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# Combined Ozonation Using Alumino-Silica Materials for the Removal of 2,4-Dimethylphenol from Water

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*This study deals with an advanced oxidation process combining adsorption and ozonation for treating petrochemical effluents. The compound 2,4-dimethylphenol (DMP) was the paradigm molecule and faujasite-Y, mordenite, ZSM-5 and  $\gamma$ -alumina were tested. Single ozonation showed rapid DMP degradation but limited by gas to liquid ozone transfer. No catalytic effect occurred during ozonation combined with any of the adsorbents: DMP removal was not accelerated. However, a good synergistic effect was observed for TOC removal with  $\gamma$ -alumina, yet the various zeolites are less efficient. Some specific oxidation by-products produced during ozonation are eliminated by adsorption in the presence of  $\gamma$ -alumina, although they persist in the other cases.*

**Keywords** Ozone, Combined Ozonation,  $\gamma$ -Alumina, Zeolites, 2, 4-Dimethylphenol

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## INTRODUCTION

Nowadays, industrial wastewaters are mainly treated by biological routes with good removal efficiencies, at least for most of the industrial branches. However, petrochemical industry generates wastewaters containing various non-biodegradable pollutants such as phenolic compounds, which must undergo specific treatment. Advanced oxidation processes (AOPs), combining simultaneous adsorption and ozonation, have been investigated by many researchers in recent years (Merle et al. 2010a; Valdes and Zaror 2005).

In these processes, various adsorbents can be used for increasing locally the concentration of a specific pollutant

while ozone is used as a powerful oxidizing agent, which reacts with the pollutant. In addition, while ozone reaction regenerates the adsorbent for further use, this one can have a catalytic effect for decomposing ozone into hydroxyl radicals HO•, which are much more powerful than ozone O<sub>3</sub> itself, thus increasing the global oxidation efficiency (Beltrán 2004; Hoigné and Bader 1976). The ideal adsorbent should act, at the same time, as a pollutant scavenger and as a catalyst for ozone decomposition.

Activated carbons and zeolites are most commonly used. Even though activated carbon is usually cheap and is highly efficient for adsorption and catalytic decomposition, its properties can be affected during ozonation (Merle et al. 2010a; Valdes et al. 2003). On the contrary, zeolites were proven to be stable under ozonation conditions as they improve refractory compounds removal (Dong et al. 2008; Fujita et al. 2004; Merle et al. 2010a; Monneyron et al. 2003; Sano et al. 2007; Valdes et al. 2009).

Thus, the present work studies the coupling of adsorption and ozonation using various types of zeolites (faujasite-Y, mordenite and ZSM-5) and  $\gamma$ -alumina, in terms of DMP removal efficiency and TOC mineralization. DMP was chosen as a paradigm non-biodegradable phenolic compound, characteristically found in effluents from petrochemical industries. First, ozone decomposition in presence of the materials was investigated. Then, interaction between DMP and ozone alone was studied. The adsorption kinetics and adsorption capacities of the various materials were also determined and, finally, the effect of the various materials on the efficiency of a coupled adsorption and ozonation process was evidenced. Finally the results observed are discussed in terms of physical and chemical properties of the alumino-silica materials used, in terms of adsorption capacities and in terms of ozonation mechanisms.

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## MATERIALS AND METHODS

### Chemicals and Zeolites

The 2,4-dimethylphenol (DMP) 99% purity was purchased from Acros Organics. Pure ethanol (analytical grade) was supplied from VWR Prolabo. The solutions were prepared with ultrapure water supplied by a Purelab Prima DV35 system.

Three commercial zeolites from TOSOH Corp, Tokyo Japan (faujasite-Y, mordenite and ZSM-5) and commercial  $\gamma$ -alumina from Alfa Aesar Company (Ward Hill, Massachusetts, USA) were used in this work. The main characteristics of these materials are given in Table 1. Prior to experimentation, the materials were washed with ultrapure water and, after draining, dried at 105 °C for 24 h and then were kept in a desiccator to prevent moisturizing.

### Experimental Setup

The dynamic adsorption and ozonation runs were conducted using the experimental setup shown in Figure 1. It consists of a jacketed semi-batch glass reactor (26 cm height and 11 cm diameter) filled up with 2 L of the DMP solution and perfectly stirred by a 6-blade Rushton turbine. The temperature was set at 25 °C.

Ozone was produced from pure oxygen by a BMT 802N ozone generator (Tübingen, Germany). A set of valves and a flow controller ensured a constant 30 L.h<sup>-1</sup> input flow into the reactor. The gas was continuously fed through a pipe located below the stirrer and collected through another pipe at the top of the reactor. Ozone concentrations in the gas phase, at the reactor inlet or outlet, were measured using a UV analyzer (Uvozon TLG200 from Trailgaz-ITT, Herford, Germany) and the off-gas flow was driven to an ozone thermal destructor (450 °C) before release to the atmosphere.

A liquid circulating loop ensured sampling for monitoring the pH value and the dissolved ozone concentration, thanks to a polarographic probe (Orbisphere Model 31330.15xx, Loveland, Colorado, USA). The pH was measured but not controlled in most experiments.

