# Improvement of Biomethane Production from Organic Fraction of Municipal Solid Waste (OFMSW) through Alkaline Hydrogen Peroxide (AHP) Pretreatment

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**Abstract:** The organic fraction resulting from the separate collection of municipal solid waste (OFMSW) is an abundant residue exploitable for biofuel production. Anaerobic digestion (AD) is one of the most attractive technologies for the treatment of organic wastes thanks to the generation of biogas with a high methane content. However, because of its complex composition, the direct digestion of OFMSW can be less effective. To overcome these difficulties, many pretreatments are under development. In this work, the efficacy of alkaline hydrogen peroxide (AHP) oxidation was assessed for the first time as a pretreatment of OFMSW to enhance its anaerobic biodegradability. In this regard, many AHP batch tests were executed at pH 9 and by changing the peroxide dosages up to 1 $g_{H2O2}/g_{COD}$, under room temperature and pressure conditions. Afterwards, biomethane potential tests (BMP) were conducted to evaluate the performance of anaerobic digestion both on raw and pretreated OFMSW. The pretreatment tests demonstrated that AHP induces only a weak reduction in the organic load, reaching a maximum COD removal of about 28%. On the other hand, notable productions of volatile fatty acids (VFA) were found. In fact, by applying a peroxide dose of just 0.025 $g_{H2O2}/g_{COD}$, there was a doubling in VFA concentration, which increased by five times with the highest $H_2O_2$ amount. These results indicate that AHP mainly causes the conversion of complex organic substrates into easily degradable compounds. This conversion made it possible to achieve much better performance during the BMP tests conducted with the pretreated waste compared to that carried out on fresh OFMSW. Indeed, a low methane production of just 37.06 $mL_{CH4}/g_{TS}$ was detected on raw OFMSW. The cumulated $CH_4$ production in the pretreated samples increased in response to the increase in $H_2O_2$ dosage applied during AHP. Maximum specific productions of about 463.7 $mL_{CH4}/g_{TS}$ and 0.31 $L_{CH4}/g_{CODremoved}$ were calculated on mixtures subjected to AHP. On these samples, the satisfactory evolution of AD was confirmed by the process parameters calculated by modeling the cumulated $CH_4$ curves through a new proposed formulation of the Gompertz equation.

**Keywords:** alkaline hydrogen peroxide; anaerobic digestion; methane; OFMSW

## 1. Introduction

The development of suitable approaches for the management and treatment of municipal solid waste (MSW) is still a critical challenge in modern societies as the global production of MSW continues to grow over the years [1]. Half of the overall amount of MSW includes plastics, cardboard, and metals, whereas the organic fraction represents about 35–40% [2,3]. In effect, because of the widespread application of recycling practices, large quantities of the organic fraction of municipal solid waste (OFMSW) are produced. Anaerobic digestion (AD) represents a suitable technology for the transformation of organic waste to valuable renewable energy [4–9]. During anaerobic processes, organic matter is

degraded, without oxygen, through a sequence of four main phases performed by several classes of microorganisms, which leads to the production of a biogas with a high methane content [4]. In the first steps, complex molecules are hydrolyzed by fermentative microorganisms into simpler compounds including sugars, fatty acids, and amino acids [4]. These compounds, in the second phase (acidogenesis), are converted into volatile fatty acids (VFA) and some other products, mainly $CO_2$ and $H_2$ [4]. In the acetogenic phase, the VFA are transformed into acetate with still production of $CO_2$ and $H_2$. Finally, the acetate is used by methanogenic archaea to generate biomethane [4,10]. A certain aliquot of methane is also produced through anaerobic respiration exploiting $CO_2$ and $H_2$ [4]. In general, hydrolysis is characterized by the slowest reaction rate, and thus represents the limiting step [10]. For this reason, the feeding of complex organic matrices in conventional digesters leads to low conversion performances [11]. OFMSW is very heterogeneous and is often mixed with courtyard wastes, which contain lignocellulosic structures and are recalcitrant to anaerobic microbial degradation [12,13]. Therefore, adequate methodologies are necessary to overcome the difficulty in the digestion of OFMSW [10]. In this regard, scientific research in recent years has taken different directions. The main approaches for the enhancement of anaerobic digestion processes can be summarized as: optimization of the process parameters, co-digestion, feedstock pre-treatment, additive supplementation, optimization of bioreactors configurations, and application of genetic technologies [10]. The first strategy aims to identify the optimal values of parameters that mainly affect the AD process to increase biogas production (pH, temperature, COD/N/P ratio, organic loading rate, etc.) [14–16]. In co-digestion processes, two or more different wastes are fed into the digesters in proper amounts to obtain a balanced mixture in terms of chemical–physical characteristics [10,17]. On the other hand, the use of pretreatments exploits physical and chemical processes to improve the characteristics of waste before the feeding into digesters [10,13]. The supplementation of additives (activated carbon, zero valent metals, zeolites, etc.) aims to enhance AD mechanisms including direct interspecies electron transfer (DIET) [18–20]. Bioreactors optimization focuses on changing digesters' geometry from single-stage to two-stage and multi-stage to improve the digestion of complex organic waste [20]. Genetic strategy exploits the manipulations of enzymes, methanogens and microbial strains to enhance biological activity [10]. Among the different strategies, waste pretreatment is often essential to obtain satisfactory efficiencies in the digestion of very complex matrices, such as OFMSW [10]. Physical pretreatments (high-pressure homogenization, ultrasonic processes, microwave techniques, etc.) consist of the destruction of recalcitrant organic compounds to facilitate subsequent biological degradation [10,13,21–23]. Compared to physical processes, chemical techniques have gained more interest because of their better results in promoting biogas generation [10]. Strong acids, alkalis, and oxidizing compounds have been tested for the pretreatment of hardly biodegradable wastes [10]. Alkali processes showed great potential even in industrial applications [24]. Nevertheless, alkali pretreatments based on the use of hydroxides, such as NaOH, require great dosages that could cause the inhibition of methanogens [25]. Moreover, the discharge of digestate with high levels of $Na^+$ induces undesirable effects such as water and soil salinization [25]. The combination of hydroxides with $H_2O_2$ proved to be very effective in bleaching and delignification treatments [26,27]. It exploits the alkaline environment to induce $H_2O_2$ decomposition with the production of highly reactive species (hydroperoxide anion, radicals, etc.) able to convert complex organic matter into simpler molecules without reaching complete mineralization [26]. This conversion guarantees a large amount of easily degradable organic compounds during a subsequent anaerobic digestion, notably enhancing biogas production [28–30]. The process is advantageous as it does not generate hazardous products and can operate under milder operating conditions (lower hydroxides additions, lower temperatures, and shorter reaction times) than conventional alkali processes [31]. Compared to typical $H_2O_2$ oxidation treatments, AHP is very profitable as it is conducted without the addition of external catalysts or other activator agents (UV, $O_3$, US, etc.); therefore, the complexity of the treatment is notably reduced [28–30]. In addition,

AHP avoids the production and the disposal of a bulky precipitate that is instead generated in catalytic processes to remove the catalyst ions after waste treatment [28–30]. In our previous works, we demonstrated that alkaline hydrogen peroxide is very effective in increasing the anaerobic biodegradability of the residues of olive oil production [28–30], while other research tested its applicability to increase the digestibility of crop residues [31–33]. In the present paper, we investigated the effectiveness of AHP in the pretreatment of OFMSW to improve the subsequent methane productions in digestion processes. This is a new strategy as, to the best of our knowledge, no published works reported the pretreatment of OFMSW through $H_2O_2$ in alkaline conditions. A series of tests was conducted to define the effects of $H_2O_2$ dosages on the process performances. Subsequently, batch digestion tests were executed to estimate the potential methane production of raw and pretreated OFMSW. A modeling of the experimental trends of methane production was also carried out.

