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Energy valorization of olive waste water, their sludge and treatmentby methane production

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Abstract

The anaerobic digestion of the two wastes: olive mill wastewater (OMWW) and sludge from their treatment, is a biological process that allows the production of energy in the form of biogas. Our study is based on the comparison of the methanogenic capacity between the biomethanization of OMWW and the sludge from their treatment. The OMWW were previously treated by electrocoagulation and then adsorption under optimal conditions. The sludge generated by the various treatments, estimated at 50 g/L of OMWW, is in turn treated by anaerobic digestion. The production of methane from the two wastes is accompanied by a reduction in their estimated pollutant load in non-biodegradable organic matter, polyphenols and fat by 39%, 45% and 39% respectively for olive mill wastewater treatment sludge and 36%, 31%, 39 for olive mill wastewater ; i.e. a total pollutant load yield of the OMWW of about 75% to 78%. The total amount of methane produced over 30 days and 49 days respectively by the OMWW and their treatment sludge is 300.7 cm3/L and 889.9cm3/L, equivalent to an energy equivalent of 2.92 Wh/L and 8.72 Wh/L. The application of the anaerobic digestion process to OMWW treatment sludge is efficient and cost-effective for methane production while eliminating its adverse effects on the environment and producing energy.

Keywords: *Olive mill wastewater, treatment sludge, anaerobic digestion, biogas, energy, loadpolluting*

1.Introduction

Morocco is the sixth largest producer of OMWW in the Mediterranean. Nearly 30% of Moroccan OMWW are "treated" by simple natural evaporation, while more than 70% are released directly into the natural environment, which poses very serious environmental problems for our country [1]. The example of the situation in Oued Sebou (Fez, Morocco) is an illustration of this scourge [2].In recent years, the study of OMWW treatment has been the subject of much research and several techniques have been proposed such as concentration, evaporation[3]., incineration, ultrafiltration/ reverse osmosis, coagulation/flocculation[4], biological treatment by aerobically activated sludge, anaerobic co-digestion[5], etc. Some of these techniques do not eliminate all pollution, others are often costly or generate secondary pollution requiring further treatment. However, none of these techniques have resulted in industrial-scale application[6]. Anaerobic digestion is an attractive alternative biological process in which organic pollutants are transformed into methane CH_4 and carbonic acid CO_2[7]. It allows the decontamination of effluents that are more or less rich in organic matter, and the production of energy in the form of biogas and compost. It uses closed reactors that occupy much less floor space than conventional wastewater treatment plants, which produce only very small quantities of sludge [8]. The organic matter present in the OMWW is transformed into biogas, a renewable energy source, during anaerobic treatment. The energy efficiency of this process depends on the type of organic matter present in the OMWW[9]. This work consists of the treatment of OMWW and sludge generated by their treatment by a process combining electrocoagulation and adsorption, by anaerobic digestion after describing the different materials and experimental methods used to obtain treatment sludge from OMWW.

2. Materials and methods

2.1. Characteristics of olive mill wastewater

The OMWW were collected from the storage basin of an olive oil mill in three phases, located in Meknassa Ben-Ali, 8 km from the city of Taza, during the olive growing season (November 2018 - March 2018). The aggregate sample is obtained from 8 samples taken from different locations and depths which are then mixed. Then put in plastic bags numbered, dated and stored in the refrigerator at 4 °C until they are analyzed according to the AFNOR standard set by Rodier[10].

2.2. Combined treatment of OMWW by electrocoagulation / adsorption

The electrocoagulation experiments were conducted in a one-litre electrochemical cell. The cell consisted of 8 aluminium plates each with a total surface area of 70 cm^2 (length 10cm × 7 width cm) arranged in parallel at a distance of 1 cm and supplied by a direct current of 5 A current, 18 V voltage and 90 W power [11]. The solution is mixed in the electrolytic cell by a magnetic stirrer placed at the bottom of the tank and located between the two electrodes. The agitation intensity is 200 rpm. In order to improve the treatment, the pretreated OMWW underwent a second treatment by adsorption on charcoal of modified and acid-activated eucalyptus sawdust. The treatment by adsorption of the pretreated OMWW is carried out under optimal conditions of stirring time which is 270 min, adsorbent load 2.4 g /L, and a pH of the medium equal to 3.

