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Jullian Vittenet, Aboussaoud Wael, Mendret Julie, Jean-Stephane Pic, Hubert Jean-Stephane, et al.. Catalytic ozonation with γ -Al₂O₃ to enhance the degradation of refractory organics in water. *Applied Catalysis A : General*, 2015, 504, pp.519-532. 10.1016/j.apcata.2014.10.037 . hal-01079847

HAL Id: hal-01079847

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Vittenet, Jullian and Aboussaoud, Wael and Mendret, Julie and Pic, Jean-Stéphane and Debellefontaine, Hubert and Lesage, Nicolas and Faucher, Karine and Manero, Marie-Hélène and Thibault-Starzyk, Frédéric and Leclerc, Hervé and Galarneau, Anne and Brosillon, Stéphan Catalytic ozonation with γ -Al₂O₃ to enhance the degradation of refractory organics in water. (2015) Applied Catalysis A General, 504. 519-532. ISSN 0926-860X

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Catalytic ozonation with γ -Al₂O₃ to enhance the degradation of refractory organics in water

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A B S T R A C T

Nowadays, heterogeneous catalytic ozonation appears as a promising way to treat industrial wastewaters containing refractory pollutants, which resist to biological treatments. Several oxides and minerals have been used and their behavior is subject to controversy with particularly the role of Lewis acid sites and/or basic sites and the effect of salts. In this study, millimetric mesoporous γ -Al₂O₃ particles suitable for industrial processes were used for enhancing the ozonation efficiency of petrochemical effluents without pH adjustment. A phenol (2,4-dimethylphenol (2,4-DMP)) was first chosen as petrochemical refractory molecule to evaluate the influence of alumina in ozonation. Single ozonation and ozonation in presence of γ -Al₂O₃ led to the disappearance of 2,4-DMP in 25 min and a decrease in pH from 4.5 to 2.5. No adsorption of 2,4-DMP occurred on γ -Al₂O₃. Adding γ -Al₂O₃ in the process resulted in an increase of the 2,4-DMP oxidation level. Indeed, the total organic carbon (TOC) removal was 14% for a single ozonation and 46% for ozonation with γ -Al₂O₃. Similarly, chemical oxygen demand (COD) removal increases from 35 to 75%, respectively. Various oxidized by-products were produced during the degradation of 2,4-DMP, but after 5 h ozonation 90% of organic by-products were acetic acid > formic acid >> oxalic acid. Some of the carboxylic acids were adsorbed on γ -Al₂O₃. The use of radical scavengers (tert-butanol) highlighted the involvement of hydroxyl radicals during catalytic ozonation with γ -Al₂O₃ in contrary to single ozonation, which mainly involved direct ozone reaction. γ -Al₂O₃ is an amphoteric solid with Lewis acid AlOH(H⁺) sites and basic Al-OH sites. After ozonation the amount of basic sites decreased due to carboxylates adsorption, while the Lewis acid sites remained constant as evidenced by FTIR. Several ozonation runs with γ -Al₂O₃ reported a progressive decrease of its catalytic activity due to the cumulative sorption of carboxylates on the basic sites. After 80 h of ozonation, a calcination at 550 °C allowed to recover all Al-OH basic sites and the initial activity of γ -Al₂O₃. A synthetic petrochemical effluent containing various petrochemicals (phenol, acetic acid, naphthenic acid, pyrene, naphthalene) was then treated with γ -Al₂O₃ with and without NaCl. Sodium ions prevented carboxylates adsorption on γ -Al₂O₃ leading to a higher efficiency of γ -Al₂O₃ in presence of NaCl and allowed to decrease the toxicity of the petrochemical effluent.

Keywords:

Catalytic ozonation

Wastewater treatment

Al₂O₃

Phenol

Advanced oxidation process

1. Introduction

In recent years, many efforts on the advanced oxidation processes (AOPs) development have been done for wastewater treatment especially in industries to treat organic compounds resistant to biological treatments [1]. Among the AOPs, processes based on ozone appear as promising technologies for the removal

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of refractory compounds [2–7]. In aqueous media, O_3 can react directly with organic compounds and/or indirectly when O_3 is decomposed into free radicals, which have higher oxidizing rate than O_3 itself [2–4,8]. Consequently, favoring this second route allows to reach higher levels of toxic pollutant mineralization. The indirect reaction in single ozonation is influenced by the pH of the solution (high pH), the solution composition and the temperature, but it is limited to a certain extend of mineralization [3,8]. In this context, some studies have focused on heterogeneous catalytic ozonation in aqueous media since the early 2000s, due to the enhancement of the production of hydroxyl radicals with materials such as activated carbons, zeolites, oxides (CeO_2 , TiO_2 , MgO , Al_2O_3 , MnO_2 , Fe_2O_3 , Co_3O_4 , NiO , CuO , ZnO , ZrO_2 , ...) and the subsequent ozone economy [4,8–17]. However, all of these materials have never been studied in identical conditions, so it is difficult to compare their efficiency. An excellent review by Nawrocki and Kassprzyk-Hordern in 2010 reported the different materials and conditions used in catalytic ozonation in this last decade [8]. They report that the following order in term of better heterogeneous catalysts appears in certain conditions (ozonation of dinitrobenzene at pH 3): $Fe_2O_3 > Co_3O_4 > MoO_3 > CuO \sim NiO > Al_2O_3 > TiO_2 > Cr_2O_3 \sim MnO_2 \sim O_3$, which seems to follow the basicity strength of the oxides ($Mn > Fe > Co > Ni > Cu > Zn$) except for MnO_2 . However, in some other studies MnO_2 was demonstrated as the more active catalyst, but leaching of some cations have been also observed, as well as for CuO . Some of these oxides need to be supported for industrial processes to avoid fine particles and the leaching of metal has to be avoided. In this review was also highlighted the wide controversy of mechanisms proposed in literature responsible for the increase of ozone activity in the presence of materials and especially the role of Lewis acid sites and/or basic sites, which remained a subject of debate. Catalytic ozonation appears as a highly suitable process for petrochemical wastewater treatments as ozone is especially active for refractory molecules of this industry such as aromatic molecules substituted with electron donor groups as alkyl-benzene (toluene, xylene, ethylbenzene), phenols (alkylphenols) and polyaromatic hydrocarbons (naphtalene, phenantrene, anthracene, ...).

It was previously shown that the catalytic activity of activated carbons in ozonation decreased after several runs by the loss of their basic sites and no regeneration was possible [5–7]. Inorganic catalysts should be preferred. Zeolites and oxides in ozonation for wastewater treatment provide many advantages: no chemicals to add, simplicity of use and high pollutant removal efficiency [15]. Concerning the zeolites in ozonation process for organic compounds removal, it seems that the reaction mechanisms are zeolite structures dependent [18]. Some studies revealed the adsorption capacity of pollutant and/or ozone into the micropores of zeolites, especially in ZSM-5 structure type, which does not confer any radical pathway but serve as reservoir of ozone and adsorbents of organic compounds [19–21]. Besides, it was also demonstrated that zeolites could catalyze ozone decomposition and enhance the generation of hydroxyl radicals (HO^\bullet) [11]. Indeed, it was recently reported that basic zeolites as LTA zeolite can enhance radicals generation by combining two pathways: the production of hydroxide ions during the cation-exchange of Na-zeolite with the protons of the solution and by the interaction of ozone with some hydroxyl groups present as defects in the material [18]. However, a decrease of the LTA catalytic activity was observed for a second run of phenol compounds ozonation due in part to the irreversibility of the cation-exchange [18]. Other porous materials especially $\gamma-Al_2O_3$ have been identified to generate free radicals from the interaction between their hydroxyl groups and ozone [20,22,23]. A study suggested that $\gamma-Al_2O_3$ combined to O_3 allowed an enhancement of HO^\bullet radical via $\bullet O_2^-$ and/or $\bullet O_3^-$ radicals, resulting in a faster

carboxylic acids removal than single ozonation [22]. Recently, Ikhlaq et al. [20] confirmed this hypothesis and pointed out also that HO^\bullet radicals can combine with themselves to produce H_2O_2 , depending on the pH of the solution. This was demonstrated after pH adjustment for pH higher than $pH=6.2$. Another catalytic reaction mechanism with aluminum oxides was also proposed due to the ir capacity to adsorb ozone and to decompose it into free radicals by interacting with the hydroxyl groups of the materials [16,24]. Moreover, the catalytic effect of $\gamma-Al_2O_3$ was preserved after several ozonation runs, indicating no poisoning of the active sites for ozone decomposition [16]. However, the increase of the pollutant removal efficiency by heterogeneous ozonation with $\gamma-Al_2O_3$ was also attributed to the adsorption of ozonation by-products. On the one hand, pharmaceutical pollutant removal experiments were performed by alternating single ozonation and catalytic ozonation with $\gamma-Al_2O_3$ in order to observe the by-products adsorption capacity of $\gamma-Al_2O_3$. The authors explain that carboxylates could be adsorbed onto $\gamma-Al_2O_3$ when the solution pH is lower than the pH_{PZC} of the material [2]. On the other hand, 2,4-dimethylphenol (2,4-DMP) removal was performed by single ozonation in order to generate oxidized by-products and, then $\gamma-Al_2O_3$ was added to examine its adsorption ability [17]. These experiments clearly evidenced no adsorption of the oxidized by-products generated after 35 min of single ozonation, but an adsorption of the by-products generated after 3 h of single ozonation. Consequently, it appears that reaction mechanisms in aluminum oxides/ozone processes are by-products dependent and are still unclear, especially concerning $\gamma-Al_2O_3$ material. The adsorption of oxidized by-products and the role of Lewis acid sites and basic sites of $\gamma-Al_2O_3$ are subject to large controversy.

In the present study, a commercial $\gamma-Al_2O_3$ with millimetric particles, suitable for industrial ozonation processes, was investigated for 2,4-DMP degradation in the presence of ozone, without adding any chemical, so without pH adjustment. Substituted phenols, such as 2,4-DMP are highly toxic compounds and are typical pollutants found in petrochemical wastewater [25,26]. The kinetics of pollutant degradation was followed, as well as the formation of the oxidized by-products by chromatography, by total organic carbon (TOC) and chemical oxygen demand (COD) measurements. Adsorption isotherms of 2,4-DMP and of the final oxidized by-products (carboxylic acids) on $\gamma-Al_2O_3$ were performed to clarify the adsorption capacity of $\gamma-Al_2O_3$. FTIR studies were performed to examine the acid and basic sites of the material before and after ozonation. The reusability of $\gamma-Al_2O_3$ was investigated by performing several ozonation runs of the pollutant. $\gamma-Al_2O_3$ was also used in the ozonation of a complex synthetic petrochemical effluent (phenol, acetic acid, naphtenic acid, pyrene, naphtalene) to confirm the observations obtained with 2,4-DMP. Toxicity tests were performed to evaluate the efficiency of $\gamma-Al_2O_3$ in ozonation.

2. Experimental procedure

2.1. Materials

Acetonitrile (ACN) and water (H_2O) for high performance liquid chromatography (HPLC) analyzes are HPLC grade (Sigma Aldrich). $\gamma-Al_2O_3$ was purchased from Alpha Degussa. All other chemicals are high grade commercially available from Sigma Aldrich: 2,4-dimethylphenol (2,4-DMP) (98%), acetic acid, formic acid, oxalic acid, phenol, pyrene, naphtalene and *tert*-butanol (*t*-BuOH). Naphtenic acid was purchased from Fluka. 2,4-DMP and carboxylic acids solutions were prepared using Millipore Milli-Q water.

2.2. Inorganic materials characterization

X-ray diffraction (XRD) pattern of the material was performed using a Bruker D8 Advance diffractometer with a Bragg-Brentano

geometry and equipped with a Bruker Lynx Eye detector. XRD pattern was recorded in the range 4° – 85° (2θ) with a 0.0197° angular step size and a 0.2 s counting time per step. Textural properties of the material were determined by N_2 adsorption/desorption at -196°C on a Micromeritics Tristar 3000 apparatus. The sample was previously outgassed in vacuum at 250°C for 12 h. The surface area was determined according to the BET method. Total pore volume was calculated at the end of the adsorption step. Mesopore diameter was evaluated using the Broekhoff and De Boer method applied to the desorption branch of the isotherm as it has been shown to be one of the more accurate method for mesopore size evaluation [27].