## 2. Description of the Experiments

### 2.1. Materials

Samples of OFMSW withdrawn from a waste treatment facility sited in Rende (Cosenza, Calabria Region, Italy) were used as feedstock. Before our sampling, the OFMSW was mechanically shredded in the treatment plant. The samples were composed, averagely in equal parts, of source-sorted organic household residues and solid wastes from gardens and parks [12]. In the laboratory, the samples were further homogenized and ground with a commercial blender (SINOTECH, 350 W), obtaining semi-fluid mixtures. Samples of digestate from an AD pilot plant treating composting leachate were exploited as inoculum for the biomethane potential tests [12]. The samples were stored in 50 L tanks at 4 °C. $H_2O_2$ (30% *w/v*) and NaOH of analytical grade were exploited to conduct the pretreatment tests.

### 2.2. Alkaline Hydrogen Peroxide Tests

The investigation aimed to define the pretreatment of OFMSW with $H_2O_2$ and NaOH. In this regard, different tests were carried out to identify the optimal $H_2O_2$ dosage to increase the anaerobic biodegradability of waste. Specifically, the dosage of peroxide was selected by referring to the ratio ($R_{HC}$) between $H_2O_2$ and COD ($g_{H2O2}/g_{COD}$), and values of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 0.75, 1 $g_{H2O2}/g_{COD}$ were tested. In our previous works, the most favorable pH for AHP treatments was found around 9 [29]. Therefore, this pH was selected to conduct the present experiments and NaOH (6 M) was used for its setting. In addition to the above experiments, a single test was carried out by only adjusting the pH, without any additions of $H_2O_2$. All experiments were carried out at room conditions of temperature (20 ± 2 °C) and pressure. During each test, the selected dosages of $H_2O_2$ and NaOH were mixed to 100 mL of OFMSW and then tap water was added to reach a total volume of 250 mL. The mixture was mechanically stirred at 300 rpm for a reaction time of about 3 h during which pH and temperature were continuously monitored. At the end of the treatment, the mixture was withdrawn and characterized.

### 2.3. Biomethane Potential Tests

BMP tests were carried out on both raw and pretreated OFMSW. Specifically, five tests were executed on OFMSW subjected to AHP pretreatment with different $R_{HC}$ ratios (0.025, 0.1, 0.25, 0.5, 1 $g_{H2O2}/g_{COD}$) and another was conducted with untreated OFMSW. Samples of digestate from a digestion process of composting leachate were used as inoculum. In each test, taking into account the low content of volatile solids (VS) of inoculum, a mixture with a total volume of 150 mL was prepared by mixing 60 mL of OFMSW (raw or pretreated) with 90 mL of digestate of composting leachate. In this way, the ratio of volatile solids of inoculum to those of OFMSW (raw or pretreated) was between 0.2 and 0.35 $g_{VS(icoulum)}/g_{VS(OFMSW)}$. With these ratios, potential limitations to the digestion process due to a lack of active biomass were prevented [34]. In addition to the tests with OFMSW, a BMP test was conducted with only the amount of inoculum. In all samples, no

chemicals were added to adjust the process parameters (pH, COD/N/P, etc.). The experiments were performed using 0.5 L dark glass bottles equipped with hermetic lids, which were connected, through HDPE (High Density Polyethylene) tubes, to cylindrical Plexiglass devices exploited for gas measurement. The gas produced was assessed through the displacement of the volume of a liquid placed in the cylinders. To remove carbon dioxide and other acid gases in the biogas, NaOH flakes were placed in little boxes positioned along the pipes that connected the bottles with the gasometers. This made it possible to measure $CH_4$ production during the anaerobic process. To start the tests, the mixtures were put in the bottles and $N_2$ was fluxed for about 5 min to create anaerobic conditions. The bottles were then sealed, connected to the $CH_4$ monitoring devices, and positioned in a thermostatic fridge provided with a magnetic stirring station. The samples were continuously mixed for 50 days (d) while keeping the temperature at 35 °C. Methane production was assessed daily. At the end of the tests, the residual digestates were analyzed in terms of the main chemical–physical parameters.

### 2.4. Analytical Methods

Temperature, pH, and conductivity were measured by a bench analyzer (Crison, MM 41, Barcelona, Spain). Total solids (TS) and volatile solids (VS) were estimated by weighing the samples dried at 105 °C and 550 °C [35]. COD, alkalinity (ALK), and $H_2O_2$ were determined by titrimetric procedures [35]. Volatile fatty acids (VFA) and total Kjeldahl nitrogen (TKN) were assessed by a preliminary distillation, followed by titration of samples with NaOH, for VFA, and HCl, for TKN [35]. The concentrations of $N-NH_4^+$, $P-PO_4^{3-}$, and $SO_4^{2-}$ were determined by colorimetric methods using a UV–Vis spectrophotometer (Thermo Genesys10uv, Waltham, MA, USA) [35]. Each analysis was conducted four times and the mean values with standard deviation were reported.

## 3. Results and Discussion

### 3.1. Characteristics of Organic Matrices

The raw OFMSW used in this work was characterized by a notable COD concentration around 254 g/L with a ratio between COD and VS of about 1.43 $g_{COD}/g_{VS}$ (Table 1), in line with the literature reports [19]. The high level of VS with respect to the total solids content (TS) (approximately 0.93 $g_{VS}/g_{TS}$) underlines that the waste was mainly composed of organic solids. The total Kjeldahl nitrogen was close to 2.2 g/L, and the ammoniacal form $N-NH_4^+$ represented only about 7% of the TKN (Table 1). The detected values show a low availability of nitrogen compared to the organic load, with a COD/TKN value of about 114.6 $g_{COD}/g_{TKN}$. The ratio between nitrogen and phosphorus (8.4 $g_{TKN}/g_P$) was adequate for biological processes [19]. Despite the fact that the pH was moderately acidic, the VFA/ALK ratio (0.194 $g_{CH3COOH}/g$ $g_{CaCO3}$) was below the threshold values (0.3–0.4 $g_{CH3COOH}/g$ $g_{CaCO3}$) that are considered tolerable for AD [4,12]. Therefore, the characteristics of OFMSW did not cause concern regarding the occurrence of inhibition phenomena due to an initial excess of volatile fatty acids [12].

**Table 1.** Characteristics of OFMSW and inoculum.

| | pH | Cond mS/cm | COD g/L | TS g/L | VS g/L | VFA $g_{CH3COOH}$/L | ALK $g_{CaCO3}$/L | $N-NH_4^+$ g/L | TKN $g_N$/L | $P-PO_4^{3-}$ mg/L | $SO_4^{2-}$ mg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Inoculum | 7.8 ± 0.1 | 23.6 ± 0.2 | 12.5 ± 0.6 | 21.6 ± 0.7 | 10.2 ± 0.4 | 0.91 ± 0.06 | 13.6 ± 0.7 | 1.415 ± 0.06 | 1.61 ± 0.05 | 215.1 ± 0.03 | 542.7 ± 21 |
| OFMSW | 5.3 ± 0.1 | 2.29 ± 0.1 | 254.4 ± 4.1 | 191.1 ± 1.6 | 178.1 ± 1.8 | 3.1 ± 0.02 | 15.98 ± 0.5 | 0.159 ± 0.007 | 2.22 ± 0.06 | 265.7 ± 12.1 | 192.1 ± 9.1 |

The characteristics of the inoculum exploited during the BMP tests were typical of mature digestates. Indeed, low residual organic matter content was detected, with values of COD and VS that resulted in about 12.5 g/L and 10.5 g/L (Table 1), respectively. Such values were mainly representative of the amount of bacterial biomass in the digestate. The high level of $N-NH_4^+$ in the inoculum, which accounted for about the total quantity of TKN, confirmed how the samples underwent an effective anaerobic degradation. The

alkaline pH was also representative of digestate taken from an anaerobic digestion process in a stable methanogenic phase.