2.3. Biomethanization treatment

The pilot for the anaerobic digestion of OMWW and treatment sludge was carried out in a system consisting of a 2-litre fermentor, maintained at a mesophilic temperature of 37°C throughout the digestion process. Sampling operations were performed manually using a syringe. The biogas produced was measured according to the principle of

displacement of a basic solution (NaOH 5M + limewater saturated solution). The experiment continues until biogas production tends towards zero [12].

Figure 1. Biomethanization assembly

2.4. Analytical techniques

On all samples of raw or treated OMWW, we have executed the following physico-chemical analyses: pH, conductivity, chemical oxygen demand, biological oxygen demand, polyphenols, ammoniacal nitrogen and fat. For the sludge, we mixed all the sludge recovered from the OMWW treatments and characterized it by measuring the same physicochemical parameters and by some heavy metals (Al, Fe, Zn....) that we carried out by ICP spectroscopy.

3. Results and Discussions

3.1. Physico-chemical characteristics of OMWW

The results of the physico-chemical characterization of the studied OMWW are presented in Table 1. The characterization of the OMWW shows that the COD/BOD_5 ratio is very high, reflecting the presence of certain non (or less) biodegradable organic substances, essentially represented by phenolic compounds whose concentration has exceeded 3 g.L-1. In addition, the OMWW contain a high concentration of fat, a low nitrogen content (NTK of 0.003 g. L-1) and are acidic in nature (pH of 4.43).

Table 1. Physico-chemical characteristics of **OMWW**.

Parameters	Value
pH	4.43 ± 0.05
Conductivity EC (mS.cm^{-1})	8.56 ± 0.02
Density	1.05
MM (%)	25.25 ± 5.46
Organic matter (%)	74.75 ± 5.46
Organic carbon (%)	43.36 ± 3.16
Fat (g/L)	7.67
NTK (mg/L)	0.003 ± 0.0004
BOD_5 (mg of O_2.L^{-1})	5650 ± 0.5
COD (mg of O_2.L^{-1})	96070 ± 0.51
Polyphenols (g.L^{-1})	3.45 ± 0.68

3.2. Treatment of OMW by electrocoagulation / adsorption

Table 2. Composition of OMWW treated by electrocoagulation**.**

Parameters	Value
pH	6.51±0.05
EC (ms.cm-1)	9.45±0.02
TKN (g.L-1)	0.0024±0.0004
BOD5 (mg of $O_2.L^{-1}$)	3898±0.5
COD (mg of $O_2.L^{-1}$)	52108±0.51
Fat g/L	3.01
Polyphenols g/L	2.56

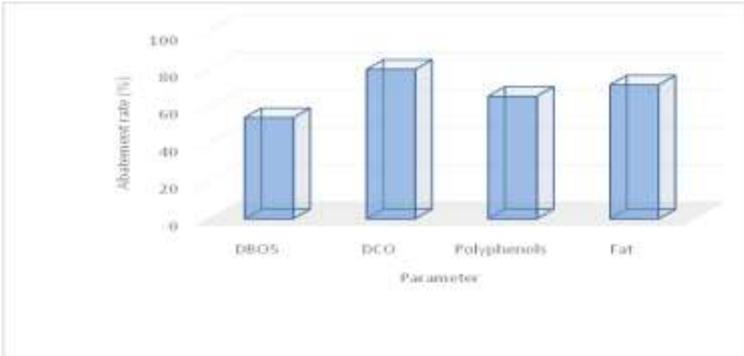

Figure 2. Treatment efficiency of OMWW by electrocoagulation.

