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A catalytic oxidation process of olive oil mill wastewaters using hydrogen peroxide and copper

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ABSTRACT

The Mediterranean region is the largest olive oil producer in the world, consequently in this area olive oil mill wastewaters have a high seasonal pollution potential. Due to the presence of phyto-toxic compounds, such as poly-phenols, the olive oil mill wastewater is not easily biodegradable, and, therefore, the direct biological treatment is not recommended. Many techniques have been proposed for the their treatment, such as catalytic wet oxidation, ozonization, photo-catalysis, etc., among which, the catalytic oxidation seems to give good results. The present paper reports the results of an experimental investigation carried out with the aim to define a new catalytic oxidation process with hydrogen peroxide using copper-based catalyst, able to reduce the phyto-toxicity of olive oil mill wastewaters and to recover the catalyst after oxidation treatment. The experimental results have showed that, operating in a slurry type reactor at mild operating conditions, it is possible to reduce the organic chemical oxygen demand down to 10% and the poly-phenols amount of wastewater down to 1%. Therefore, the process is able to increase the rapidly biodegradable substrate content up to 80%, to remove color and total suspend solid amount and to minimize the metal loss of the catalyst after oxidation process, with a recover of about 80% with respect to its initial amount, permitting to reuse it for a long life cycle.

Keywords: Catalytic oxidation; Copper; H_2O_2; Poly-phenols

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1. Introduction

Olive oil production implies a large amount of wastewaters. The Mediterranean region is the largest olive oil producer in the world, consequently in this area OOMW represent a high seasonal pollution potential. Due to the presence of phyto-toxic compounds, such as poly-phenols, the OOMW are hardly biodegradable and able to lead to the complete inhibition of activated sludge processes [3,4,14,30]. So these wastewaters cannot be discharged to traditional wastewater treatment plant without a suitable pre-treatment [23]. Many techniques have been proposed for the removal of phyto-toxic compounds such as wet and catalytic wet air oxidation, ozonization, photo-catalysis, Fenton and photo-Fenton etc. [2–4,6,10,12,16,18,20,21,24,25,30,31]. Among these techniques catalytic oxidation processes using hydrogen peroxide (Fenton and Fenton-like processes) give good results for the removal of various classes of organic pollutants. In fact the catalysed hydrogen peroxide decomposition results in the formation of highly reactive free radicals, particularly hydroxyl radicals, which are capable of oxidizing many organic pollutants to lower molecular weight compounds and eventually to carbon dioxide and water [22].

Esplugas have been studied and compared the effectiveness of different advanced oxidation processes, (ozone and its combination, photolysis and UV/H_2O_2, Fenton and photocatalysis) for the degradation of phenol in aqueous solution demonstrating as Fenton process is

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characterized by the fastest degradation rate [13]. Furthermore, several researches have been carried out with the aim to investigate the use of other transition metals, in homogeneous and heterogeneous form, in conjunction with hydrogen peroxide to treat hardly biodegradable compounds [5,8,17,22,26,28,29]. In particular Mantzavinos demonstrated that the H_2O_2–Cu^{II} system is generally more effective than the typical Fenton process (H_2O_2–Fe^{II}) [22], in agreement with Pecci [26], showing, beside, how the TOC removal rates increase with the increase of process temperature between 25° and 80 °C.

However, while traditionally Fenton process using a ferrous salt, has been tested also as a raw OOMW treatment technology [2,3,23], homogenous system using copper as catalyst has been applied generally on artificially prepared wastewaters.

In the present paper the authors report the results of an experimental investigation carried out on raw wastewaters with the aim to define a catalytic oxidation process with hydrogen peroxide and copper as catalyst, able to reduce the organic load and the phyto-toxicity of OOMW. For this purpose, several tests were carried out to identify the optimal chemical reagents amounts, and the process temperature. With the operating conditions defined, at the end of the catalytic oxidation, without further operations, it is possible to recover, in powder form, about 80% of initial catalyst amount that can be reused for subsequent raw OOMW oxidation treatments. In this way is possible to greatly reduce the costs of catalyst consumptions and to avoid the formation of a large volume sludge that, instead, is generally produced in traditionally Fenton process due to the catalyst removal carried out by chemical flocculation.

