Article

Energetic Valorization of Wet Olive Mill Wastes through a Suitable Integrated Treatment: H_2O_2 with Lime and Anaerobic Digestion

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Abstract: In the Mediterranean region, the disposal of residues of olive oil industries represents an important environmental issue. In recent years, many techniques were proposed to improve the characteristics of these wastes with the aim to use them for methane generation in anaerobic digestion processes. Nevertheless, these techniques, in many cases, result costly as well as difficult to perform. In the present work, a simple and useful process that exploits H_2O_2 in conjunction with lime is developed to enhance the anaerobic biodegradability of wet olive mill wastes (WMOW). Several tests were performed to investigate the influence of lime amount and H_2O_2 addition modality. The treatment efficiency was positively affected by the increase of lime dosage and by the sequential addition of hydrogen peroxide. The developed process allows reaching phenols abatements up to 80% and volatile fatty acids productions up to 90% by using H_2O_2 and $Ca(OH)_2$ amounts of 0.05 gH_2O_2/gCOD and 35 g/L, respectively. The results of many batch anaerobic digestion tests, carried out by means of laboratory equipment, proved that the biogas production from fresh wet olive mill wastes is hardly achievable. On the contrary, organic matter abatements, around to 78%, and great methane yields, up to 0.34–0.35 L_{CH4}/$g_{CODremoved}$, were obtained on pretreated wastes.

Keywords: anaerobic digestion; hydrogen peroxide; methane; olive mill wastes

1. Introduction

The development of sustainable approaches for valorization of agricultural co-products, by-products and wastes is an important environmental and economic challenge. Indeed, nowadays, these residues represent an important polluting source and they are often not properly exploited also in a view of a potential recovery. The Mediterranean area is mainly affected by the management and disposal of olive mill residues derived from the olive oil production [1–5]. Indeed, in this region, the olive mill by-products surpass 30 million m^3 per year [5]. The uncontrolled disposal of these residues causes serious pollution problems, such as the deterioration of natural water bodies characteristics and soil quality. The oil extraction systems largely affect the characteristics of olive milling by-products [2]. The wet olive mill wastes (WOMW), generated by the new two phase decanters, are generally more complex to treat and manage compared with the by-products produced by means of the conventional extraction systems. Indeed, wet olive mill wastes show an extremely high content of COD (chemical oxygen demand) and total solids (20%–30%), as well as a great amount of phenolic compounds, which make the treatment in conventional wastewaters treatment plants very complex [6,7]. Due to the seasonal production and the high availability of organic compounds, anaerobic digestion (AD) may represent a valid solution for the valorization of olive mill wastes. In fact, by means of this technique, a valuable biogas is produced and the nitrogen rich residual slurry

(digestate) could be exploited for agronomic applications as organic fertilizer or amendment [8,9]. Anaerobic digestion, furthermore, can be efficiently applied both in large-scale industrial installations and in small agro-industrial plants [8,9]. However, the presence of antimicrobial phenolic compounds makes particularly difficult the biological treatment of WOMW. Therefore, wet olive mill wastes must be preliminarily pre-treated to reduce the phenols amount [10–12]. There are many methods available for the pre-treatment of olive mill residues, such as the physical-chemical treatments and advanced oxidation processes (AOPs) [10–29]. AOPs include several techniques: Fenton like and ultraviolet/ozone (UV/O_3) processes, wet and wet catalytic air oxidation, supercritical water oxidation, sonication processes, UV/TiO_2, solar photocatalysis, ultraviolet/hydrogen peroxide (UV/H_2O_2), ozone/hydrogenperoxide (O_3/H_2O_2) processes, etc. These processes lead to the production of highly reactive free radicals, able to oxidize many recalcitrant organic molecules to more biodegradable compounds. Thus, the treated waste is less toxic and exploitable in a subsequent AD process for biogas production. Nevertheless, in many cases, the treatment methods practiced on a large scale are costly or difficult to manage. A suitable method, which exploits the hydrogen peroxide, was successfully applied by the authors to improve the anaerobic treatability of olive mill wastes and wastewaters [30,31]. This treatment provides alkaline conditions to promote the decomposition of H_2O_2, resulting in the formation of radicals species. The process is conducted without the addition of external catalysts or other activator agents (UV, O_3, US, etc.); therefore, the costs and the complexity of the treatment are notably reduced. An effective conversion of recalcitrant compounds into easily biodegradable molecules, without a complete mineralization, occurs during the treatment. This ensures the availability of high amounts of degradable organic substrate for a subsequent anaerobic digestion treatment. This process has been tested in our previous studies by using NaOH to set the process pH [30,31]. In the present work, it has been evaluated the applicability of Ca(OH)$_2$, a very cheap and easy to find compound, to generate the alkaline environment required for the treatment. Actually, contrary to common chemical-physical applications, calcium hydroxide has not been exploited as flocculating agent, but exclusively to create the operating conditions for H_2O_2 decomposition. Several tests were performed on wet olive mill wastes to identify the effects of lime addition and H_2O_2 dosage procedure on process performances. Furthermore, many batch digestion tests were conducted to verify the methane production potential both of raw and pretreated olive mill wastes. Finally, an economic analysis was conducted.

2. Description of the Experiments

2.1. Materials

During the experiments, samples of wet olive mill wastes withdrawn from two-phase extraction system were used. Furthermore, samples of livestock manure (LM) and livestock manure digestate (LMD) were exploited, as inoculum, to perform the AD tests. The main properties of used wastes are reported in Tables 1 and 2. The research was initially aimed to the definition of the oxidation process with H_2O_2 and Ca(OH)$_2$. In the next phase, batch digestion tests were conducted in a lab-scale equipment to evaluate the methane production detectable both on pre-treated and fresh WOMW. Hydrogen peroxide and Ca(OH)$_2$ of industrial grade were used during the experiments.

Table 1. Characteristics of fresh wet olive mill waste.

pH	Cond. mS/cm	COD g/L	TP g/L	VFA g/L	ALK g/L
4.41 ± 0.11	10.0 ± 0.26	276.7 ± 0.86	4.85 ± 0.10	4.39 ± 0.11	1.84 ± 0.04
TKN g/L	**NH_4^+-N g/L**	**PO_4^{-3}-P g/L**	**TS g/L**	**VS g/L**	
1.89 ± 0.07	0.18 ± 0.006	0.39 ± 0.012	337.5 ± 1.35	317.6 ± 1.41	

Table 2. Characteristics of livestock manure (LM) and livestock manure digestate (LMD).

