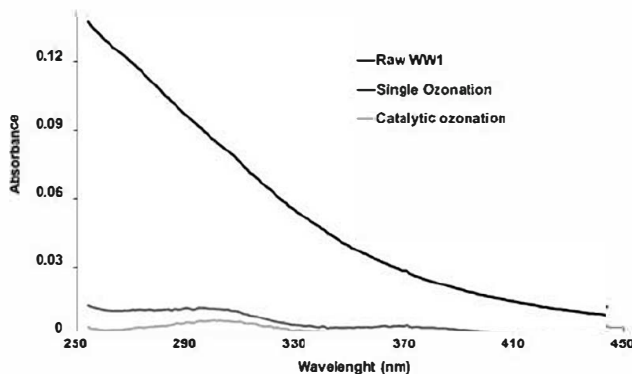


Figure 11. UV Absorbance spectra in the range 250–450 nm for raw WW1 and after single and catalytic ozonation.

Figure 12 stress the main differences in absorbance spectra for raw WW1 and after the different treatments. Major absorbance occurred in the region with wavelengths under 250 nm.

Regarding absorbance spectra in the range 250 nm–450 nm (Figure 11), one can observe first that both oxidation systems greatly affected UV absorbance spectra. It can be noticed that proteins (specific amino acids as tyrosine and tryptophan) and compounds absorbing at 280 nm were only present into raw water. In a general way single ozonation showed higher final values of absorbance compared to catalytic ozonation. The absorbance peak at 210 nm was still remaining whatever the treatment applied. Aromatic compounds absorbing at 254 nm (Silverstein et al. 1998) were highly reduced in both treatments but single ozonation was less efficient than catalytic ozonation (nearly total removal). Regarding higher wavelengths values, only raw water sample has shown some UV absorption. This indicates that the corresponding compounds were then removed during both oxidation processes.

Figure 12 corresponds to the spectra of the samples with eightfold dilution because of absorbance saturation in this wavelength area. A high absorbance at wavelengths around 210 nm was noticed in all cases, corresponding to compounds such as aldehydes, carboxyl, esters, nitrates, and numerous other organic compounds (Silverstein et al. 1998). Single ozonation showed a slight increment in absorbance values compared to raw WW1. This can be due to the compounds absorbing at higher wavelengths (as aromatics) that are converted into by-products absorbing at lower wavelengths during reaction. Regarding catalytic ozonation experiment, a reduction around 20% of 210 nm absorbance can be noticed. This shows an enhancement of oxidation yields for catalytic ozonation compared to single ozonation.

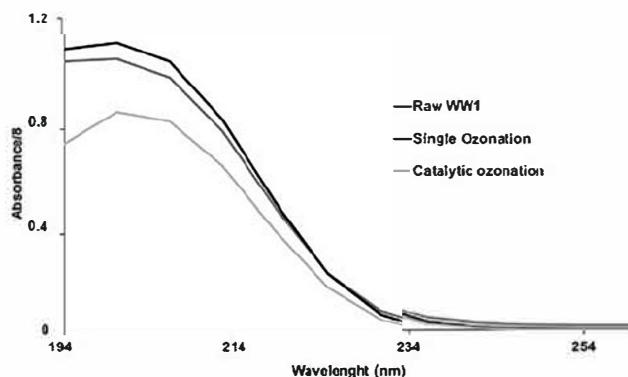


Figure 12. Diluted (eightfold) UV Absorbance spectra in the range 190–250 nm for raw WW1 and after single and catalytic ozonation.

All complementary analyses showed that catalytic ozonation is more efficient for reducing wastewater characteristic polluting parameters compared to single ozonation. Catalytic ozonation therefore enhances the reduction of the organic compounds present in the wastewater matrix, particularly aromatic compounds that represented a part of resistant pollutants so far.

Conclusions

Experiments have been carried out on urban wastewaters for comparing single ozonation, single adsorption and catalytic ozonation according to the TOCCATA® process, in terms of organic matter removal efficiency and ozone transfer.