The process, reducing the COD content by almost 90%, removing the poly-phenols amount and increasing OOMW biodegradability allows their disposal to the municipal wastewater treatment plants. This was confirmed by several respiration inhibition tests that demonstrated how the toxicities of raw OOMW were almost completely removed after catalytic oxidation.

2. Experimental investigations

2.1. Catalytic tests

Experimental investigations were carried out on OOMW collected from a continuous process. The OOMW samples, stored at 4 °C, were analyzed with the respect to the main chemical parameters (Table 1) and the wastewater biodegradability.

Batch catalytic tests were carried out at atmospheric pressure in three neck glass flask of about 1000 ml capacity, equipped with mechanic stirrer. The reactor was thermostated by means of a digester supplied by Carlo Erba and provided with water refrigerating coil to avoid the volatilization of organic matter compounds. Experimental investigations were carried out on raw not filtered wastewater and, being the OOMW enough acid, without pH adjustment. In this way it was possible to reduce the chemical additions and avoid the production of a high concentrated waste that should be separately treated. During each tests, a volume of about 750 ml of reaction mixture, was prepared by adding, to the OOMW samples, different amounts of a hydrogen peroxide solution at 35% (w/w) and a copper nitrate solution at 30% (w/w). The solution was heated up to the desired temperature and stirred for about three hours. A temperature probe housed inside a glass tube was used to control the liquid phase temperature. The process effectiveness was evaluated by monitoring the COD and poly-phenols amounts on treated OOMW. Besides hydrogen peroxide an copper concentrations were determined.

Table 1
Chemicals parameters of OOMW

Parameter	Unit	Value
pH	–	4.73
COD	gO_2/l	34.3
SCOD	gO_2/l	16.7
TBC	gO_2/l	13.1
RBC	gO_2/l	1.96
TP	g gallic a./l	1.1
$N–NH_4^+$	mg/l	37.2
$N–NO_2^-$	mg/l	1.0
$N–NO_3^-$	mg/l	21.0
$P–PO_4^{3-}$	mg/l	2.73
TSS	g/l	21.1
VSS	g/l	15.8

2.2. Analytical methods

Analyses of COD, copper, nitrogen compounds (NH_4^+–N, NO_2^- N, NO_4^3 –N), reactive phosphorus (NO_4^{3-}–P), TSS and VSS were carried out according to standard methods [1]. The pH was controlled by means of a Hanna pH-meter. The SCOD was assessed by means a flocculation pretreatment as proposed by Mamais [19], the poly-phenols content according to Folin-Ciocalteau's method [15] and hydrogen peroxide amount by iodometric titration method [5,12]. On treated samples, to avoid the positive interference in COD measurement derived from the presence of H_2O_2, [4,18] the residual peroxide was eliminated by adjusting the pH to 11 and heating at 100 °C the corrected solutions for one hour. This operation was carried out in flasks provided with adeguate condenser (equipments for COD analysis) to avoid possible loss or volatile compounds.

The TBC and RBC were determined by means of respirometric tests [9,32] conducted in a Chemitec S250 OUR test, which consists of a thermostated and aerated (without oxygen exchange with ambient) batch reactor of 500 ml, magnetically stirred and provided of a probe for the measurement of the dissolved oxygen and temperature.

The same equipment has been used to assess the inhibitory effects of fresh and treated OOMW on suspended biomass activity. For this purpose activated sludge samples were mixed with different volumes of raw and treated wastewaters (10–200% volumetric dilutions) and aerated for about 12 h. After this period the test mixtures were transferred to the respiration vessel and fed with a suitable amount of sodium acetate before OUR estimation. For each test, the percent inhibition was calculated by comparing the OUR value to the rate of a control test carried out by adding only acetate to biomass, without any wastewater addition. All respirometric investigations were carried out at constant temperature (20 ± 2 °C), using activated sludge samples directly withdrawn from the aeration tank of domestic wastewater treatment plant in Cosenza (Italy).