### 3.2. Alkaline Hydrogen Peroxide Tests

Alkaline hydrogen peroxide tests were carried out at values of pH (9) and temperature ($20 \pm 2 \, °C$) milder than those commonly applied in the pretreatment of crop residues through AHP [31–33]. Under the above conditions, different tests were executed by varying the $H_2O_2$ dosage between 0 and 1 $g_{H2O2}/g_{COD}$.

Due to the weak operating conditions applied in terms of pH and temperature and due to the short reaction time, the initial content of COD was substantially unchanged in the test without the dosage of $H_2O_2$. Anyway, the results of experiments conducted by increasing the $H_2O_2$ dosage proved that alkaline oxidation causes only a weak abatement of the organic matter content (Figure 1). In fact, during the experiments, a slight COD reduction was observed. In particular, the removal yield was negligible with the lowest peroxide dosage tested and then linearly increased, reaching a value of about 12% with a ratio of 0.1 $g_{H2O2}/g_{COD}$ (Figure 1). Above this dosage, the abatements increased more slowly up to a maximum yield of about 28% using a dose of 1 $g_{H2O2}/g_{COD}$. The results are in agreement with those of our previous works on the treatment of olive oil mill wastes by using $H_2O_2$ and NaOH [29,30]. The COD abatements obtained with AHP were significantly lower than those generally detectable with other oxidation pretreatments [36]. AHP also caused a small abatement of the volatile solids amount, which showed a removal trend similar to that observed for COD. Consequently, the reduction in total solids concentration was quite low. From these findings, it can be stated that alkaline oxidation induces only a limited mineralization of the organic matter. In effect, the use of $H_2O_2$ in a basic medium generally produces only partial transformations of complex organic substrates into simpler and more biodegradable compounds [33]. This was confirmed by the trend of VFA concentration, whose initial value was around 1.5 $g_{CH3COOH}/L$. As shown in Figure 2, VFA were produced when $H_2O_2$ was applied, and increasing quantities were obtained with the rise in $R_{HC}$. It is interesting to note that the volatile fatty acids content doubled with the lowest $R_{HC}$ (0.01 $g_{H2O2}/g_{COD}$) tested in this study. Such results proved how the method guarantees a remarkable enhancement in biodegradable compounds even at very low reactant dosages. Above the $R_{HC}$ ratio of 0.01 $g_{H2O2}/g_{COD}$, the level of VFA rose slowly and a concentration of about 4 $g_{CH3COOH}/L$ was reached for a dose of 0.1 $g_{H2O2}/g_{COD}$ (Figure 2). By further increasing the dosage of $H_2O_2$, the VFA amount grew linearly, attaining a value close to 7.6 $g_{CH3COOH}/L$, which corresponds to five times the initial concentration.



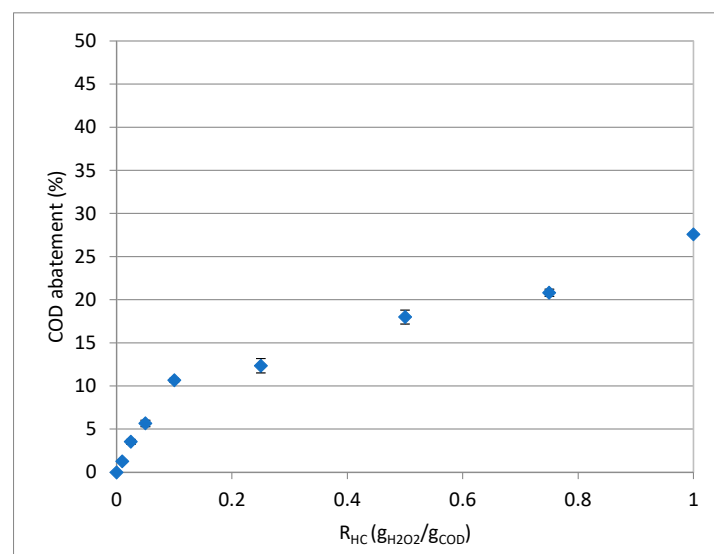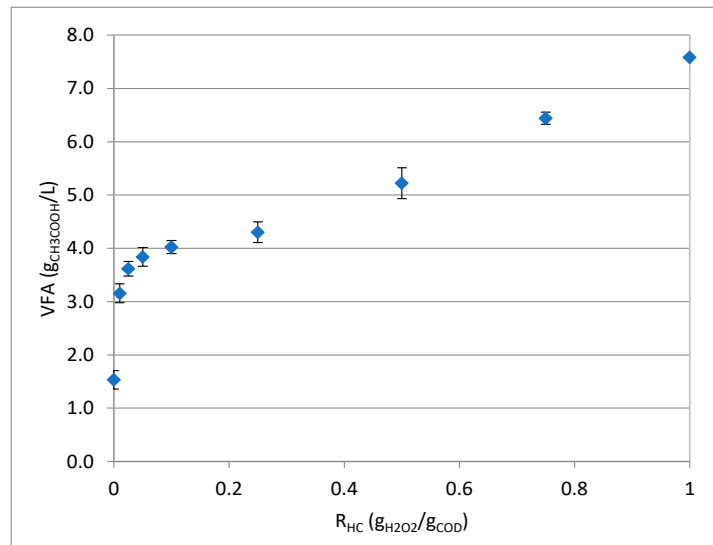**Figure 1.** COD abatements detected in the AHP tests conducted with different $H_2O_2$ dosages.

**Figure 2.** VFA concentrations detected in the AHP tests conducted with different $H_2O_2$ dosages.

VFA production is justified by alkaline hydrogen peroxide decomposition, which leads to the formation of hydroperoxide anions $HO_2^-$ and then to highly reactive hydroxyl radicals [26]:

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

$$H_2O_2 + HO_2^- \rightarrow OH\cdot + O_2^-\cdot + H_2O \tag{2}$$
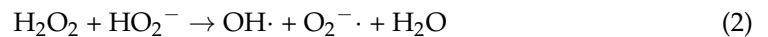
The generated $OH\cdot$ may attack organic compounds by extracting a hydrogen atom from the molecules (RH: general expression of organic molecules) [37,38]:

$$RH + OH\cdot \rightarrow H_2O + R\cdot \tag{3}$$

This mechanism triggers a series of further reactions that involve radical species and cause the oxidation of complex molecules into simpler compounds [37,38]:

$$R\cdot + H_2O_2 \rightarrow ROH + OH\cdot \tag{4}$$

$$R\cdot + O_2 \rightarrow ROO\cdot \tag{5}$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \tag{6}$$

Equation (6) shows the formation of molecules characterized by a chemical composition associable to that of carboxylic acids (ROOH), thus of VFA, which cannot be further oxidized by radicals [39,40].

The production of intermediate organic species, mainly carboxylic acids, in the advanced oxidation process was stated in many previous studies [39,40]. Our works on the residues of olive oil production demonstrated that VFA were actually generated during alkaline hydrogen peroxide oxidation [28–30], in agreement with the results of the present study.