The ^{13}C MAS NMR spectrum of $\gamma\text{-Al}_2\text{O}_3$ after 5 h ozonation was performed on filtered and dried material and was obtained on a Varian VNMRS 300 MHz spectrometer with a magnetic field of 7.05 T. The operating frequency for ^{13}C was 75.43 MHz. The sample was packed in a 7.5 mm ZrO_2 rotor. The chemical shifts are presented in parts per million.

FTIR analyses of $\gamma\text{-Al}_2\text{O}_3$ were performed on dried materials before and after ozonation. Samples were pressed ($\sim 10^6$ Torr) into self-supported disks (2 cm^2 area, $7\text{--}10\text{ mg cm}^{-2}$) and placed in a quartz cell equipped with KBr windows. A movable quartz sample holder permits one to adjust the pellet in the infrared beam for spectra recording and to displace it into a furnace at the top of the cell for thermal treatment. The cell was connected to a vacuum line for evacuation ($P_{\text{residual}} \approx 10^{-6}$ Torr) and for the introduction of gases into the infrared cell. The gas pressure inside the cell was measured by a pressure gauge (10^{-2} – 10^3 Torr range). A Bruker Vertex 80 V spectrometer equipped with a mercury cadmium telluride (MCT) cryodetector and an extended KBr beam splitter was used for the acquisition of spectra recorded at room temperature, in the $600\text{--}5500\text{ cm}^{-1}$ range. The resolution of the spectra was 4 cm^{-1} , and 128 scans were accumulated for each spectrum. Strength of acid sites of the materials was obtained by pyridine adsorption followed by FTIR spectroscopy for different temperatures of desorption. Basic sites of the materials were analyzed by CO_2 adsorption/desorption.

2.3. Adsorption and ozonation experiments

Prior to ozonation experiments, 2,4-DMP adsorption capacity of $\gamma\text{-Al}_2\text{O}_3$ was assessed to quantify its possible contribution to the degradation of the pollutant. Adsorption of the pollutant was performed at 25°C in abiotic conditions: 0.2 g of $\gamma\text{-Al}_2\text{O}_3$ were stirred in a glass bottle containing 100 mL of pollutant solution until the equilibrium was reached, which was corresponding to 4 h. Equilibrium isotherms of adsorption were plotted for 2,4-DMP concentrations ranging from 1 to 400 mg L^{-1} . Equilibrium isotherms of carboxylic acids adsorption (acetic acid, formic acid, oxalic acid) were performed following the same procedure than for 2,4-DMP adsorption.

The ozone decomposition of the pollutant was assessed in a glass stirred batch reactor of 2 L as previously described [18]. Experiments were conducted at 25°C , feeding the reactor with a 40 L h^{-1} O_3 gas flow rate with a 2 g Nm^{-3} O_3 concentration (obtained from air). In a typical run, 3 g of $\gamma\text{-Al}_2\text{O}_3$ were added in the reactor with 1.5 L of 2,4-DMP solution at 50 mg L^{-1} . The solution was stirred at 400 rpm at 25°C and O_3 was injected to the reactor immediately after introducing $\gamma\text{-Al}_2\text{O}_3$. In order to avoid limitation by O_3 gas to liquid transfer, the stirring velocity of the reactor was optimized by progressively increasing the velocity from 200 to 400 rpm and optimal stirrer velocity was found at 400 rpm [18]. The pollutant removal and its oxidized by-products were monitored taking samples within time through PTFE syringe filters ($0.45\ \mu\text{m}$).

The reuse and regeneration of $\gamma\text{-Al}_2\text{O}_3$ were also investigated by performing several ozonation runs of the 2,4-DMP degradation.

These experiments were performed using another lab scale reactor described elsewhere [17], similar to the first one but with a volume of solution of 2 L, an amount of $\gamma\text{-Al}_2\text{O}_3$ of 5 g L^{-1} , a O_3 gas flow rate is 30 L h^{-1} and O_3 gas concentration is 5 g Nm^{-3} (obtained from O_2).

A synthetic petrochemical effluent was also ozonized with $\gamma\text{-Al}_2\text{O}_3$ without and with NaCl (50 g L^{-1}). These experiments were performed in a third pilot plant scale reactor described elsewhere [28] with a volume of solution of 1.5 L, an amount of $\gamma\text{-Al}_2\text{O}_3$ of 2 g L^{-1} , a O_3 gas flow rate of 24 L h^{-1} and a gas concentration of $5\text{ g O}_3\text{ Nm}^{-3}$. The complex synthetic effluent was a mixture of several aromatic hydrocarbons and associated acids: phenol, acetic acid, naphthenic acid, pyrene, naphthalene with initial concentration of 200, 200, 25, 0.05, 0.95 mg L^{-1} , respectively, corresponding to $\text{TOC} = 230\text{ mg L}^{-1}$ and $\text{COD} = 750\text{ mg L}^{-1}$. Toxicity tests were performed on the experiments performed in presence of NaCl (50 g L^{-1}). Non-standardized toxicity tests (Toxkits), named ARTOXKIT and ROTOXKIT, were performed using two different seawater organisms *Artemia franciscana* and *Brachionus calyciflorus*, respectively. Toxicity tests were performed after pH adjustment at pH 7 of the effluent treated by 150 and 300 min of ozonation with $\gamma\text{-Al}_2\text{O}_3$. The efficiency of the process was assessed by the effluent concentration able to provoke 50% mortality of the species after 24 h of exposure (LC_{50} 24 h). Results were expressed in toxic unit: $\text{Equitox/m}^3 = 100/\text{LC}_{50}$ 24 h.

2.4. Analysis of soluble pollutant and by-products

The 2,4-DMP concentration in the aqueous solutions was monitored by HPLC (Waters 600E controller and pump, 717 plus Autosampler) equipped with an UV detector (2996 PDA, fixed wavelength $\lambda = 279\text{ nm}$). HPLC analyzes was performed on a C18 grafted silica column (Interchim, Uptisphere[®] C18-ODB, $150\text{ mm} \times 4.6\text{ mm} \times 5\ \mu\text{m}$). $20\ \mu\text{l}$ sample were injected and a mobile phase composed of 45/55 (ACN/ H_2O) at 0.8 ml min^{-1} was used. Solutions were filtered before analysis with a PTFE syringe filter ($0.45\ \mu\text{m}$). Under these analytical conditions, the retention time of 2,4-DMP was about 5 min.

The total organic carbon (TOC) values of the solutions were determined with a Shimadzu TOC-V meter. The gas flow-rate (air) was set to 130 mL min^{-1} and the gas pressure was 190 kPa. The TOC measurement is based on the oxidation of the organic matter (except volatile organic compounds) by thermal oxidation. The solution is first acidified with HCl (2 N) to transform carbonates into CO_2 . Air is then bubbled in the solution to remove CO_2 . Samples are then injected in an oven heated at 680°C containing a catalyst (Pt) to transform the organics into CO_2 , which is therefore analyzed by an IR detector.

The chemical oxygen demand (COD) is the quantity of oxygen necessary to chemically oxidize all molecules in water. This analysis is performed using oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ in closed containers in acidic medium in presence of Ag_2SO_4 catalyst. HgSO_4 is also added to precipitate chloride anions. After addition of 2 mL of polluted water solution in tubes containing the oxidative reactants at different concentrations to analyze COD between 0 and $150\text{ mg O}_2\text{ L}^{-1}$ (purchased to Hash), the mixtures were heated at 150°C for 2 h. The amount of produced Cr^{3+} was measured by spectrophotometry (Hash instrument) at 600 nm, which allowed to calculate COD.

The carboxylic acids concentrations were determined by ionic chromatography (IC) using a Dionex ICS 1000 system equipped with an ASRS 4 mm ionization system and a Dionex AS19 column. $25\ \mu\text{l}$ samples were injected. Eluent was a KOH solution at 1 mL min^{-1} and with the following gradient conditions: 10 mM from 0 to 10 min, then 45 mM from 10 to 40 min and finally 10 mM from 40 to 50 min.

LC-MS analyses were achieved with a UPLC Acquity H-Class (Waters) and a Synapt G2-S (Waters) detector equipped with a

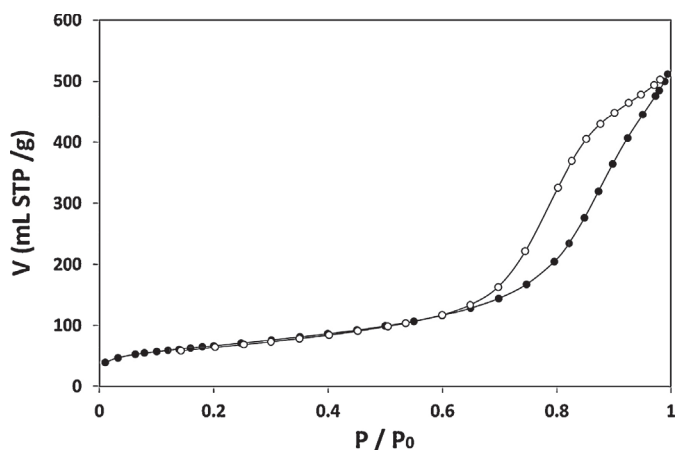


Fig. 1. N_2 adsorption (●) and desorption (○) isotherms of $\gamma\text{-Al}_2\text{O}_3$ at -196°C .

dual electro-spray (ESCl). $10\ \mu\text{L}$ samples were injected, a column Acquity BEH I was used (C18, $50\ \text{mm} \times 2.1\ \text{mm} \times 1.7\ \mu\text{m}$) and the mobile phase was constituted of ACN and H_2O at $0.8\ \text{ml min}^{-1}$.

3. Results and discussion

3.1. Characterization of $\gamma\text{-Al}_2\text{O}_3$

$\gamma\text{-Al}_2\text{O}_3$ was purchased as 3–5 mm cylindrical pellets (Fig. S1), which is a suitable size for industrial ozonation processes. XRD pattern indicated principally three broad peaks around 35 , 45 and 66° in 2θ (Fig. S2), which showed the gamma crystalline phase of this alumina oxide [29]. N_2 adsorption/desorption isotherm of $\gamma\text{-Al}_2\text{O}_3$ is of type IV according to IUPAC classification characteristic of a mesoporous material (Fig. 1). A hysteresis loop (H1) was observed at high relative pressures revealing cylindrical pores of mean pore diameter of 15 nm. The material featured a BET specific surface area of $236\ \text{m}^2\ \text{g}^{-1}$ and a mesopore volume of $0.60\ \text{cm}^3\ \text{g}^{-1}$.

3.2. Adsorption of 2,4-DMP on $\gamma\text{-Al}_2\text{O}_3$

Prior to O_3 experiments, adsorption of the pollutant on $\gamma\text{-Al}_2\text{O}_3$ was verified to assess the adsorption contribution in the 2,4-DMP removal. First, adsorption kinetic was monitored at 25°C by stirring a 2,4-DMP solution ($50\ \text{mg L}^{-1}$) with $\gamma\text{-Al}_2\text{O}_3$ ($2\ \text{g L}^{-1}$) in order to estimate the time necessary to reach equilibrium. The expected maximum adsorption would be $25\ \text{mg}$ 2,4-DMP per gram $\gamma\text{-Al}_2\text{O}_3$. Equilibrium was reached after 4 h and only $0.2\ \text{mg}$ 2,4-DMP per gram $\gamma\text{-Al}_2\text{O}_3$ was obtained. The 2,4-DMP adsorption isotherm was then built for an equilibrium time of 4 h and by varying the 2,4-DMP concentration from 1 to $400\ \text{mg L}^{-1}$. For the highest 2,4-DMP concentration ($400\ \text{mg L}^{-1}$) only $3.2\ \text{mg}$ 2,4-DMP were adsorbed per gram of $\gamma\text{-Al}_2\text{O}_3$ (Fig. S3). Therefore, in this study (using a 2,4-DMP solution of $50\ \text{mg L}^{-1}$) the contribution of the pollutant adsorption in the ozonation process can be neglected.