3. Results and discussion

3.1. Definition of operation conditions

The OOMW used in this work were characterized by an organic matter content of about 34.3 gCOD/l with a soluble fraction of 49% and the biodegradable and rapidly biodegradable fractions of 39.5% and 5.7% respectively (Table 1). The ammonium nitrogen and reactive phosphorus concentrations were low if compared to organic load, the poly-phenols content higher than 1 g/l and pH less than 5 (Table 1). The first investigations were carried out with the aim to identify the optimal catalyst and hydrogen peroxide amounts for the treatment. Using a DCu value of 500 mg/l [11] and a r_{HC} ratio between 1 and 11, in each test carried out heating the reaction solutions up to 100 °C, almost a complete reduction of TP was observed, while the COD abatement increased onwards up to a maximum efficiency of about 90% for a r_{HC} ratio of 5 gH_2O_2/gCOD, value that is estimated as optimal for the peroxide amount (Fig. 1). In order to try out to reduce the catalyst amount, holding the r_{HC} = 5 gH_2O_2/gCOD and the process temperature of 100 °C, different tests were conducted changing DCu between 5 mg/l and 500 mg/l. The results showed always the complete TP reduction and a COD removal of about 90% with a DCu value of 50 mg/l (Fig. 2). This concentration is much lower than the catalyst dosages typically used in classical Fenton process for the OOMW treatment [3,6,23], confirming the higher efficiency of processes catalyzed by copper. Using the dosages defined, further investigations were carried out in order to evaluate the influence of process temperature between 25 °C and 100 °C, on the oxidation efficiency. While a TP abatement higher than 90% was observed at any temperature, only 50% COD reduction was obtained at 25 °C and 50 °C (Fig. 3). The organic matter removal, instead, rapidly increases, with a linear trend, in the range 50–100 °C (Fig. 3). In particular each increase of 10 °C implies an efficiency increase of about 10%. These results suggest that the oxidation rate of H_2O_2–Cu^{II} system increases with the temperature faster than the peroxide decomposition into water and oxygen.

3.2. Analysis of process evolution

Once defined the optimal peroxide and catalyst amount (r_{HC} = 5gH_2O_2/gCOD, DCu = 50 mgCu^{II}/l) and

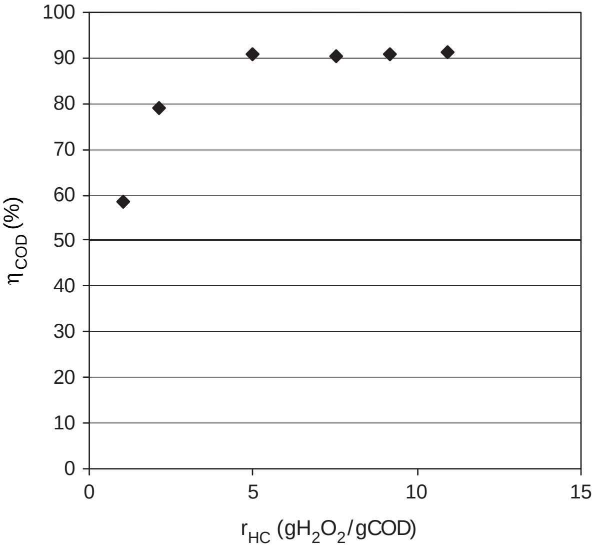

Fig. 1. η_{COD} vs. r_{HC} with DCu = 500 mgCu^{II}/l.