Sample	pH	Cond. mS/cm	COD g/L	TP g/L	VFA g/L	ALK g/L
LM	7.72 ± 0.09	8.81 ± 0.30	121.8 ± 1.46	1.59 ± 0.06	6.02 ± 0.21	11.1 ± 0.3
LMD	7.90 ± 0.12	18.3 ± 0.27	35.45 ± 1.27	1.38 ± 0.02	2.64 ± 0.10	19.7 ± 0.37
Sample	**TKN g/L**	**NH_4^+-N g/L**	**PO_4^{-3}-P g/L**	**TS g/L**	**VS g/L**	
LM	2.54 ± 0.09	1.67 ± 0.047	0.532 ± 0.021	60.9 ± 0.78	44.2 ± 1.12	
LMD	1.95 ± 0.052	1.5 ± 0.038	0.52 ± 0.020	40.7 ± 0.56	27.5 ± 0.98	

2.2. Tests with H_2O_2 and $Ca(OH)_2$

To create the alkaline conditions required for oxidation process, $Ca(OH)_2$ amounts equal to 15 g/L, 25 g/L and 35 g/L were tested. On the basis of findings of our previous works [30,31], all the oxidation tests were carried out using an overall hydrogen peroxide amount of 0.05 gH_2O_2/gCOD. In a first set of tests, the overall H_2O_2 quantity was dosed in a single step (Table 3, modality D1). In a next set of experiments, three sequential dosage modalities were tested. In particular, for all these procedures, half of total peroxide amount (0.025 gH_2O_2/gCOD) was fed at the start of the oxidation treatment. The remaining dose was added after 15 min for the second procedure (modality D2); while for the third (modality D3) and fourth procedure (modality D4), two and three doses of 0.0125 gH_2O_2/gCOD and 0.0083 gH_2O_2/gCOD, respectively, were provided at progressive time intervals of 15 min of each other (Table 3). The experiments were conducted in batch mode, at room temperature and pressure, in beakers of 250 mL equipped with mechanical stirrers. During each test, the lime was added to 100 mL of raw wet olive mill waste. Afterwards, the mixture was stirred at a speed of 300 rpm, able to ensure an efficient mixing, for approximately 2 h, up to reach the stabilization of pH. No operation for suspended solids separation was then conducted. After the above time, the H_2O_2 was dosed according to the aforementioned procedures (Table 3). From the initial H_2O_2 dose, the mixture was stirred at 300 rpm for a reaction time of about 3 h, adequate to complete the oxidation process. A multiparameter probe was used for pH and temperature control. The samples were withdrawn and characterized once reached the pH stabilization (just before the first H_2O_2 addition) and during the oxidation process. To verify the compounds adsorption on lime, the samples were subjected to an acidification procedure before the analytical determinations. In particular, HCl (1:1) was added to the samples, up to reach a pH of about 5, in order to promote the release of compounds incorporated by $Ca(OH)_2$.

Table 3. Dosing modalities of H_2O_2 tested during the experiments. Each modality was applied for the three used lime dosage (15 g/L, 25 g/L and 35 g/L).

Progressive Dosing Time of H_2O_2 (min)		0	15	30	45
	modality D1	0.05	0	0	0
H_2O_2 quantity	modality D2	0.025	0.025	0	0
(gH_2O_2/gCOD)	modality D3	0.025	0.0125	0.0125	0
	modality D4	0.025	0.0083	0.0083	0.0083

2.3. Digestion Tests

A total of 5 AD tests were performed using raw and pre-treated wet olive mill wastes. In particular, three tests were conducted with WOMW pre-treated with H_2O_2 and different lime dosages (15 g/L, 25 g/L and 35 g/L). The other two tests were carried out, respectively, with the raw WOMW and with the waste pretreated with only lime (25 g/L). Samples of livestock manure (LM) and livestock manure digestate (LMD), as inoculum, were used. In particular, in each test, a mixture volume of 150 mL was prepared by mixing 85 mL of olive mill waste (raw or pretreated), 50 mL of livestock manure digestate and 15 mL of livestock manure. No other external compounds were used. The batch

tests were conducted in small laboratory equipment developed for the purpose. Specifically, 0.5 L dark glass bottles were provided with hermetic closing caps. These caps were linked, through HDPE (High Density Polyethylene) pipes, to proper volumetric gasometers, made of Plexiglas cylinders. To neutralize the CO_2 and others acid gases in the produced biogas, sodium hydroxide flakes were put in small containers located along the connecting tubes in HDPE. In this way, it was mainly monitored the methane volume produced during the AD tests. The prepared mixtures were inserted in bottles, and then a flux of nitrogen gas was fed for about of 3–4 min to cause the oxygen stripping. Afterwards, the bottles were closed and connected to the system for methane measurement. The prepared mixtures were then placed in a thermostatic fridge at 35 °C and constantly stirred for 120 days by means of magnetic mixer. The CH_4 production was monitored every day. After four months, the residual slurries were analyzed with respect to the main chemical parameters.

2.4. Analytical Methods

The pH, temperature and conductivity were estimated by a multiparametric probe; total solids (TS) and volatile solids (VS) by drying the sample at 105 °C and 550 °C, respectively; the COD, alkalinity (ALK) and H_2O_2 amount by the titrimetric methods; NH_4^+-N and PO_4^{3-}-P by spectrophotometric analysis; total Kjeldhal Nitrogen (TKN) and Volatile Fatty Acids (VFA, expressed in term of acetic acid) by the distillation technique [32]; total phenols (TP, expressed in term of gallic acid) by the Folin and Ciocalteu method [33]. On the pre-treated samples, the positive interference in COD estimation, due to the presence of eventual residual H_2O_2 concentration, was accounted by means of the procedure proposed by Mantzavinos [34]. Each analysis was conducted four times, the mean value and the standard deviation were shown. The reported performances were representative of the actual removal or production of the compounds. Therefore, the values were not affected by the dilutions due to the reactant additions in the various processes.

## 3. Results and Discussion

3.1. Characteristics of WOMW

The characterization of WOMW showed values of pH and conductivity of about 4.4 and 10.0 mS/cm, respectively (Table 1). The total solids were around to 337.5 g/L, with a particularly high volatile fraction, approximately of 94%. The COD was of about 277 g/L; the total Kjeldhal nitrogen resulted close to 1.9 g/L, while the free ammonium nitrogen was much lower, equal just to 0.18 g/L. The concentration of total phenols, of about 4.85 g/L, confirmed the great phytotoxic potential of wet olive mill wastes. These values show that the polluting load of WOMW is notably greater than that of wastewaters generated by three phase extraction system [24,26].