In addition to Equations (1)–(6), the produced $OH\cdot$ can also react with $H_2O_2$, leading to the formation of less reactive $HO_2\cdot$ radicals (Equation (7)), which reduces the process effectiveness [41]. It is conceivable that such a condition is accentuated by high doses of hydrogen peroxide. This hypothesis justifies the trend of the VFA production index $I_{VH}$ (defined as the amount of VFA generated per unit of $H_2O_2$ dosed), which shows a decreasing trend in response to the increase in $R_{HC}$ (Figure 3).

$$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O \tag{7}$$
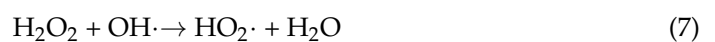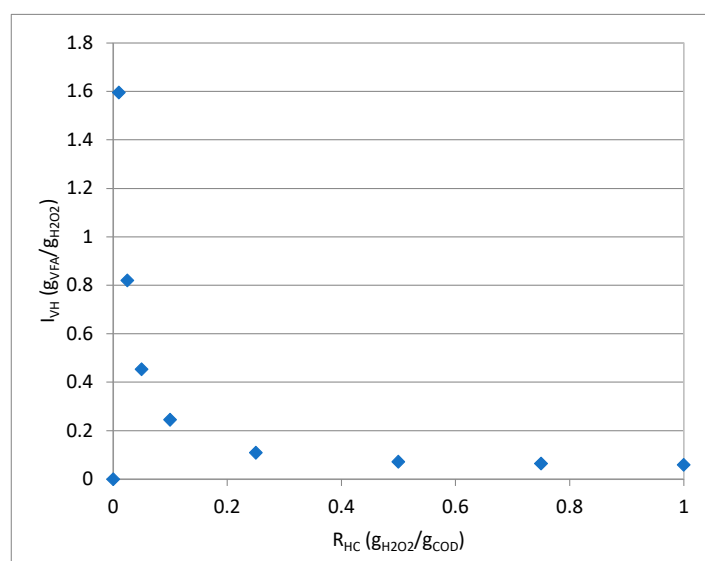
**Figure 3.** $I_{VH}$ ratio detected in the AHP tests conducted with different $H_2O_2$ dosages.

This behavior underlines how AHP was more advantageous at low dosages in terms of an effective utilization of $H_2O_2$, while at high dosages, the marked interaction between $H_2O_2$ and OH· probably caused a worse consumption of hydrogen peroxide. Despite these considerations, the VFA content kept growing with the $H_2O_2$ dose. In the perspective of a subsequent treatment of OFMSW in anaerobic digestion, VFA production during AHP is clearly a meaningful aspect due to the high biodegradability of low-molecular carboxylic acids. In fact, the conversion of complex substrates into VFA permits us to feed to AD a waste with a high content of bioavailable compounds. This allows a reduction in the extension of the hydrolysis and acidification phases and an increase in $CH_4$ generation. As a consequence of substrates' conversion into VFA, the restricted COD abatement induced by the alkaline hydrogen peroxide pretreatment also represents a beneficial feature. Indeed, a great quantity of residual organic matter with a large portion of VFA could guarantee a better performance in anaerobic digestion.

AHP is further advantageous because, with all the dosages applied, the concentrations of $H_2O_2$ at the end of the conducted tests were negligible. Thus, there is no need for additional treatments for the elimination of residual $H_2O_2$ before feeding OFMSW to anaerobic digestion [42]. Furthermore, in comparison with catalytic oxidation pretreatments (Fenton and Fenton-like processes), the absence of metal catalysts simplifies the process management and avoids potential inhibition phenomena during AD.

*3.3. Biomethane Potential Tests*

To assess the effect on methane production induced by the alkaline hydrogen peroxide pretreatment, a series of BMP tests on raw and pretreated OFMSW was conducted. In particular, the experiments discussed above proved that an increase in $H_2O_2$ dosage promotes the production of easily degradable organic acids, although the $I_{VH}$ decreases and the $H_2O_2$ utilization worsens. Considering these aspects, five samples pretreated with different $H_2O_2$ dosages (0.025, 0.1, 0.25, 0.5, 1 $g_{H2O2}/g_{COD}$, named, respectively, samples SP1, SP2, SP3, SP4, SP5) were subjected to AD tests. Moreover, anaerobic digestion was investigated on a mixture with raw OFMSW (sample SR) and on a sample made by the inoculum only (SI). The samples were prepared for BMP tests as described in Section 2.3. The chemical properties of mixtures are reported in Table 2.

**Table 2.** Characteristics of samples subjected to BMP tests.

| Sample | SI | SR | SP1 | SP2 | SP3 | SP4 | SP5 |
|---|---|---|---|---|---|---|---|
| pH | $7.2 \pm 0.1$ | $6.85 \pm 0.1$ | $7.4 \pm 0.2$ | $7.56 \pm 0.1$ | $7.61 \pm 0.1$ | $7.43 \pm 0.1$ | $7.60 \pm 0.1$ |
| Cond (mS/cm) | $14.2 \pm 0.11$ | $14.35 \pm 0.09$ | $17.26 \pm 0.07$ | $18.28 \pm 0.10$ | $18.00 \pm 0.08$ | $17.78 \pm 0.04$ | $19.08 \pm 0.09$ |
| COD (g/L) | $7.34 \pm 0.21$ | $48.20 \pm 0.92$ | $45.08 \pm 0.86$ | $41.83 \pm 1.4$ | $42.52 \pm 0.45$ | $38.32 \pm 1.23$ | $33.90 \pm 0.35$ |
| TS (g/L) | $13.1 \pm 0.34$ | $43.54 \pm 1,4$ | $41.16 \pm 1.7$ | $37.92 \pm 0.63$ | $38.44 \pm 1.21$ | $35.32 \pm 0.46$ | $32.50 \pm 0.98$ |
| VS (g/L) | $6.22 \pm 0.23$ | $34.61 \pm 1.07$ | $32.78 \pm 0.65$ | $29.76 \pm 0.24$ | $30.27 \pm 1.43$ | $27.3 \pm 0.76$ | $24.16 \pm 1.10$ |
| VFA ($g_{CH3COOH}$/L) | $0.49 \pm 0.02$ | $1.14 \pm 0.04$ | $2.07 \pm 0.08$ | $2.17 \pm 0.03$ | $2.22 \pm 0.02$ | $2.54 \pm 0.05$ | $3.65 \pm 0.07$ |
| ALK ($g_{CaCO3}$/L) | $7.99 \pm 0.35$ | $10.71 \pm 0.45$ | $13.24 \pm 0.56$ | $13.17 \pm 0.27$ | $13.21 \pm 0.49$ | $13.26 \pm 0.61$ | $13.31 \pm 0.38$ |
| N-$NH_4^+$ (g/L) | $0.856 \pm 0.023$ | $0.874 \pm 0.011$ | $0.904 \pm 0.029$ | $0.903 \pm 0.034$ | $0.899 \pm 0.025$ | $0.895 \pm 0.040$ | $0.890 \pm 0.038$ |
| TKN ($g_N$/L) | $0.954 \pm 0.041$ | $1.323 \pm 0.021$ | $1.705 \pm 0.012$ | $1.539 \pm 0.056$ | $1.513 \pm 0.067$ | $1.437 \pm 0.034$ | $1.406 \pm 0.052$ |
| P-$PO_4^{3-}$ (mg/L) | $129.6 \pm 7.4$ | $170.6 \pm 10.8$ | $303.7 \pm 15.1$ | $358.8 \pm 7.8$ | $348.6 \pm 12.8$ | $333.15 \pm 14.5$ | $353.9 \pm 12.9$ |
| $SO_4^{2-}$ (mg/L) | $302.6 \pm 9.76$ | $356.3 \pm 7.89$ | $355.9 \pm 10.54$ | $352.8 \pm 4.89$ | $353.6 \pm 12.71$ | $349.8 \pm 5.26$ | $345.3 \pm 15.15$ |
| VFA/ALK ($g_{CH3COOH}$/$g_{CaCO3}$) | 0.061 | 0.106 | 0.156 | 0.165 | 0.168 | 0.191 | 0.274 |
| COD/TKN (g/g) | 7.69 | 36.43 | 26.44 | 27.18 | 28.10 | 26.67 | 24.11 |

