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Wet hydrogen peroxide catalytic oxidation of olive oil mill wastewaters using Cu-zeolite and Cu-pillared clay catalysts

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Abstract

The use of catalysts to improve the performances of water treatment technologies is well known; in the last years more scientific attention was given to the treatment of the olive oil mill wastewaters. This problem affects especially the Mediterranean area because this region is the largest world olive oil producer. In this paper, the results of the wet hydrogen peroxide catalytic oxidation on olive oil mill wastewaters using Fenton-like type catalysts (Cu-Silicalite-1 and Cu-pillared clay) are presented. Both the catalysts showed a high conversion in the oxidation of poly-phenols and were able to drastically reduce the chemical oxygen demand, the biochemical oxygen demand and the non-biodegradability of the olive oil mill wastewaters.

Keywords: Cu-zeolite and Cu-pillared clay catalysts; OOMW; Biodegradable COD; WHPCO

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1. Introduction

The actual industrial processes for the production of olive oil, based on the olive milling, cause a large amount of wastewaters, more than 10^7 m^3/year [1]. In the last years the world productions ranged from 2.5 to 3.0 millions of tonnes (3.0 in 2004 and 2.58 in 2005). The Mediterranean region is the largest olive oil producer in the world (2005 production: Spain 880×10^3 tonnes, Italy 600×10^3 tonnes, Greece 424×10^3 tonnes, Morocco, Tunisia and Syria from 100 to 200×10^3 tonnes) [2]; consequently in this area there is a considerable production of olive oil mill wastewaters (OOMW). Due to the presence of phytotoxic compound, such as poly-phenols, the OOMW is not biodegradable, and, as a result, the direct biological treatment is not recommended. Many techniques have been proposed for the OOMW treatment, such as catalytic wet oxidation, ozonation, photo-catalysis, etc. [3–5], but probably the combination of a catalytic oxidation followed by a usual biological treatment is an interesting answer [6]. The main disadvantages of catalytic wet oxidation or photo-catalysis methods are the high cost of the reactor and the not easily manageable process. Different papers in the literature report the good performances of Fenton-like catalysts in the oxidation of poly-phenols [7–11]. The Fenton mechanism uses iron or copper ions as catalyst that react with hydrogen peroxide (HP) in order to generate hydroxyl radicals [12]. The main disadvantages of the homogeneous Fenton catalysts are: the need of recovering iron or other transition metal used after the catalytic treatment, the side reactions such as the oxidation and the complexation of the reduced transition metal ions [8], and the high cost of the HP reactant. This last problem can be solved by the new advanced in situ direct synthesis of HP from a hydrogen/oxygen mixture [13,14]. The use of solid Fenton-type catalysts as an alternative to the homogeneous salts in solution could limit these disadvantages, because of the easy recover of the catalyst after the oxidation treatment, of the low contamination of the effluents with metals which negatively influence the successive biological treatment step and of the wide operative pH range [8]. The development of the solid Fenton-type catalysts has recently obtained great

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research efforts. Zeolites containing transition metal [12,15], copper-montmorillonites [16], iron containing pillared clays [17,18] and metal organic framework [19] have been presented as active catalysts for the oxidation of different organic compounds. These catalysts show a good rate of conversion of the pollutants and especially exhibit marginal leaching of the cations, and they also maintain their activity during several reaction runs [17,18]. Various authors clearly show the contribution of heterogeneous catalysis using the Fenton-like catalysts [11,20–22].

The aim of this work is to study the copper-based zeolite and pillared clay catalysts performances in the poly-phenols degradation. The Fenton-like heterogeneous catalysts will be tested on real OOMWs by the wet hydrogen peroxide catalytic oxidation (WHPCO) reaction. This reaction is an interesting process for the phyto-toxicity reduction, due to the mild operating conditions and to the high activity of Fenton-like catalysts for the poly-phenols degradation [23]. In this paper the synthesis of Cu-Silicalite-1 zeolite type and of Cu-pillared clay catalysts, the leaching showed by the catalysts, and, finally, their catalytic behavior for the WHPCO of OOMWs are presented.