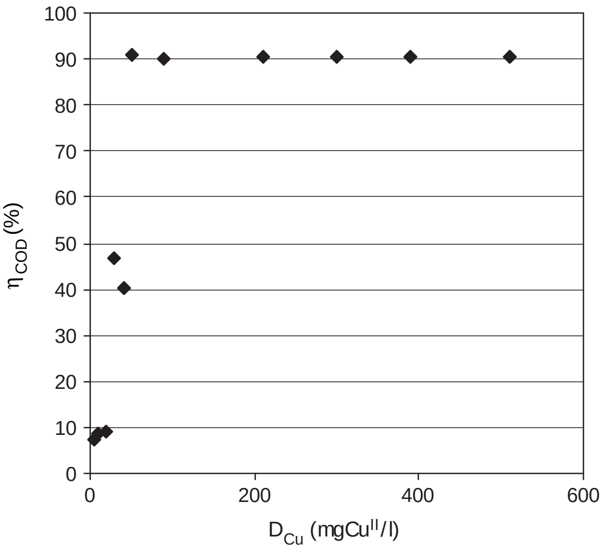

Fig. 2. η_{COD} vs. DCu with r_{HC} = 5gH_2O_2/gCOD.

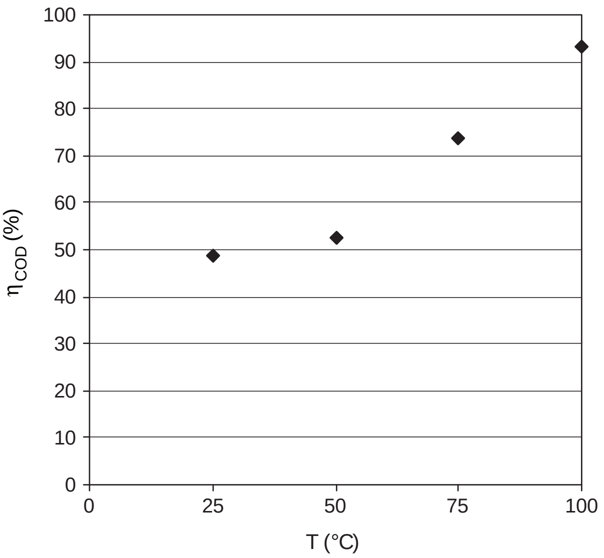

Fig. 3. η_{COD} vs. T with DCu = 50 mgCu^{II}/l and r_{HC} = 5 gH_2O_2/gCOD.

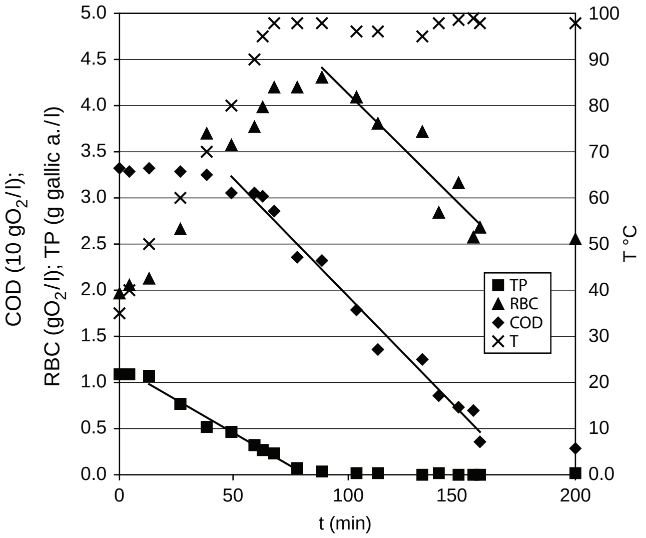

Fig. 4. COD, RBC and TP vs. t during catalytic tests carried out with DCu = 50 mgCu^{II} /l and r_{HC} = 5 gH_2O_2/gCOD.

the process temperature (T = 100 °C), in order to evaluate the process transformations, during a typical test, at different reaction time, 20 ml of mixture were withdrawn and immediately cooled in ice, to quench the catalyst oxidation, before being analysed with respect to pH, COD, RBC, TP, HP and Cu concentrations.

The results of analysis carried out on samples withdrawn at different reaction times, showed as the TP content began to decline after 10 min at a temperature near to 50 °C and proceeded according to a zero order kinetic, with a removal rate about of 0.86 g gallic a./lh, reaching concentrations almost equal to zero (Fig. 4).