The treatment of OMWW by electrocoagulation under the above-mentioned conditions led to their neutrality and allowed a reduction in their pollutant load in polyphenols 25.79%, fat 60.75%, non-biodegradable organic matter 45.76% and biodegradable organic matter 31%. In order to improve these yields, the pretreated OMWW underwent a second treatment by adsorption in a static reactor on charcoal of activated eucalyptus sawdust. Table 3 summarizes the results of the adsorption tests on charcoal of activated sawdust and also figure 3 shows the abatement rate of this treatment (COD, BOD_5, polyphenols, fat).

Table 3. Composition of OMWW treated by electrocoagulation-adsorption.

Parameters	Value
EC ($ms.cm^{-1}$)	6.23±0.02
TKN ($g.L^{-1}$)	0.0017±0.15
BOD5 (mg of $O_2.L^{-1}$)	2583±0.5
COD (mg of $O_2.L^{-1}$)	19069±0.5
Polyphenols g/L	1.21

The combined treatment of OMWW under optimal conditions of time has reduced the non-biodegradable organic load by 80.15%, 54.28% biodegradable organic load, 65.78% phenolic compounds and 65.78% fat and also from black to pale yellow[13].

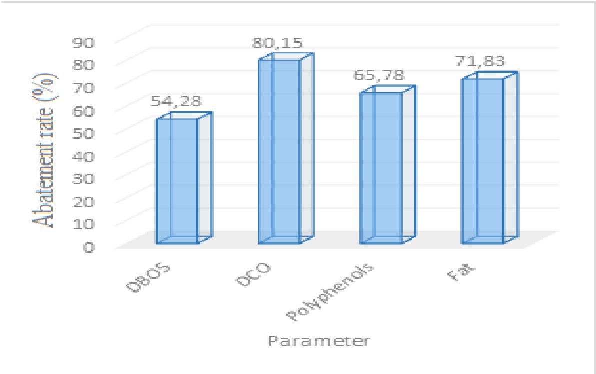

Figure 3. Treatment efficiency of OMWW by electrocoagulation-adsorption.

3.3. Physicochemical characterization of OMWW sludge

The sludge recovered after treatment of the OMWW is black in colour. Their physicochemical characterization shows that the COD/BOD_5 ratio is very low, which explains why the biodegradable organic matter of the OMWW is released into the sludge and adsorbed onto the charcoal of the sawdust contains a high concentration of aluminium which, due to the treatment of the OMWW by electrocoagulation using aluminium plates (Al of 531, 3 $mg.L^{-1}$) and is almost neutral in nature (pH of 6.47)[14].

Table 4. Physicochemical Characteristics of OMWW sludge

Parameters	Values
pH	6,47 ± 0.05
Conductivity (ms /cm)	6,45 ± 0.02
MM(%)	34.28 ± 5.46
MO (%)	65.72 ± 5.46
CO (%)	52.42 ± 3.16
Fat (g/L)	4.76
NTK (mg/L)	_
BOD_5 (mg of $O_2.L^{-1}$)	9561
COD (mg of $O_2.L^{-1}$)	4560 ± 0.51
Polyphenols (g .L^{-1})	1.42 ± 0.68
Al (mg /L)	531.3
Fe (mg /L)	7.885
Zn (mg /L)	6,015
Cr (mg /L)	3,26
Na (mg /L)	356,385
Mg (mg /L)	509.1

3.4. Biomethanization of OMWW and sludge from their treatment

3.4.1. Methane production

The anaerobic digestion of OMWW begins with hydrolysis to form long-chain fatty acids and glycerin, then these products will be transformed by bacteria into H_2, acetates and carbon dioxide which will be transformed into methane and carbon dioxide by methanogens according to the following reactions [15, 16]:

Hydrolysis: $C_6H_{10}O_5)$ n + $nH_2O \rightarrow nC_6H_{12}O_6$

Acidogenesis: $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$

$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2CH_2COOH + 2H_2 + 2CO_2$

$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$

Metagenesis: $CH_3COOH \rightarrow CH_4 + CO_2$

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Monitoring of biogas production for both experiments shows an increase in methane production from day one until it reaches stability on day 49 with a total production of 898.6 cm3/L of methane for the biomethanization of OMWW treatment sludge. For OMWW, methane production is low and in increments of 5 until there was a slight increase in this rate with a total production of 300.7cm3/L (Figure 4). As a result, it can be concluded that the OMWW treatment sludge has more favourable survival conditions (nutrients) and methanogenic bacteria development. Based on the results obtained (Table 5), the fermentation of OMWW and treatment sludge produces biogas with a high methane content and traces of sulphate.