2. Experimental

2.1. Catalyst synthesis and characterization

The Cu-Silicalite-1 zeolite catalyst was obtained by direct hydrothermal synthesis. The molar composition of the starting hydrogel system was $0.12Na_2O–0.08TPABr–1SiO_2–0.02Cu(NO_3)_2/0.06H_3PO_4–wH_2O$, were w is the distilled water molar content. The sources of materials used were: precipitated silica (BDH) or fumed silica (F200), copper nitrate tri-hydrate, phosphoric acid, distilled water and the organic compound TPABr (tetrapropylammonium bromide). Due to the different solubility of silica sources, in order to obtain in fast time the complete homogenization of the starting hydrogel, it was used 20 or 40 mol of water (w) for BDH and for F200 silica source, respectively.

Two Cu-Silicalite-1 samples were prepared: the (Na)S1 sample was synthesized using BDH silica source and ageing the total starting hydrogel for 3 days at 80 °C; the (Na)S2 sample was obtained using F200 silica source, ageing the sodium-organic-silica hydrogel for 3 days at 80 °C and then adding the phosphoric acid/copper solution. The synthesis temperature to obtain the desired zeolite is 170 °C, under autogenously pressure, hydrothermal static condition and a crystallization time of 1 day. Both the Cu-Silicalite-1 samples were activated by calcination at 550 °C (reached at 2 °C/min) for 5 h in air flow. A part of the (Na)S2 calcined catalyst was treated with 1 M NH_4Cl solution at 80 °C for 2 h in order to obtain the zeolite in the protonic form. The exchange procedure was repeated twice and afterwards the sample was re-calcined, obtaining the named (H)S2 sample.

The Cu-pillared clay (Cu-AZA) catalyst was prepared by pillaring procedure of a clay (commercial bentonite from Sigma–Aldrich), using a diluted aqueous solution of NaOH containing Al^{3+}/Cu^{2+} ions [24]. The cationic solution containing respectively 0.18 and 0.02 mol/l of $AlCl_3$ and $CuCl_2$ was prepared by slow addition of a 0.2 M NaOH solution to the solution containing the metal salt up to arrive to an OH/metal ratio of about 2 under constant stirring at a temperature of 70 °C. Then the intercalating solution was added very slowly at room temperature to the previously prepared aqueous suspension of the clay (2 wt.%). The final ratio (Al + Cu)/clay was 3.8 mol/kg. After an ageing period of 20 h in the presence of the mother liquor, the solid was recovered by filtration. It was then washed for a long time with distilled water till complete elimination of Cl^- ions from the washing solution. The solid was then dried at 70 °C and calcined at 500 °C (reached at 2 °C/min) for 2 h. The preparation was well reproducible.

Both zeolite and pillared clay 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. The copper content of all the samples was measured by a Perkin Elmer ELAN DRC-e inductively coupled plasma mass spectroscopy (ICP-MS), and the BET surface areas were obtained by the N_2 adsorption/desorption analysis at 77 K using an ASAP 2020 Micromeritics instrument, after overnight activation in vacuum.

2.2. Olive oil mill wastewaters

The fresh OOMW effluents were obtained from three phase continuous oil mill plants, located in Calabria (southern Italy) and using olives from the Carolea *cultivar* type. Fresh samples were stored in plastic containers and kept in the dark at 4 °C, and, when necessary, aliquots of crude OOMW were diluted with distilled water to the required values.

2.3. Catalytic tests

The reaction tests were carried out in a thermostated stirred batch reactor. The (Na)S1 and the (H)S2 samples were used to oxidize the poly-phenols contained in the OOMW-1, while the (H)S2 sample was used for the OOMW-2 oxidation, and the Cu-AZA sample for the OOMW-3 oxidation. As a function of the catalyst, an amount of 0.6 g/l OOMW (Cu-Silicalite-1) or 5 g/l OOMW (Cu-AZA) was used at 50 °C (Cu-Silicalite-1) or at 80 °C (Cu-AZA) and atmospheric pressure. The solution of hydrogen peroxide (HP, 35%, w/w) was added step by step in the case of OOMW-1 and OOMW-2. The HP solution amount was determined assuming that the total chemical oxygen demand (COD_{TOT}) of OOMW is totally due to phenol (model compound) and setting the HP/phenol molar ratio to 10. The obtained value was divided into 11 steps and periodically added (2 min time interval) to the heated OOMW. In the case of OOMW-3, the HP solution was added with a peristaltic pump at a rate of 0.5 ml/h.

The Cu-AZA catalyst was also used to oxidize a 500 mg/l solution of *p*-coumaric acid, at 80 °C, atmospheric pressure, with an HP addition rate of 0.5 ml/h and 5 g/l of catalyst.