Together with the TP reduction, a remarkable increase of RBC contents occurred, suggesting a conversion of hardly biodegradable compounds into easily biodegradable acids. In fact, the complete poly-phenols abatement stops the RBC production which, after about 50 min, is oxidized according to a zero order kinetics and a removal rate about of 1.44 gO_2/lh (Fig. 4).

The COD removal started after 50 min at 70 °C and, beyond this temperature, went on according to a linear trend characterized by a removal rate, about of 15.2 gO_2/lh, one order of magnitude higher than that RBC abatement (Fig. 4). This has a justification in fact that the RBC fraction is more difficult to treat by catalytic oxidation (Fig. 4).

After the initial peroxide and copper addition to the OOMW, the pH dropped from 4.73 down to 4.2 and during the catalytic oxidation it progressively decreased as temperature increased, reaching a minimum value near to 3 at 80 °C (Fig. 5). This initial pH decay trend is consequence of the partial oxidation of poly-phenols into easily biodegradable acids, while, after the minimum pH point, the increasing trend corresponds to the COD abatement [20,21].

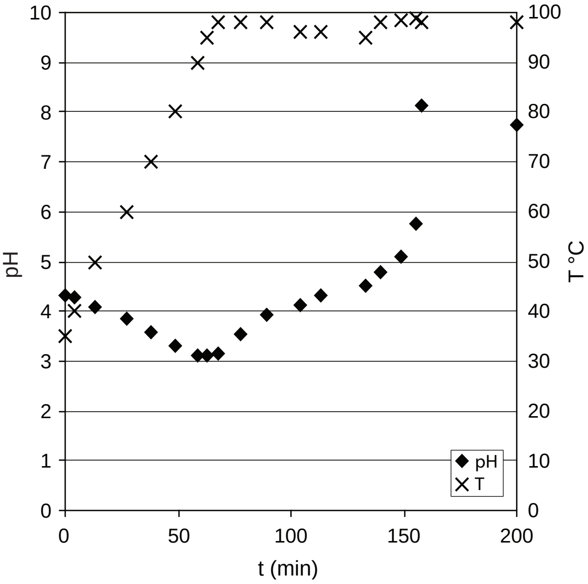

Fig. 5. pH vs t during catalytic tests carried out with DCu = 50 mgCu^{II}/l and r_{HC} = 5 gH_2O_2/gCOD.

Between 50 °C and 70 °C, hydrogen peroxide was initially consumed only for the poly-phenols oxidation, then it was reduced faster, according to a first order reaction, due to COD removal (Fig. 6).

The process stops when the pH increases up to eight causing, at a temperature about of 100 °C, a rapid hydrogen peroxide decomposition into water and oxygen with a high skim formation.

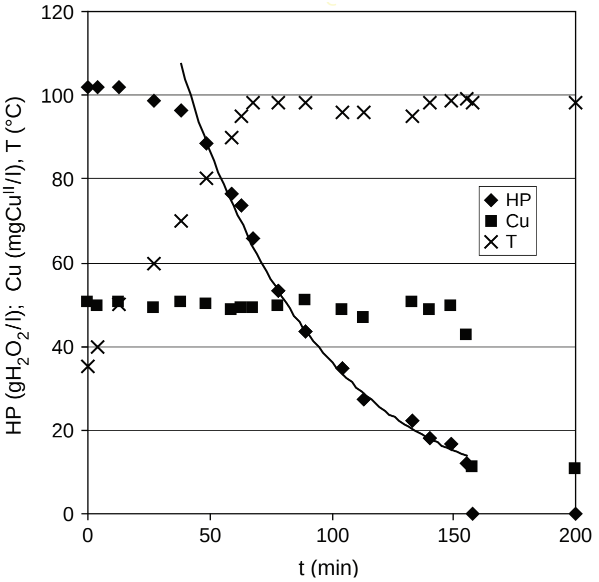

Fig. 6. HP and Cu vs. *t* during catalytic tests carried out with DCu = 50 mgCU^{II}/l and r_{HC} = 5 gH$_2$O$_2$/gCOD.

