

## Chemical Pretreatment of Olive Oil Mill Wastewater Using a Metal-Organic Framework Catalyst

SALVATORE DE ROSA,<sup>†</sup> GIROLAMO GIORDANO,<sup>‡</sup> TERESA GRANATO,<sup>\*,‡</sup>  
ANDREA KATOVIC,<sup>‡</sup> ALESSIO SICILIANO,<sup>†</sup> AND FRANCESCO TRIPICCHIO<sup>†</sup>

Dipartimento di Difesa del Suolo "V. Marone", Università della Calabria, I-87030 Rende (CS), Italy,  
and Dipartimento di Ingegneria Chimica e dei Materiali, Università della Calabria,  
I-87030 Rende (CS), Italy

Olive oil mill wastewaters (OOMW) are not suited for direct biological treatment because of their nonbiodegradable and phytotoxic compound (such as polyphenols) content. Advanced technologies for treatment of OOMW consider mainly the use of solid catalysts in processes that can be operated at room conditions. A system based on combined actions of catalytic oxidations and microbial technologies was studied. The wet hydrogen peroxide catalytic oxidation (WHPCO) process is one of the new emerging oxidation processes particularly attractive for the pretreatment of highly polluted OOMW containing polyphenols that are not suited for classical treatments. In this work, the biodegradability of OOMW was evaluated before and after treating the wastewater samples by the WHPCO process using a metal-organic framework (MOF) as a catalyst. This material, containing Cu and prepared with benzene-1,3,5-tricarboxylic acid (BTC), is a robust metal-organic polymer with a microporous structure that is reminiscent of the topology of zeolite frameworks.

**KEYWORDS:** Fenton's reagent; olive oil mill wastewater; biodegradation; copper; metal-organic framework; heterogeneous catalysis

### INTRODUCTION

Olive oil mill wastewaters (OOMW) have a high seasonal pollution potential, especially in the Mediterranean region. The annual OOMW production in this region is estimated to be over  $10^7$  m<sup>3</sup> (1). The phytotoxicity and antimicrobial activity of OOMW, mainly determined by its phenolic content, usually make the direct biological treatment difficult for OOMW. Among the different chemical technologies studied to treat polyphenol containing model effluents or real OOMW (such as noncatalytic and catalytic wet oxidation, ozonation, solar light photocatalysis, etc.), the combination of catalytic oxidation pretreatment with biological posttreatment (aerobic or anaerobic) is an attractive solution. In recent studies, great attention has been focused on the Fenton reagent, a homogeneous catalytic system comprising hydrogen peroxide (HP) and a ferrous salt (2–6). Iron-catalyzed HP decomposition determines the formation of highly reactive free hydroxyl radicals (HO•), second only to fluorine radicals in terms of oxidizing power, that are capable of oxidizing many organic pollutants to lower molecular weight compounds and eventually to carbon dioxide and water (7). The main disadvantage of Fenton and Fenton-like reagents is the need of recovering iron or other transition metal used after the catalytic treatment (4). These drawbacks can be overcome in principle

using heterogeneous Fenton-type catalysts, with minimal, if any, leaching of the transition metal.

The aim of the present work is to develop an efficient heterogeneous catalytic pretreatment that can be used to increase the biodegradability of the OOMW, to make possible the subsequent biological oxidation. In this work, the nonbiodegradable compounds present in OOMW are oxidized by means of wet hydrogen peroxide catalytic oxidation (WHPCO), and the catalyst used is a metal-organic framework (MOF) compound containing copper, Cu<sub>3</sub>(BTC)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub> (BTC = benzene 1,3,5-tricarboxylic acid). The high micropore volume, large pore sizes, crystallinity, and high metal content render this new and emerging class of porous materials very interesting as catalysts for reactions catalyzed at low temperatures, such as liquid-phase transformation (8). The efficiency of the WHPCO of polyphenols was evaluated by a complete characterization of the biodegradability of fresh and treated samples. Biological aerobic kinetics of the OOMW organic substrate was evaluated using an activated sludge taken from the wastewater treatment plant of Montalto Uffugo (Calabria, South Italy).