### 3.2. Tests with H_2O_2 and $Ca(OH)_2$

The experiments were conducted using a hydrogen peroxide amount equal to 0.05 gH_2O_2/gCOD. This value was set on the basis of previous works of authors in which it was verified the good performance of alkaline oxidation, using the above H_2O_2 dose and NaOH to set the pH [31]. In this study, to create the basic environment, $Ca(OH)_2$ amounts of 15 g/L, 25 g/L and 35 g/L were tested. These quantities were mechanically mixed with fresh WOMW samples for about 2 h. After this period, for each of tested lime dose, the pH of mixture reached values equal to about 9.2, 10.1 and 11.1, respectively. During the tests, it was primarily verified the effect of lime additions on WOMW characteristics. The analyzed samples, withdrawn just before the hydrogen peroxide dosage, showed a reduction of phenols (TP) that ranged from 41% to 63% in response to the increase of lime amount. However, these abatements are attributable exclusively to the TP adsorption/incorporation by lime, without any conversion of these recalcitrant molecules. These mechanisms were well investigated by Aktas et al. [35], who demonstrated that the many phenolic molecules can be incorporated by lime. The adsorbed substances, however, can be easily released in an acid environment because the

dissolution of lime takes place. In fact, in our experiments, by subjecting, before the analytical determinations, the WOMW samples mixed with lime to the acidification procedure with HCl, an almost complete release of phenols was observed. This is clearly a negative aspect if the samples were subjected to a next AD process. Indeed, due to the organic acids production during anaerobic digestion, the phenolic compounds could be totally or partially released by causing the inhibition of methanogenic biomass. To avoid this phenomenon, a separation of suspended solids should be conducted before the AD. In this way, also the phenols adsorbed by lime particles would be removed. Nevertheless, this treatment would cause a drastic reduction of organic load of the samples and, thus, also a notably lower methane yield during the subsequent anaerobic digestion. The drawbacks due to the use of lime for the treatment of olive oil residues were also verified by Madani et al. [14]. Contrary to the effect of $Ca(OH)_2$ alone, the dosage of H_2O_2 in a single step (modality D1) produced an actual phenols removal that linearly increased, from 52% up to about of 79%, with the lime dosage (Figure 1). These abatements remained substantially unchanged by monitoring the phenols content after the acidification procedure of samples. This indicates that an effective oxidation of TP occurred. Furthermore, besides the phenols reduction, the pre-treatment caused the enhancement of easily biodegradable substances. In fact, as shown in Figure 2 (modality D1), consistent to phenols oxidation, a VFA growing trend was monitored. This increase of volatile fatty acids content indicates a conversion of low biodegradable organic matters to rapidly biodegradable carboxylic acids [36]. This transformation clearly represents a positive aspect of the proposed pre-treatment. In fact, the partial oxidation of complex molecules to VFA shortens the extension of hydrolytic and acid phases in a next anaerobic digestion, by increasing the biogas yields.

The small COD abatements (modality D1), comprised between 18.4% and 24% (Figure 3), confirmed that the pre-treatment with H_2O_2 and lime produces mainly a partial oxidation of complex substances to easier biodegradable molecules, with only a restricted mineralization of organic load.
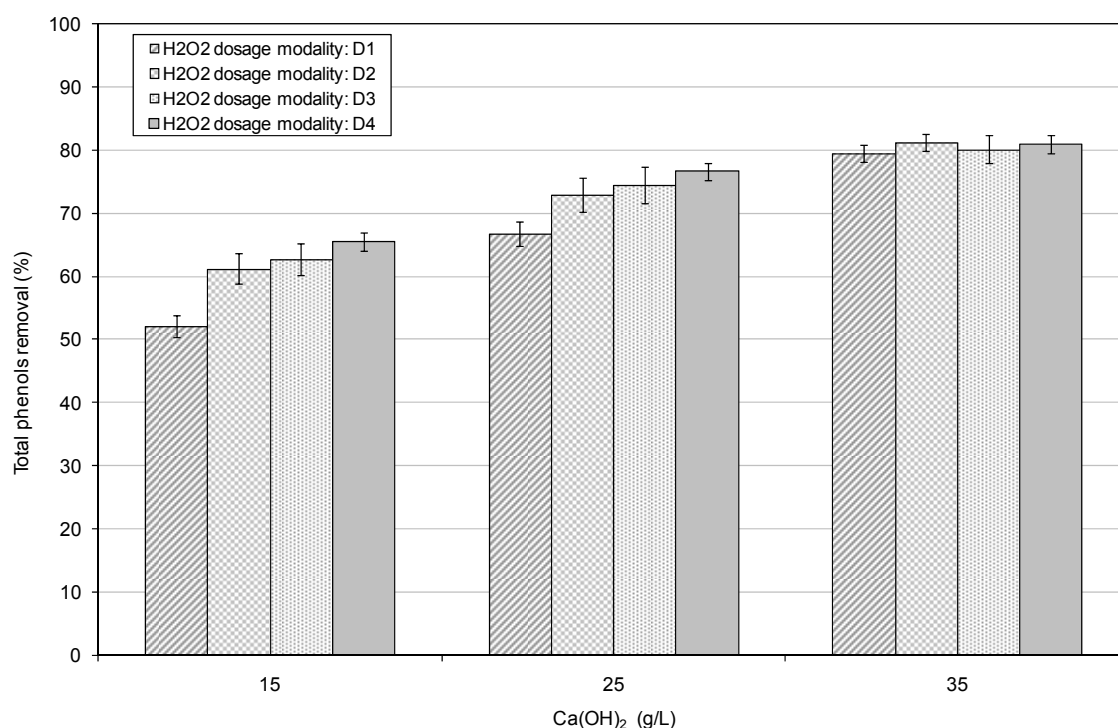
Figure 1. Phenols removals detected in the experiments conducted by changing the lime quantity (15 g/L, 25 g/L and 35 g/L) and by dosing the H_2O_2 amount (0.05 gH_2O_2/gCOD) with four different modalities (D1: single addition; D2: two additions; D3: three additions; and D4: four additions).
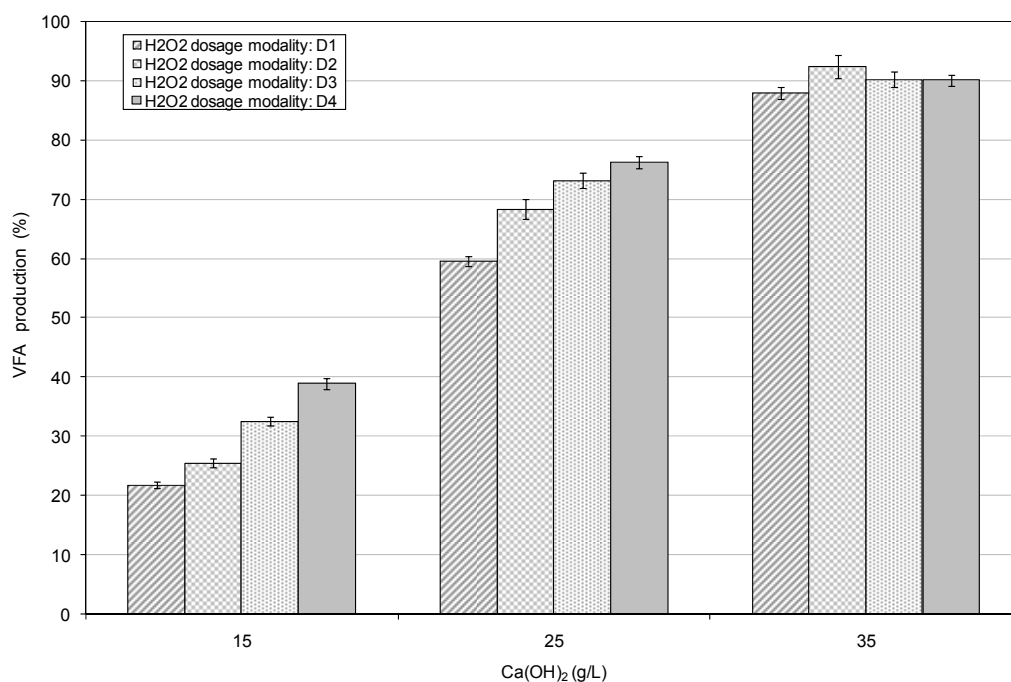
Figure 2. VFA productions detected in the experiments conducted by changing the lime quantity (15 g/L, 25 g/L and 35 g/L) and by dosing the H_2O_2 amount (0.05 gH_2O_2/gCOD) with four different modalities (D1: single addition; D2: two additions; D3: three additions; and D4: four additions).
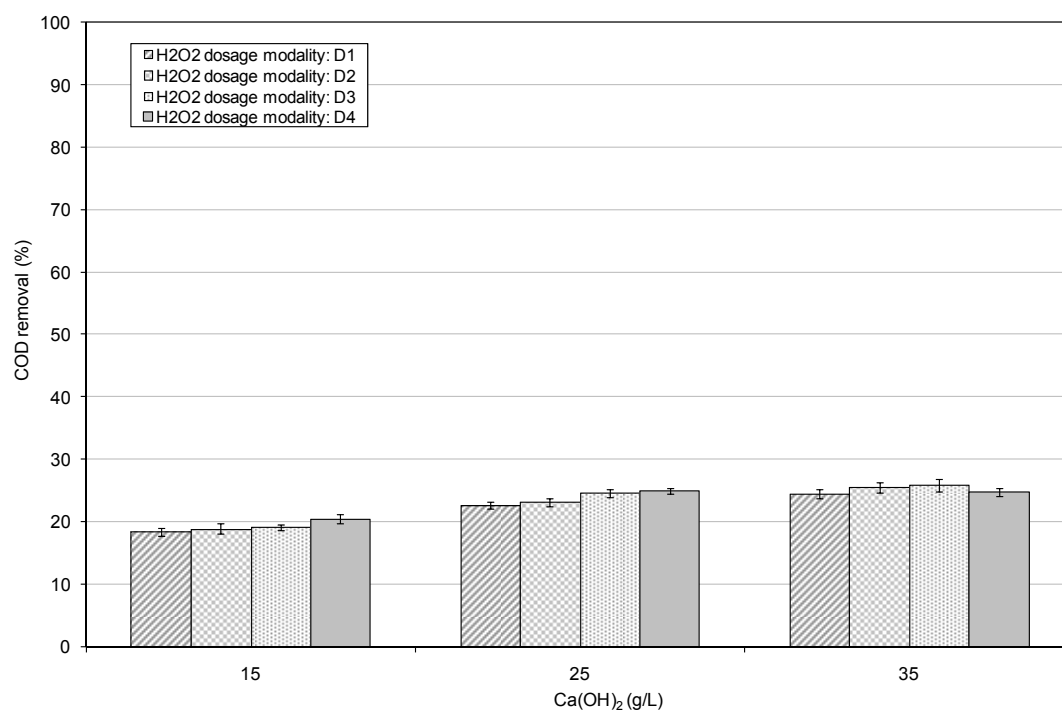