A data acquisition system recorded the ozone concentrations in gas and liquid phases and the pH every 5 s. Considering the flow rate of the recirculation pump, the flow rate of the gas and the limited volume of the various pipes, the values recorded can be considered as the actual values within the reactor, without significant bias.

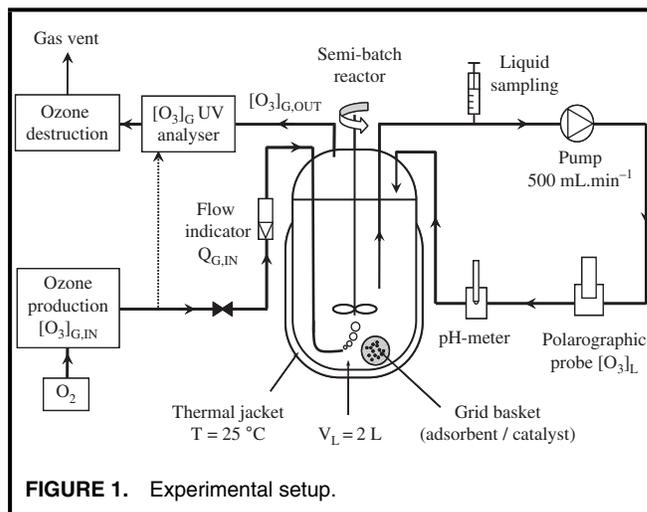


FIGURE 1. Experimental setup.

### Analytical Methods

In order to limit the impact of sampling on the reactor total volume, small solution volumes (12 mL; 2 mL for HPLC measurement and 10 mL for TOC measurement) were sampled. Samples were first passed through a 0.45- $\mu$ m PTFE filter before analysis in order to remove non-soluble compounds.

The concentration of the pollutants was determined by High Performance Liquid Chromatography using a HP 1050 series chromatograph equipped with a Diode Array Detector (Agilent Technologies HP 1200 series) and a ZORBAX Eclipse XDB-C18 column, 4.6  $\times$  150 mm, 5  $\mu$ m. Isocratic elution mode with a solvent mixture of 60% ethanol and 40% ultra-purified water (volume ratio) was applied at a flow rate of 1 mL.min<sup>-1</sup> and at ambient temperature. The retention time of DMP was 3 min and its concentration was measured according to the peak area at 280 nm. The retention time of the oxidation by-products was around 1.5 min. Oxidation by-products were not namely identified but the evolution of the area of the corresponding peaks was monitored at 254 nm.

The total organic carbon (TOC) was determined using a Shimadzu TOC-V series (Kyoto, Japan). A small amount of hydrochloric acid is added to acidify the sample; this converts all inorganic carbon (IC) in the sample to carbon dioxide. The sample is then treated with sparging gas in order to drive this CO<sub>2</sub> out of the sample solution. The TOC concentration is

TABLE 1. Main Characteristics of the Zeolites and  $\gamma$ -Alumina

Type	Faujasite-Y	Mordenite	ZSM-5	$\gamma$ -Alumina
Pore diameter (Å)	7.4 + 13.0	(6.5 $\times$ 7.0) + (2.6 $\times$ 5.7)	(5.3 $\times$ 5.6) + (5.1 $\times$ 5.5)	150
Si/Al (mol/mol)	28	460	4200	0
BET surface (m <sup>2</sup> /g)	608	509	308	237
Pore volume (cm <sup>3</sup> /g)	0.24	0.20	0.12	0.65
Binder type (% weight)	Clay (20%)	Alumina (20%)	Clay (20%)	—
Pellet diameter (mm)	1.5	3.0	1.5	3.0

determined by measuring the total carbon (TC) of the sample after the IC has been eliminated.

## RESULTS AND DISCUSSION

### Effect of Alumino-Silica Materials Concentration on the Kinetic Constant of Ozone Decomposition

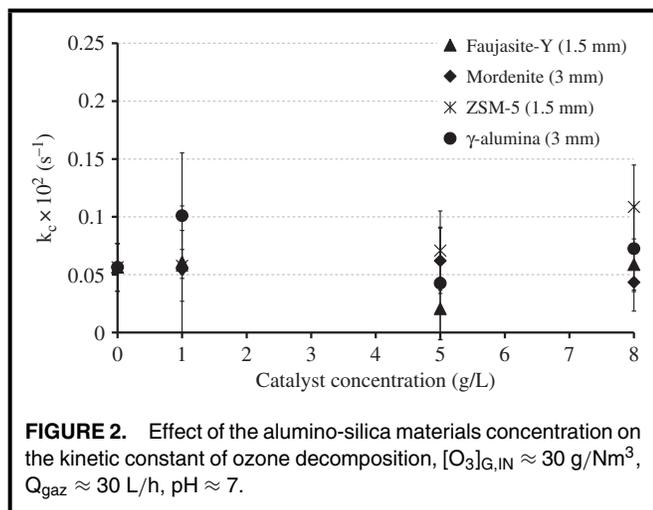
The pseudo-first-order kinetic constant of ozone decomposition ( $k_c$ ) was determined in absence and in the presence of the different materials in the reactor filled with 2 L of ultrapure water buffered at pH 7. The methodology was developed in former works (López-López et al. 2007a; Merle et al. 2009; Reungoat et al. 2010) and the  $k_c$  value was calculated according to Equation [1]. The results obtained for 30 mg.L<sup>-1</sup> ozone inlet concentration are presented in Figure 2.  $k_c$  is very sensitive to  $([O_3]_{G,IN} - [O_3]_{G,OUT}^\infty)$  and this term is small in comparison to  $[O_3]_{G,IN}$  and  $[O_3]_{G,OUT}^\infty$ . Thus, the incertitude of  $k_c$  is important.