The reaction time was at least of 3 h. During the HP addition and during the reaction test, both temperature and pH of the reaction mixture were continuously monitored. At the end of the reaction test, the catalyst was recovered from the reaction mixture by centrifugation and re-characterized before the next use.

2.4. Analytical methods

Analyses of total chemical oxygen demand (COD_{TOT}), soluble COD (COD_{SOL}) and total suspended solids (TSS) of OOMW-1 and OOMW-2 were determined using standard methods for the examination of water and wastewater [25]. The COD_{SOL}, in particular, was measured by means of a flocculation pre-treatment, as proposed by Mamais et al. [26]. In order to avoid the positive interference derived from the presence of HP in COD measurement of the treated OOMWs [27,28], the residual HP was eliminated by an adequate chemical treatment (with K_3RuCl_6) of the samples prior to the analysis. The fresh and treated OOMW-1 and OOMW-2 samples were analyzed respect to the biodegradable COD (BCOD), the rapidly biodegradable COD (RBCOD), the slowly biodegradable COD (SBCOD) and the not-biodegradable COD (nonbiod.COD) by respirometric methods [29,30], and to copper content by ICP-MS. 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^3, continuously stirred and provided of a probe for the measurement of the dissolved oxygen and temperature. The total poly-phenols content was measured both in the fresh and treated OOMW-1 and OOMW-2 samples.

The fresh and treated OOMW-3 were characterized respect to COD_{TOT}, total organic carbon (TOC) and total poly-phenols. The TOC of the solution was determined with a TOC analyzer mod. 5000 A (Shimadzu).

The determination of poly-phenol compounds is obtained by the Folin–Ciocalteau method, based on the use of the Folin–Ciocalteau reagent, an aqueous mixture of phosphotungstic acid ($H_3PW_{12}O_{40}$) and phosphomolybdic acid ($H_3PMo_{12}O_{40}$) that forms a tungsten and molybdenum oxides mixture (W_8O_{23} and Mo_8O_{23}) by oxidation of phenols. This blue mixture after 2 h shows a maximum absorption peak at 765 nm. The total content of poly-phenol compounds is expressed as concentration of gallic acid (ppm-g.a.).

The concentration of the HP at various reaction times was determined by a modified iodometric titration method, using a solution of potassium iodide, sulphuric acid and ammonium-molibdate. The HP first oxidizes iodide to iodine and this is further titrated by sodium thiosulphate. Starch may help in the indication of the endpoint, if added when the dark color of iodine is hardly seen [31].

3. Results and discussion

3.1. Characterization of the catalysts

In Fig. 1, the XRD patterns of the (Na)S1 and (Na)S2 zeolites are reported. They correspond exactly to the XRD pattern characteristic of a MFI type zeolite structure. Both the (Na)S1 and (Na)S2 samples showed brick-shape crystals, with a uniform morphology and size, as can be observed in the SEM images reported in Fig. 2. The (Na)S1 sample, in particular, has a crystals dimension of about 20 μm × 20 μm, while the sample (Na)S2 of about 2 μm × 1 μm. The difference in crystals dimension can be attributed to the different ageing method used to prepare the two zeolites, while the different silica sources do not influence the crystal size.

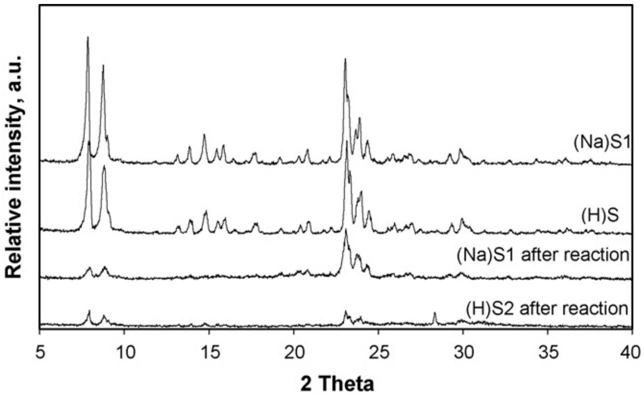

Fig. 1. XRD patterns of Cu-Silicalite-1 zeolites before and after reaction test.