Single ozonation was selective for reducing wastewater organic matter (only 39% DOC removal and 27% mineralization), probably because of the presence of compounds refractory to molecular ozone. Catalytic ozonation according to the TOCCATA process was able to enhance the oxidation extent achieving 90% DOC removal and 98% mineralization under similar conditions. As expected, adsorption contributed to DOC decrease during the catalytic process as the first step of catalytic mechanism. A pseudo-second-order kinetic model was presented for single adsorption, and some specific sorption parameters have been deduced such as the equilibrium sorption capacity and the rate constant. An apparent first-order kinetic model was proposed for DOC mineralization during catalytic ozonation which fitted well to experimental data.

Carbon balances stressed that catalytic ozonation achieved a high organic carbon mineralization compared to single ozonation. Besides, ozone mass transfer was enhanced from 24% to 68%, when ozone reaction took place in the presence of catalyst, and dissolved ozone concentration was much lower. Ozone transfer enhancement was therefore highlighted under catalytic reaction.

UV absorbance showed that more organic compounds were oxidized during catalytic ozonation compared to single ozonation, particularly aromatic compounds that absorb at 254 nm.

The TOCCATA® catalytic process was therefore much more efficient than traditional single ozonation for reducing recalcitrant organic matter with ozone transfer and reactivity enhancement.

Nomenclature and abbreviations

Abbreviations/ Nomenclature	Significance	Unit
WW	Wastewater	
COD	Chemical Oxygen Demand	$\text{mgO}_2\text{L}^{-1}$
DOC	Dissolved Organic Carbon	mgC.L^{-1}
DIC	Dissolved Inorganic Carbon	mgC.L^{-1}
IC	Inorganic carbon: CO_2 trapped at the gaseous output	mgC.L^{-1}
Q_G	Gaseous volumetric flow	L.h^{-1}
Q_L	Liquid volumetric flow	L.h^{-1}
U_L	Empty Bed Liquid Superficial velocity	m.h^{-1}
U_G	Empty Bed Gaseous Superficial velocity	m.h^{-1}
$[\text{O}_3]_{\text{GIN}}$	Inlet ozone concentration	$\text{mgO}_3\text{L}^{-1}$
$[\text{O}_3]_{\text{GOUT}}$	Outlet ozone concentration	$\text{mgO}_3\text{L}^{-1}$
$[\text{O}_3]_L$	Dissolved ozone concentration	$\text{mgO}_3\text{L}^{-1}$
k_{CO}	Apparent first order kinetic constant for catalytic ozonation	min^{-1}
$\text{O}_3_{\text{applied}}$	Ozone amount applied during reaction	g
$\text{O}_3_{\text{consumed}}$	Ozone amount consumed during reaction	g
$\text{O}_3_{\text{transferred}}$	Ozone amount transferred during reaction	g
V_d	Reactor dead volume	L
$k_{\text{single}_\text{O}_3}$	Single O_3 second order constant	$\text{L.mol}^{-1}.\text{min}^{-1}$
R^2	Linearization correlation parameter	
t_c	Contact time	min
t	Reaction time	min
V_{tot}	Total liquid volume	L
V_L	Volume of liquid in the reactor	L
q_e	Amount of DOC adsorbed at equilibrium	$\text{mg}_{\text{DOC}}.\text{g}_{\text{catalyst}}^{-1}$
q_t	Amount of DOC adsorbed on the surface of the catalyst at any time t	$\text{mg}_{\text{DOC}}.\text{g}_{\text{catalyst}}^{-1}$
k_1	Pseudo first order chemical sorption rate constant	min^{-1}
k_2	Pseudo second order chemical sorption rate constant	$\frac{\text{g}_{\text{catalyst}}}{\text{mg}_{\text{DOC}}.\text{min}}.$
k_d	Intraparticle diffusion rate constant	$\frac{\text{mg}_{\text{DOC}}}{\text{min}^{1/2}}.$
c	Intercept for Weber and Morris model	$\frac{\text{mg}_{\text{DOC}}}{\text{g}_{\text{catalyst}}}$
α, β	Elovich rate constants	$\frac{\text{g}_{\text{catalyst}}}{\text{mg}_{\text{DOC}}.\text{min}^{-1}}.$
q_{exp}	Experimental maximum adsorbed amount	$\text{mg}_{\text{DOC}}.\text{g}_{\text{catalyst}}^{-1}$
η_{O_3}	Ozone transfer yield	%

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