Figure 3. COD removals detected in the experiments conducted by changing the lime quantity (15 g/L, 25 g/L and 35 g/L) and by dosing the H_2O_2 amount (0.05 gH_2O_2/gCOD) with four different modalities (D1: single addition; D2: two additions; D3: three additions; and D4: four additions).

The increase of process performance, in response to the lime amount, is attributable to the corresponding increase in mixture pH. Indeed, the lime dosages tested in this study allowed to reach

pH values able to efficiently promote the hydrogen peroxide decomposition, leading the sequential production of HO_2^- and $OH\cdot$

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O \tag{1}$$

$$H_2O_2 + HO_2^- \rightarrow OH\cdot + O_2^{-}\cdot + H_2O \tag{2}$$
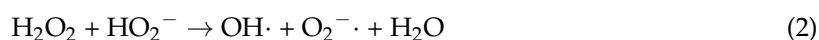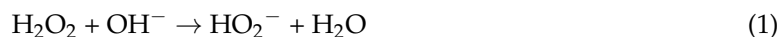
Clearly, the pH growth, from 9.2 to 11.1, in response to lime dosage, favors the generation of hydroperoxide anions and hydroxide radicals, accentuating the phenols removal and the production of volatile fatty acids (Figures 1 and 2). The pH values, due to the ability of $Ca(OH)_2$ to neutralize the acids compounds, remained substantially unchanged during the oxidation process.

The hydroxide radicals formed by means of Reactions (1) and (2) can further react with hydrogen peroxide with the production of less reactive $HO_2\cdot$ species.

$$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O \tag{3}$$

This disadvantageous consumption of $OH\cdot$ could be reduced by dosing the overall H_2O_2 amount in more subsequent steps, resulting in an increase of the process performance.

This hypothesis was confirmed by the results of experiments carried out by testing different modalities of hydrogen peroxide dosage. In particular, the higher benefits were obtained with the lowest amount of lime tested. In this case, by dosing the H_2O_2 amount in two steps (modality D2), it was observed an enhancement in phenols removal of about 10%, compared with the abatement detected by adding the peroxide in a single step (modality D1) (Figure 1). Further slight performance enhancements were reached by providing the hydrogen peroxide dosage in three and four additions (modalities D3 and D4), up to a maximum abatement around to 66% (Figure 1). The benefits due to the sequential addition of H_2O_2 can be easily observed by comparing the trends of phenols and H_2O_2 concentrations monitored in the tests with the dosage modalities D1 and D4. The curves reported in Figure 4 show a more gradual H_2O_2 consumption during the test with the subsequent dosages. This allowed obtaining a higher TP removal (Figure 5). In fact, in response to each H_2O_2 addition, a progressive phenols reduction occurred up to reach, in about 90 minutes, a concentration lower of about 0.7 g/L compared with the residual concentration obtained with the modality D1 (Figure 5). In the test with a single dosage, the higher initial concentration of H_2O_2 probably accentuates the $OH\cdot$ scavenger, according to Reaction (3), reducing the overall oxidation power. This mechanism, furthermore, causes also an adverse consumption of H_2O_2. These undesirable effects are, presumably, less marked by performing the dosage of hydrogen peroxide in subsequent steps.