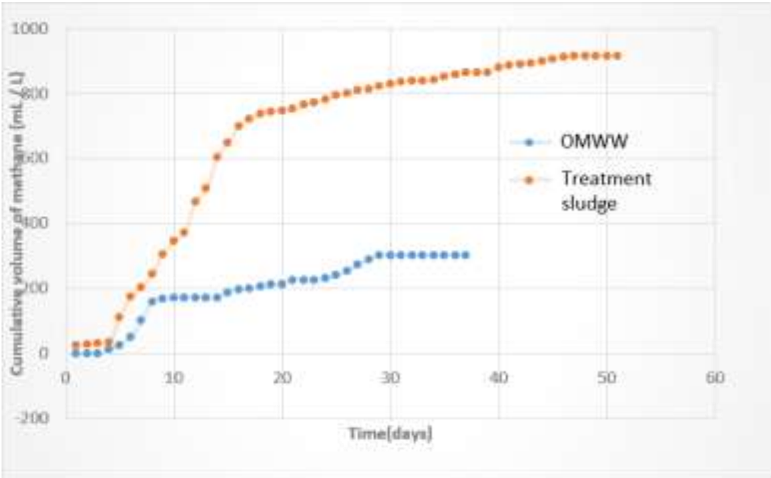

Figure 4. Evolution of cumulated volume of OMWW methane and treatment sludge.

Table 5: Volume composition of biogas

Gas	Rawvegetable water	Treatment residues
Methane CH_4 (%)	72.55	75.32
Carbon dioxide CO_2 (%)	27.45	24.68
Hydrogen sulfide H_2 S (%)	Traces	Traces

3.4.2. Effect of the biomethanization of OMWW and their sludge on physico-chemical parameters as a function of time

The pH, the concentration of COD, BOD_5 and polyphenols of vegetable waters are important parameters for the OMW fermentation. The anaerobic digestion performance of OMW and sludge from their treatment was evaluated for more than a month. Methane production data: biogas yield, pH, conductivity, COD, BOD_5, total lipids, concentration of polyphenols measured throughout the digestion experiment are presented in the graphs (5-10). The pH, COD, BOD_5 and polyphenol concentration of the OMWW are important parameters for the fermentation of the OMWW.

The anaerobic digestion performance of OMWW and sludge from their treatment was evaluated for more than a month. Dataon methane production : biogas yield, pH, conductivity, COD, BOD_5, total lipids, concentration of polyphenols measured throughout the digestion experiment are presented in the graphs (5 to 10). As shown in Figure 5, we noticed a slight decrease in pH from day one for both cases. This acidification of the environment could be attributed to incomplete oxidation of the organic matter leading to the production of organic fatty acids under anaerobic conditions with the accumulation of volatile fatty acid and the release of H^+ proton. The effects of pH variation on microbial kinetics are not negligible. Studies by Andres Donoso and al. [17] have shown that pH inhibits anaerobic digestion. However, pH is only a factor protagonist and was not involved in optimizing pH-methane production ratios. The balance of digestion depends on the non-accumulation of intermediate degradation products. Thus, hydrolysis and acidification of lipids do not occur with a pH below 6, because the accumulation of H+ protons implies the blocking of methanogenic activity. Also, high salinity (high conductivity) (Figure 6) could cause a decrease in dry matter by decreasing nitrogen availability, in addition to their toxicity to some microorganisms [18].