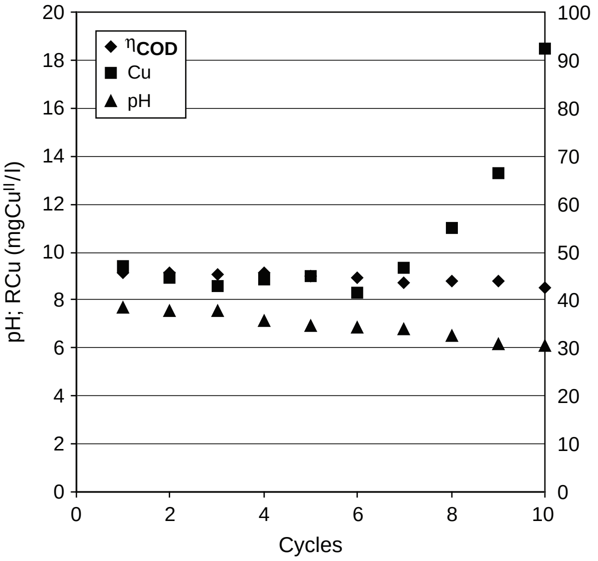

Fig. 7. RCu, η_{COD} and final pH at several cycles carried out reusing copper recovered and with partial fresh catalyst make up.

The copper ions concentrations remain essentially unchanged until the end of the process when the solution becomes alkaline (Fig. 6). The basic pH allows the copper hydroxide formation that, being in powder form, can be easily removed by settling, so that, only the 20% of initial catalyst amount remain dissolved probably as $[Cu(NH_3)_4]^{II}$ complex.

3.3. Catalyst recovering ad reuse

The absence of suspended solids in the treated OOMW allows an easy catalyst recovery, allowing its reuse for subsequent raw OOMW oxidation treatments. Being the copper hydroxide soluble in many organic acids, the recovered catalyst added to fresh OOMW is immediately dissolved, so that the copper is again available in homogenous form for the next treatment. The possibility of recovering the catalyst without further treatment, and of reusing it ensures the reduction of the costs of chemical consumptions and avoids the formation of a large volume of sludge, that instead, is generally produced by chemical flocculation in classical Fenton process for iron removal.

In order to assess how many cycles could be carried out reusing the recovered catalyst, at the begin of every cycle, was restored only the fraction, about of 9 mgCu^{II}/l, lost as solute during the previous treatment. The results showed a low decrease of COD abatement (Fig. 7), but, over the seventh cycle, a rapid growth of residual dissolved copper up to 18 mg/l at tenth round (Fig. 7).

This residual catalyst enhancement is probably due to lower pH values reached at the end of the last cycles, which impedes the catalyst precipitation (Fig. 7). These results suggest a maximum cycles number of about seven, that could be carried out with only a partial fresh catalyst make up.

With the aim of evaluating the hypothesis of reuse only the catalyst recovered without fresh copper make up, further experimentations were carried out with initial DCu values between 50 and 100 mg/l, and with no any catalyst addition during next cycles.

For each initial catalyst amount, the COD removal efficiency remained around 90% during the first three cycles, while, in subsequent tests it was progressively reduced up to seventh cycle, with 10% difference between tests started with 50 mg/l and 100 mg/l (Fig. 8). RCu and pH showed always gradual reduction (Figs. 9–10).

On the basis of these results, it seems that the treatment could be carried out with an initial catalyst dosage of about 50 mg/l, for seven consecutive cycles, without any further copper addition.