In the texts carried out with a lime dosage of 25 g/L, the sequential dosage of H_2O_2 produced a growth of phenols abatement from 67% to 77%, by increasing the steps for hydrogen peroxide additions. Instead, for the maximum quantity of tested lime, the modality of H_2O_2 addition did not cause any significant process modification (Figure 1). The lower effect of sequential peroxide dosage with the increase of lime amount is attributable to the corresponding pH increase, which clearly accentuates the oxidative power and makes less meaning the $OH\cdot$ scavenger. The abatements reached in the present study are in line with those detected by the authors using NaOH to create the alkaline conditions [31]. Moreover, similar performances are reported in other researches concerning the treatment of olive mill wastewaters. In particular, phenols removals of about 60% were obtained by Bettazzi et al. [22] with Fenton process, using doses of approximately 0.15 and 0.25 $gH_2O_2/gCOD$. Similar findings were obtained by Canepa et al. [23] and Khoufi et al. [25] by applying, respectively, photo-Fenton and electro-Fenton processes in the treatment of wastewaters of three phase production systems. Better performances were reached when hydrogen peroxide dosages, significantly greater than that applied in this study, were used [11].
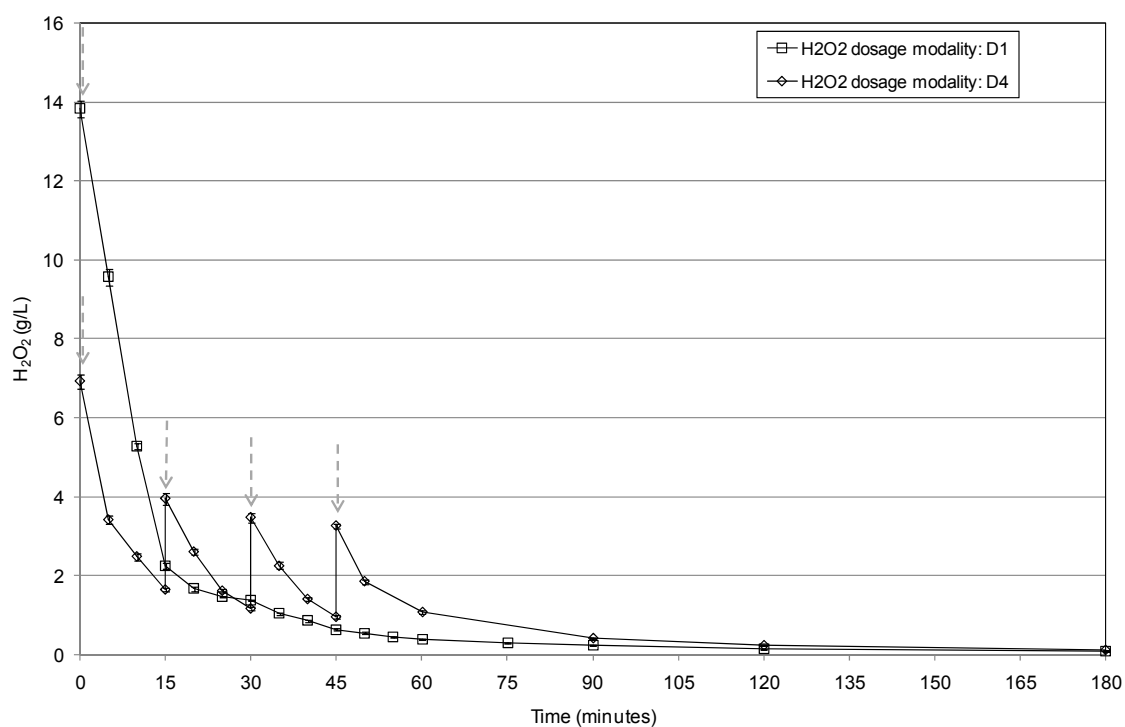
Figure 4. H_2O_2 concentrations monitored during the tests conducted with a lime amount of 15 g/L and by dosing the hydrogen peroxide in a single step (modality D1) and in four additions (modality D4). The arrows indicate the H_2O_2 additions.
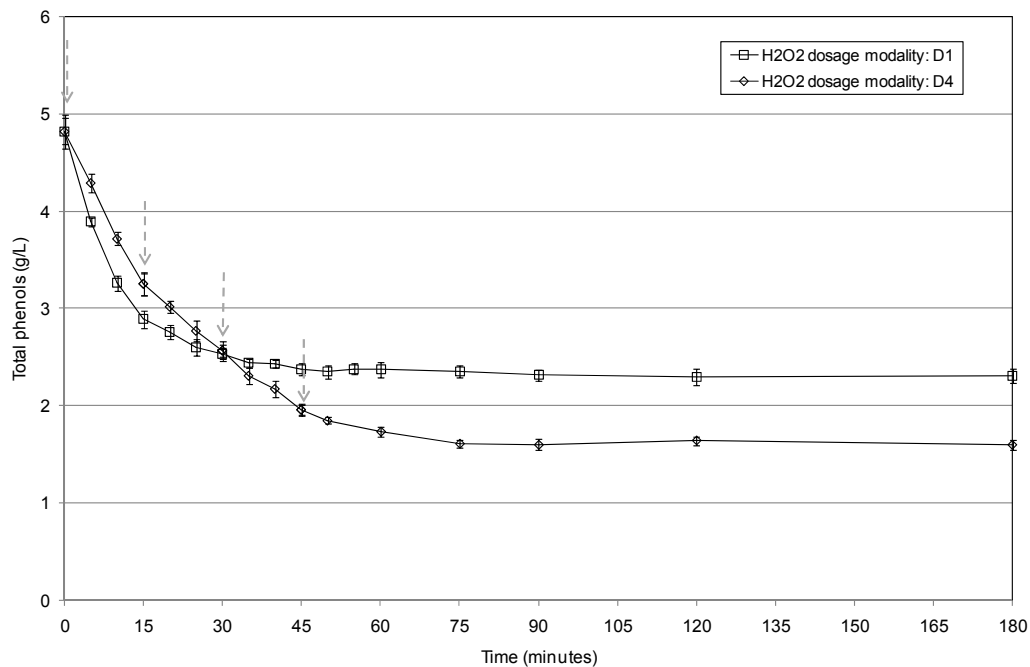
Figure 5. Phenols concentrations monitored during the tests conducted with a lime amount of 15 g/L and by dosing the hydrogen peroxide in a single step (modality D1) and in four additions (modality D4). The arrows indicate the H_2O_2 additions.

The trends of phenols abatement detected during the experiments were consistent with those of VFA productions. In fact, by dosing the hydrogen peroxide in multiple steps, remarkable VFA increases

were observed with the lime amounts of 15 g/L and 25 g/L (Figure 2). No appreciable benefits were detected by using the highest $Ca(OH)_2$ dose (Figure 2). For each lime dosages, the maximum VFA concentration was, respectively, 6.1, 7.7 and 8.5 g(acetic acic)/L. These values, being the theoretical COD/(acetic acid) ratio of about 1.06, approximately correspond to the COD amount due to volatile fatty acids.

The abatements of total COD, for every lime amount and H_2O_2 dosage modality, were always restricted (Figure 3). The pre-treatment with H_2O_2 caused also a negligible reduction of volatile solids (VS) content, always lower than 5%. This confirms that the alkaline oxidation causes only a limited mineralization of organic matter. The observed abatements of total COD were lower than those detected by means of other pre-treatment techniques. In particular, organic load removals greater than 80% were reached by treating olive mill wastewaters with Fenton process [11,14]. Nevertheless, the low reduction of COD content caused by the proposed pre-treatment is clearly a positive aspect if the WOMW were further treated in anaerobic digestion. In fact, the high amount of residual organic substrate could ensure notable methane yields during AD. The proposed process is also advantageous because, for each process conditions applied, the concentration of H_2O_2 after the pretreatment was completely negligible. Therefore, further treatments aimed to the removal of residual hydrogen peroxide are unnecessary. Moreover, compared with conventional Fenton pre-treatments, the absence of external catalysts notably simplifies the process management. In addition, the proposed treatment cancels the costs for the disposal of bulky precipitate produced by the chemical precipitation of catalyst ions.