3.3. Ozonation of 2,4-DMP in aqueous solution with and without $\gamma\text{-Al}_2\text{O}_3$

Ozonation experiments were conducted with 2,4-DMP solutions ($50\ \text{mg L}^{-1}$) at 25°C with an initial pH of deionized water around 4.5. No chemicals were added in the solution in accordance of industrial process requirement (no buffer or base added). The pH was continuously measured but not controlled. The pH value of the 2,4-DMP solutions with and without $\gamma\text{-Al}_2\text{O}_3$ was monitored during the ozonation experiments (Fig. S4). The pollutant removal over time was monitored as well as the total organic carbon (TOC)

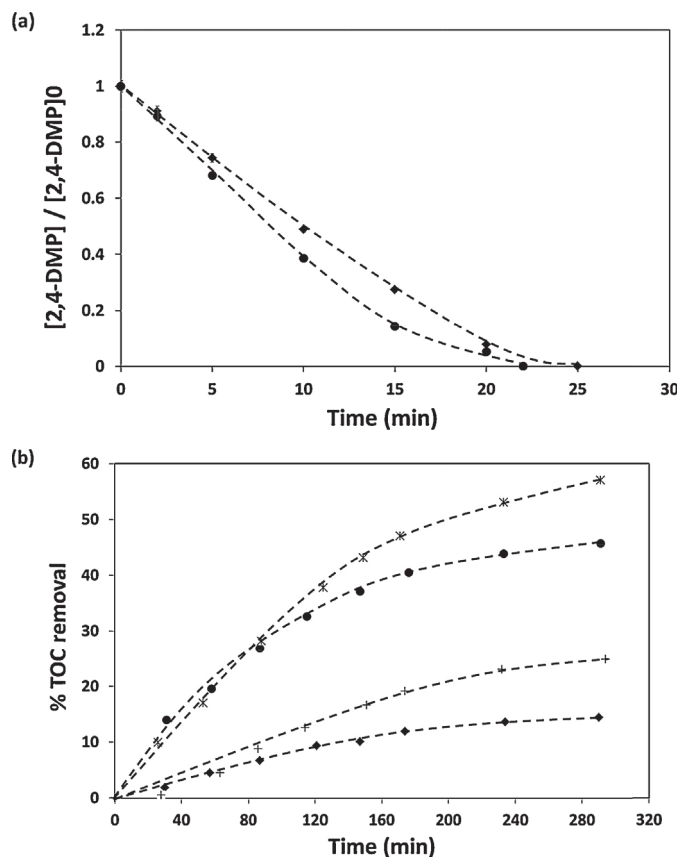


Fig. 2. 2,4-DMP removal (a) and TOC removal (b) during single ozonation (◆) and during ozone/ $\gamma\text{-Al}_2\text{O}_3$ coupled treatment with different amount of $\gamma\text{-Al}_2\text{O}_3$: $1\ \text{g L}^{-1}$ (+); $2\ \text{g L}^{-1}$ (●); $5\ \text{g L}^{-1}$ (*). Temperature: 25°C . O_3 flow rate: $40\ \text{L h}^{-1}$. $[\text{O}_3]_{\text{inlet}}$: $2\ \text{g Nm}^{-3}$. $[\text{2,4-DMP}]_0$: $50\ \text{mg L}^{-1}$. Volume of solution: $1.5\ \text{L}$.

(Fig. 2) and the chemical oxygen demand (COD) (Fig. 3; Table 1) with and without $\gamma\text{-Al}_2\text{O}_3$. Some 2,4-DMP oxidized by-products were identified and followed within time (Table 2).

3.3.1. Removal of 2,4-DMP from the water solution

By single ozonation (without materials) 2,4-DMP was totally removed from the solution after 25 min even with low ozone concentration ($2\ \text{g Nm}^{-3}$) (Fig. 2a). Similar fast 2,4-DMP removal by single ozonation was also previously noticed with similar initial concentration indicating a high reactivity of this pollutant with ozone [17,18,30]. Adding $\gamma\text{-Al}_2\text{O}_3$ ($2\ \text{g L}^{-1}$) in the ozonation process led to a slight increase of 2,4-DMP removal rate with a complete removal after 22 min (Fig. 2a), as observed also previously using zeolites in similar conditions [17,18]. The initial degradation of 2,4-DMP seems independent of the presence of any inorganic catalysts and encountered presumably to fast direct reaction of ozone with 2,4-DMP. Ozone reacts preferentially with organic molecules featuring double bonds (Scheme 1) and activated aromatics. 2,4-DMP is an aromatic molecule substituted by three electron donor groups (one hydroxyl strongly e^- donor and two methyl) and is therefore very favorable to ozonation degradation. Two simplified pathways can be imagined for direct ozonation of 2,4-DMP due to the

Table 1

Rate constants for COD removal during 2,4-DMP ozonation for single ozonation and ozonation with $\gamma\text{-Al}_2\text{O}_3$.

	$k_{\text{COD fast}} \times 10^5\ (\text{s}^{-1})$	$k_{\text{COD slow}} \times 10^5\ (\text{s}^{-1})$
Single ozonation	7.8 ± 0.1	1.1 ± 0.1
$\text{O}_3/\gamma\text{-Al}_2\text{O}_3$	11.9 ± 0.1	5.8 ± 0.1

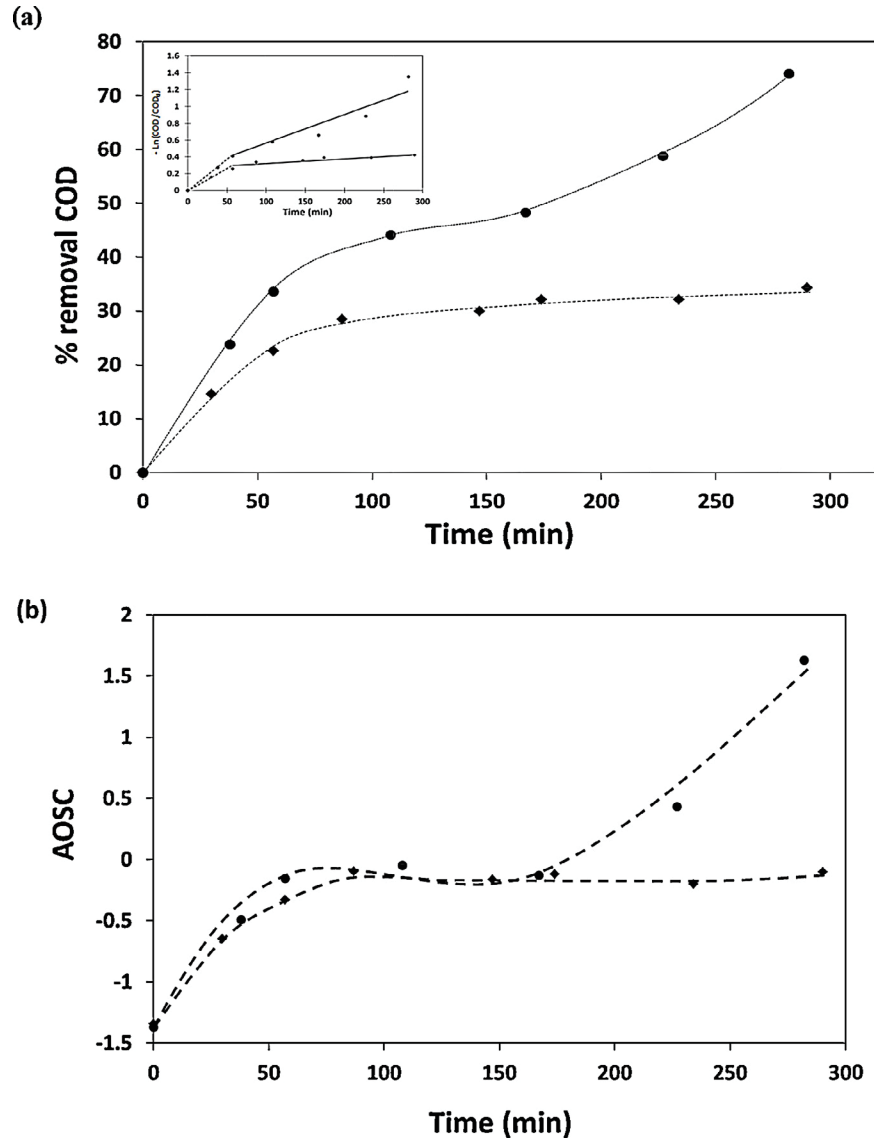
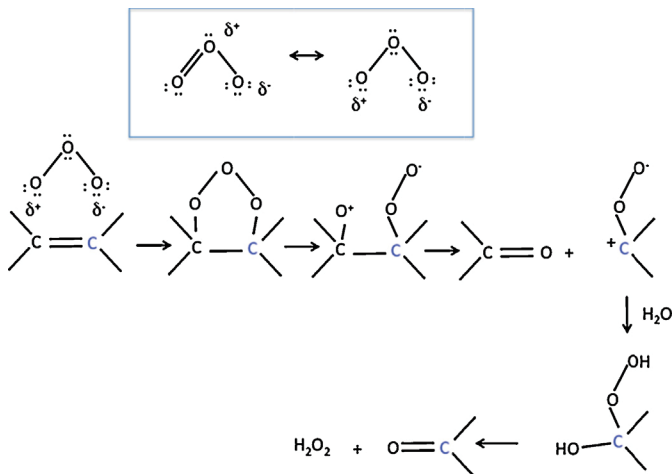


Fig. 3. COD removal (Inset: logarithm representation for rate constant calculation) (a) and AOSC factor evolution (b) during single ozonation (◆) and during ozone/ γ -Al₂O₃ coupled treatment (●). Temperature: 25 °C; O₃ flow rate: 40 L h⁻¹; [O₃]_{inlet}: 2 g Nm⁻³; [2,4-DMP]₀: 50 mg L⁻¹; volume of solution: 1.5 L; γ -Al₂O₃: 2 g L⁻¹.



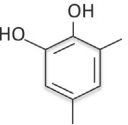
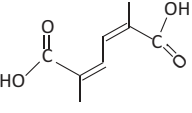
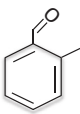
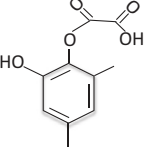
Scheme 1. Schematic representation of direct O₃ reaction with unsaturated bond.

polarizability of the double bond bearing the OH group (Scheme 2). Different intermediary by-products are however expected as for nitrobenzene ozonation [31]. Expected final products are carboxylic acids. They are very stable against ozonation as acetic acid but not formic acid, which reacts with ozone to give CO₂.

3.3.2. Removal of total organic carbon from the water solution

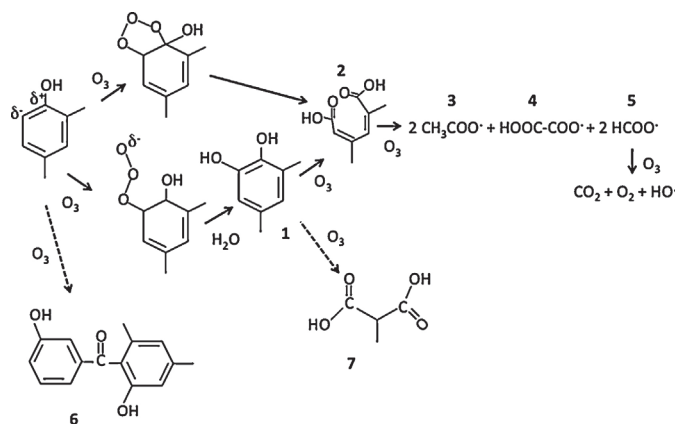
The removal of specific pollutant (as 2,4-DMP in our case) is one of the objectives of the water treatment. However, the efficiency of a water treatment process should also assess the amount of total organic carbons (TOC) remaining in the solution resulting from the degradation of the initial product. Indeed oxidized by-products of pollutants may have also a toxic character and sometimes are even more toxic than the initial pollutant, as it will be shown in the last part of this study. So, it is of prime importance to estimate the oxidation efficiency of a water treatment process through TOC measurement [32,33]. If no adsorption of pollutants or by-products is noticed, TOC removal corresponds to the mineralization level of the pollutant. Concerning single ozonation, only 14% TOC removal was reached after 5 h ozonation. Adding

Table 2
Identification by LC-MS of some 2,4-DMP oxidized by-products after single ozonation and ozonation with γ -Al₂O₃.