### EXPERIMENTAL INVESTIGATION

**Analytical Methods.** Analyses of total chemical oxygen demand (COD<sub>TOT</sub>), soluble COD (COD<sub>SOL</sub>), NH<sub>4</sub><sup>+</sup>-N, NO<sub>2</sub><sup>-</sup>-N, NO<sub>3</sub><sup>-</sup>-N, PO<sub>4</sub><sup>3-</sup>-P, SST, and SSV were determined using standard methods (9). The COD<sub>SOL</sub>, in particular, was measured by means of a flocculation pretreatment, as proposed by Mamais et al. (10). To avoid the positive

\* Author to whom correspondence should be addressed. Tel: +39.0984.496712; fax: +39.0984.496655; e-mail: granato@unical.it.

<sup>†</sup> Dipartimento di Difesa del Suolo "V. Marone".

<sup>‡</sup> Dipartimento di Ingegneria Chimica e dei Materiali.

**Table 1.** Chemical Parameters of OOMW

parameters	unit	values
COD <sub>TOT</sub>	g L <sup>-1</sup>	74.4
COD <sub>SOL</sub>	g L <sup>-1</sup>	57.7
polyphenols	g L <sup>-1</sup>	2.65
sugars	g L <sup>-1</sup>	20.6
NH <sub>4</sub> <sup>+</sup> -N	mg L <sup>-1</sup>	70
NO <sub>2</sub> <sup>-</sup> -N	mg L <sup>-1</sup>	8.6
NO <sub>3</sub> <sup>-</sup> -N	mg L <sup>-1</sup>	91
PO <sub>4</sub> <sup>3-</sup> -P	mg L <sup>-1</sup>	232
SSV	g L <sup>-1</sup>	43.0
SST	g L <sup>-1</sup>	52.4
pH		3.58

interference derived from the presence of HP in COD measurement (11, 12), the residual HP was eliminated by an adequate thermal treatment of the samples prior to the analysis.

The total reducing sugar content was determined by the ADNS spectrophotometric method at 550 nm (13). The polyphenol content was determined by using a UV-vis spectrophotometer at 710 nm and after removing sugars. This method utilizes a reagent (Folin-Ciocalteu's phenol reagent) that in the presence of polyphenols or sugar forms a blue compound. To determine the exact amount of polyphenols in the OOMW, the interferences due to the sugar molecules have been eliminated using a C18 column (14).

The fresh and treated OOMW samples were analyzed with respect to the biodegradable COD (BCOD), the rapidly biodegradable COD (RBCOD), and the slowly biodegradable COD (SBCOD) by respirometric methods (15, 16). The respirometric tests were done by means of a Chemitec S250 OUR test, which consists of a thermostated and aerated (without oxygen exchange with ambient) batch reactor of 500 cm<sup>3</sup>, continuously stirred and provided of a probe for the measurement of the dissolved oxygen and temperature. The biological aerobic kinetics was evaluated by adding 20–30 mL of OOMW (diluted 10-fold) to 480–470 cm<sup>3</sup> of activated sludge, continuously stirred and aerated, to maintain the dissolved oxygen amount at about 5–7 ppm. The activated sludge was preaerated for 5 h to remove its own COD. Every 30 min, an aliquot of 15 mL of mixed liquor was taken from the batch reactor, filtered at 0.45 μm, and analyzed by the direct COD measurement.

**Catalyst Synthesis and Characterization.** The synthesis procedure for the preparation of MOF material was taken from literature (17), and it is a synthesis process for large-scale manufacture resulting from an optimization of literature recipes (18, 19). The as-made sample is a powder of intense blue crystals of Cu-BTC. The postsynthesis treatment consisted of drying the sample at 383 K overnight.

The Cu-BTC samples' powder X-ray diffraction (XRD) patterns were obtained using a Philips PW 1710 diffractometer with Cu Kα radiation. Scanning electron microscope (SEM) images were obtained using a Cambridge Stereoscan 360 SEM, and copper content of the samples were measured by an electron-dispersive X-ray (EDAX) analysis in the SEM chamber. Thermal analysis was performed by a Netzsch STA 409 instrument in air flow (5 mL/min) between 293 and 1123 K at a heating rate of 10 K/min (TG-DTG-DSC).

**WHPCO Test.** The Cu-BTC sample was used as a catalyst to oxidize the polyphenols contained in the OOMW sample in a thermostated stirred batch reactor. A catalyst amount of 243 mg was introduced into 250 mL of OOMW at room temperature and atmospheric pressure. An amount of 113.2 mg/L of HP (solution 30% w/w) was added in aliquots of 10 mL every 2 minutes. Then, the reaction time was started. After 27 h, the catalyst was recovered from the reaction mixture by decantation.