All samples were characterized by pH values and VFA/ALK ratios suitable for anaerobic digestion [4,12]. In effect, the higher volatile fatty acids concentrations in pretreated OFMSW were balanced by proper alkalinity values due to the pH setting during the AHP tests [29,30]. Because of the high nitrogen content in the inoculum, the COD/TKN was always below the theoretical minimum ratio of 50/1 [12]. This condition indicates a quite large availability of nitrogen, which represents the major nutrient to support bacterial metabolism [4,12]. The BMP tests were prolonged until digestion stopped, and no methane production was stably monitored.

The trends of cumulative $CH_4$ reported in Figure 4 show how the production started almost immediately on the sample containing the inoculum only, but it stopped after just one week, reaching a negligible volume of 55 $mL_{CH4}$. This confirms that the inoculum had a very low amount of available degradable organic matter.
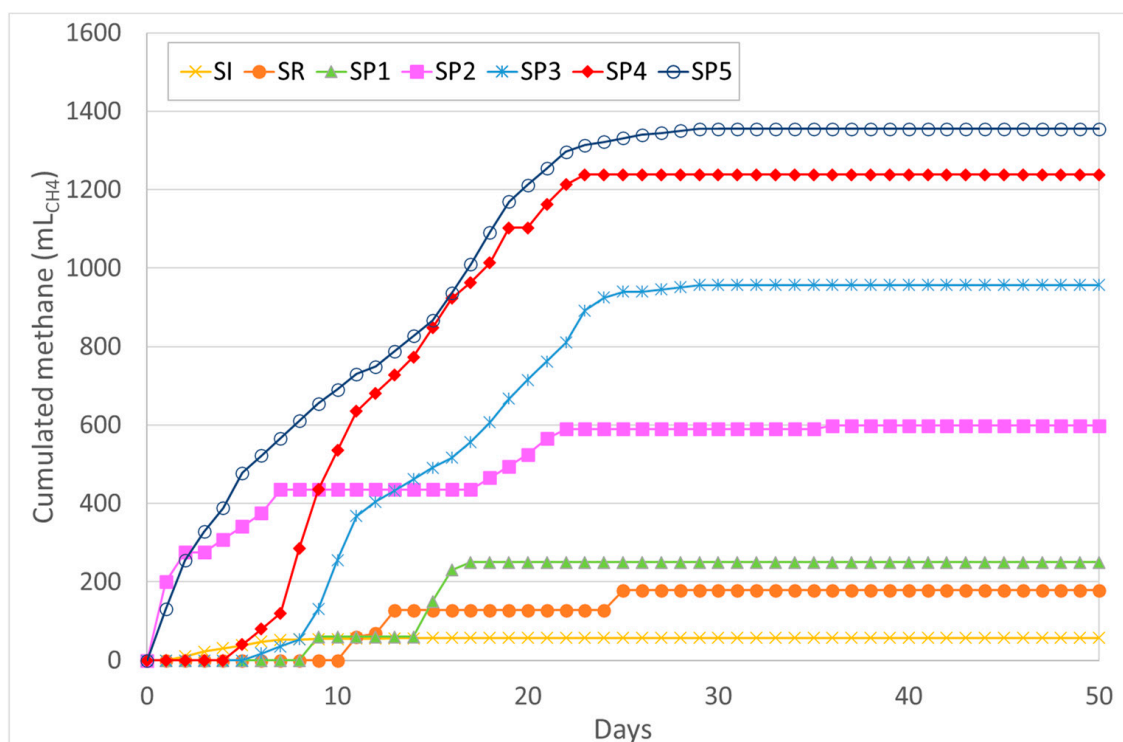


**Figure 4.** Cumulated methane volumes detected during the BMP tests.

Unsatisfactory productions were detected on the mixture prepared with untreated OFMSW (mixture SR). Indeed, methanization began on day 10 and continued with slow steps up to an overall cumulated production of about 170 mL$_{CH4}$. This behavior clearly proved the difficulty in degrading such a complex matrix. The poor efficiency is also underlined by the specific cumulated methane production index I$_{MS}$ (referring to the initial solids content of OFMSW added), which was just 37.06 mL$_{CH4}$/g$_{TS}$ (Table 3). It must be pointed out that previous works reported higher values of this parameter than that detected in the present study [34,43]. The low CH$_4$ production in our test with raw OFMSW finds a motivation in an excessive formation of VFA during the digestion process that probably caused the inhibition of methanogens activity. Indeed, despite an adequate initial VFA/ALK ratio (Table 2) [4], the volatile fatty acids reached a concentration of about 6.6 g$_{CH3COOH}$/L, which led to a pH around 6.3 (Table 4), able to inactivate the methanization phase [12]. Such a condition confirms that the conversion of complex organic matter during hydrolysis and fermentation phases represents the limiting factor in the digestion of OFMSW, and it could potentially arrest the process. Much better results were monitored on mixtures prepared using pretreated OFMSW (Figure 4). First of all, the time required for the beginning of methane generation, except for sample SP2, was progressively shorter in the samples pretreated with higher H$_2$O$_2$ dosages (Figure 4). This condition is attributable to the increasing amounts of rapidly biodegradable compounds (VFA) obtained with the increase in hydrogen peroxide used in AHP pretreatment.

**Table 3.** Values of I$_{MS}$ and Y$_{MC}$ calculated at the end of BMP tests.

| Sample | SI | SR | SP1 | SP2 | SP3 | SP4 | SP5 |
|---|---|---|---|---|---|---|---|
| I$_{MS}$ (mL$_{CH4}$/g$_{TS}$) | 29.32 | 37.06 | 59.10 | 159.72 | 250.13 | 369.11 | 463.72 |
| Y$_{MC}$ (L$_{CH4}$/g$_{CODremoved}$) | 0.138 | 0.059 | 0.064 | 0.149 | 0.242 | 0.281 | 0.314 |