2,4-DMP oxidized by-products	m/z	O ₃		O ₃ / γ -Al ₂ O ₃		
		t _r (min)	t _d (min)	t _r (min)	t _d (min)	
	C ₈ H ₁₀ O ₂	139	1.30	61	1.35	61
	C ₈ H ₁₀ O ₄	171	0.70	91	0.71	91
	C ₈ H ₈ O	121	1.27	91	1.32	85
	C ₁₀ H ₁₀ O ₅	211	0.71	91	0.71	91

t_r: retention time; t_d: complete removal time.

γ -Al₂O₃ (2 g L⁻¹) to the ozonation process allowed a remarkable increase of the TOC removal corresponding to 46% of organic carbons removal (Fig. 2b). TOC removal increased linearly during about 60 min and then became slower (especially after ca. 170 min), which probably indicated that some oxidized by-products are very stable towards ozonation. Moreover, this slowdown in the mineralization rate can be explained by the low ozone dosage chosen in this study (2 g Nm⁻³) in comparison with usual industrial conditions (25 to 100 g Nm⁻³). Increasing the amount of γ -Al₂O₃ from 1 to 5 g L⁻¹ in the ozonation process yielded to an increase of TOC removal from 26 to 57%, respectively. However, TOC removal



Scheme 2. Schematic representation of expected direct O₃ reaction with 2,4-DMP (plain arrows). Possible dimerization route (6) and methylmalonic acid (7) formation is presented in dashed line.

efficiencies for 2 and 5 g L⁻¹ γ -Al₂O₃ were overlapping during 90 min of reaction. We may explain this fact considering two parallel reactions: catalytic ozonation and adsorption on γ -Al₂O₃ of highly oxidized by-products formed after 90 min ozonation. Similar catalytic ozonation efficiency between 2 and 5 g L⁻¹ γ -Al₂O₃ is suspected, whereas adsorption ability of highly oxidized by-products is enhanced with higher amount of γ -Al₂O₃ adsorbent.

3.3.3. Chemical oxygen demand (COD) removal

The chemical oxygen demand (COD) is another way to indirectly measure the amount of organic compounds remaining in water. TOC measures the organic matter that can be oxidized by thermal treatment (expressed in mg of C per L), whereas COD measures the organic matter that can be oxidized chemically. COD is expressed in mg of O₂ per L, which indicates the mass of oxygen consumed per liter of solution to oxidize organics [11]. Single 2,4-DMP ozonation led to 35% COD removal corresponding to a decrease from 130 to 83 mg O₂ L⁻¹ after 5 h treatment. Similarly to the TOC evolution, the COD decreased more rapidly in the presence of γ -Al₂O₃. Indeed, adding γ -Al₂O₃ (2 g L⁻¹) in the process allowed a significant reduction of the COD from 143 to 37 mg O₂ L⁻¹, corresponding to 75% COD removal. The kinetics of COD removal was modeled using a two-pathways first-order kinetic model [2]. This model distinguishes organic compounds oxidizing fast during the ozonation experiments from those oxidizing slowly. The experimental data for fast and slow oxidations were fitted with the first order kinetic model (Eq. (1)) and reported in Fig. 3a. In each pathway of the model the corresponding rate constants for COD removal were higher in the presence of γ -Al₂O₃ (Table 1). The change of regime was clearly observed after 60 min of ozonation (Fig. 3a).

$$\frac{d[\text{COD}]_x}{dt} = k[\text{COD}]_x$$

$$\frac{d[\text{COD}]_x}{[\text{COD}]_x} = k dt \quad (1)$$

$$-\ln\left(\frac{\text{COD}_x}{\text{COD}_0}\right) = kt + \text{constant}$$

with x = fast or slow.

An interesting factor to consider is the average oxidation state of carbon (AOSC) [2,34,35], which informs indirectly about the average oxidation state of the organic compounds remaining in the solution by comparing thermal oxidation (TOC) with chemical oxidation (COD) according to Eq. (2).

$$\text{AOSC} = 4 - \left(4 \times 0.375 \frac{\text{COD}}{\text{TOC}}\right) \quad (2)$$

with 0.375 being the ratio between the molecular mass of C and O₂ to expressed COD and TOC in mmol.

Higher AOSC values will be obtained for higher oxygenated molecules. AOSC values are in the range [-4 to +4] with -4 accounting for low oxidation state as methane and +4 for high oxidation state as CO₂. The AOSC value of the starting 2,4-DMP solution is around -1.4, as the average oxidation state of the molecule is low. For single ozonation, the average oxidation level of the organic compounds increased to -0.2 after 4 h indicating an increase of the average oxidation states of the organics in solution, which however remains low. Adding γ -Al₂O₃ during the ozonation process resulted in a three steps process: from 0 to 60 min (AOSC from -1.4 to -0.2), from 60 to 170 min (AOSC = -0.2) and above 170 min with a remarkable increase of the AOSC from -0.2 to +1.6 between 3 and 5 h ozonation (Fig. 3b). This evidences that the by-products obtained after 170 min of ozonation with γ -Al₂O₃ are different to the one obtained by single ozonation and have a higher level of oxidation state.

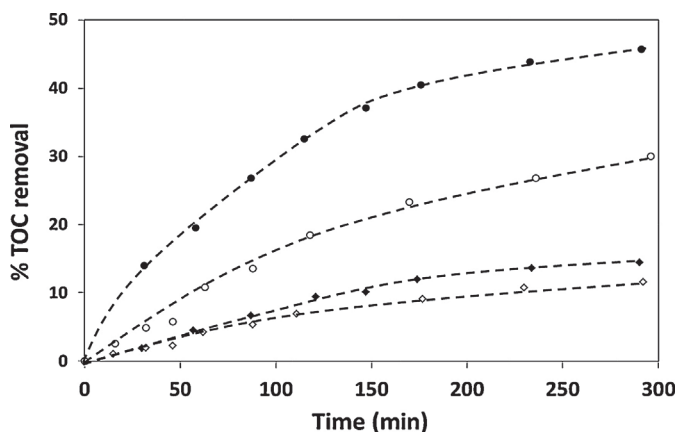


Fig. 4. TOC removal during single ozonation with (\diamond) and without (\bullet) *t*-BuOH radical scavenger and during ozone/ γ - Al_2O_3 coupled treatment with (\circ) and without (\bullet) *t*-BuOH. Temperature: 25 °C; O_3 flow rate: 40 L h^{-1} ; $[\text{O}_3]_{\text{inlet}}$: 2 g Nm^{-3} ; $[\text{2,4-DMP}]_0$: 50 mg L^{-1} ; volume of solution: 1.5 L; γ - Al_2O_3 : 2 g L^{-1} ; [*t*-BuOH]: 25 mg L^{-1} .

3.4. Ozonation of 2,4-DMP in presence of HO^\bullet radical scavenger (*t*-BuOH)

The pH value of the 2,4-DMP solutions with and without γ - Al_2O_3 was monitored during the ozonation experiments (Fig. S4). For single ozonation, a decrease in the pH value was observed from 4.0 to 2.8. This is very likely due to the formation of carboxylic acids during ozonation as reported elsewhere [36–39]. A higher pH decrease was noticed for ozonation in presence of γ - Al_2O_3 from 4.5 to 2.5 after 5 h. In both cases (with and without γ - Al_2O_3) the promotion of HO^\bullet radicals due to basic pH is not possible due to very low OH^- concentration at the pH of this study. As mentioned previously, O_3 can react by two routes in aqueous media: the direct O_3 ozonation (Schemes 1 and 2) and the radical type reaction. This later route implies the generation of HO^\bullet radicals during ozone self-decomposition. The radical reaction is more efficient for removing refractory compounds [3,8]. In order to evidence HO^\bullet generation in the ozonation with γ - Al_2O_3 a stable radical scavenger as tert-butanol (*t*-BuOH at 25 mg L^{-1}) was introduced in the 2,4-DMP solution. This amount of *t*-BuOH was previously demonstrated to be enough in heterogeneous catalytic ozonation to annihilate radical type reaction [40]. Single ozonation in presence of *t*-BuOH revealed a slight decrease in the TOC removal efficiency from 14 to 11% (Fig. 4) showing that single ozonation was principally governed by direct reaction of ozone with the organics present in the solution. For ozonation in the presence of γ - Al_2O_3 , adding *t*-BuOH induced a decrease of the TOC removal from 46 to 30%. This highlighted that γ - Al_2O_3 promotes the formation of HO^\bullet as no *t*-BuOH was adsorbed on the material (not shown). As reported in several studies [16,20,22,24], the aluminum oxides might enhance free radicals generation due to their surface hydroxyl groups, which can interact with O_3 . However, as TOC removal in presence of *t*-BuOH remained higher (30%) with γ - Al_2O_3 in comparison to single ozonation (11%), it can be reasonably assumed that adsorption of oxidized by-products occurred on γ - Al_2O_3 and contributed to decrease the TOC of the solution. If the direct ozone reaction is at the same level with γ - Al_2O_3 than for single ozonation therefore 11%, the contribution of adsorption in TOC removal for γ - Al_2O_3 could be 19% and the contribution of radical reaction 16%.

3.5. Identification of by-products obtained during 2,4-DMP ozonation

3.5.1. By-products identified by LC-MS during single ozonation

As oxidized phenolic compounds are known to have a possible toxic character, their identification can give information about the

toxicity level of the solution [32,33]. The identification of the first by-products from 2,4-DMP oxidation during single ozonation was attempted by LC-MS analysis. The non-exhaustive list of the products observed is presented in Table 2. Considering the products identified, several types of reactions were involved in the oxidation process: (i) Hydroxylation of the aromatic ring: hydroxylation of the aromatic ring, producing $\text{C}_8\text{H}_{10}\text{O}_2$ (product 1 in Scheme 2) is consistent with hydroxylation products usually observed during phenol ozonation [40,41]. This by-product was the most abundant (Fig. S5). It appeared since the beginning of the reaction, reached an optimum after 25 min ozonation and was totally degraded after 61 min of reaction (Table 2). (ii) Opening of the aromatic ring by direct addition of ozone (Criegee mechanism): the identification of $\text{C}_8\text{H}_{10}\text{O}_4$ (product 2 in Scheme 2) confirms that the direct addition of ozone on 2,4-DMP led to opening the aromatic ring and produced dimethyl muconic acid. Indeed, muconic acid is considered as one of the major transient products during ozonation of phenol [41,42]. This transient product was at its maximum in 20 min and was totally degraded after 91 min (Fig. S5; Table 2). (iii) Dimerization of 2,4-DMP: during the first minutes of ozonation the solution became turbid indicating the apparition of less soluble products. The compound $\text{C}_{10}\text{H}_{10}\text{O}_5$ (Table 2; Fig. S5) has a higher molar mass than 2,4-DMP, which could result from the reaction of oxalic acid with $\text{C}_8\text{H}_{10}\text{O}_2$ (product 1 in Scheme 2) and/or a degradation of a dimer. Dimerization of phenoxy radicals in acidic water was previously observed leading to non-soluble species [30,43]. Such a dimerization of dimethylphenols was also observed in oxidizing conditions in presence of ozone or copper [41,44,45]. Another compound $\text{C}_8\text{H}_8\text{O}$ observed by LC-MS is considered as a by-product of $\text{C}_{10}\text{H}_{10}\text{O}_5$ after several successive demethylations of the ring and decarboxylation of the aliphatic chain bonded with the first carbon of the aromatic ring. These two by-products were at their maximum at 15 min and were completely degraded after 91 min of ozonation (Fig. S5; Table 2).