The change of the polyphenol concentration during the oxidation reaction was measured utilizing the Folin-Ciocalteu reagent, while the concentration of the HP at various reaction times was determined by a modified iodometric titration method. The temperature and pH of the reaction mixture were continuously monitored. Aliquots of the reaction mixture after 3 h and 27 h (final reaction mixture) were analyzed with respect to BCOD, RBCOD, and SBCOD.

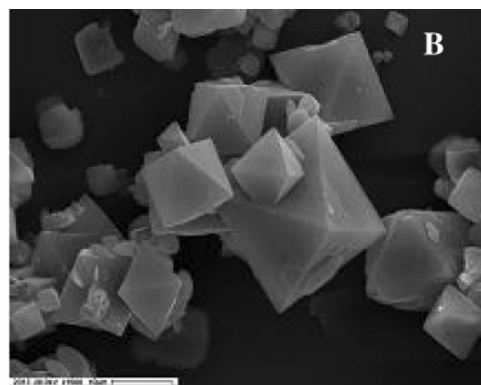
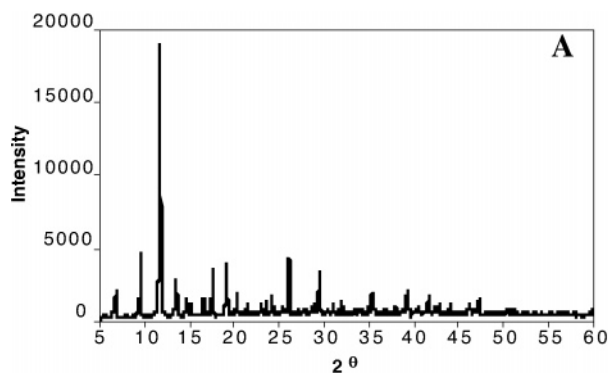
## RESULTS AND DISCUSSION

**Characterization of the OOMW.** The chemical parameters of fresh OOMW are reported in Table 1. The OOMW used in this work was characterized by an elevated COD<sub>TOT</sub> value and a high fraction of COD<sub>SOL</sub> (which is 77.6% of COD<sub>TOT</sub>). For samples having a high COD<sub>SOL</sub> fraction, as in the studied case, the catalytic oxidation pretreatment could be an attractive solution. The concentration of ammonium nitrogen and reactive phosphorus was low if compared to COD<sub>TOT</sub>. The low content of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P creates the necessity to add ammonium and phosphorus salts to have a complete conversion of the biodegradable organic substrate by biological oxidation reactions in wastewater treatment plants. As it can be observed from the concentration of the total suspended solids, a settling pretreatment was not advantageous.

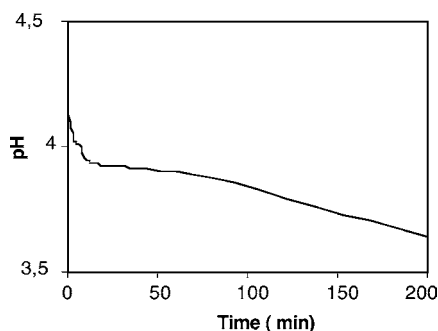
**Characterization of the Cu-BTC Catalyst.** In Figure 1, the XRD pattern and SEM image of the Cu-BTC catalyst are reported. As expected from the indication reported by Wang et al. (17), the Cu-BTC sample synthesized under hydrothermal conditions was obtained as cube-shaped crystals having a crystal-size dimension of 10–30 μm.

The fully hydrated as-synthesized Cu-BTC material contains about 20 wt % of water and is stable up to 573 K.

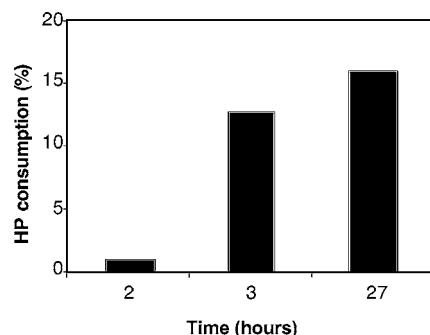
**WHPCO of the OOMW.** The chemical pretreatment oxidation process on the OOMW was carried out at room temperature and atmospheric pressure, using a catalyst amount of 0.97 g-cat L<sup>-1</sup>. The HP amount used was 113.2 mg/L, determined choosing phenol as probe molecule of the total COD and considering an HP/phenol initial molar ratio of 10 (substoichiometric). The oxidation was expected to be immediate and highly exothermic (11), and so to prevent excessive heating, HP was added in aliquots. The temperature of the reaction mixture reached, after 3 h, the highest value of 306 K. The pH of the reaction mixture, during the HP adding, decreased rapidly to 3.9; for 60 min, the