**Table 4.** Characteristics of samples at the end of BMP tests.

| Sample | SI | SR | SP1 | SP2 | SP3 | SP4 | SP5 |
|---|---|---|---|---|---|---|---|
| pH | 7.9 ± 0.1 | 6.34 ± 0.1 | 7.22 ± 0.1 | 7.12 ± 0.1 | 7.53 ± 0.1 | 7.55 ± 0.1 | 7.61 ± 0.1 |
| Cond (mS/cm) | 14.82 ± 0.15 | 14.75 ± 0.11 | 18.12 ± 0.04 | 18.75 ± 0.06 | 19.34 ± 0.10 | 18.34 ± 0.05 | 19.52 ± 0.12 |
| COD (g/L) | 4.60 ± 0.14 | 29.01 ± 0.11 | 19.22 ± 0.75 | 15.13 ± 0.67 | 16.23 ± 0.59 | 9.04 ± 0.41 | 5.21 ± 0.14 |
| TS (g/L) | 9.57 ± 0.27 | 27.54 ± 0.95 | 21.01 ± 1.0 | 18.97 ± 0.52 | 18.94 ± 0.71 | 13.82 ± 0.58 | 12.00 ± 0.56 |
| VS (g/L) | 3.68 ± 0.11 | 19.54 ± 0.76 | 13.23 ± 0.52 | 11.01 ± 0.50 | 11.26 ± 0.39 | 6.08 ± 0.29 | 3.67 ± 0.18 |
| VFA (g$_{CH3COOH}$/L) | 0.40 ± 0.01 | 6.60 ± 0.09 | 0.82 ± 0.03 | 1.23 ± 0.05 | 0.95 ± 0.03 | 1.04 ± 0.04 | 1.02 ± 0.05 |
| ALK (g$_{CaCO3}$/L) | 7.12 ± 0.24 | 8.96 ± 0.27 | 12.46 ± 0.35 | 11.56 ± 0.39 | 10.60 ± 0.65 | 11.5 ± 0.42 | 11.21 ± 0.47 |
| N-NH$_4^+$ (g/L) | 0.914 ± 0.041 | 0.918 ± 0.037 | 0.978 ± 0.026 | 0.994 ± 0.025 | 1.011 ± 0.03 | 1.108 ± 0.036 | 1.204 ± 0.040 |
| TKN (g/L) | 0.947 ± 0.026 | 1.30 ± 0.043 | 1.678 ± 0.029 | 1.426 ± 0.032 | 1.407 ± 0.045 | 1.387 ± 0.051 | 1.325 ± 0.044 |
| P-PO$_4^{3-}$ (mg/L) | 139 ± 3.49 | 158.1 ± 9.8 | 301.5 ± 15.3 | 284.8 ± 16.0 | 295.0 ± 13.8 | 271.8 ± 12.5 | 205.38 ± 9.44 |
| SO$_4^{2-}$ (mg/L) | 347.6 ± 11.9 | 378.9 ± 14.6 | 394.6 ± 11.4 | 375.3 ± 15.7 | 398.2 ± 14.7 | 394.4 ± 17.6 | 395.8 ± 11.8 |
| VFA/ALK (g$_{CH3COOH}$/g$_{CaCO3}$) | 0.056 | 0.736 | 0.066 | 0.106 | 0.089 | 0.090 | 0.091 |
| COD/TKN (g/g) | 4.857 | 22.38 | 11.45 | 10.61 | 11.53 | 6.51 | 3.93 |

Besides the shorter start-up time, the higher doses in the pretreatment generally induced a more effective evolution of the digestion process. Indeed, the samples SP1 and SP2, pretreated with lower H$_2$O$_2$ dosages, showed periods of stagnation in the production of methane. These phases suggest the occurrence of reactions for the transformation of complex organic substances into compounds that can be assimilated by microorganisms responsible for the generation of CH$_4$. Methane production evolved without stagnation periods in the mixtures SP3, SP4, and SP5 with OFMSW pretreated using H$_2$O$_2$ amounts ≥ 0.25 g$_{H2O2}$/g$_{COD}$. Each of these curves showed phases characterized by different production rates and representative of the degradation of substrates with different biodegradability. The overall CH$_4$ volume detected at the end of digestion progressively

grew in response to the amounts of peroxide dosed during the AHP tests. However, it can be noted that in the sample SP1, the maximum methane production was barely greater than that reached with raw OFMSW (Figure 4). Therefore, the $H_2O_2$ amount was not enough to adequately improve the digestion process. On the other hand, large increases in the final cumulated $CH_4$ volume were observed with the progressive rise in the applied peroxide amount up to a dosage of 0.5 $g_{H2O2}/g_{COD}$ (mixture SP4). Beyond this dose, the beneficial effect on anaerobic digestion was less marked. Indeed, with the mixture SP5, although the $H_2O_2$ was doubled, an overall $CH_4$ increase around 9% was monitored in comparison with the mixture SP4. The high performance reached on samples SP4 and SP5 was confirmed by the values of specific productions $I_{MS}$ that were equal to 369.1 and 463.7 $mL_{CH4}/g_{TS}$, respectively (Table 3). These values are greater than those found in BMP tests conducted in other works on raw OFMSW [34]. The positive effect of AHP pretreatment on the digestion process is also clear by referring to the COD removal detected at the end of the BMP tests. In effect, the abatement of organic matter was only 40% on raw waste. On the other hand, COD removal progressively increased in the pretreated samples in response to the increase in $H_2O_2$ dosage applied during the AHP tests (Figure 5).
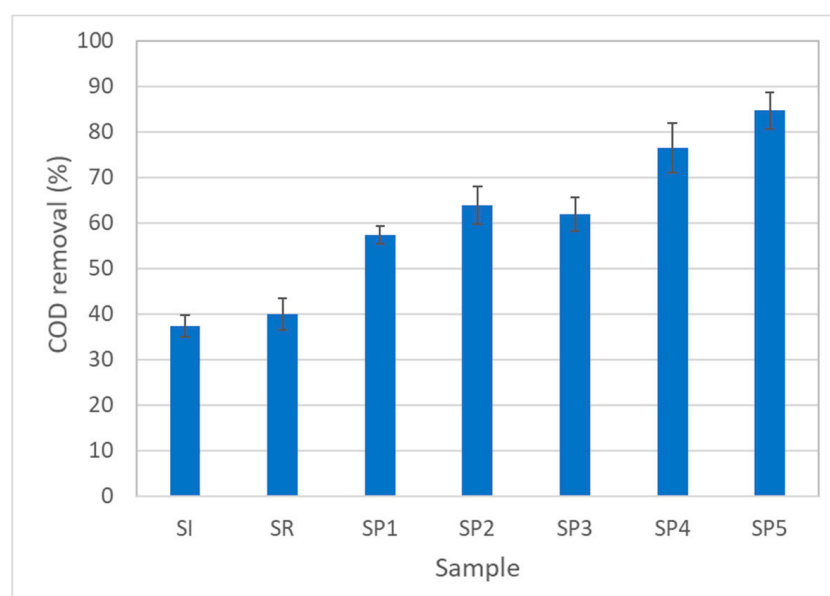


**Figure 5.** COD removal in the BMP tests.

The efficient degradation of organic substrates led to effective methane productions, reaching specific yields $Y_{MC}$, expressed in terms of COD removed, of 0.28 and 0.31 $L_{CH4}/g_{CODremoved}$ in the case of mixtures SP4 and SP5 (Table 3). These values are around 70–77% of the theoretical methane production yield that, at a temperature of 35 °C, amounts to 0.4 $L_{CH4}/g_{CODremoved}$ [44].

The results presented above clearly showed a notable beneficial effect of AHP pretreatment on methane production during the anaerobic digestion of OFMSW. Contrary to our results, Bolado-Rodríguez et al. [31] observed an unfavorable evolution of digestion processes on wheat straw and sugarcane bagasse pretreated through AHP (pH 11.5, T = 50 °C and 5% *w/w* $H_2O_2$). The authors justified the poor results with the potential presence of residual chemicals from pretreatment able to inhibit the anaerobic biomass activity. However, using similar peroxide dosages, we found that the residual $H_2O_2$ was completely negligible at the end of our tests. Therefore, the better behavior of the digestion process detected in the present study was probably due to the lower pH (9) applied during AHP pretreatment, which avoided excessive additions of NaOH that could hinder methane production. The inhibition of the AD process caused by high amounts of NaOH was stated by other authors and it is considered one of the main drawbacks of conventional

alkaline processes [10,25]. In effect, the generation of recalcitrant compounds, such as complex aromatic compounds, because of waste pretreatment under high NaOH levels was reported in several works [45]. Clearly, the presence of such molecules in pretreated waste can inhibit the microbial activity of methanogens during anaerobic digestion [45]. Moreover, adverse effects on methanogenesis were attributed to high concentrations of sodium and to the excessive presence of residual hydroxide ions ($OH^-$) [46,47].