3.5.2. By-products identified by LC-MS during ozonation in the presence of γ - Al_2O_3

During the degradation of the pollutant in presence of γ - Al_2O_3 , LC-MS analyzes revealed the same by-products than for the single ozonation and thus the same oxidation pathways. The maximum apparition and the complete removal of these by-products occurred at the same time than for single ozonation. All of these by-products have been degraded after 90 min (Table 2; Fig. S5). The main difference consists in the amount of these by-products, which is much abundant in presence of γ - Al_2O_3 (except for $\text{C}_{10}\text{H}_{10}\text{O}_5$, which was formed in similar amount) (Fig. S5).

3.5.3. Identification and quantification of carboxylic acids obtained during single ozonation

Ionic chromatography analysis allowed to identify and quantify the carboxylic acids formed during 2,4-DMP ozonation. Three carboxylic acids were mainly formed in the following increasing amount (Fig. 5a): acetic acid > formic acid \gg oxalic acid (products 3, 5, 4 in Scheme 2). Acetic acid was the most abundant reaching a plateau after 100 min, which corresponded to a final concentration of 62 mg L^{-1} . The formation of acetic acid is a consequence of an opening of the aromatic ring that could occur from the beginning of the ozonation reaction and of the oxidation of the by-products (Scheme 2). It must be noticed that acetic acid is a highly refractory molecule that is very stable against ozonation and will not be oxidized in formic acid or oxalic acid. The release of formic acid can correspond to a demethylation of 2,4-DMP from the beginning of the reaction and/or to the oxidation of other by-products after several breakages of the C–C bonds. The highest formic acid concentration (28 mg L^{-1}) was observed after 60 min of reaction and then decreased to reach a concentration

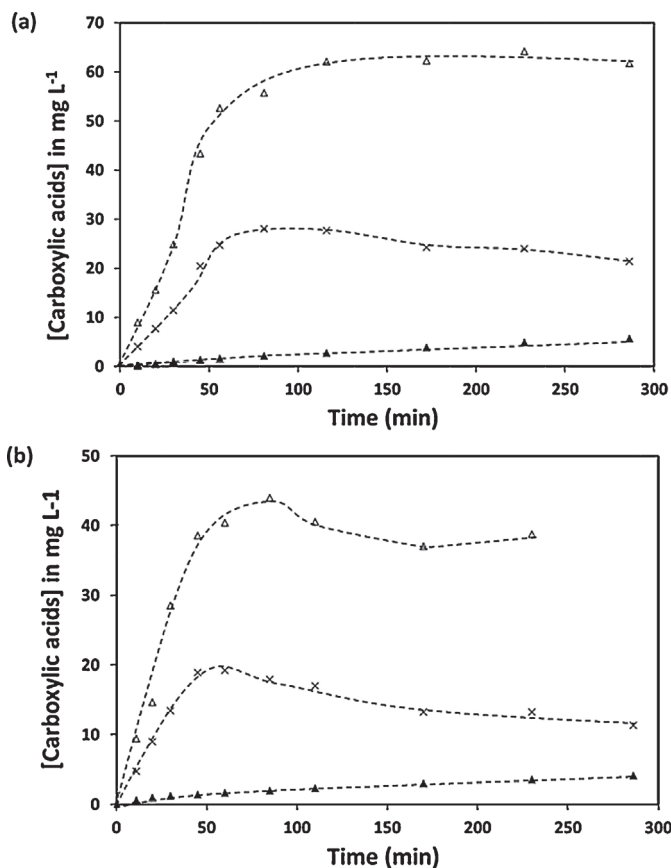


Fig. 5. Kinetic of acetic acid (Δ), formic acid (\times) and oxalic acid (\blacktriangle) formation during single ozonation (a) and during ozone/ γ - Al_2O_3 coupled treatment (b). Temperature: 25 °C; O_3 flow rate: 40 L h^{-1} ; $[\text{O}_3]_{\text{inlet}}$: 2 g Nm^{-3} ; $[\text{2,4-DMP}]_0$: 50 mg L^{-1} ; volume of solution: 1.5 L; γ - Al_2O_3 : 2 g L^{-1} .

of 21 mg L^{-1} after 5 h. This decrease is due to its oxidation into carbon dioxide (Scheme 2). Concerning oxalic acid, a slight and steady increase of its concentration was noticed to reach a value of 6 mg L^{-1} after 5 h ozonation. Oxalic acid can be released from an opening of the aromatic ring and/or from the oxidation of dimers. The study of mass balance of the process (Table 3) indicated that after 1 h of reaction 0.41 mmol of 2,4-DMP was transformed into 1 mmol CH_3COOH , 0.65 mmol HCOOH and 0.02 mmol HOOC-COOH , which corresponds to the transformation of 1 molecule of 2,4-DMP into 2.4 molecules of CH_3COOH , 1.6 molecules of HCOOH and 0.05 molecule of HOOC-COOH . This result is close to the expected simplified direct ozonation of 2,4-DMP into acetic acid and formic acid

Table 3
Mass balance after 1 and 5 h of single ozonation and ozonation with γ - Al_2O_3 of 2,4-DMP.

Ozonation time	O_3		$\text{O}_3 + \gamma\text{-Al}_2\text{O}_3$	
	1 h	5 h	1 h	5 h
CH_3COOH (mmol L^{-1})	1	1	0.71	0.60
HCOOH (mmol L^{-1})	0.65	0.45	0.43	0.24
HOOC-COOH (mmol L^{-1})	0.02	0.05	0.02	0.04
Other by-products (mmol CL^{-1})	0.43	0.27	0.73	0.25
Total by-products (mmol CL^{-1})	3.12	2.82	2.62	1.77
Produced CO_2 (mmol CL^{-1})	0.16	0.46		
Produced CO_2 + adsorbated by-products (mmol CL^{-1})			0.66	1.51

Initial concentration 2,4-DMP: 50 mg L^{-1} (0.41 mmol L^{-1} ; 3.28 mmol CL^{-1}).

(Scheme 2). The higher amount of acetic acid and the lower amount of formic acid were presumably due to the route implying dimerization of 2,4-DMP. The very low amount of oxalic acid could result from its reaction with the bihydroxylated by-product (product 1 in Scheme 2) as soon as it was produced. Taking into account TOC measurement and the initial amount of 2,4-DMP (3.28 mmol CL^{-1}) it was possible to determine the amount of organics remaining in the solution and the level of mineralization (Table 3). After 5 h of single ozonation 2.82 mmol CL^{-1} remained in the solution composed at 90% of carboxylic acid and 10% of unknown by-products.

3.5.4. Identification and quantification of carboxylic acids obtained during ozonation with γ - Al_2O_3

During ozonation with γ - Al_2O_3 the same carboxylic acids as for single ozonation were identified and quantified: 1 molecule of 2,4-DMP was converted into 1.7 molecules CH_3COOH , 1.0 molecule HCOOH and 0.05 molecule HOOC-COOH . Lower amounts of carboxylic acids were obtained for ozonation with γ - Al_2O_3 except for oxalic acid, which followed the same trend as for single ozonation (Fig. 5b). By allowing the generation of HO^\bullet radicals γ - Al_2O_3 favors a different oxidation mechanism leading to less acetic acid and less formic acid. It could also be hypothesized that a non-reactive phenomenon occurred such as the adsorption of the carboxylic acids on the solid. Indeed the maximum concentration of acetic acid was reached after 75 min and then decreased, which cannot be due to the oxidation of acetic acid. Adsorption of carboxylic acids was thus investigated in the following paragraph. Concerning mass balance calculated from TOC and from the amount of carboxylic acids (Table 3) it was demonstrated that ozonation in presence of γ - Al_2O_3 generated after 1 h ozonation more by-products (other than carboxylic acids) due to the different mechanism pathway using HO^\bullet radicals with 0.73 $\text{mmol C}_{\text{by-product}} \text{L}^{-1}$ after 1 h for ozonation with γ - Al_2O_3 , whereas single ozonation produced only 0.43 $\text{mmol C}_{\text{by-product}} \text{L}^{-1}$. After 5 h ozonation the amount of by-products (other than carboxylic acids) decreased and reached a similar value of $\sim 0.26 \text{ mmol C}_{\text{by-product}} \text{L}^{-1}$ for both ozonation processes. However, the remaining by-products (other than carboxylic acids) resulting from 5 h ozonation with γ - Al_2O_3 are different from those obtained by single ozonation as they featured a higher level of oxidation state as previously demonstrated from AOSC measurements. Carboxylic acids represent 86% of the carbon remaining in the solution after 5 h ozonation. Ozonation with γ - Al_2O_3 allowed after 5 h to decrease the amount of organics in water from 3.28 to 1.77 mmol CL^{-1} , whereas single ozonation reached only 2.82 mmol CL^{-1} .

3.6. Adsorption of carboxylic acids on γ - Al_2O_3

3.6.1. Adsorption isotherms of carboxylic acids on γ - Al_2O_3

During 2,4-DMP oxidation, three carboxylic acids (acetic acid, formic acid and oxalic acid) have been identified and γ - Al_2O_3 adsorption properties towards these acids have been studied. The adsorption isotherms of the three carboxylic acids were carried out varying the acids concentrations from 5 to 400 mg L^{-1} (Fig. 6). The adsorption capacity of γ - Al_2O_3 became significant for equilibrium acid concentration higher than 25 mg L^{-1} . For the highest acid concentration (400 mg L^{-1}) an adsorption 20, 23, 35 mg g^{-1} (or 0.33, 0.50 and 0.38 mmol g^{-1}) was obtained for acetic acid, formic acid and oxalic acid, respectively. During ozonation with γ - Al_2O_3 the maximum acid equilibrium concentrations were found after 1 h and corresponded to 43, 20 and 2 mg L^{-1} , for acetic acid, formic acid and oxalic acid, respectively. Considering the adsorption isotherms, an adsorption capacity on γ - Al_2O_3 of 3.4, 3.7 and 0.9 mg g^{-1} (or 0.06, 0.08 and 0.01 mmol g^{-1}) for acetic acid, formic acid and oxalic acid, respectively, could be expected, which will contribute as 0.43 mmol CL^{-1} in TOC removal. Adsorption of

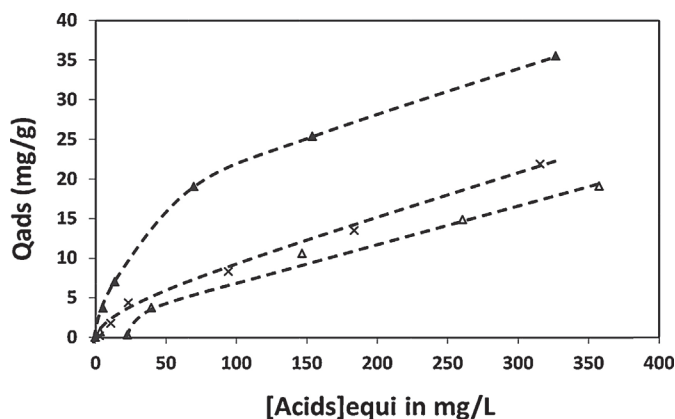


Fig. 6. Adsorption isotherms of acetic acid (Δ), formic acid (\times) and oxalic acid (\blacktriangle) onto γ - Al_2O_3 at 25 °C. $[\text{Acids}]_0$: from 5 to 400 mg L^{-1} .

carboxylic will give a participation of 13% in the 46% TOC removal with γ - Al_2O_3 , which is below to what was predicted (19%) considering 11% of direct ozonation reaction (as for single ozonation) and 16% of radical reaction. Three possibilities could be considered: (1) other by-products could be adsorbed as dimethyl muconic acid, (2) the contribution of direct ozonation is higher (17%) in presence of alumina due to ozone adsorption at the surface of the particles and (3) the amount of adsorbed carboxylic acids is higher in presence of ozone. Indeed during adsorption experiments of carboxylic acids on γ - Al_2O_3 the pH of the solution increased from 4.5 to 7.6. In this range of pH carboxylic acids are under carboxylates form (CH_3COO^- , HCOO^- , $-\text{OOC}-\text{COO}^-$) as pH is higher than the pK_A of the acids ($\text{pK}_\text{A}-\text{CH}_3\text{COOH} = 4.76$, $\text{pK}_\text{A}-\text{HCOOH} = 3.74$, $\text{pK}_\text{A}-\text{HOOC}-\text{COOH} = 1.25$ and 4.27). The adsorption of the carboxylates (RCOO^-) on γ - Al_2O_3 occurs via a ligand exchange with $\text{Al}-\text{OH}$ groups forming $\text{Al}-\text{O}(\text{CO})\text{R}$ groups and liberates OH^- responsible for the increase of pH. In ozonation with γ - Al_2O_3 the mechanism of adsorption is different as in contrary a decrease of pH from 4.5 to 2.5 was observed. At these pH carboxylic acids are under their protonated forms: CH_3COOH , HCOOH , $\text{HOOC}-\text{COO}^-$, which could encountered for a different mechanism of adsorption and maybe a higher adsorption. Therefore, it is difficult from adsorption experiments to accurately estimate the amount of carboxylic acids adsorbed on γ - Al_2O_3 during ozonation.