$$k_c = \frac{Q_G \cdot \left( [O_3]_{G,IN} - [O_3]_{G,OUT}^\infty \right)}{[O_3]_L^\infty \cdot V_L} \quad [1]$$

With:

- $k_c$  = kinetic constant of ozone decomposition (s<sup>-1</sup>);
- $Q_G$  = volumetric gas flow rate (m<sup>3</sup>.s<sup>-1</sup>);
- $[O_3]_{G,IN}$  = ozone concentration in inlet gas (g.m<sup>-3</sup>);
- $[O_3]_{G,OUT}^\infty$  = ozone concentration in outlet gas at steady state (g.m<sup>-3</sup>);
- $[O_3]_L^\infty$  = ozone concentration in liquid at steady state (g.m<sup>-3</sup>);
- $V_L$  = liquid volume in the reactor (m<sup>3</sup>)

The values of  $k_c$  without solid are similar to those obtained by López-López et al. (2007b) and by Merle et al. (2010b). In addition, it is obvious that none of the tested alumino-silica materials does promote ozone decomposition even at high



concentration of solid in water. So, these materials would probably not act as catalysts for ozone decomposition in water, contrarily to other materials such as activated carbon (Merle et al. 2010a). About ZSM-5, the same commercial material was tested on ozone abatement in the gas phase and showed a catalytic effect on ozone decomposition, because of the Lewis acid sites of the ZSM-5 (Brodu et al. 2013).

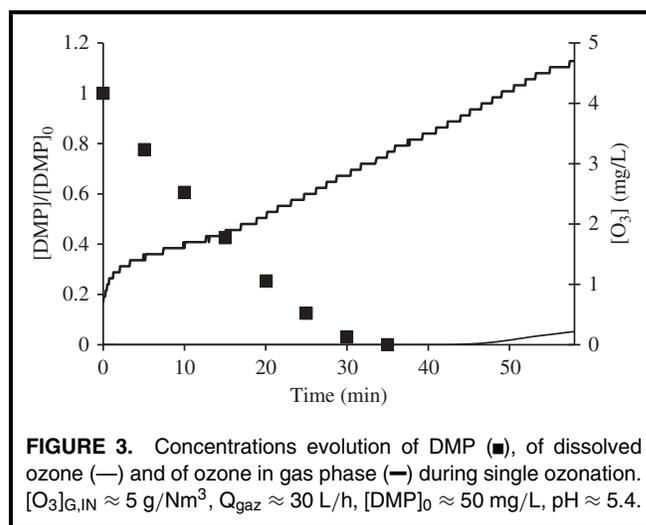
### 2,4-dimethylphenol Single Ozonation

Before ozonation experiments, a preliminary test was conducted to verify that the pollutant is not stripped off during ozonation. The experiment was performed in the semi-batch reactor, replacing ozone by nitrogen at a 30 L.h<sup>-1</sup> input flow; the DMP initial concentration was 50 mg.L<sup>-1</sup>. This test showed that there is no stripping of DMP by the gas during the experiments. So, if there is an evolution of the DMP concentration during the ozonation experiment, it will only be the result of DMP oxidation.

Single ozonation was performed in the semi-batch reactor with an ozone inlet concentration of 5 g.Nm<sup>-3</sup>; the DMP initial concentration was 50 mg.L<sup>-1</sup>. Figure 3 shows the evolution of the concentrations of DMP and ozone in the liquid and of ozone at the outlet gas during this single ozonation experiment. When the samples were taken, no dissolved ozone concentration was found in the reactor, which confirms that there was no oxidation of the samples between the sampling time and the analytical measurement time.

First, it is noticeable that DMP decrease was fast and quite linear during the first 30 min. This behavior indicates an apparent zero order for the reaction and suggests that the limiting phenomenon was ozone mass transfer rather than the chemical reaction itself.

Moreover, ozone concentration in the liquid phase remained null all over the period of DMP degradation and even a few minutes after DMP total removal, indicating the beginning of degradation of oxidation by-products. Then it started to rise gradually. This profile clearly demonstrates



that the reaction between ozone and organics (DMP and its direct oxidation by-products) is fast and that interfacial ozone mass transfer controls the oxidation kinetics. The profile for gaseous ozone is also consistent with this hypothesis since it increases progressively until finally reaching the inlet value.