Therefore, the use of lime in conjunction with H_2O_2 can represent a suitable process for the pretreatment of wet olive mill wastes before a subsequent anaerobic digestion.

3.3. Anaerobic Digestion Tests

With the aim to verify the CH_4 yields detectable after the alkaline oxidation, the samples pre-treated by dosing the hydrogen peroxide amount in four steps, for each investigated lime amount, were subjected to batch anaerobic digestion tests (samples ST1, ST2 and ST3 prepared with WOMW treated by using, respectively, 15 g/L, 25 g/L and 35 g/L of lime and by dosing H_2O_2 in four steps). Furthermore, the methane potential was investigated on untreated waste (sample STQ) and on WOMW after the treatment with only lime (sample SL). In this last case, the AD test was conducted on the sample mixed with a $Ca(OH)_2$ quantity equal to 25 g/L (sample SL). All tests were carried out without any addition of external compounds to set the process parameters (COD/N/P, VFA/ALK, etc.); therefore, no external compounds were used. Only the pH of sample prepared with fresh WOMW was set around to 7.1 with $Ca(OH)_2$. The properties of samples prepared for batch AD tests, according to the procedures mentioned in material and methods section, are reported in Table 4. The concentration of TP exceeded 3.6 g/L in the mixture with raw WOMW, while it was significantly lower in those prepared with WOMW pre-treated with lime and H_2O_2. These mixtures, as consequence of oxidation process, were characterized by the higher VFA amounts. Moreover, the concentrations of volatile fatty acids were also balanced by adequate alkalinity values, due to the pH setting performed during the pre-treatment. Indeed, the VFA/ALK ratios, lower than 0.25, were particularly suitable for anaerobic digestion [31]. In addition, also in the mixture with raw WOMW, after the pH setting to 7.1, the VFA/ALK ratio reached a value compatible for biogas production. The COD/TKN ratios were higher than values considered optimal for anaerobic digestion [30], but, as aforementioned, no nutrient compounds were fed to set this parameter. No reliable considerations can be done about the organic load/bacteria ratio, because the VS amounts in the mixtures are mainly representative of particulate organic matter instead of bacteria concentration.

From the analysis of experimental results (Figure 6), it can be noticed the very low methane production for the mixture with untreated WOMW (STQ). In fact, although the pH of the waste was corrected to prevent initial acidic conditions (Table 4), only a methane volume of about 260 mL was detected (Figure 6). This negligible production confirms the extremely low anaerobic biodegradability

of raw wet olive mill wastes [31]. Indeed, in the mixture with untreated sample, the high phenols concentration probably caused the arrest of AD process. Thus, the findings of conducted tests indicate that an effective biogas generation is hardly detectable on WOMW, also if the mixture were prepared using suitable inoculum quantity, equal to 45% of the overall amount. Consistent with the poor methane production, a small COD abatement, of about 29%, was monitored at the end of anaerobic digestion (Figure 7). These findings are in agreement with the statements of other researches, which indicated that the CH_4 generation could be possible exclusively with extremely high dilution ratio of raw olive mill residues [37,38]. However, this workaround is not applicable for olive milling plants that cannot mix the WOMW with other types of waste. Furthermore, the high amounts of olive mill by-products that are commonly produced in a very restricted period cannot be easily stored. Thus, it is important to treat high WOMW quantities in a short time.

Table 4. Characteristics of samples subjected to digestion tests. The samples were prepared by mixing raw or pre-treated WOMW (85 mL) with livestock manure (15 mL) and livestock manure digestate (50 mL). STQ: raw WOMW; SL: WOMW pre-treated with 25 g/L of $Ca(OH)_2$; ST1, ST2 and ST3: WOMW pre-treated with 0.05 $gH_2O_2/gCOD$ and, respectively, 15 g/L, 25 g/L and 35 g/L of $Ca(OH)_2$, (the H_2O_2 was dosed in four additions).

Sample	pH	Cond. mS/cm	COD g/L	TP g/L	VFA g/L	ALK g/L	VFA/ALK g/g
STQ	7.11 ± 0.06	11.9 ± 0.26	189.5 ± 1.56	3.65 ± 0.08	4.44 ± 0.11	16.84 ± 0.42	0.26 ± 0.009
SL	8.12 ± 0.11	12.9 ± 0.40	176.9 ± 1.94	1.98 ± 0.02	4.52 ± 0.12	26.71 ± 0.96	0.17 ± 0.007
ST1	7.33 ± 0.09	13.2 ± 0.47	149.6 ± 1.34	1.69 ± 0.05	4.69 ± 0.19	19.15 ± 0.40	0.245 ± 0.01
ST2	7.47 ± 0.07	13.9 ± 0.26	146.5 ± 1.89	1.43 ± 0.03	5.88 ± 0.10	26.50 ± 0.79	0.220 ± 0.007
ST3	7.54 ± 0.07	14.3 ± 0.53	144.6 ± 1.12	1.10 ± 0.02	6.93 ± 0.17	33.51 ± 0.60	0.206 ± 0.006