**Figure 1.** Cu-BTC: (A) XRD pattern; (B) SEM image.



**Figure 2.** pH versus reaction time (first 200 min) in the WHPCO of polyphenols present in OOMW.



**Figure 3.** HP consumption versus reaction time in WHPCO of polyphenols present in OOMW.

**Table 2.** COD Fractions of the Fresh and Treated OOMW

	COD <sub>TOT</sub> (gL <sup>-1</sup> )	COD <sub>SOL</sub> (gL <sup>-1</sup> )	BCOD (gL <sup>-1</sup> )	RBCOD (gL <sup>-1</sup> )	SBCOD (gL <sup>-1</sup> )	nonbiodegrad. COD (gL <sup>-1</sup> )
fresh	74.4	57.7	9.62	8.90	0.72	64.8
fresh <sup>a</sup>	74.4	57.7	38.7	16.0	22.7	35.7
treated	60.8	56.0	14.3	11.0	3.3	46.5
treated <sup>a</sup>	60.8	56.0	51.4	30.8	20.6	9.4

<sup>a</sup> With ammonium sulfate and potassium phosphate bihydrate.

pH value was stable and, finally, it decreased again down to 3.4 after 27 h (Figure 2).

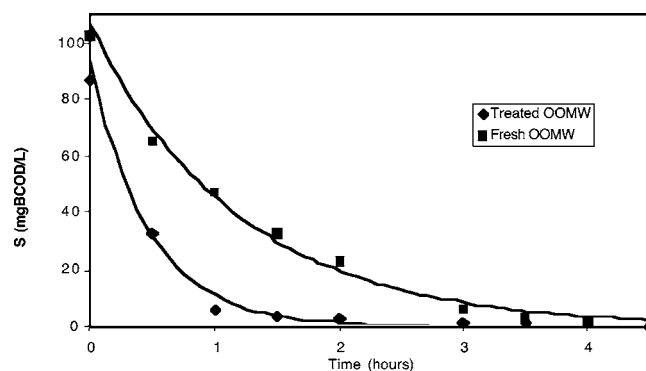
HP consumption at various reaction times was measured and the obtained results are reported in Figure 3. It can be seen that the highest amount of HP was consumed during the third hour of treatment, while from the 3rd to the 27th hour of the WHPCO there was only a 3.5% residual increase of HP consumption.

The polyphenol content after 27 h of oxidation decreased down to 0.10 g L<sup>-1</sup>, with a reduction with respect to fresh sample of 96%.

The recovery of catalyst was made by settling, but the amount of recovered catalyst available was too small for the "after reaction" characterization.

**COD Measurements and Kinetic Tests.** After the WHPCO of polyphenols, the catalyst-free reaction mixture was reanalyzed with respect to COD<sub>TOT</sub>, COD<sub>SOL</sub>, BCOD, RBCOD, and SBCOD. Both fresh and treated OOMW were also analyzed after setting the COD<sub>TOT</sub>/N/P ratio at the optimal value by adding ammonium sulfate and potassium phosphate bihydrate. The obtained results are reported in Table 2.

As expected, the respirometric results obtained on samples confirm the effective necessity of the addition of nitrogen and phosphorus to achieve complete biological oxidation; however, the fresh OOMW sample, also after the nutrient addition, shows a low biodegradability, and as matter of fact,



**Figure 4.** BCOD removing kinetic tests on the fresh and treated OOMW samples.

the nonbiodegradable COD fraction is 48% of COD<sub>TOT</sub> (Table 2).

After the WHPCO pretreatment, the biodegradability of the OOMW increased from 52 to 84.5%, with a COD<sub>TOT</sub> reduction of 18%. This is an interesting result, because it indicates the selectivity of HP with respect to nonbiodegradable compounds. The increase of RBCOD (from 16 to 30.8 gL<sup>-1</sup>) suggests that, after the chemical oxidation, the transformation of complex organic molecules into rapidly biodegradable organic acids took place. This is confirmed by the reduction of the pH during the reaction test (Figure 2). The SBCOD fraction remained almost equal (at 34%) after the WHPCO pretreatment.