The copper and silicon contents in the (Na)S1, (Na)S2 and (H)S2 zeolites, measured by the ICP-MS, are reported in Table 1. The Si/Cu molar ratio in the starting hydrogel system was at 50 for all samples. The values of Si/Cu molar ratio in the (Na)S1 and (Na)S2 zeolites are related with the theoretical value of the starting hydrogel systems. In the (Na)S2 sample the copper content is of about 4% higher than that of the (Na)S1 sample. This is probably due to the different procedures used for the preparation. As can be noted in Table 1, the copper content in the (Na)S2 sample is drastically reduced after the ionic exchange treatment to obtain the zeolite protonic form, (H)S2. The copper leaching during the ionic exchange is at about 71% and this is probably due to the acid pH of the ionic exchange solution (at 4.63). BET surface areas were at about 370 m^2/g for both (Na)S1 and (Na)S2 samples.

The XRD pattern of the Cu-AZA sample is reported in Fig. 3, while the Cu-AZA SEM image is showed in Fig. 4. The content of copper in the Cu-AZA catalyst was 2.0 wt.% (Table 1), and the surface area was at 107 m^2/g.

3.2. Characterization of the OOMW samples

The chemical parameters of the fresh OOMW samples are reported in Table 2.

The OOMW-1 sample was characterized by a relatively low COD_{TOT}, because it was left in a settler for about 1 year. During this period of time, the suspended fraction of the OOMW was partially decanted and a natural fermentation process occurred, causing the COD reduction [27]. The OOMW-2 is, instead, a wastewater just produced and it is in fact characterized by a COD value typical of an OOMW. The OOMWs were chosen with different COD in order to test how the pre-treatment oxidation process is influenced by the starting organic substrate concentration. As it can be observed from the concentration of

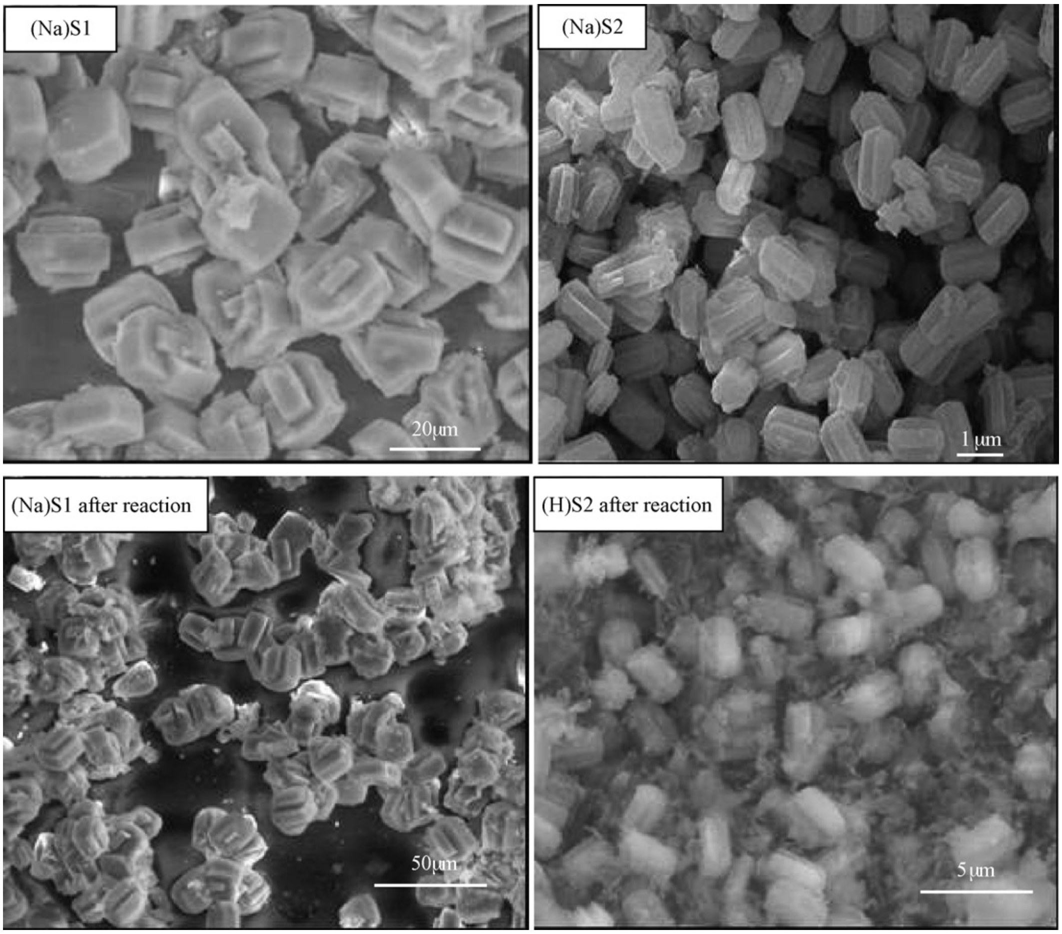

Fig. 2. SEM images of Cu-Silicalite-1 zeolites before and after reaction test.