## 2,4-Dimethylphenol Adsorption onto Alumino-Silica Materials

Adsorption kinetics were studied for all adsorbents in granular form in the semi-batch reactor using a concentration of  $1 \text{ g.L}^{-1}$  of adsorbent for each experiment. The volume of the DMP solution was 2 L and the DMP initial concentration was  $50 \text{ mg.L}^{-1}$ . Adsorbents were ground to have approximately the same particle size, distributed between 0.5 and 1 mm. Results of this adsorption kinetics study are presented in Figure 4; best adsorption kinetics was obtained with faujasite-Y followed by mordenite. A plateau was observed in the case of ZSM-5 and  $\gamma$ -alumina, indicating that these two materials do not adsorb DMP or adsorb only extremely slowly. Because of intra-particle mass transfer resistance, the adsorption kinetics would be obviously slower if using the materials in their original pellet form.

The adsorption equilibrium isotherms of the different materials were also investigated at the temperature of  $25 \text{ }^\circ\text{C}$ . These adsorption equilibrium curves are presented in Figure 5. Adsorption capacities determination was based on the generalized Langmuir-Freundlich isotherm model using Equation 2 (Kano et al. 2000). The fitted values of Langmuir-Freundlich parameters and the estimated maximum adsorption capacities are summarized in Table 2.

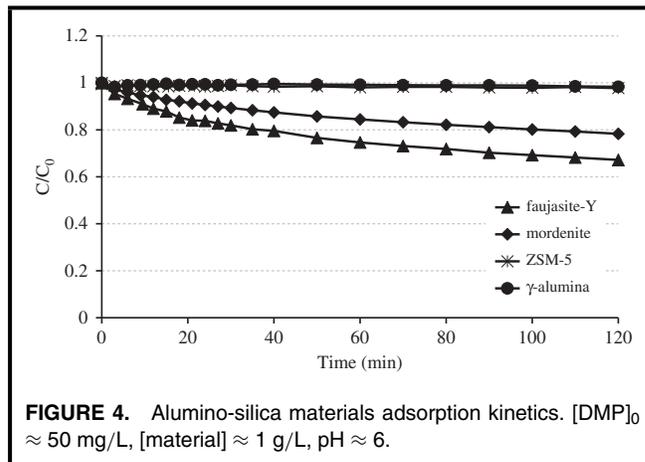


FIGURE 4. Alumino-silica materials adsorption kinetics.  $[\text{DMP}]_0 \approx 50 \text{ mg/L}$ ,  $[\text{material}] \approx 1 \text{ g/L}$ ,  $\text{pH} \approx 6$ .

Adsorption capacities of zeolites are different from each other with the following decreasing order: faujasite-Y, mordenite and ZSM-5.  $\gamma$ -alumina shows no adsorption at all. The adsorption capacity depends on the Si/Al ratio and on the pore size. The difference in the adsorption capacities of the various zeolites can be explained by the difference in their physical properties (pore size and pore volume) allowing the adsorption of the pollutant within the pores: faujasite-Y and mordenite contain an important pore volume, comparing to ZSM-5.

Despite its large mesopores, the  $\gamma$ -alumina does not show any adsorption capacity for DMP due to its hydrophilic character because of the absence of silica ( $\text{Si/Al} = 0$ ). These results are similar to those obtained by Reungoat et al. (2007), who showed that the adsorption capacity of zeolites depends on the Si/Al ratio (hydrophobic or hydrophilic character)