3.4. Activated sludge inhibition tests

The inhibition tests carried out with treated OOMW samples characterized by a RCu concentration equal to 9.1 mgCu^{II}/l, showed a reduction of biomass activity less than 5% up to dosages of 25 ml and an inhibition effect close to 10% diluting OOMW ten fold (Fig. 11). So the investigations prove that, up to a 1:10 dilution ratio, the copper amounts of treated OOMW not significantly affect the respiration rate of activated sludge. These results are in agreement with several researches that

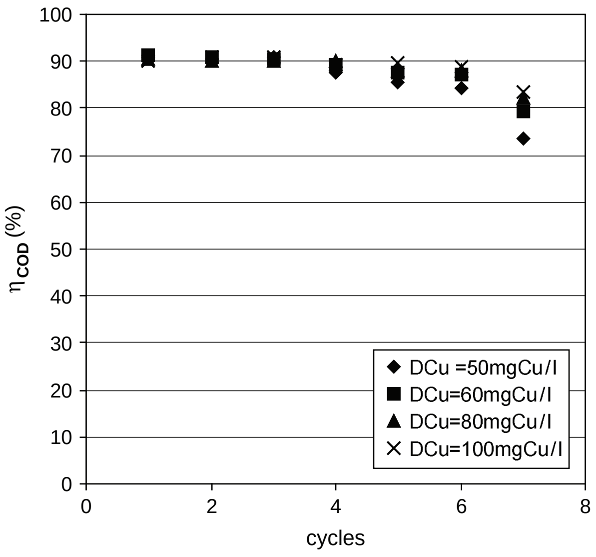

Fig. 8. η_{COD} for different initial DCu values at several cycles carried out reusing only the copper recovered and without fresh catalyst make up.

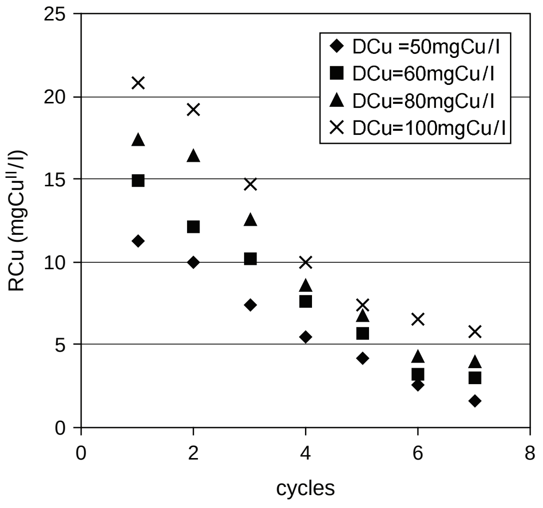

Fig. 9. RCu for different initial DCu at several cycles carried out reusing only the copper recovered and without fresh catalyst make up.

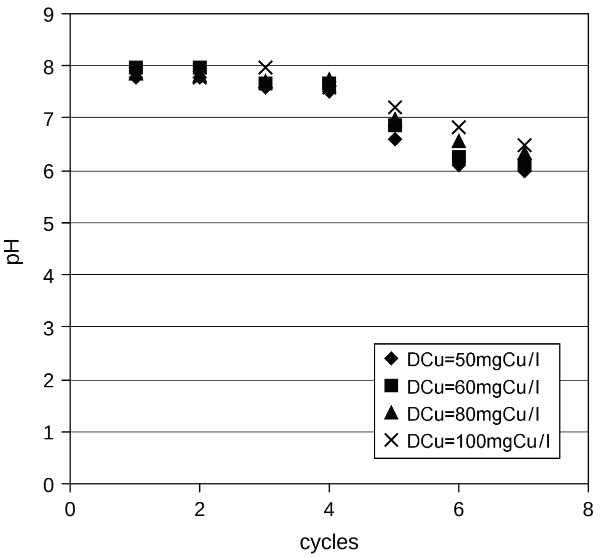

Fig. 10. Final pH for different initial DCu at several cycles carried out reusing only the copper recovered and without fresh catalyst make up.