the total suspended solids, a settling pre-treatment of the OOMW-2 was not advantageous. The OOMW-3 was characterized by an intermediate poly-phenols content and TOC value, but by a very high COD_{TOT} value. In order to thoroughly analyze the reactivity data, the solid suspended matter of OOMW-3 was removed sieving the wastewater at 400 mesh.

3.3. Catalytic tests

3.3.1. OOMW-1 and OOMW-2 oxidation tests

The total HP amount during the chemical oxidation processes carried out on the OOMW-1 and OOMW-2, as said, was added step by step. During the HP addition (20 min long), the pH of the reaction mixture underwent a little decrease for both OOMW-1 and OOMW-2, varying between 5.2 and 5.1 for OOMW-1 and 4.6 and 4.2 for OOMW-2.

Table 1
Cu and Si content in the Cu-Silicalite-1 zeolites and Cu content in the Cu-AZA sample

Sample	Cu (wt.%)	Si/Cu (mol/mol)
(Na)S1	2.25	47.1
(Na)S2	2.34	45.3
(H)S2	0.68	155
Cu-AZA	2.0	

Due to the difference in the poly-phenols amount, the total reaction time was of 3 h for OOMW-1 and of 21.5 h for OOMW-2.

The OOMW-1 was treated using the (Na)S1 and the (H)S2 samples, in order to evaluate the most active and efficient catalyst between the two Cu-Silicalite-1 samples. The poly-phenol abatement after 3 h of reaction was at 97% and 94.5% respectively with (Na)S1 and (H)S2. The OOMWs after the reaction tests were analyzed respect to copper content by ICP-MS and the results showed a higher copper leaching occurred to

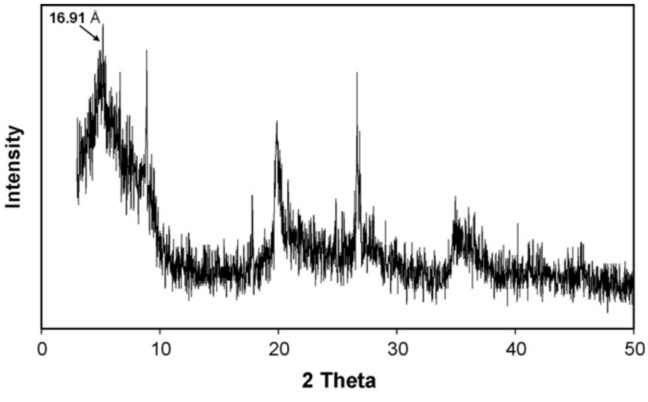

Fig. 3. XRD pattern of Cu-AZA.

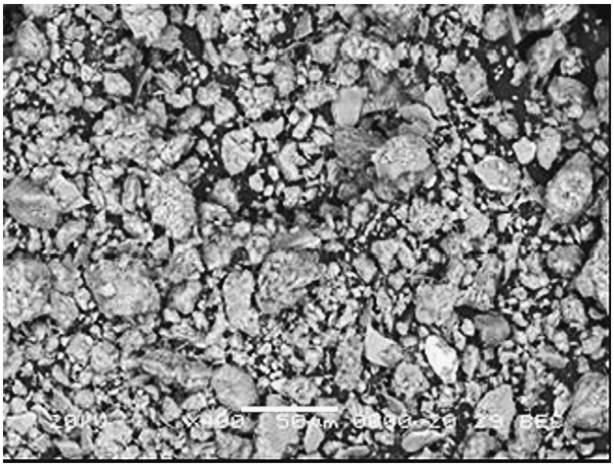

Fig. 4. SEM image of Cu-AZA.

the (Na)S1 (about 23 wt.%) respect to the (H)S2 sample (7 wt.%). Due to this result, the OOMW-2 (higher COD_{TOT} and poly-phenol respect to the OOMW-1) was oxidized with the (H)S2 catalyst, that showed a high catalytic efficiency respect to the poly-phenol abatement and, especially, a higher copper stability respect to the (Na)S1 sample. The Cu-leaching results indicate that a dilution factor ranging between 1.5 and 2.5 can be used to obtain the copper content at the accepted limit of 0.4 mg_{Cu}/l [32].