Sample	TKN gN/L	NH_4^+-N g/L	PO_4^{-3}-P g/L	COD/TKN g/g	TS g/L	VS g/L
STQ	2.02 ± 0.038	0.70 ± 0.027	0.46 ± 0.011	93.8 ± 1.92	201.6 ± 1.01	190.1 ± 1.21
SL	1.98 ± 0.06	0.19 ± 0.003	0.16 ± 0.006	89.3 ± 2.87	202.3 ± 0.95	192.1 ± 1.45
ST1	1.91 ± 0.07	0.18 ± 0.002	0.22 ± 0.007	78.3 ± 2.90	201.9 ± 1.4	189.4 ± 1.62
ST2	1.96 ± 0.07	0.20 ± 0.002	0.15 ± 0.005	74.7 ± 2.83	202.6 ± 1.1	189.1 ± 0.86
ST3	1.88 ± 0.06	0.16 ± 0.003	0.15 ± 0.003	76.9 ± 2.52	203.4 ± 1.8	189.0 ± 0.74
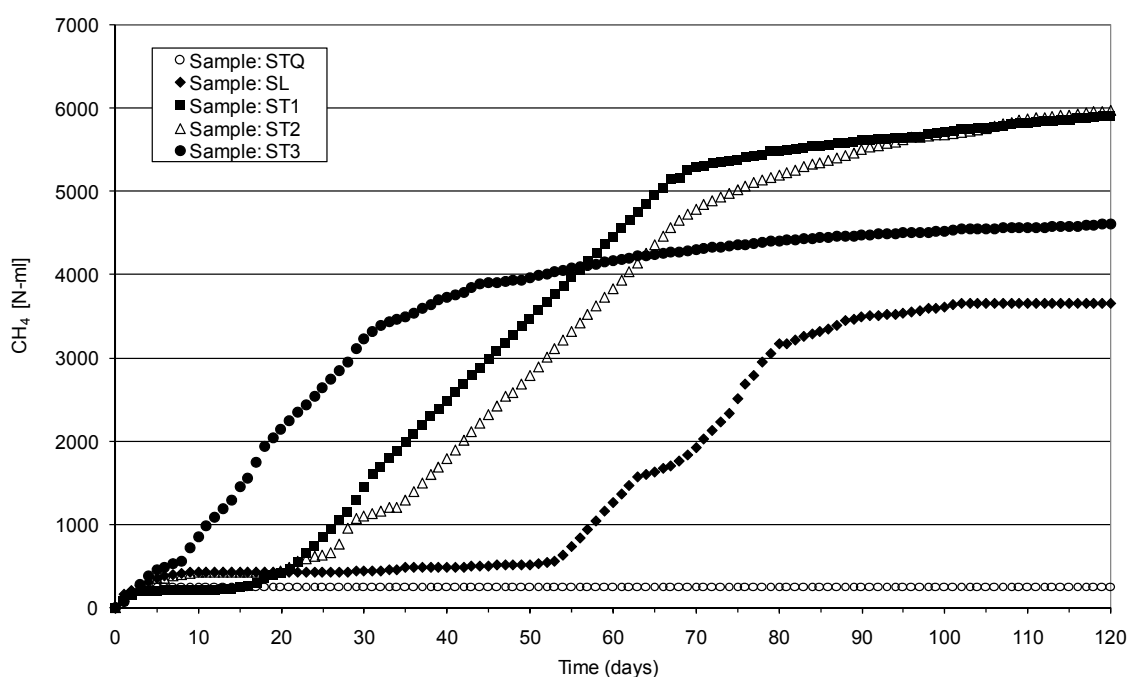
Figure 6. Methane productions detected during the digestion tests.
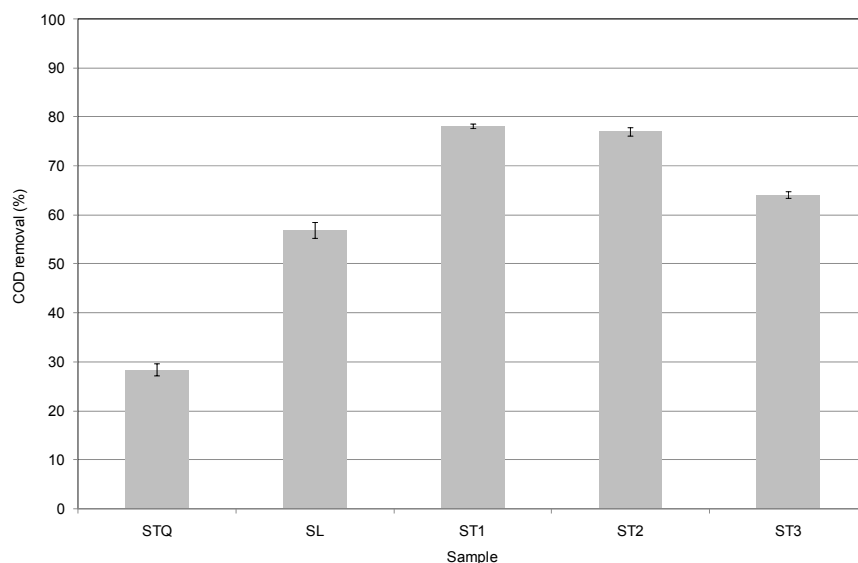
Figure 7. COD removals detected on the digested samples.

On the contrary, of the negligible production detected with fresh waste, notable digestion performances were observed on pre-treated samples (Figure 6). In particular, on the mixture with the WOMW treated using H_2O_2 and the greatest lime amount (sample ST3), the exponential CH_4 production started almost immediately, without that an acclimation phase was necessary (Figure 6). This was due to the properties of this sample, which had the lowest phenols amount and the highest VFA concentration (Table 4). Furthermore, the VFA amount was also balanced by adequate alkalinity values as results from the VFA/ALK ratio [39]. These characteristics clearly promoted the immediate methane production. Nevertheless, in this case, the conversion of organic matter, of about 64%, was lower than those obtained on samples with H_2O_2 and lime dosages of 15 g/L (sample ST1) and 25 g/L (sample ST2) (Table 5, Figures 6 and 7). This is likely attributable to a remarkable incorporation of organic matter by the greatest lime amount (35 g/L), which hindered the methane production. In fact, a cumulate volume of approximately 4.6 L was reached.

In samples ST1 and ST2, due to the higher phenols concentrations, an acclimatization period of about 20 days occurred. Nevertheless, after this delay time, the methane productions followed exponential trends, attaining overall volumes of about 6 L. These productions are mainly attributable to the degradation of COD of WOMW. In fact, the amount of degradable organic matter of the added inoculum can be estimated at only 10% of total COD of prepared samples. Moreover, the exponential phases, during which the main COD conversion occurred, were accomplished in a period of around 40 days. This time is of the same order of magnitude of the sludge retention time in conventional anaerobic digestion of complex agro-industrial wastes, conducted in semi-continuous systems [39]. The goodness of anaerobic digestion was underlined by the remarkable CH_4 yields, that reached values around to 0.34–0.35 $L_{CH4}/g_{CODremoved}$ (Table 5), almost equal to the sthoichiometric value [40]. These yields are in line with the values reported in other studies. In particular, Khoufi et al. [25] observed maximum yields of about 0.32–0.34 $L_{CH4}/g_{CODremoved}$ on olive mill residues pretreated by means of electro-Fenton process. Some works stated that, in batch conditions, the biogas production by the treatment of olive mill residues is possible only with low values of initial COD amount. In particular, Hamdi et al. [38] demonstrated that the anaerobic biodegradation of olive mill wastewaters is effective in treating samples with COD concentrations up to 20 g/L. Sabbah et al. [37] observed that COD concentrations greater than 50 gCOD/L could not be removed in batch anaerobic reactor. In the present study, the notable methane yields were obtained despite the extremely high initial organic loads, close to 140 gCOD/L, of the mixtures subjected to AD tests. This confirmed the reduction of phyto-toxic power of WOWM caused by the proposed pre-treatment.

The enhancement of anaerobic degradability of WOMW was further confirmed by the remarkable COD reductions, monitored on the digested wastes (Table 5, Figure 7). In particular, the abatements detected on samples ST1 and ST2, around 78%, are comparable with the efficiencies reached by El-Gohary et al. [11] on olive mill wastewaters pre-treated by conventional Fenton process. The residual COD concentrations were around 33 g/L (Table 5), in line with the value of livestock digestate used in this study. Similar reductions, of about 71%, were monitored with regard to the volatile solids concentration, which reached values close to 56 g/L (Table 5).