After 3.5 h of chemical oxidation, an aliquot of the reaction mixture was analyzed with respect to COD<sub>TOT</sub>, and the obtained value was 58.0 gL<sup>-1</sup>. This value is practically equal to that measured after 27 h. From this result, it can be concluded that the oxidation reaction time of about 3.5 h is sufficient to obtain the maximum oxidation efficiency. As noted before, the HP consumption occurred only during the first 3 h of reaction (Figure 3).

In Figure 4, the results of kinetic tests for the BCOD removing are reported. The maximum specific growth rate ( $\mu_{max}$ ) and the half-saturation coefficient ( $K_S$ ) were evaluated by means of an interpolation on the basis of the Monod kinetics (20). The value of  $\mu_{max}$  for the fresh sample was 1.12 d<sup>-1</sup> and for the treated sample was 1.62 d<sup>-1</sup>, so the obtained increase after the oxidation treatment was at 45%. A positive effect was also obtained for  $K_S$ , which for the fresh sample was at 200 mgBCOD/L and for the treated sample was at 105 mgBCOD/L (with a reduction of about 50%). The half-saturation coefficient decrease suggests that the content of toxic substances was reduced after the oxidation treatment. This hypothesis can be verified carrying out inhibition tests. The BCOD removing rate was increased both by  $\mu_{max}$  increase as well as by  $K_S$  decrease. For instance, to obtain a 80 mg L<sup>-1</sup> reduction of BCOD, the fresh sample needs a 2-h treatment while for the treated sample 1-h treatment is enough.

This positive result can be observed in Figure 5; the reaction rate is higher for the treated sample and, in particular, the asymptotic value for the fresh sample was at 180 mg BCOD/Lh, while after the oxidation treatment this value is at 280 mg BCOD/Lh. This result is directly correlated to the necessary biological treatment time, which is significantly reduced in the case of the treated sample.

In conclusion, the experimental results showed that with the WHPCO process it is possible to improve significantly the biodegradability of the OOMW and that the Cu-MOF cat-

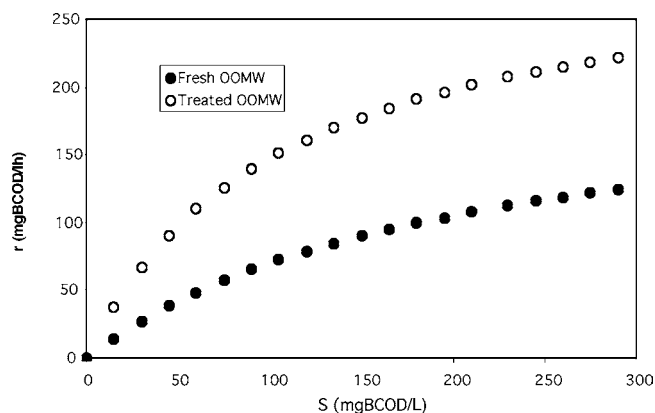


Figure 5. Monod kinetics rate for the fresh and treated OOMW samples.

alyst is selective with respect to nonbiodegradable compounds. In fact, this process increased the BCOD fraction from 52.0 to 84.5%, with a polyphenol abatement of 96%, and it showed also a significant reduction of other nonbiodegradable compounds and a small reduction of COD<sub>TOT</sub> (18%). The kinetic tests showed that, after the WHPCO, the BCOD fraction removing rate increased. This means that the biological treatment time is significantly reduced and that the OOMW can be sent to the biological treatment plant. The principal advantage of the use of the Cu-MOF heterogeneous catalyst, as an alternative to homogeneous Fenton reagent system (Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>), is the possibility to recover the catalyst and to reuse it.