As shown in Figure 8, we noted a decrease in fat content over time from anaerobic digestion on the first day in both cases. In fact, this reflects the proper functioning of the anaerobic digestion process and the stability of the fermentation medium, i.e. there is no accumulation of fatty acids in the medium and they have been transformed into methane by the methanogens as they are produced. Indeed, OMWW contain on the one hand easily fermentable products e. g. sugar and glucose, and on the other hand compounds that are difficult to degrade e. g. fatty acids and polyphenols. These polyphenols have an inhibitory effect on anaerobic digestion [19]. However, in the presence of methanogenic activities, they are partially degradable (Figure 8). In addition, the two experiments lead to a significant reduction in COD of 56% for the biomethanization of OMWW and 39% for that of treatment sludge. This decrease is explained by the degradation of organic substances that are transformed into intermediate products. Similarly, anaerobic digestion of OMWW and treatment sludge leads to a decrease in biological oxygen demand during digestion time [20].

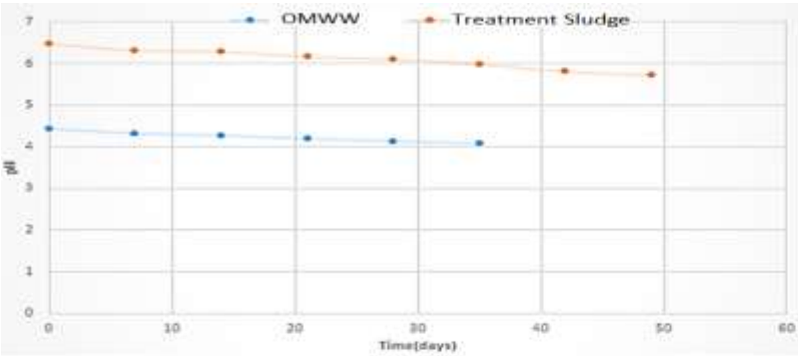

Figure 5. Evolution of the OMWW pH and their sludge as a time function.

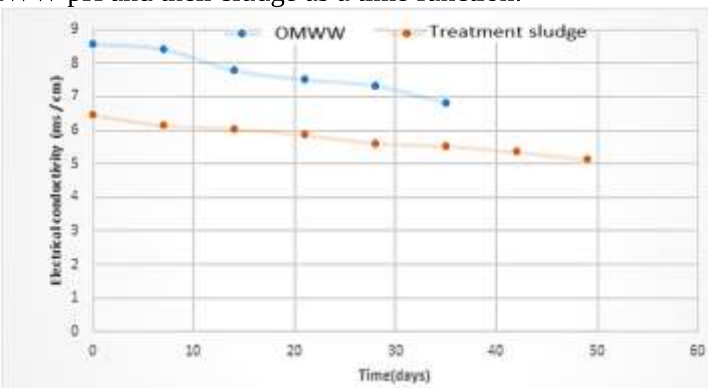

Figure 6. Evolution of the OMWW conductivity and their sludge as a time function.

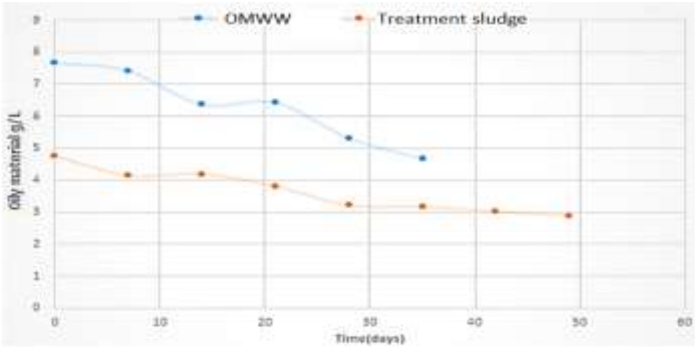

Figure 7. Evolution of fat of OMWW and their sludge as a time function.