3.6.2. Identification of carboxylic acids adsorbed on γ - Al_2O_3 after ozonation by ^{13}C CP MAS NMR

In order to confirm the adsorption of carboxylic acids on γ - Al_2O_3 in presence of ozone, solid state ^{13}C CP MAS NMR was performed on the materials after ozonation. ^{13}C NMR spectrum (Fig. S6) exhibited three major peaks with chemical shifts at 178, 164 and 21 ppm, confirming the adsorption of acetic acid, formic acid and/or oxalic acid at the surface of γ - Al_2O_3 [46,47]. It is difficult to assign the peak at 164 ppm to either formic acid or oxalic acid. Indeed in liquid ^{13}C NMR, formic acid is identified by a peak (COO) at 165.8 ppm and oxalic acid by a peak (COO) at 160.9 ppm. For acetic acid the two peaks at 178.1 (COO) and 22 (CH_3) ppm were clearly identified. Additional peaks of lower intensity of unidentified products are present on the spectrum at 142, 131, 81, 42 and 29 ppm. The peaks at 142, 131 and 29 could come from the adsorption of some dimethyl muconic acid, as muconic acid in solution presents three peaks at 166, 140 and 129 ppm and the peak at 29 ppm could come from the contribution of methyl groups. The peak at 42 ppm could come from the adsorption of methyl malonic acid (Product 7 in Scheme 2), as malonic acid in solution presents two peaks at 178 and 49 ppm. However, it is very difficult to quantify each of these adsorbed products due to their very low amount on the material

giving peaks just higher than the background noise on the spectrum.

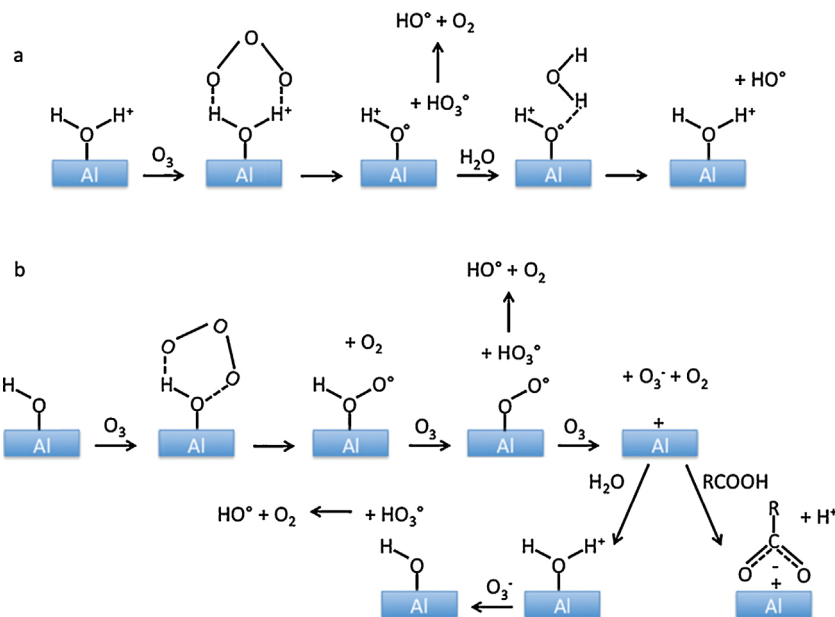
3.6.3. Identification of carboxylates adsorbed on γ - Al_2O_3 after ozonation by FTIR

The adsorption of the carboxylic acids on γ - Al_2O_3 in presence of ozone was also confirmed by FTIR (Fig. S7). In comparison to FTIR spectrum of γ - Al_2O_3 before ozonation several additional vibrational bands of low intensity were found on the FTIR spectrum of γ - Al_2O_3 after ozonation after outgassing the sample at 150 °C to remove the adsorbed water (large bending vibration of water at 1639 cm^{-1}): at 1254, 1312, 1375, 1392, 1460, 1505, 1550, 1572, 1589, 1615 cm^{-1} . For each carboxylic acids four bands are expected: the symmetric and antisymmetric modes of $\text{C}=\text{O}$ stretching are in the ranges 1625–1687 and $1660\text{--}1740\text{ cm}^{-1}$, respectively, the $\text{C}-\text{O}-\text{H}$ in-plane bending at $1395\text{--}1440\text{ cm}^{-1}$ and the $\text{C}-\text{O}$ stretch at $1315\text{--}1280\text{ cm}^{-1}$. However, no bands above 1625 cm^{-1} have been observed in the spectrum of γ - Al_2O_3 after ozonation revealing that carboxylic acids are under their carboxylates form. Indeed, for carboxylate salts only two vibrations for each salts are expected as $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bonds of the acid are replaced by two equivalent $\text{C}-\text{O}$ “bond-and-a-half” bonds. These CO_2^- bonds interact out-of-phase and in-phase to give two bands. The antisymmetric CO_2^- stretch band is usually seen at $1540\text{--}1650\text{ cm}^{-1}$ and the symmetric CO_2^- stretch band is usually seen at $1360\text{--}1450\text{ cm}^{-1}$. Acetate salts bands are usually observed at $1400\text{--}1450$ and $1550\text{--}1600\text{ cm}^{-1}$, formate at 1360 and 1600 cm^{-1} and oxalate at 1320 and 1620 cm^{-1} . Considering the vibrational bands observed in the spectrum of γ - Al_2O_3 after ozonation, the bands relative to carboxylates adsorbed on γ - Al_2O_3 surface could therefore be assigned as follows: for acetate bands at 1460 and 1550 cm^{-1} ; for formate bands at 1375 and 1589 cm^{-1} ; for oxalate bands at 1312 and 1615 cm^{-1} . The remaining bands correspond to unidentified adsorbed products (1254 , 1392 , 1505 , 1572 cm^{-1}), which could result from the adsorption of other carboxylate by-products as dimethyl muconic acid, as assumed by ^{13}C NMR. Quantification of these products by FTIR was not possible as in too low amounts.

3.7. Basic and acid sites of γ - Al_2O_3 before and after ozonation by FTIR

γ - Al_2O_3 is an amphoteric solid with Lewis acid $\text{AlOH}(\text{H}^+)$ sites and basic $\text{Al}-\text{OH}$ sites (Scheme 3). The acidic properties of γ - Al_2O_3 before and after ozonation have been determined by FTIR after pyridine adsorption on dried materials (Fig. S8). FTIR/pyridine spectrum of γ - Al_2O_3 before ozonation featured no band at 1547 cm^{-1} characteristic of Brønsted acid site, and after ozonation a very weak band appeared, which disappeared at 100 °C under vacuum, featuring very low amount of weak Brønsted sites. This could come from free COOH group on the surface of γ - Al_2O_3 after ozonation as in the case of oxalic acid adsorption. The band at 1596 cm^{-1} is relative to H-bonding between OH surface groups and pyridine. This band disappeared after outgassing at 100 °C . Three similar intense bands at 1455 , 1496 and 1625 cm^{-1} were observed in FTIR/pyridine spectra of γ - Al_2O_3 before and after ozonation, which remained after outgassing at 500 °C . These bands are characteristic of strong Lewis acid sites. The Lewis acid sites of γ - Al_2O_3 were not modified during ozonation. If the Lewis acid sites of γ - Al_2O_3 participate to the ozonation process they are entirely regenerated during ozonation as already proposed in literature [8]. An example of simplified possible mechanism is given in Scheme 3. Furthermore, the acid sites of γ - Al_2O_3 are not affected by the adsorption of carboxylic acids, they are not the adsorption sites.

The basic properties of γ - Al_2O_3 before and after ozonation have been determined by FTIR after CO_2 adsorption on dried materials (Fig. S9). For both materials, CO_2 adsorption has revealed the



Scheme 3. Expected interaction of O_3 with (a) acid and (b) basic sites of $\gamma\text{-Al}_2\text{O}_3$ (scheme adapted and modified from Ref. [8]). (b) Hypothesis for adsorption mechanism of carboxylic acids with the basic sites of $\gamma\text{-Al}_2\text{O}_3$ during ozonation.

presence of Al^{3+} extra-framework species evidenced by a fine band at 2365 cm^{-1} of CO_2 is linearly coordinated to these Al species. FTIR spectra of CO_2 adsorbed on $\gamma\text{-Al}_2\text{O}_3$ before and after ozonation showed also similar four major peaks at 1231, 1482, 1644 and 1774 cm^{-1} characteristic of the formation of carbonates at the surface of the material due to the chemisorption of CO_2 on the Al-OH basic sites. Lower amount of carbonates were observed on $\gamma\text{-Al}_2\text{O}_3$ after ozonation. Furthermore, chemisorbed carbonates were desorbed at 250°C for $\gamma\text{-Al}_2\text{O}_3$ before ozonation featuring a medium force of the basic sites and at lower temperature (200°C) on $\gamma\text{-Al}_2\text{O}_3$ after ozonation revealing a slightly lower force of the basic sites. Ozonation implied a decrease of the basicity of Al-OH species in number and in force due most probably to carboxylates adsorption on the basic sites. An example of simplified possible mechanisms is given in Scheme 3 to explain the competition between Al-OH as active site for catalytic ozonation and Al-OH as adsorption sites for carboxylates. This hypothesis allows to explain the additional decrease of pH during ozonation with $\gamma\text{-Al}_2\text{O}_3$ due to the chemisorption of RCOOH on an intermediate site Al(+) (formed during ozonation), which liberates a proton to give an electrostatic interaction $\text{RCOO}^- - \text{Al}(+)$ and contributes to decrease the pH (Scheme 3). The amount of Al-OH species could not be calculated at 25°C due to the presence of water hiding FTIR bands of the OH region ($3000\text{--}4000\text{ cm}^{-1}$). After outgassing the samples at 500°C , which implies water removal but also carboxylates removal, similar FTIR spectra of Al-OH bands at 3793, 3774, 3730, 3689, 3675 cm^{-1} were observed for $\gamma\text{-Al}_2\text{O}_3$ before and after ozonation with an amount of OH groups $\sim 1.1\text{ mmol OH g}^{-1}$ (Fig. S10). Basic Al-OH sites are affected by carboxylates adsorption and their number decreased during ozonation, however the recovery of all Al-OH groups after outgassing suggests a possible regeneration of $\gamma\text{-Al}_2\text{O}_3$ by calcination at 500°C .