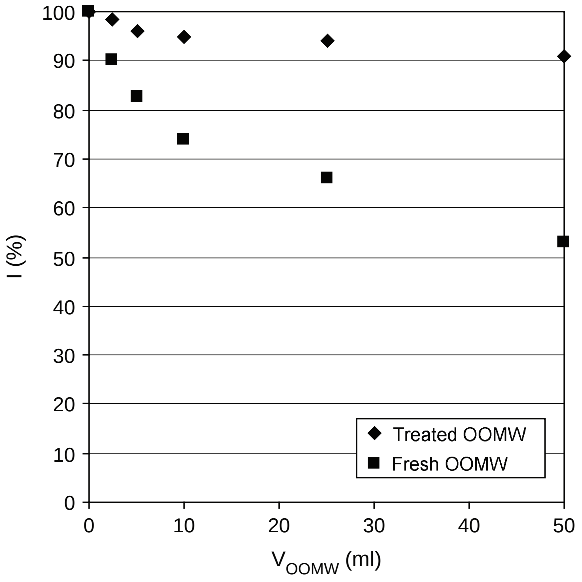

Fig. 11. I vs. wastewaters additions.

reported an appreciable metabolic activity reduction of activated sludge samples characterized by copper concentrations higher than 5 mg/l [7].

The experimental investigations carried out demonstrated also as the fresh OOMW are able to reduce the oxygen uptake rate of about 18% with a dilution ratio about of 1:100, and approximately of 48% for an addition of 50 ml, confirming their high phyto-toxicity power (Fig. 11). So a direct biological process is not suitable for their treatment; in fact, to avoid a considerable efficiency decrease, the OOMW should be mixed with the inlet flow to wastewater treatment plants with a high dilution ratio. Instead, being the inhibition effects almost completely removed after the catalytic oxidation, OOMW could be fed to municipal treatment plants with a low dilution ratio without excessive efficiency loss.

4. Conclusions

The experimental investigations allowed to define a catalytic oxidation treatment of OOMW, that, operating in a slurry type reactor at mild operating conditions with hydrogen peroxide and copper as catalyst, makes possible to reduce the COD content down to 10% and the polyphenols amount down to 1%, to increase the rapidly biodegradable substrate content up to 80% and to remove color and suspended solids amount. The process is carried out with copper additions much lower than the catalyst dosages typically used in classical Fenton process for the OOMW treatment, allowing the reduction of the costs of chemical consumptions. Besides, the process is able to minimize the metal loss of the catalyst after oxidation process, with a consequent recover of about 80% of his initial addition that can be reused for a long life cycle. This possibility allows to avoid further treatments for catalyst removal after catalytic oxidation.

The process, moreover, makes possible the direct disposal of treated OOMW to the municipal wastewater treatment plants; in fact they don't contain suspended solids and phyto-toxic compounds, and are characterized by an organic load, that even greater than that municipal wastewaters, is almost totally rapidly biodegradable.

This was confirmed by several respiration inhibition tests that demonstrated how the toxicities of raw OOMW were almost completely removed after catalytic oxidation.

Due to the high innovation degree this process was submitted for a patent.

Acknowledgement

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Symbols

COD — Chemical Oxygen Demand (gO_2/l)
Cu — Copper concentration ($mgCu^{II}/l$)
DCu — Catalyst dosage ($mgCu^{II}/l$)
HP — Hydrogen peroxide concentration (gH_2O_2/l)
I — Inhibition index (%)
OOMW — Olive Oil Mill Wastewaters
OUR — Oxygen Uptake Rate (mgO_2/lh)
RBC — Rapidly Biodegradable COD (gO_2/l)
RCu — Residual dissolved copper at the end of the catalytic oxidation ($mgCu^{II}/l$)
r_{HC} — Hydrogen peroxide/COD ratio ($gH_2O_2/gCOD$)
SCOD — Soluble COD (gO_2/l)
t — Time (min)
T — Temperature (°C)
TBC — Total Biodegradable COD (gO_2/l)
TOC — Total organic Carbon (gC/l)
TP — Total poly-phenols concentration (g gallic a./l)
TSS — Total Suspended Solids (g/l)
V_{OOMW} — Volume of OOMW added during the inhibition tests (ml)
VSS — Volatile Suspended Solids (g/l)
η_{COD} — COD removal efficiency (%)

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