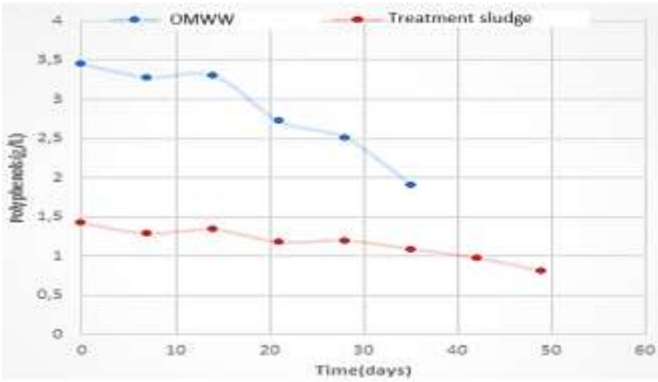

Figure 8. Evolution of the polyphenol content of OMWW and their sludge as a time function.

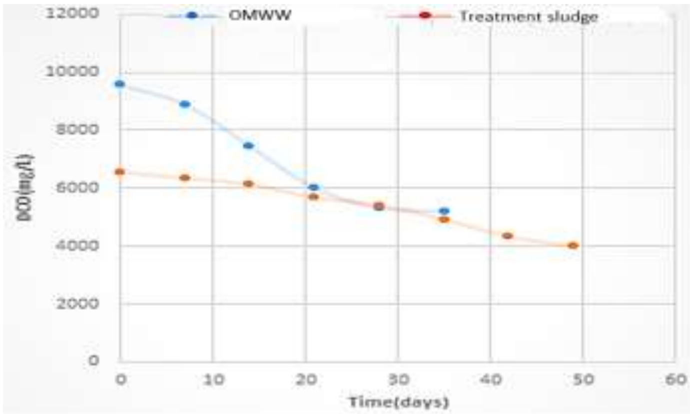

Figure 9: Evolution of the chemical oxygen demand of OMWW and their sludge as a time function

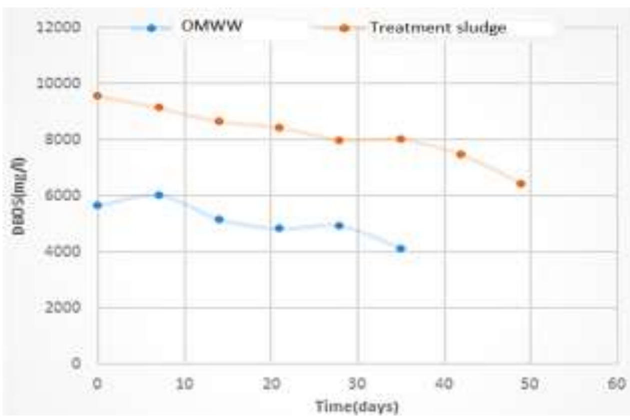

Figure 10: Evolution of the biological oxygen demand of OMWW and their sludge as a time function

4.Conclusion

This study reveals the importance of anaerobic fermentation of OMWW treatment sludge since it reduces its undesirable effect on the environment; through its ability to degrade, on the one hand, harmful organic matter (COD and polyphenols) under the action of biomass bacteria, and on the other hand, to produce energy in the form of biogas. This gas is largely methane since the other gases released: NH_3, H_2S, CO_2,...are absorbed either by the sulphuric acid solution or by the sodium hydroxide solution. However, we record that OMWW treatment sludge produces 3 times more biogas than OMWW. The quantity of methane produced is the equivalent of 8.72 Wh/L in electrical energy. Since the biogas production coefficient varies according to the nature of the effluents to be treated and the time required for complete fermentation, the gas released becomes low at the end of each experiment following the decrease in the content of organic matter present (decrease in COD), and/or the probable accumulation of compounds inhibiting methanization (volatile fatty acids, CO_2...). OMWW treatment sludge promotes higher gas production than raw marine sludge. Despite several unclear points (residence time and conditions of the culture medium...) this treatment remains a means to enhance these effluents known for their harmful effect on the environment, and to produce, at the same time, an energy source.

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