The HP concentration was measured at different reaction times, and the HP consumption was calculated considering that the starting value is the one measured at the end of the HP addition. The values obtained are shown in Fig. 5. During the pre-treatment test done on the OOMW-1 with the (Na)S1 sample, the HP was consumed up to 12%, and the HP consumption is near to be linear versus reaction time. In the case of the OOMW-2, instead, between the first and the fifth hour of reaction test there was the most of the HP consumption (ranged between 2% and 10%), while during the rest of the reaction test only a little amount of HP was still consumed (at 21.5 h about 12% of HP consumption).

The poly-phenol content was reduced of about 97% (after 3 h of oxidation test) and 92% (after 4.5 h of oxidation test) for the OOMW-1 (with (Na)S1) and OOMW-2, respectively. When the OOMW-1 was treated with the (Na)S1 catalyst, the copper content was at 13.5 $mg_{Cu\text{-}CAT}/l_{OOMW}$ (see Table 1). In the case of the OOMW-2, the used catalyst was the (H)S2 sample, so the copper content was so at 4.1 $mg_{Cu\text{-}CAT}/l_{OOMW}$ (see Table 1). Despite to the lower copper content, also in the case of OOMW-2 oxidation test, the obtained poly-phenol abatement was higher than 90%. This result suggests to suppose that the copper contained in the (H)S2 catalyst is totally active for the oxidation reaction, also considering that, particularly in the case of the OOMW-2, the nominal value of the poly-phenol content is about 10-times higher than that of the OOMW-1.

At the end of each reaction tests, the catalyst was separated from the treated OOMW by centrifugation at 7000 rpm for 7 min. The recovered materials were re-characterized in order to evaluate if they underwent any damage. The XRD patterns confirm in both cases that the crystal structure of the Cu-Silicalite-1 catalysts was not varied after the catalytic test, as reported in Fig. 1. The decrease in the peak intensity is probably due to the presence of organic materials deposit from OOMW on the catalyst surface. A confirmation of this hypothesis is given from the SEM images of materials recovered after the

Table 2
Chemical parameters of the fresh OOMW samples

Parameters	Unit	Values			
		OOMW-1	OOMW-2	OOMW-3	OOMW-3 sifted (400 mesh)
COD_{TOT}	g/l	8.23	87.6	124	117
COD_{SOL}	g/l	3.54	52.5		
Poly-phenols	g/l	0.42	3.6	2.77	2.38
TSS	g/l	4.6	60.4		
pH	–	5.25	4.61	4.5–5.5	4.5–5.5
TOC	g/l		26.35	28.00	20.36

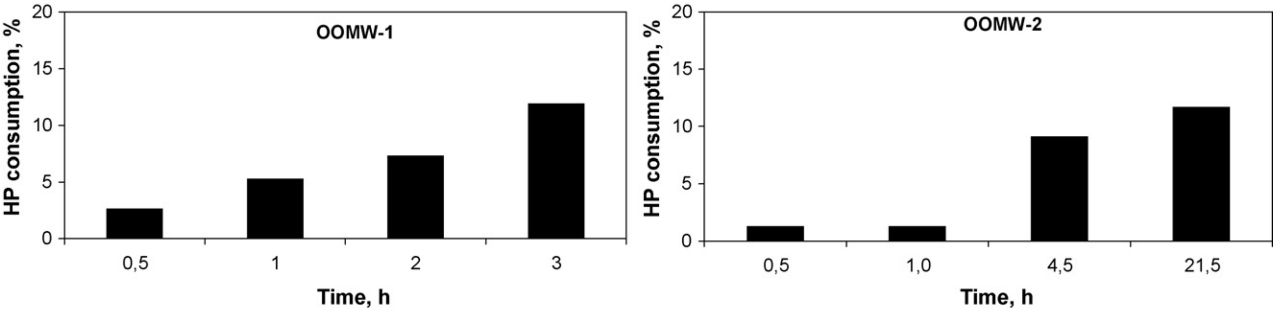

Fig. 5. HP consumption vs. reaction time during the OOMW-1 and OOMW-2 oxidation tests.