In our tests, the effective evolution of the digestion process on pretreated samples was also confirmed by the values of parameters detected at the end of BMP tests (Table 4). Indeed, contrary to what was observed in the mixture with raw OFMSW, pH and VFA/ALK ratios typical of digestates from a suitable methanogenic phase were detected [12]. The COD/TKN was always quite low because of the substantial removal of organic matter. These results indicate that the availability of nitrogen was not a limiting factor for the digestion process. The TKN was mainly composed of $N-NH_4^+$ due to the transformation of organic nitrogen into reduced ionic forms. Anyway, the ammonium levels were much lower than the maximum concentration, around 3 g/L, that is assumed to be acceptable in anaerobic digestion [4]. Thus, inhibition phenomena imputable to excessive quantities of ammoniacal species did not occur.

Potential inhibitory and competing conditions caused by the oxidation of organic matter through sulfate-reducing mechanisms were also prevented [48]. Indeed, the ratio $COD/SO_4^{2-}$ was always higher than the threshold value of 10, below which sulfate-reducing bacteria (SRB) can compete with methanogens and produce toxic species such as sulfides [48].

In addition to these aspects, the concentrations of the parameters (Table 4) are compatible for the exploitation of digestate in agronomic practices if an adequate disposal modality is adopted to take the salinity values under control [49].

### 3.4. Modeling of Cumulated Methane Productions

The evolution of the anaerobic digestion process in batch reactors is generally modeled through the modified Gompertz equation (Equation (8)) [31,50]. The original expression was formulated to describe the bacterial dynamic through a logistic curve composed of a lag period followed by an exponential growth and an exhaustion phase. Lay et al. [51] assumed that the dynamic growth of methanogens is directly proportional to the $CH_4$ production rate according to the following version:

$$P = P_m \cdot exp\left\{-exp\left[\frac{R_m \cdot e}{P_m}(\lambda - t) + 1\right]\right\} \tag{8}$$

where $P$ is the cumulated methane ($mL_{CH4}$) at the digestion time $t$ (d); $P_m$ is the maximum cumulated volume of methane ($mL_{CH4}$); $R_m$ is the maximum daily rate ($mL_{CH4}$/d); $\lambda$ is the lag phase (d) for the beginning of methane production; and $e$ is the number of Napier (2.718).

As described above, the trends found in our experiments showed subsequent phases characterized by different production rates. To model this type of curve, we defined a new formulation of the Gompertz equation composed of a series of $n$ logistic trends that can describe the degradation of substrates characterized by different degradability:

$$P = \sum_{i=1}^{n} P_{m_i} \cdot exp\left\{-exp\left[\frac{R_{mi} \cdot e}{P_{m_i}}(\lambda_i - t) + 1\right]\right\} \tag{9}$$

In the above equation, for each phase $i$, the symbols have the same meaning as those described for Equation (8). In the case of the mixture with the inoculum, an accurate simulation was obtained through the conventional model (Equation (8)) (Figure 6a). Indeed, as previously mentioned, the sample SI showed a typical logistic curve that can be well described by the Gompertz model. Obviously, the values of the parameters confirmed an extremely weak methane production (Table 5). In the case of mixtures with raw and

pretreated OFMSW, much better fittings (Figure 6b–g) were obtained with the proposed expression (Equation (9)). In effect, the $R^2$ was always higher than 0.99 with this model (Table 6). Except for sample SP2, the number $n$ in the series of Equation (9) was equal to 2 (Table 6). This means that two sequential methanization phases occurred during the digestion process. Each of these phases showed a lag period ($\lambda$ values) attributable to the conversion of complex organic matter to easily degradable compounds. The values of the first lag phase ($\lambda_1$) progressively decreased from sample SR to sample SP5 (by excluding the sample SP2, which showed a singular trend) (Table 6). This, as previously discussed, is attributable to the formation of short-chain carboxylic acids during AHP pretreatment, which promoted the rapid initiation of methanization. The second production phase began after similar periods ($\lambda_2$) in the pretreated samples.

**Table 5.** Parameters of Gompertz model (Equation (8)) obtained from the interpolation of the experimental curves: $P_m$ (mL$_{CH4}$), $R_m$ (mL$_{CH4}$/d), $\lambda$ (d).

| SI | SR | SP1 | SP2 | SP3 | SP4 | SP5 |
|---|---|---|---|---|---|---|
| $P_m$ | $P_m$ | $P_m$ | $P_m$ | $P_m$ | $P_m$ | $P_m$ |
| 57 | 170 | 250 | 598.5 | 976.5 | 1249 | 1401 |
| $R_m$ | $R_m$ | $R_m$ | $R_m$ | $R_m$ | $R_m$ | $R_m$ |
| 12.5 | 26.2 | 62.5 | 48.7 | 64.1 | 100.9 | 65.2 |
| $\lambda$ | $\lambda$ | $\lambda$ | $\lambda$ | $\lambda$ | $\lambda$ | $\lambda$ |
| 1.8 | 12.5 | 10.5 | $10^{-5}$ | 6.8 | 5.3 | $10^{-5}$ |
| $R^2$ | $R^2$ | $R^2$ | $R^2$ | $R^2$ | $R^2$ | $R^2$ |
| 0.990 | 0.848 | 0.907 | 0.855 | 0.986 | 0.990 | 0.980 |

**Table 6.** Parameters of new Gompertz model (Equation (9)) obtained from the interpolation of the experimental curves: $P_m$ (mL$_{CH4}$), $R_m$ (mL$_{CH4}$/d), $\lambda$ (d).