3.8. Reuse and regeneration of $\gamma\text{-Al}_2\text{O}_3$

3.8.1. Reuse of $\gamma\text{-Al}_2\text{O}_3$ in successive ozonation reactions

To establish the durability of $\gamma\text{-Al}_2\text{O}_3$ during ozonation, the material has been reused in 10 successive runs with a higher amount of solid (5 g L^{-1}) and a higher amount of entering O_3 (5 g Nm^{-3} produced from O_2). This slightly harder condition of

ozonation allowed for the first run to reach a higher level of TOC removal with 71% after 8 h with $\gamma\text{-Al}_2\text{O}_3$, whereas for single ozonation TOC removal was only 30% (Fig. 7). Then a series of 10 ozonation runs was performed using the same $\gamma\text{-Al}_2\text{O}_3$ sample, in order to assess the stability of the material (Fig. 7). Each run lasted about 8 h and $\gamma\text{-Al}_2\text{O}_3$ was reused without any regeneration or specific treatment. Millimetric $\gamma\text{-Al}_2\text{O}_3$ particles were put in a perforated basket easy to immerse in the solution and easy to remove and to place in another batch of effluent. TOC removal clearly progressively decreased during the successive runs with $\gamma\text{-Al}_2\text{O}_3$. After 7–10 runs with $\gamma\text{-Al}_2\text{O}_3$ TOC removal was quite reproducible with 40% TOC removal, which remained higher than single ozonation (30% TOC removal). The decrease of TOC removal with $\gamma\text{-Al}_2\text{O}_3$ is due to the decrease of the amount of basic Al-OH sites by irreversible chemisorption of carboxylates (Scheme 3). If for each run 0.15 mmol of carboxylates per gram of $\gamma\text{-Al}_2\text{O}_3$ are chemisorbed on Al-OH (as found in Section 3.6.1), seven runs will be enough to eliminate all Al-OH groups of $\gamma\text{-Al}_2\text{O}_3$ ($1.1\text{ mmol OH g}^{-1}$), which is consistent with the result obtained in this reuse study.

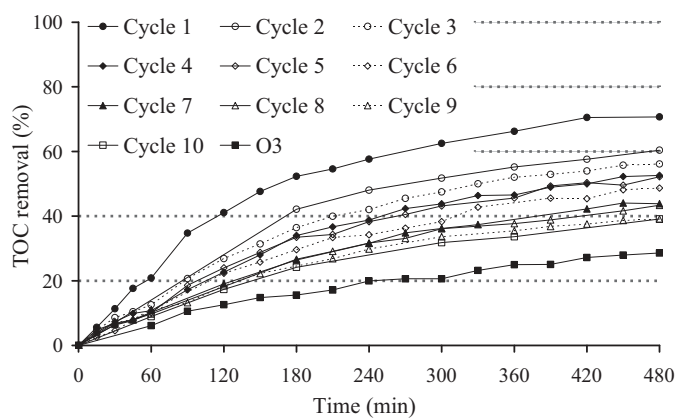


Fig. 7. TOC removal during single ozonation (■) and during a series of 10 successive ozone/ $\gamma\text{-Al}_2\text{O}_3$ coupled treatment runs using the same solid without regeneration. First run (●), fifth run (◇) and tenth run (○). Temperature: 25°C ; O_3 flow rate: 30 L h^{-1} ; $[\text{O}_3]_{\text{inlet}}$: 5 g Nm^{-3} ; $[\text{2,4-DMP}]_0$: 50 mg L^{-1} ; volume of solution: 2 L ; $\gamma\text{-Al}_2\text{O}_3$: 5 g L^{-1} .

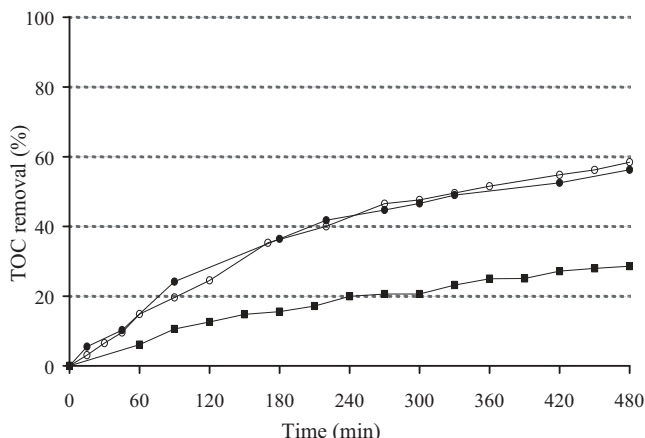


Fig. 8. TOC removal during single ozonation (■) and during ozone/ γ -Al₂O₃ coupled treatment using a fresh sample of alumina (●) and a thermally regenerated sample of alumina (○). Temperature: 25 °C; O₃ flow rate: 30 L h⁻¹; [O₃]_{inlet}: 5 g Nm⁻³; [2,4-DMP]₀: 50 mg L⁻¹; volume of solution: 2 L; γ -Al₂O₃: 1.85 g L⁻¹.

The remaining stable activity of γ -Al₂O₃ after 7–10 runs, which is 10% higher than single ozonation is due either to reversible catalytic activity of Lewis sites of γ -Al₂O₃ or to a higher efficiency of direct O₃ reaction at the solid surface. As for the previous study 16% TOC removal were assigned to radical reaction (Section 3.4), radicals are produced either by acid sites or acidic sites (Scheme 3), it seems that basic sites are also involved in the catalytic activity of γ -Al₂O₃. Basic sites of γ -Al₂O₃ act in TOC removal as carboxylic acids adsorbents and also as basic catalytic sites, which are lost at each carboxylate adsorption.

3.8.2. Regeneration of γ -Al₂O₃ after ozonation

After 10 runs of ozonation (80 h ozonation), γ -Al₂O₃ was removed from the solution, dried at 120 °C during 20 min and calcined at 500 °C during 6 h. A part of the resulting material (1.85 g L⁻¹) was then used in a new ozonation experiment and its performance was compared to the same amount of a fresh γ -Al₂O₃ sample. The thermally regenerated γ -Al₂O₃ showed a similar efficiency of the new γ -Al₂O₃ with 60% TOC removal after 8 h (Fig. 8). As observed earlier by FTIR (Section 3.7), a calcination at 500 °C allowed to remove adsorbed carboxylates and to recover all basic Al-OH groups of γ -Al₂O₃. Therefore, a calcination at 500 °C allows to regenerate and reuse this catalyst without any loss of performances.

3.9. Ozonation of a synthetic petroleum effluent

3.9.1. Ozonation of a synthetic petroleum effluent without any additive

A synthetic petrochemical effluent containing various petrochemicals was treated with γ -Al₂O₃. This experiment was performed in a third pilot plant scale reactor described elsewhere [28]. The complex synthetic effluent was a mixture of several aromatic hydrocarbons and associated acids: phenol, acetic acid, naphthenic acid, pyrene, naphthalene with initial concentration of 200, 200, 25, 0.05, 0.95 mg L⁻¹, respectively, corresponding to TOC = 230 mg L⁻¹. With γ -Al₂O₃ TOC removal was much faster than for single ozonation during the first 50 min and then stopped and remained at 50% equivalent to single ozonation (Fig. 9). In the synthetic effluent a large amount (200 mg L⁻¹) of acetic acid was added, which blocked Al-OH basic sites of γ -Al₂O₃ from the beginning of the process. Considering the adsorption isotherm (Fig. 6) a concentration of acetic acid of 200 mg L⁻¹ will correspond to 12 mg g⁻¹ (0.20 mmol g⁻¹) of acetate adsorbed on the

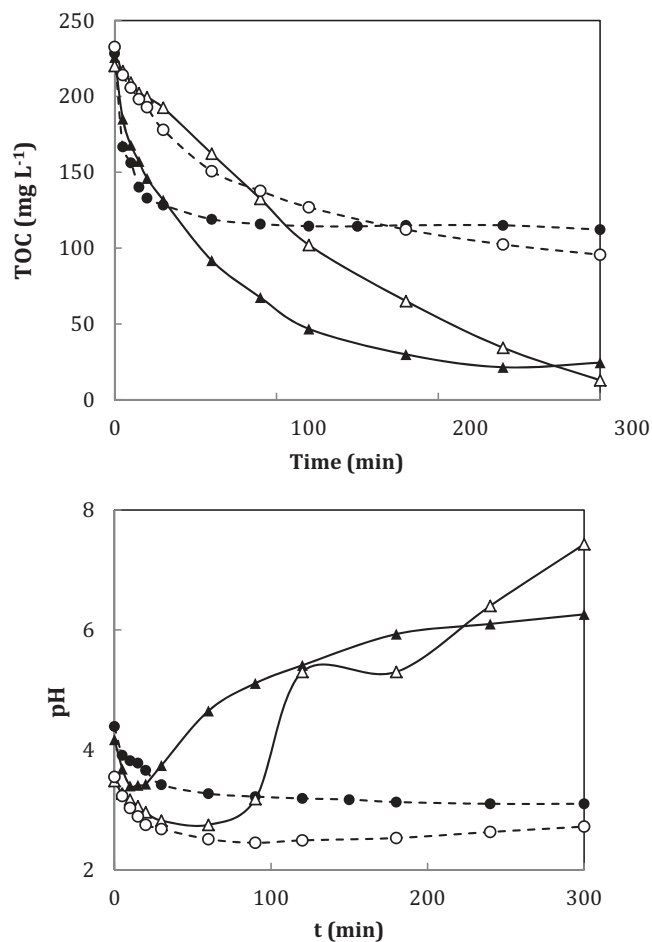


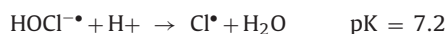
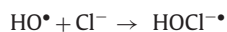
Fig. 9. TOC and pH evolution during single ozonation (open symbols) and during ozonation with γ -Al₂O₃ (plain symbols) without (circles) and with (triangles) NaCl 50 g L⁻¹ of a synthetic petrochemical effluent containing various petrochemicals: 200 mg L⁻¹ phenol, 200 mg L⁻¹ acetic acid, 25 mg L⁻¹ naphthenic acid, 0.05 mg L⁻¹ pyrene, 0.95 mg L⁻¹ naphthalene. Temperature: 35 °C; O₃ flow rate: 24 L h⁻¹; [O₃]_{inlet}: 5 g Nm⁻³; [TOC]₀: 250 mg L⁻¹; volume of solution: 1.5 L; γ -Al₂O₃: 2 g L⁻¹.

solid. A large amount of phenol (200 mg L⁻¹, 2.1 mmol L⁻¹) was also added and if we consider a similar mechanism as for 2,4-DMP (Section 3.5.4) 1 mol of phenol will produce 1.7 mol acetic acid, 1 mol formic acid and 0.05 mol oxalic acid. This will correspond to a production of 216 mg L⁻¹ of acetic acid, 100 mg L⁻¹ formic acid and 9 mg L⁻¹ oxalic acid and therefore an adsorption capacity (calculated from the adsorption isotherms in Fig. 6) on γ -Al₂O₃ of 13 mg g⁻¹ (0.22 mmol g⁻¹), 10 mg g⁻¹ (0.21 mmol g⁻¹), 6 mg g⁻¹ (0.07 mmol g⁻¹) for each acid, respectively. The total of expected carboxylates adsorbed on the solid will be therefore at least 0.7 mmol g⁻¹, which means that for only two molecules (acetic acid and phenol) already ~65% of Al-OH basic sites will be rapidly blocked. The stopover of the reaction after 50 min with γ -Al₂O₃ is therefore due to the total obstruction of Al-OH basic sites by adsorbed carboxylates. For single ozonation a slightly higher TOC removal is obtained after 300 min (58% TOC removal). The fact that γ -Al₂O₃ presents no better activity than single ozonation when all of the basic sites are blocked let suppose that the Lewis acid sites of γ -Al₂O₃ do not participate to the ozonation process. We have previously observed that Lewis acid sites were not affected during ozonation (Section 3.7). We therefore proposed that the catalytic activity of oxides in water ozonation is due principally to the basic sites (M-OH) of the materials (Scheme 3). The Lewis acid sites previously demonstrated as responsible for catalytic ozonation in

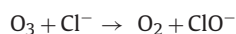
gaseous phase [48,49] cannot participate to the reaction in water, as these sites are surely blocked by water molecules that O₃ cannot displace.