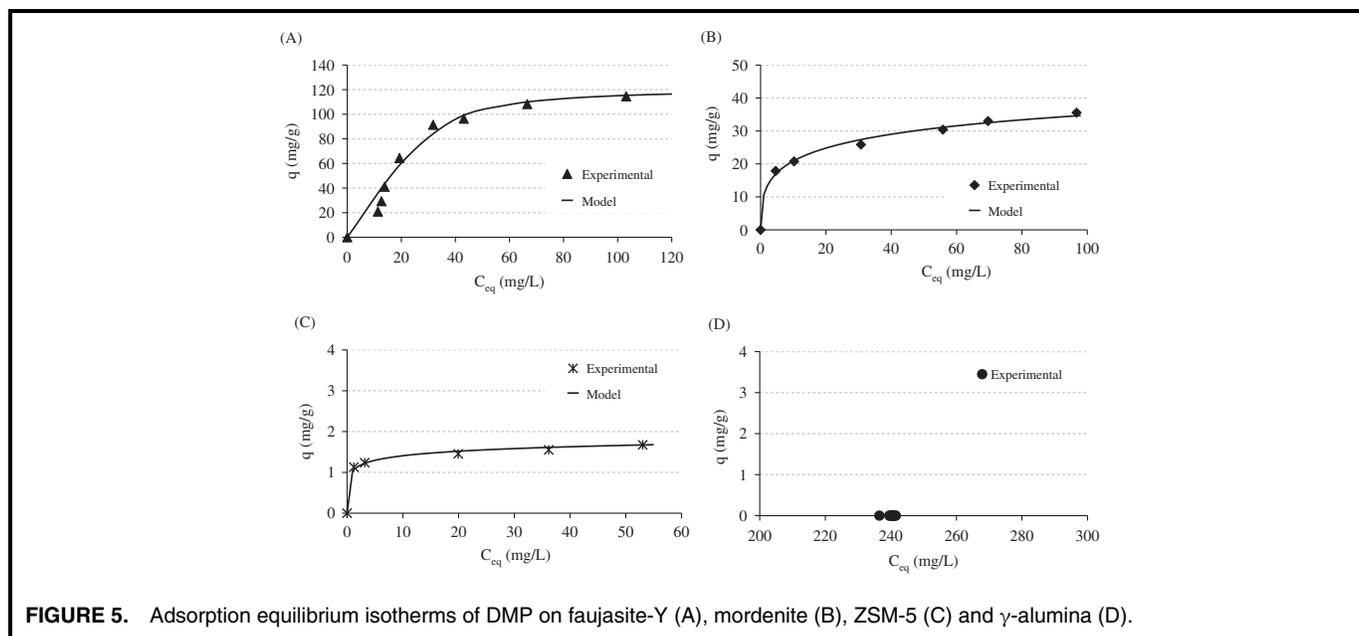


FIGURE 5. Adsorption equilibrium isotherms of DMP on faujasite-Y (A), mordenite (B), ZSM-5 (C) and  $\gamma$ -alumina (D).

**TABLE 2.** Fitted Values of Langmuir-Freundlich Parameters for Adsorption of DMP on the Zeolites and  $\gamma$ -Alumina

	$R^2$	$q_{\max}$ (mg.g <sup>-1</sup> )	$b$ ( $\times 10^2$ )	$1/n$
Faujasite-Y	0.98	120	5.03	2.00
Mordenite	0.98	67.4	1.19	0.38
ZSM-5	0.99	2.80	9.55	0.23
$\gamma$ -Alumina	—	0.00	—	—

for ratios lower than 100 and on the zeolite structure for higher ratios.

$$q = q_{\max} \times \frac{(b \cdot C_{eq})^{(1/n)}}{1 + (b \cdot C_{eq})^{(1/n)}} \quad [2]$$

With:

- $q$  = adsorption quantity (mg.g<sup>-1</sup>);
- $q_{\max}$  = maximum adsorption quantity (mg.g<sup>-1</sup>);
- $C_{eq}$  = equilibrium concentration in the liquid phase (mg.L<sup>-1</sup>);
- $b$  = generalized Langmuir-Freundlich constant (L.mg<sup>-1</sup>);
- $1/n$  = generalized Langmuir-Freundlich exponent (dimensionless);

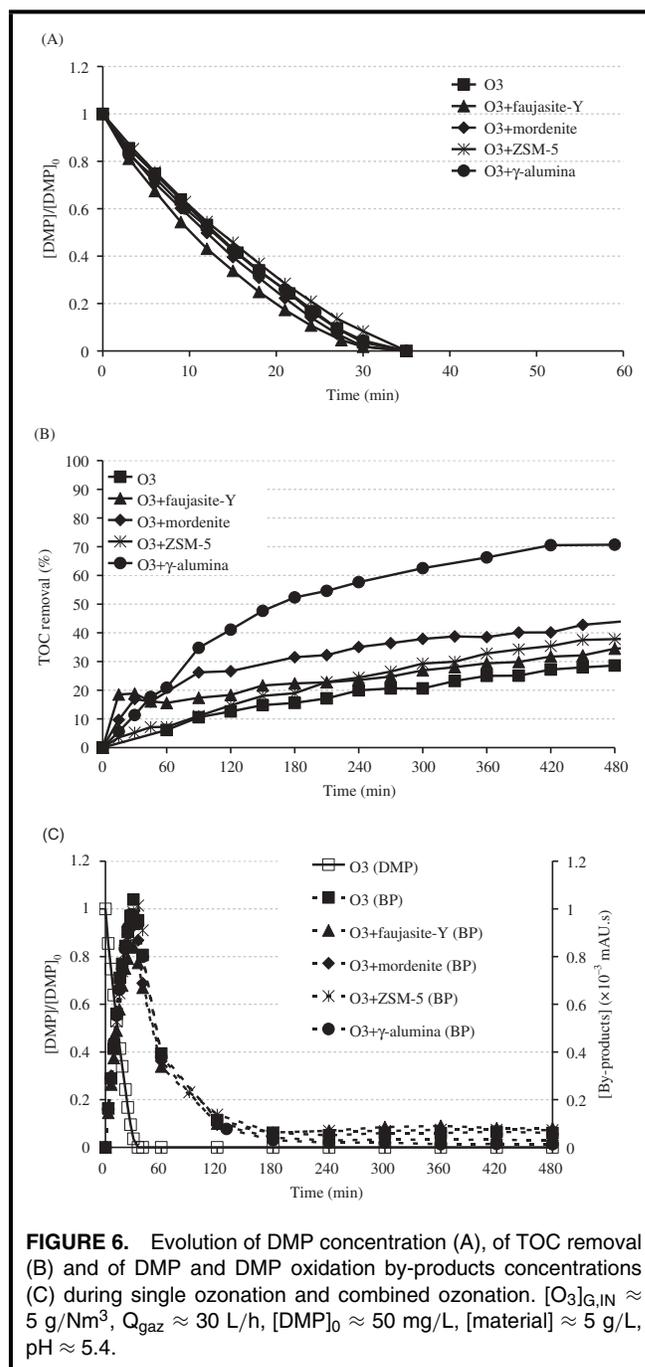
## 2,4-Dimethylphenol Single Ozonation Versus Combined Ozonation

Ozonation of 2,4-dimethylphenol was conducted in absence and in the presence of 5 g.L<sup>-1</sup> of materials in their original pellets form, moving freely inside the reactor filled with 2 L of DMP solution. The initial concentration of the DMP solution was 50 mg.L<sup>-1</sup>.