| SR | | SP$_1$ | | SP$_2$ | | | SP$_3$ | | SP$_4$ | | SP$_5$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n$ | | $n$ | | $n$ | | | $n$ | | $n$ | | $n$ | |
| 2 | | 2 | | 3 | | | 2 | | 2 | | 2 | |
| $P_{m1}$ | $P_{m2}$ | $P_{m1}$ | $P_{m2}$ | $P_{m1}$ | $P_{m2}$ | $P_{m3}$ | $P_{m1}$ | $P_{m2}$ | $P_{m1}$ | $P_{m2}$ | $P_{m1}$ | $P_{m2}$ |
| 120 | 50 | 60.1 | 190 | 279.5 | 161.2 | 154.6 | 601.2 | 355.4 | 853.6 | 388 | 833.4 | 521.6 |
| $R_{m1}$ | $R_{m2}$ | $R_{m1}$ | $R_{m2}$ | $R_{m1}$ | $R_{m2}$ | $R_{m3}$ | $R_{m1}$ | $R_{m2}$ | $R_{m1}$ | $R_{m2}$ | $R_{m1}$ | $R_{m2}$ |
| 5.9 | 59.5 | 131 | 152 | 198.5 | 41.9 | 38.3 | 81.5 | 81.2 | 135.3 | 55.9 | 85.6 | 79.5 |
| $\lambda_1$ | $\lambda_2$ | $\lambda_1$ | $\lambda_2$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\lambda_1$ | $\lambda_2$ | $\lambda_1$ | $\lambda_2$ | $\lambda_1$ | $\lambda_2$ |
| 10.1 | 24.2 | 8.3 | 14.5 | $10^{-5}$ | 3.5 | 17.7 | 6.1 | 17.2 | 4.9 | 13.5 | $10^{-5}$ | 14.2 |
| $R^2$ | | $R^2$ | | $R^2$ | | | $R^2$ | | $R^2$ | | $R^2$ | |
| 0.995 | | 0.999 | | 0.997 | | | 0.998 | | 0.999 | | 0.997 | |
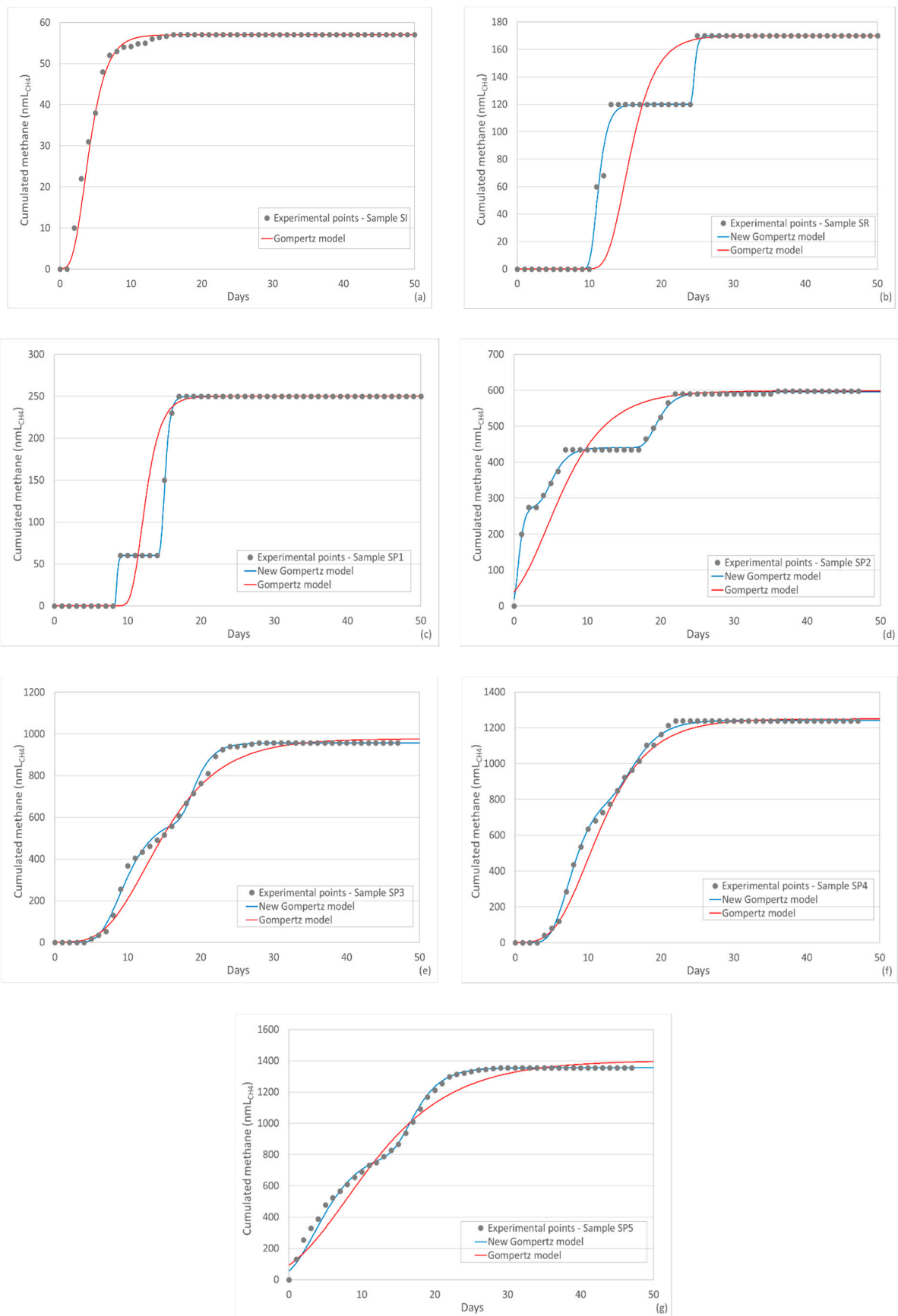
**Figure 6.** Interpolation of experimental curves through the Gompertz equation (Equation (8)) and the new proposed model (Equation (9)): mixtures SI (**a**), SR (**b**), SP1 (**c**), SP2 (**d**), SP3 (**e**), SP4 (**f**), SP5 (**g**).

The daily rates were high in the sample SP1 and in the sample SP2 for the first methanization phase ($R_{m1}$), but the production reached unsatisfactory cumulative volumes. In samples SP3 and SP5, the daily methane rate was around 80–85 $mL_{CH4}/d$ in both production phases, while in sample SP4 a higher rate, equal to about 135 $mL_{CH4}/d$, was calculated for the first exponential step (Table 6). This value was found to be about 29.22 $mL_{CH4}/(g_{COD}\cdot d)$ and 40.25 $mL_{CH4}/(g_{TS}\cdot d)$ by referring, respectively, to the COD and TS of waste subjected to AD. These values were largely greater than those detected by Boulanger on raw waste [34], proving the positive effect of AHP on biogas production from OFMSW. This was further confirmed by the time necessary to produce 80% of the overall methane volume, defined as technical digestion time $T_{80}$ [45]. $T_{80}$ is often used as a guideline for hydraulic retention time (HRT) in the design of anaerobic digesters. The value of $T_{80}$ for raw OFMSW was calculated around 24 days (reaching a very low methane production). In comparison, the values $T_{80}$ of the samples SP4 and SP5, which showed the greatest yields, were approximately 16 days. Therefore, the alkaline hydrogen peroxide pretreatment, in addition to higher methane productions, allows a considerable reduction in hydraulic retention times. This, clearly, permits a reduction in the volume of the digesters.

## 4. Conclusions

In the present work, the effects of alkaline peroxide pretreatment on the methane production achievable from OFMSW were assessed. In this regard, a set of AHP tests at mild conditions was conducted and then a series of BMP tests was executed on raw and pretreated OFMSW. A maximum COD removal of just 28% was reached during the AHP tests. On the contrary, a notable formation of volatile fatty acids was observed. In fact, the VFAs rapidly increased, attaining a fivefold increase with the maximum $H_2O_2$ dosage tested. These results proved that AHP caused mainly the conversion of complex organic matter into compounds that are easily degradable in anaerobic digestion processes. The BMP tests showed a poor methane production on raw OFMSW, while a notable improvement was obtained with the pretreated samples. The maximum productions of 463.7 $mL_{CH4}/g_{TS}$ and 0.31 $L_{CH4}/g_{CODremoved}$ were obtained on the sample pretreated with $R_{HC}=1\ g_{H2O2}/g_{COD}$. However, satisfactory productions (369.1 $mL_{CH4}/g_{TS}$ and 0.28 $L_{CH4}/g_{CODremoved}$) were reached by halving the peroxide amount. With this dose (0.5 $g_{H2O2}/g_{COD}$), the methane production rate, calculated with a new proposed formulation of the Gompertz equation, reached the highest value of 40.25 $mL_{CH4}/(g_{TS}\cdot d)$. In conclusion, the results of the conducted experiments support the applicability of alkaline peroxide oxidation as a pretreatment of OFMSW to enhance the yields in AD. Anyway, further research would be advisable to optimize some technical aspects. In particular, it could be interesting to test the dosage of $H_2O_2$ in sequential steps to further improve the performance of AHP and reduce peroxide consumption. This would allow us to limit the costs for chemical reagents, which represents the main outlay in these types of processes. Moreover, the anaerobic digestion of pretreated OFMSW in continuous or semi-continuous reactors must be investigated.

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