#### LITERATURE CITED

- Yesilada, O.; Sik, S.; Sam, M. Biodegradation of olive oil mill wastewater by *Coriolus versicolor* and *Funalia trogii*: effects of agitation, initial COD concentration, inoculum size and immobilization. *World J. Microbiol. Biotechnol.* **1998**, *14*, 37–42.
- Debellefontaine, H.; Chakchouk, M.; Foussard, J. N.; Tissot, D.; Striolo, P. Treatment of organic aqueous wastes: wet air oxidation and wet peroxide oxidation. *Environ. Pollut.* **1995**, *92*, 155–164.
- Greagor, K. H.; Bigini, S.; Cavadore, A. Processo FSR: una nuova tecnologia Fenton per il trattamento delle acque reflue industriali. *Inquinamento* **1999**, *5*, 88–91.
- Centi, G.; Perathoner, S.; Torre, T.; Verduna, M. G. Catalytic wet oxidation with H<sub>2</sub>O<sub>2</sub> of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts. *Catal. Today* **2000**, *55*, 61–69.
- Lee, Y.; Lee, C.; Yoon, J. High temperature dependence of 2,4-dichlorophenoxyacetic acid degradation by Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> system. *Chemosphere* **2003**, *51*, 963–971.
- Kuznetsova, E. V.; Savinov, E. N.; Vostrikova, L. A.; Parmon, V. N Heterogeneous catalysis in the Fenton-type system FeZSM-5/H<sub>2</sub>O<sub>2</sub>. *Appl. Catal., B* **2004**, *51*, 165–170.

- Mantzavinos, D. Removal of cinnamic acid derivatives from aqueous effluents by fenton and fenton-like processes as an alternative to direct biological treatment. *Water, Air, Soil Pollut.* **2003**, *3*, 211–221.
- Schlichte, K.; Kratzke, T.; Kaskel, S. Improved synthesis, thermal stability and catalytic properties of the metal-organic framework compound Cu<sub>3</sub>(BTC)<sub>2</sub>. *Microporous Mesoporous Mater.* **2004**, *73*, 81–88.
- APHA-AWWA-WEF Standard methods for the examination of water and wastewater. *Am. Public Health Assoc. New York* **1992**.
- Mamais, D.; Jenkins, D.; Pitt, P. A rapid physical-chemical method for the determination of readily biodegradable soluble COD in municipal wastewater. *Water Res.* **1992**, *27*, 195–197.
- Bressan, M.; Liberatore, L.; D'Alessandro, N.; Tonucci, L.; Belli, C.; Ranalli, G. Improved combined chemical and biological treatments of olive oil mill wastewaters. *J. Agric. Food Chem.* **2004**, *52*, 1228–1233.
- Rivas, F. J.; Beltrán, F. J.; Gimeno, O.; Frades, J. Treatment of olive oil mill wastewater by Fenton's reagent. *J. Agric. Food Chem.* **2001**, *49*, 1873–1880.
- Bailey, M. J.; Biely, P.; Poutanen, K. Interlaboratory testing of methods for assay of xylanase activity. *J. Biotechnol.* **1992**, *23*, 257–270.
- Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu – Methods in Enzymology*; Academic Press Inc.: London, 1999; Vol. 299, pp 152–178.
- Copp, J. B.; Spanjers, H.; Vanrolleghem, P. A. Respirometry in control of the activated sludge process: benchmarking control Strategies. *IWA Scientific and Technical report No 11* **2002**.
- Ziglio, G.; Andreottola, G.; Foladori, P.; Ragazzi, M. Experimental validation of a single-OUR method for wastewater RBCOD characterisation. *Water Sci. Technol.* **2001**, *43* (11), 119–126.
- Wang, Q. M.; Shen, D.; Bülow, M.; Lau, M. L.; Deng, S.; Fitch, F. R.; Lemcoff, N. O.; Semancin, J. Metallo-organic molecular sieve for gas separation and purification. *Microporous Mesoporous Mater.* **2002**, *55*, 217–230.
- Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, J. D. A chemically functionalizable nanoporous material [Cu<sub>3</sub>(TMA)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>. *Science* **1999**, *283*, 1148–1150.
- Yaghi, O. M.; Li, G.; Li, H. Selective binding and removal of guests in a microporous metal-organic framework. *Nature* **1995**, *378*, 703–706.
- Henze, M.; Harremoës, P.; Jansen, J. I. C.; Arvin, E. *Wastewater treatment, biological and chemical processes*, Ed.; Springer-Verlag: Berlin Heidelberg, 1995.

Received for review May 30, 2005. Revised manuscript received July 29, 2005. Accepted August 1, 2005. The authors thank the PRIN 2004 project “New eco-sustainable catalytic processes based on the synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub>/O<sub>2</sub> and its integrated use in selective oxidation and depuration of emission processes” for partial financial support.

JF0512609