Figure 6A compares the evolution of DMP concentration during single ozonation and combined ozonation experiments. When running combined ozonation in the presence of any of the tested catalysts, the elimination rate of DMP was not different from single ozonation and the global elimination yield remained constant. None of the materials tested did improve the global kinetics for DMP removal. Even if some of the tested materials adsorb DMP, such as the faujasite-Y and mordenite, the global degradation rate remains the same because the reaction of ozone with DMP is faster than adsorption into the pores of the materials.

When using faujasite-Y, the curve of DMP degradation was slightly different from the rest of the curves. This is due to the high adsorption kinetics and adsorption capacity of this material comparing to the other tested materials.

To identify if there is an effect on the TOC removal when using the alumino-silica materials in combined ozonation, the TOC removal during single ozonation and combined



**FIGURE 6.** Evolution of DMP concentration (A), of TOC removal (B) and of DMP and DMP oxidation by-products concentrations (C) during single ozonation and combined ozonation.  $[O_3]_{G,IN} \approx 5$  g/Nm<sup>3</sup>,  $Q_{gaz} \approx 30$  L/h,  $[DMP]_0 \approx 50$  mg/L,  $[material] \approx 5$  g/L,  $pH \approx 5.4$ .

ozonation experiments were compared. The results are presented in Figure 6B. TOC samples were analyzed immediately after sampling. The effect of remaining dissolved ozone was neglected, considering that the reaction of oxidation of DMP by-products was limited by the chemical regime. For the first minutes of experiment, an effect on TOC removal is observed in the case of faujasite-Y and mordenite due to the DMP adsorption capacity and kinetics on these two materials, but the global TOC removal after 8 h of experiment is not significantly better comparing to single ozonation.

But, although the performances of the different materials tested are almost similar in terms of DMP degradation, a positive effect was observed in terms of TOC removal during combined ozonation:  $\gamma$ -alumina clearly promotes the TOC removal efficiency. The mordenite also has a positive effect that could be explained by the nature of the binder used to make the zeolite pellets: mordenite contains 20% weight of  $\gamma$ -alumina as a binder.

In order to understand the different behaviors observed during single ozonation and ozonation using the zeolites and  $\gamma$ -alumina, the evolution of the oxidation by-products concentration during the ozonation experiments was investigated. Figure 6C compares the evolution of DMP concentration and DMP oxidation by-products concentration during single ozonation and combined ozonation.

During the first 35 min of ozonation (in the presence or in absence of materials), DMP is reacting with ozone and its concentration decreases while its oxidation by-products concentration is increasing. During this first period of experiments, the pH of the solution quickly decreases from 5.4 to 4. The dissolved ozone remained close to zero. After 35 min, there is no more DMP in the solution (DMP is totally transformed to oxidation by-products), ozone then reacts only with these DMP oxidation by-products and the concentration of these by-products begins to decrease. During this second period of experiments, dissolved ozone concentration increases until a maximum value of  $1.1 \text{ mg}\cdot\text{L}^{-1}$  and the pH remains constant around 4. These profiles evidence that the reaction between dissolved ozone and oxidation by-products is limited by the chemical regime. It is observed that an ozonation time of 3 h allows decomposing the major part of the DMP oxidation by-products. Nevertheless, after 3 h of ozonation (in presence or in absence of materials), a plateau is observed indicating that some by-products remain in the solution and are hardly oxidized by ozone. Figure 6C also shows that, during the first 3 h, the by-products concentration profile is almost identical in case of single ozonation or combined ozonation indicating no role of the materials. On the contrary, after 3 h, the by-products concentration profile is lower in the case of  $\gamma$ -alumina than for single ozonation or ozonation using zeolites.

To confirm whether the decrease of the DMP oxidation by-products concentration over time during single ozonation experiment is due to reaction with ozone, a stripping test on DMP oxidation by-products was conducted to evidence if these by-products remain in the reaction medium or are stripped. During this experiment, the DMP oxidation by-products were generated by ozonizing the solution during 35 min; after that, the gas containing ozone was replaced by nitrogen. The test demonstrated that DMP oxidation by-products are not stripped and remain in the solution if ozone is not injected in the reactor. This confirms that the DMP oxidation by-products react with ozone in case of single ozonation, and react with ozone and may also be adsorbed by the materials in case of combined ozonation.