3.9.2. Ozonation of a synthetic petroleum effluent in presence of NaCl and toxicity tests

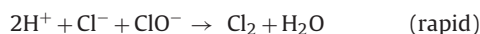
The effect of NaCl in ozonation processes is very important as some wastewater contains some salts as NaCl, which can be present in high concentration level in tannery and dye manufacturing wastewater, for instance, and also in lower amount in produced water from off-shore oil extraction. An excess of NaCl (50 g L⁻¹) was added to the ozonation process whereas in seawater NaCl concentration is around 10 g L⁻¹. Adding NaCl to the solution containing various chemicals (phenol, acetic acid, naphthenic acid, pyrene, naphthalene) led to an increase in TOC removal for both processes single ozonation and ozonation with γ-Al₂O₃ (Fig. 9). The inverse phenomenon was observed previously in ozonation of 2,4-DMP with basic Na-LTA zeolites with the same amount of NaCl [18]. It was observed that Cl⁻ ions were scavenging HO• radicals similarly as *t*-BuOH for a pH solution varying from pH 5 to 7 and no effect (or a slight negative effect) was observed for the single ozonation [18]. It was showed in literature that the efficiency of chloride ions as HO• scavenger increases by a factor of 100 then pH decreases from 6 to 3 and then the concentration of NaCl increases from 1.5 to 73 g L⁻¹ [50]. For low salinity water (<1.5 g L⁻¹) and at pH 5 no effect of chloride ions was observed. For concentration of NaCl > 75, 50 and 10 g L⁻¹ 75, 70 and 25% of HO• were removed, respectively. As in the present study the salinity of the solution is high (50 g L⁻¹) and the pH of the solution is acidic (4 > pH > 3) chloride ions should present a very strong scavenging effect on HO• radicals produced during ozonation with γ-Al₂O₃. The equations corresponding to the reaction of chloride ions with HO• are the following [50]:



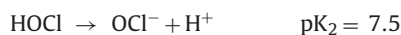
The first reaction is fast and the second reaction is five times more rapid than the first one. At pH < 7.2 Cl• is the dominant species. Although HO• should be seriously scavenged by Cl⁻ a remarkable positive effect of NaCl was noticed with TOC removal reaching 90% against 50% without NaCl. This high level of TOC removal indicates that acetic acid has been mineralized during the ozonation process with NaCl. NaCl avoid carboxylates to block the basic sites of γ-Al₂O₃ with presumably sodium cations interacting with carboxylic acids to give the corresponding salts. Considering single ozonation the only difference with our previous study about ozonation in presence of zeolites and NaCl [18] is the solution composition and mainly the presence of polycyclic aromatic hydrocarbons (PAH). Ozone in presence of chloride anions in acidic aqueous medium reacts following the proposed equations [51,52]:



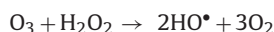
(ratedeterminingreaction, veryslowreaction)



Cl₂ has been observed as the main and only product resulting from O₃ decomposition in presence of NaCl [52] although Cl₂ in water is in equilibrium with other products [53]:



For pH < 3.3 Cl₂ will be the main species, for 3.3 < pH < 7.5 HOCl and for pH > 7.5 OCl⁻ [53]. At low initial pH (pH < 2.5) chlorine species are able to degrade efficiently some carboxylic acids (oxalic ≫ citric > maleic acids) leading to a pH increase from 2.5 to 9 [53]. However, acetic acid is barely decomposed except if a new source of HO• radical is produced as for instance by UV irradiation [53]. However, under UV, generally an intermediate product as H₂O₂ is produced as for O₃/UV [50]:



As in our study HO• are most probably highly scavenged by Cl⁻, therefore we propose that H₂O₂ could be also produced as an intermediary product during ozonation of PAH in presence of NaCl to explain the higher oxidation level of single ozonation and the mineralization of acetic acid. Indeed H₂O₂ could react with acetic acid to give peracetic acid, which is a powerful oxidant. We suggest that PAH compounds react with Cl• or Cl₂ to produce H₂O₂ and HO•. Indeed PAHs are known to decompose in water by chlorine [55] and give the corresponding quinones [56]. Industrially H₂O₂ is produced from the oxidation of dihydroxyanthracene by O₂ giving anthraquinone and H₂O₂. For ozonation in presence of NaCl and PAH we suggest the formation of an intermediate dihydroxypolyaromatic compounds giving corresponding quinone and H₂O₂. It has been demonstrated that pyrene with chlorine decomposes into pyrene-4,5-dione and 1-chloropyrene by both oxidation and chlorine-substitution reactions, respectively [57]. Authors evidenced that pyrene decomposition was associated with the formation of other reactive species than chlorine and they suggest the formation of HO• radicals. These reactive species produced during pyrene decomposition in chlorination have not been identified but are reacting with ethanol. As we previously showed that acetic acid could not decomposed by HO• radicals, we suggest that one of these reactive species could be H₂O₂. The increase of TOC removal in the presence of NaCl was accompanied by the increase of the pH of the solution (Fig. 9) from 3.5 to 6 with γ-Al₂O₃ after 25 min revealing the degradation of the sodium carboxylates liberating CO₂ and HO⁻. For single ozonation, the pH of the solution increased from 3 to 7 after 100 min due to the degradation of the carboxylic acids. The faster efficiency observed with γ-Al₂O₃ is most probably due to the faster formation of Cl• from HO• in comparison to the slow formation of Cl₂ from O₃. After 5 h the two processes have equivalent TOC removal (90%).

It was previously demonstrated in literature that the toxicity of a solution containing pollutants increased when single ozonation was performed in presence of NaCl [54]. Toxicity tests were therefore performed for ozonation with γ-Al₂O₃ in presence of NaCl using two non-standardized toxkits named ARTOXKIT and ROTOXKIT exploiting two different seawater organisms *Artemia franciscana* and *Brachionus calyciflorus*, respectively. The toxicity tests were performed after pH adjustment at pH 7 of the synthetic effluent treated after 150 and 300 min of ozonation with γ-Al₂O₃. The efficiency of the process was assessed by the effluent concentration able to induce 50% of mortality of the species after 24 h of exposure to the aqueous solution (LC₅₀ 24 h). The results were expressed in toxic unit: Equitox m⁻³ = 100/LC₅₀ 24 h (Table 4). After 150 min of ozonation with γ-Al₂O₃ the toxicity level of the solution increased revealing that the first by-products produced during ozonation are more toxic than the initial pollutants. After 300 min of ozonation with γ-Al₂O₃ the toxicity level of the solution decreased. The synthetic effluent, which was initially considered as slightly toxic, became non-toxic for at least one seawater organism.

Table 4

Percentage of TOC removal and toxicity index of the synthetic petrochemical effluent (phenol, acetic acid, naphthenic acid, pyrene, naphthalene) after ozonation with γ -Al₂O₃ after 150 and 300 min treatment.

	TOC removal (%)	ARTOXKIT (toxic unit ^a)	ROTOXKIT (toxic unit ^a)	Toxicity
Initial solution	0	5.2	5.9	Slightly toxic
O ₃ / γ -Al ₂ O ₃ (150 min)	82	10.1	8.4	Slightly toxic
O ₃ / γ -Al ₂ O ₃ (300 min)	89	2.6	5.0	Non-toxic and slightly toxic

^a Toxic unit: non-toxic < 3; 3 < slightly toxic < 10; 10 < toxic < 50; 50 < very toxic < 100; extremely toxic > 100. Temperature: 35 °C; O₃ flow rate: 24 L h⁻¹; [O₃]_{inlet}: 5 g Nm⁻³; TOC_{initial} = 230 mg L⁻¹; volume of solution: 1.5 L; γ -Al₂O₃: 2 g L⁻¹; NaCl: 50 g L⁻¹.

Catalytic ozonation in presence of NaCl with γ -Al₂O₃ allowed to decrease the toxicity of the petrochemical effluent.

4. Conclusion

The effect of γ -Al₂O₃ during ozonation for 2,4-DMP removal was investigated through different experiments. It appeared clearly that the material allowed increasing the oxidation efficiency of the initial pollutant in comparison to single ozonation. The beneficial effect of γ -Al₂O₃ was linked to two phenomena: its adsorption capacity for carboxylic acids by-products (acetic acid, formic acid and oxalic acid) and its ability to generate •OH radicals. The identification of different by-products during 2,4-DMP ozonation confirmed that both mechanisms of direct O₃ reaction and radical type reaction coexisted during ozonation with γ -Al₂O₃, in contrary to single ozonation, which is mainly governed by direct O₃ reaction. Radical type reaction for ozonation with γ -Al₂O₃ produced initially more by-products (other than acetic, formic and oxalic acids) than single ozonation leading at the end to less carboxylic acids formation. After 5 h ozonation similar amount of by-products (other than carboxylic acids) were found for both processes, but final by-products were more oxidized with γ -Al₂O₃ than those resulting of single ozonation. Cumulative adsorption of carboxylic acids on the basic Al-OH sites of γ -Al₂O₃ resulted in a progressive decrease of the TOC removal during successive runs of ozonation until all Al-OH groups were blocked by carboxylates. Lewis acid sites of γ -Al₂O₃ were not affected during ozonation. A complete regeneration of Al-OH basic sites was obtained by thermal treatment at 500 °C without altering the properties of the solid. Finally, γ -Al₂O₃ was used to treat a synthetic petrochemical effluent containing different pollutants (phenol, naphthenic acid, pyrene, naphthalene) and a large amount of acetic acid. TOC removal with γ -Al₂O₃ was very fast in the first hour of ozonation, much faster than single ozonation, and then stopped due to the inhibition of all Al-OH groups by carboxylates. A similar activity as single ozonation was then obtained with 50% TOC removal. This result allows us to propose that only Al-OH basic sites are involved in catalytic ozonation in water. By adding NaCl to the ozonation processes remarkable higher TOC removals were reached for single ozonation and for ozonation with γ -Al₂O₃ with 90% TOC after 5 h. Two antagonism mechanisms occur with γ -Al₂O₃: sodium cations prevent the adsorption of carboxylates on the basic sites of γ -Al₂O₃ by forming preferentially sodium carboxylates in solution, while chloride ions are strong •OH scavengers especially in the conditions of the study (low pH and high NaCl concentration). The higher TOC removal is concomitant with the increase of pH due presumably to the degradation of carboxylates liberating hydroxyl ions. The reaction is faster with γ -Al₂O₃ in comparison to single ozonation due to different mechanism pathways between chloride ions with •OH and with O₃, respectively. The enhancement of the mineralization of the solution is also conjointly most probably induced by the formation of H₂O₂ resulting from oxidation reactions between polycyclic aromatic hydrocarbon (PAH) and •Cl or Cl₂ for ozonation with γ -Al₂O₃ and for single ozonation, respectively. Ozonation with γ -Al₂O₃ in presence of large amount of NaCl led to a first increase of the toxicity of the effluent (after

1.5 h) and then to a decrease of the toxicity below the initial toxicity (after 5 h). γ -Al₂O₃ is therefore a good candidate for catalytic ozonation of refinery wastewater containing refractory PAH and should be better performing in lower salinity water as seawater. The large controversy observed in ozonation in water is because ozonation depends of a lot of parameters as pH, presence of salts, nature of the catalysts, but also is effluent composition dependent.

Acknowledgments

The authors acknowledge the French National Agency for Research (ANR) for supporting this study through the convention ANR ECOTECH 2010 project PETZEKO (1081C0230/ANR-10-ECOT-011-03). Special thanks are addressed to Bruno Navarra for his help for the development of the ozonation pilot, to Eddy Petit (HPLC-UV), Valérie Bonniol (Ionic chromatography) and Guillaume Cazals (LC-MS) for their precious help in by-products identification.

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