Table 3
COD fractions of the fresh and oxidized OOMW-1 and OOMW-2

	COD_{TOT} (g/l)	COD_{SOL} (g/l)	BCOD (g/l)	RBCOD (g/l)	SBCOD (g/l)	nonbiod.COD (g/l)
OOMW-1	8.2	3.5	3.7	1.4	2.3	4.5
OOMW-2	87.6	52.5	28.2	27.2	1.0	59.4
OOMW-1 (180 min)[a]	1.04	0.78	0.78	0.78	0	0.26
OOMW-2 (270 min)[a]	19.4	19.1	18.5	12.9	5.6	0.9

	COD_{TOT}	COD_{SOL}	BCOD	RBCOD	nonbiod.COD
Reduction (%)					
OOMW-1 (180 min)[a]	87.3	77.7	78.9	44.3	94.2
OOMW-2 (270 min)[a]	77.8	63.6	34.4	52.6	98.5

[a] After oxidation treatment.

catalytic tests reported in Fig. 2, in which is showed that the zeolite morphology remains the same of the as-made form for both catalysts.

The fresh OOMW-1 and OOMW-2 were analyzed with respect to COD_{TOT}, COD_{SOL}, BCOD, RBCOD, SBCOD, and non-biodegradable COD, after setting the COD_{TOT}/N/P ratio at the optimal value by adding ammonium sulphate and potassium phosphate bi-hydrate. The obtained results are reported in Table 3. The OOMW-2 has a COD_{TOT} value 10-times higher than the OOMW-1, and it is also characterized by a non-biodegradable fraction of 67.8%. In the case of the OOMW-1, instead, the non-biodegradable fraction is at 55%. For the OOMW-2 the RBCOD is the 96.5% of the BCOD. The high value of RBCOD, due to the presence of low molecular weight carboxylic acids (such as acetic acid), could justify the low pH value measured for the OOMW-2 (at 4.6). Even to its low COD_{TOT} value, the OOMW-1 showed a high SBCOD if compared to the OOMW-2, for which, instead, the SBCOD could be neglected respect to its COD_{TOT}.

The treated OOMW-1 and OOMW-2 were analyzed with respect to COD_{TOT}, COD_{SOL}, BCOD, RBCOD, SBCOD, and non-biodegradable COD, and the obtained results were reported in Table 3. For the OOMW-1 and OOMW-2 a COD_{TOT} fractions of 7.16 g/l (87.3%) and 68.2 g/l (77.8%) were respectively oxidized. It can be observed that the (H)S2 catalyst showed a good oxidation activity for the COD_{TOT} abatement. For the OOMW-1 the COD_{SOL}/COD_{TOT} ratio increased from 43% to 75% after the treatment; for the OOMW-2 it increased from 60% to 98.5%. These results show that the particulate fraction of both the OOMWs is almost totally oxidized.

Regarding the BCOD (see Table 3), for the OOMW-1, it is exactly equal to the soluble fraction and to RBCOD, so the slowly BCOD is near to zero. For the OOMW-2, the BCOD is constituted of the most part of RBCOD and of an SBCOD part. The SBCOD, in particular, is increased respect to the value of the fresh OOMW-2 (from 1.0 to 5.6), and this result can be explained by a partial conversion of the non-biodegradable COD into SBCOD components.

The better performances of the (H)S2 catalyst respect to the (Na)S1 catalyst can be noted also for the RBCOD and non-biodegradable COD abatements, especially in terms of nominal value reduction of organic substrate. As a matter of fact, in the case of the OOMW-2, the RBCOD was reduced of 14.3 g/l (52.6%), versus the RBCOD reduction of 0.62 g/l (44.3%) obtained for the OOMW-1 with the (Na)S1 catalyst. The non-biodegradable COD reduction, for the OOMW-2 was of 58.5 g/l (98.5%), while for the OOMW-1 it was of 4.24 g/l (94.2%).

The RBCOD values versus reaction time were reported in Fig. 6. As can be noted, after a reaction time of 30 min the RBCOD reduction was at 47% for OOMW-1 and at 63% for OOMW-2; in both cases after 30 min an increase in RBCOD value was observed. This result suggests that after 30 min only the conversion of the SBCOD and non-biodegradable COD into RBCOD probably occurs, and the complete organic substrate oxidation does not take place. The gain in terms of RBCOD after 30 min is not so relevant to justify a higher reaction time. For these reasons, 30 min can be considered as the optimal reaction time value.