## Mechanism Investigation

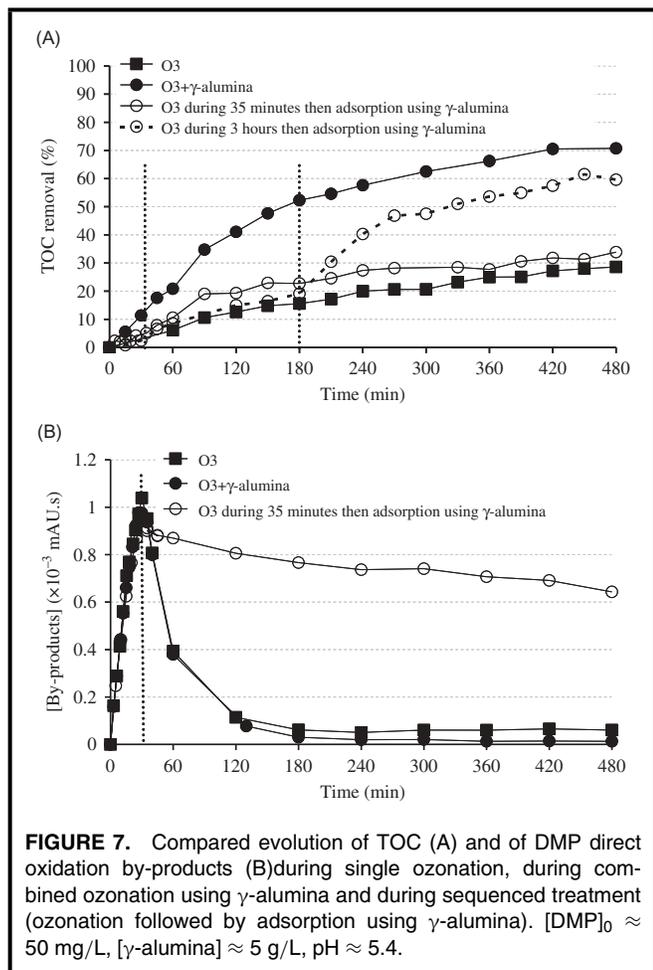
Several phenomena can be involved during combined ozonation; DMP can, at the same time, be adsorbed (not in the case of ZSM-5 and  $\gamma$ -alumina) into the material pores and consumed by reaction with ozone. Oxidation by-products can also be adsorbed or continue to react with ozone to give other by-products. The mechanisms involved in the case of using  $\gamma$ -alumina (the best material tested in terms of TOC removal) and faujasite-Y (the best material tested in terms of DMP adsorption) are investigated in this paragraph.

To understand if the TOC removal enhancement observed in the case of ozonation using  $\gamma$ -alumina results from adsorption of the DMP oxidation by-products, or from oxidation or from both phenomena, two experiments were conducted, which are a single ozonation sequence followed by a single adsorption sequence. In the first experiment, a single ozonation step was conducted during 35 min, this means until DMP is totally removed from the solution. Then the gas containing ozone was replaced by nitrogen and  $\gamma$ -alumina was then added to the reaction medium to allow for adsorption. The second experiment is identical to the first one but the single ozonation step was conducted during 3 h before stopping ozone gas, replacing it by nitrogen and adding  $\gamma$ -alumina.

The results of these two experiments were compared to the results of single ozonation and combined ozonation using  $\gamma$ -alumina in terms of TOC removal and in terms of evolution of the oxidation by-products concentration. The results are presented simultaneously in Figure 7A and Figure 7B. These results clearly show that the effect observed during continuous ozonation using  $\gamma$ -alumina is mainly an adsorption effect of some specific oxidation by-products: more precisely  $\gamma$ -alumina hardly adsorbs the primary by-products—generated during the first 35-min period of single ozonation—whereas the material easily adsorbs the subsequent secondary by-products generated during the second period of single ozonation, between 35 min and 3 h. For this reason, it seems to be necessary to conduct single ozonation for 3 h, in order to generate the greatest amount of secondary oxidation by-products which are easily adsorbable by  $\gamma$ -alumina. This can reduce ozone consumption very significantly with regard to an 8-h single ozonation treatment.

Figure 7A evidences that the TOC removal efficiency in the case of the two steps experiment (single ozonation during 3 h and then single adsorption for 5 h) is quite similar to the one observed during the continuous combined ozonation experiment. This proves that the chief phenomenon occurring in the second period of the experiment is the adsorption of specific by-products and not a catalytic phenomenon. Under the experimental conditions, adsorbable by-products start to appear after about 35 min of ozonation but continue to appear until 3 h of ozonation.

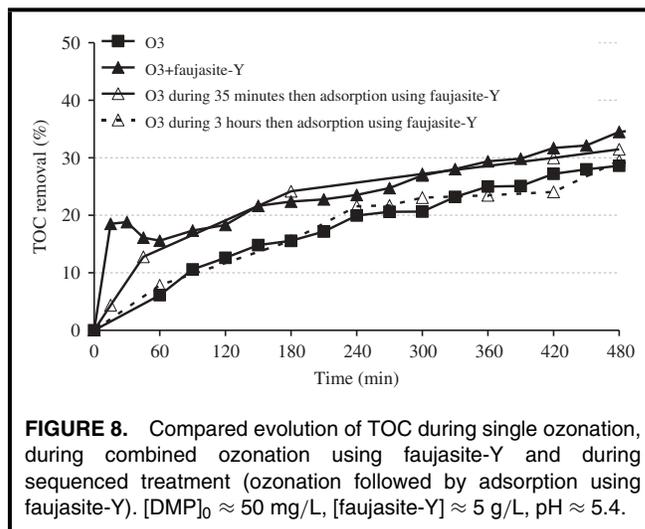
Figure 7B confirms that the direct DMP oxidation by-products, generated during the first 35 minutes of ozonation, are practically not adsorbable by  $\gamma$ -alumina. The plot corresponding to the by-products evolution when  $\gamma$ -alumina was introduced in the reactor after 3 h of single ozonation is not



mentioned on this Figure 7-B: the corresponding by-products are highly oxidized molecules which have totally lost their aromatic feature and are not detected during HPLC analysis at 254 nm.