On the contrary, the sample treated with lime alone (SL) showed a methane production and a COD reduction notably lower than those detected on samples subjected to the oxidation with hydrogen peroxide (Table 5, Figures 6 and 7). Moreover, the particularly high acclimatization period, observed before the start of exponential methanogenic phase, confirmed a remarkable inhibition power of WOMW treated with only lime additions. Thus, the conducted experiments proved that, to efficiently exploit the WOMW for methane production, a proper pre-treatment with lime and H_2O_2 is preferable. In particular, the experimental results indicate that, to maximize the methane yield, a lime amount of 15 g/L, to pre-treat the WOMW with H_2O_2, is adequate. In addition to the notable CH_4 volumes, the anaerobic digestion of pretreated wastes generates a slurry exploitable for agronomic purposes [41,42]. Indeed, the values of chemical parameters detected on digested samples (Table 5) were comparable with the characteristics of digestates of livestock manure and maize-oat silage [43]. Albuquerque et al. [43] proved that this type of digestates can be effectively used as organic fertilizer if an adequate utilization modality is adopted to control the salinity values.

Table 5. Characteristics of samples after the digestion tests.

Sample	pH	Cond. mS/cm	COD g/L	$CH_4/CODr$ L/g	TP g/L	VFA g/L	ALK g/L
STQ	7.56 ± 0.11	13.1 ± 0.37	135.6 ± 2.03	0.03 ± 0.001	3.60 ± 0.039	3.50 ± 0.084	6.70 ± 0.16
SL	7.95 ± 0.08	13.36 ± 0.41	76.19 ± 2.74	0.24 ± 0.015	1.95 ± 0.035	1.61 ± 0.034	14.14 ± 0.23
ST1	7.89 ± 0.07	13.69 ± 0.29	32.60 ± 0.55	0.34 ± 0.003	1.56 ± 0.021	1.56 ± 0.019	11.35 ± 0.41
ST2	7.76 ± 0.11	14.31 ± 0.39	33.50 ± 1.23	0.35 ± 0.014	1.40 ± 0.027	1.25 ± 0.03	15.76 ± 0.67
ST3	7.95 ± 0.012	15.73 ± 0.47	51.95 ± 0.88	0.33 ± 0.008	1.07 ± 0.019	1.04 ± 0.011	18.34 ± 0.75

Sample	TKN g/L	NH_4^+-N g/L	PO_4^{-3}-P g/L	COD/TKN g/g	TS g/L	VS g/L
STQ	1.92 ± 0.058	0.74 ± 0.02	0.150 ± 0.005	70.62 ± 2.4	185.6 ± 2.04	171.1 ± 1.98
SL	1.29 ± 0.033	0.63 ± 0.024	0.074 ± 0.003	59.06 ± 2.6	118.7 ± 1.54	94.3 ± 1.64
ST1	1.06 ± 0.025	0.82 ± 0.031	0.067 ± 0.002	33.95 ± 0.89	70.8 ± 1.13	56.4 ± 0.97
ST2	1.16 ± 0.019	0.84 ± 0.024	0.105 ± 0.003	28.87 ± 1.16	68.9 ± 1.25	55.9 ± 0.45
ST3	1.04 ± 0.014	0.79 ± 0.028	0.086 ± 0.001	49.95 ± 1.08	74.6 ± 1.48	67.9 ± 1.01

3.4. Economic Analysis

On the basis of the conducted experiments, it is sufficient a lime quantity of 15 g/L and a hydrogen peroxide amount of 0.05 $gH_2O_2/gCOD$ to improve the anaerobic biodegradability of raw WOMW, obtaining high methane yields. With this conditions, to treat 1 m^3 of WOMW, with the characteristics of that used in this study, an amount of about 39.6 L of H_2O_2 and 15 kg of $Ca(OH)_2$ are required. Through an analysis of chemicals industrial market, the price of H_2O_2 (35% *w/v*) and lime can be assumed of about 300 €/m^3 and 90 €/ton, respectively. Therefore, an overall expense around 13.2 €/m^3_{WOMW} can be estimated. This cost is significantly lower than that found if NaOH were used instead of lime. In fact, in this case, approximately 25.6 L of Na(OH) (40% *w/v*) would be necessary in order to correct the pH of WOMW at the values required to apply the proposed oxidation process. Assuming a cost for caustic soda of 240 €/ton, the expense is around to 6.1 €/m^3_{WOMW}, therefore the overall cost would be close to 18 €/m^3_{WOMW}, about 35% greater than that with lime use. A comparative analysis with other techniques is hard to carry out because the cost of treatment depends by several aspects, such as the waste characteristics, the removal yields of pollutants and the adopted operating conditions. Furthermore, there is a lack of studies concerning the expense required for the pre-treatment of olive mill wastes produced by means of two extraction systems.

The proposed pretreatment becomes more favorable by considering the gain detectable by exploiting the biogas for energy cogeneration. Indeed, the CH_4 yields (0.34–0.35 m^3_{CH4}/$kg_{CODremoved}$) and the COD abatements (78%) reached in this study, through the digestion of pretreated WOMW, allow obtaining a specific methane production of approximately 58.8 m^3_{CH4}/m^3_{WOMW}. With the hypothesis of an electric rate of 3.52 kWh/m^3_{CH4}, the above yield corresponds to 206.9 kWh/m^3_{WOMW}. The Italian directives, for example, grant a benefit of 0.233 €/kWh for the generation of renewable energy by means of anaerobic digestion of biomasses. With this incentive, a gain around 48.2 €/m^3_{WOMW} is achievable. Therefore, by subtracting the outlay due to WOMW pre-treatment, the actual profit results approximately of 35.0 €/m^3_{WOMW}. A more accurate definition of the economic viability of the integrated treatment will be possible only after the application in a demonstration plant at an adequate scale. In this regard, the main issues for scale-up are related to the construction and the costs of digesters, while, the proposed pre-treatment require simple reactors, whose capital costs are normally low.

4. Conclusions

The present research demonstrated the effectiveness of using hydrogen peroxide with lime, in absence of catalysts, for the pre-treatment of wet olive mill wastes. In particular, the experimental results showed that it is possible to obtain phenols removals next to 80% and VFA increases up to 90%, with a hydrogen peroxide dosage of only 0.05 gH_2O_2/gCOD. The process performance increased in response to the lime increase, due to the corresponding pH enhancement. Moreover, it was verified that, for lime dosage of 15 g/L and 25 g/L, the sequential addition of hydrogen peroxide produced a progressive reduction of phenols and the enhancement of volatile fatty acids amount. The COD abatements were always lower than 25%, while the residual H_2O_2 was completely negligible. Consequently, after the developed pre-treatment, the WOMW can be efficiently exploited for biogas production in anaerobic digestion. In fact, the batch digestion tests showed COD conversions up to 78% and remarkable methane yields of around 0.34–0.35 m^3_{CH4}/$kg_{CODremoved}$ on pre-treated samples. These yields guarantee a remarkable economic benefit by using the produced biogas for energy cogeneration. Therefore, the integrated treatment developed in this study may represent a suitable approach for the valorization of olive mill wastes. Nevertheless, additional studies should be carried out to investigate the applicability of this approach in industrial plants.

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