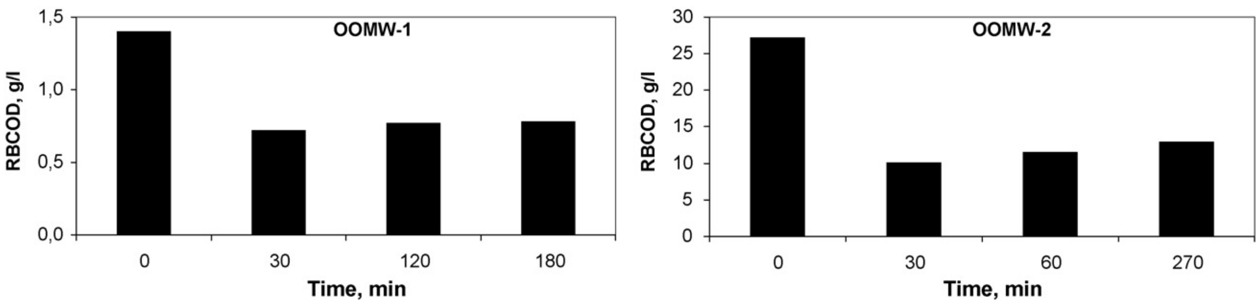

Fig. 6. RBCOD vs. reaction time for OOMW-1 (treated with (Na)S1) and for OOMW-2 (treated with (H)S2).

3.3.2. Re-use of the catalyst (Na)S1

The (Na)S1 catalyst recovered after the first reaction cycle and after a re-calcination cycle was used again for the OOMW-1 oxidation. The second reaction cycle was carried out for 3 h. The COD_{TOT} oxidized was at 84.5%, while during the first reaction cycle it was at 87.3%. The HP consumption after 3 h was of 24.8%, so it was higher than the one observed during the first cycle (7.3%). The poly-phenol abatement obtained during the second reaction cycle (80%) decreased respect to the one measured after the first reaction cycle (97%). The lower COD_{TOT} and poly-phenol abatement resulted during the re-use of the (Na)S1 sample is probably due to the reduction of the Cu present in the catalyst after the first reaction cycle, caused by the partial copper leaching occurred.

3.3.3. OOMW-3 oxidation test

The OOMW-3 was treated using Cu-AZA catalyst. The experiments were carried out at 80 °C adding the HP continuously in a minimum amount (0.5 ml/h) in order to prevent squandering of the oxidant and the presence of residual HP after the reaction cycle, which causes problems in the subsequent biological treatment, if the oxidation process is integrated.

The TOC abatement was at 13.5% after 6 h. The maximum poly-phenols removal after 6 h of reaction with Cu-AZA was only at 45%, showing that this catalyst has a lower catalytic activity respect to the Cu-Silicalite-1 type.

In the overall catalytic performances comparison between Cu-zeolites and Cu-pillared clays, it must be considered that the lower activity of pillared clays is compensated by the absence of Cu leaching, which improves the possibility of catalyst re-use. In fact, using a 500 mg/l solution of *p*-coumaric acid as model compound for poly-phenols present in OOMW, in three consecutive reaction cycles, after filtration and drying at 80 °C of the Cu-AZA catalyst, with an HP addition rate of 0.5 ml/h and with a catalyst amount of 0.5, 0.3 and 0.2 g, a near constant TOC removal (83, 75, and 75%, respectively) was observed, even if the total amount of catalyst decreased.

4. Conclusions

The Cu-Silicalite-1 catalysts showed a high catalytic activity respect to the non-biodegradable compounds (poly-phenol) and also to the organic substrate. An elevated COD_{TOT} abatement was, in fact, observed for both OOMW-1 and OOMW-2. After a re-calcination treatment, the zeolites were re-used for a second reaction cycle, and they show good results. A partial copper leaching was observed, but the value of metal concentration in the treated wastewater can be settled at the accepted limit ($0.4\ mg_{Cu}/l$) [32] with a dilution factor (such as 2.5) usual in the wastewater plants.

The Cu-AZA catalyst showed minor performances in TOC abatement and in the poly-phenol degradation compared to zeolitic samples, but it can be re-used for several reaction cycles, because it showed no copper leaching during the oxidation reactions.

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