The primary by-products of DMP oxidation—produced during the first 35 min of single ozonation—are mainly aromatic compounds with a hydrophobic character, which explains why these by-products are hardly adsorbed onto  $\gamma$ -alumina. On the other hand the oxidation by-products generated between 35 min and 3 h of single ozonation are mainly hydrophilic aliphatic acids (such as acetic, formic, or oxalic). Considering that  $\gamma$ -alumina is characterized by a strong hydrophilic character, these categories of by-products can be easily adsorbed.

To understand the difference observed between the TOC removal enhancement in the case of  $\gamma$ -alumina and in the case of faujasite-Y, a series of experiments identical to those depicted above for  $\gamma$ -alumina were also conducted with faujasite-Y. The results of these experiments are presented in Figure 8 for the TOC removal. The results show that, unlike  $\gamma$ -alumina, and although faujasite-Y adsorbs DMP, this material does not adsorb the oxidation by-products of DMP, which reduces considerably its efficiency comparing to  $\gamma$ -alumina.



Indeed faujasite-Y, which is characterized by a hydrophobic character, does not adsorb the hydrophilic aliphatic acids produced between 35 min and 3 h of single ozonation. Similar results were obtained by Merle et al. (2009).

## CONCLUSIONS

This work aims to study the effectiveness of combined ozonation as an advanced oxidation process for the degradation and mineralization of refractory organic compounds from water. The selection of the material that will be combined to ozonation is one of the key parameters towards efficiency of this kind of process, as efficient adsorption properties are usually suspected to determine the material activity. Three types of zeolites (faujasite-Y, mordenite and ZSM-5) and  $\gamma$ -alumina were selected and their effect regarding oxidation was evaluated under the same reaction conditions (5 g/L material in the form of pellets, 0.075 g/L/h ozone input), using a 2-L semi-batch reactor and 2,4-dimethylphenol ( $[\text{DMP}] = 50$  mg/L) as a model molecule.

To understand this three-phase system (liquid/gas/solid), binary interactions between ozone, material and DMP were studied independently. First, the effect of the concentration of material on ozone decomposition was studied. Neither the zeolites nor  $\gamma$ -alumina do enhance ozone decomposition. Yet, it seems that no radical species (such as  $\text{HO}\cdot$ ) are produced and that molecular ozone alone ensures oxidation.

The interaction between DMP and ozone alone was studied in a batch reactor. The DMP degradation rate is rapid and quite constant, indicating an apparent zero-order reaction and evidencing that the limiting phenomenon is interfacial ozone mass transfer, which controls the oxidation kinetics.

The DMP adsorption kinetics and adsorption capacities onto the materials were also evaluated. The various adsorption

kinetics are slow compared to the single ozonation kinetics. The best adsorption capacities were obtained with faujasite-Y, followed by mordenite. ZSM-5 and  $\gamma$ -alumina did not show any adsorption potential for DMP.

For all the materials tested, the results obtained by single ozonation and combined ozonation were identical in terms of DMP degradation over time, suggesting no catalytic effect on DMP degradation kinetics and confirming that there is no effect of the materials on ozone decomposition into radicals. However, a synergistic effect was observed in terms of total mineralization (TOC removal) during combined ozonation. The zeolites do not enhance significantly the TOC removal but very better results were obtained with  $\gamma$ -alumina. The DMP oxidation by-products were monitored and the evolution of their concentration over time was studied. The evolution, during ozonation, of these oxidation by-products exhibited two different features:

- The primary oxidation by-products of DMP, produced during the first 35 min of single ozonation, are mainly aromatic products with a hydrophobic character;
- The subsequent oxidation by-products generated between 35 min and 3 h of single ozonation are mainly hydrophilic aliphatic acids.

The mechanisms involved in the case of combined ozonation using  $\gamma$ -alumina and faujasite-Y were investigated by adding the materials to the reaction medium after 35 min or after 3 h of single ozonation: the synergetic effect observed in the case of  $\gamma$ -alumina is essentially due to the adsorption of the secondary oxidation by-products produced after 35 min of single ozonation. These by-products are mainly hydrophilic aliphatic acids, well matching with the strong hydrophilic character of the  $\gamma$ -alumina but not with the hydrophobic character of the faujasite-Y.

At last, in terms of reactor operation, it seems that a procedure consisting of 3 h single ozonation followed by a 5-h adsorption period should be a good compromise allowing at the same time DMP and aromatic by products destruction, 60 to 70% TOC removal while reducing ozone consumption compared to a 8-h continuous combined ozonation procedure. Moreover the duration of the adsorption phase should probably be reduced when improving mass transfer properties of the material and the reactor.

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