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Treatment and valorization of oil mill wastewater by methanation process

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Abstract

Olive oil extraction process generates a considerable amounts of olive mill wastewaters (OMWW). Theses effluents constitute a major environmental risk due to their high concentration of organic phenolic compounds. The objective of this study is to make a complete physicochemical characterization of raw OMWs and treat it by anaerobic digestion in order to produce the methane and to reduce their toxicants. a semi continuous anaerobic digester was conducted in mesophilic mesophilic temperature. The physicochemical analyzes show that the substrate studied are characterized by a high acidity (pH = 5.8), high content of suspended matter (SM), methane yield reached avalueof250 ml / g VS, a significant increase of volatile solid (VS) indicating an accumulation of organic compounds. The digestate remaining in the digester can be used as fertilizer in agriculture or as inoculum to make easy starting other experiences of anaerobic digestion. This digestate obtained from the digester treating olive mill wastes was characterized (NH_4, P, K, Mg…) to evaluate its agricultural quality.

Keywords: Olive wastewaters, Meknes, Polyphenol, Methane, Acidity, Methanogenic potential.

Full length article **Corresponding Author*, e-mail: *y.zaid@um5r.ac.ma*

1. Introduction

In Morocco, the olive oil industry plays a very important role in socio-economic terms, but it generates a large amount of wastes consisting of olive pomace (solid waste) and olive mill wastewater (liquid effluent) that must be treated to face the risks of pollution [1-3]. The volume of OMWW is generally estimated as follows: 1kg of olive provides about 1 to 1.5 liters of OMWs depending on the extraction system used [4]. Phytotoxicity of OMWS can be attributed to the presence of lipids and polyphenolic compounds [5]. Anaerobic fermentation is one of the main treatments for reducing the content of the olive wastewaters and to generate, at the same time, energy in the form of biogas used for the production of the electricity and heat**.** However, this process seems to be unstable due to the inhibitory effect of polyphenol and acidity of OMWW (pH between 4.5 and 5). Valorization of organic waste not only reduces environmental pollution, but also has potential for providing significant amount of renewable energy [6]. Many difficulties have been noted when applying the process of anaerobic digestion of OMWW, these difficulties are due essentially to its high concentration in organic compounds (TCOD = 80 to 140 g COD/l, total phenol = 8 to 14 g/l). Also, OMW is an acid effluent (pH = 5) characterized by low alkalinity (1 to 2 g $CaCO_3$/l) and nitrogen deficiency (0.2 to 0.5 g N/l) [8, 9]. Several pretreatments have been used to remove this problem such as dilution pretreatment by aerobic culture.

The aim of this work is treating the raw OMW without any pretreatment to evaluate its methane yield by anaerobic digestion, the main advantage of this process is that the product can be used as a vehicle fuel or for co-generation of electricity and heat, and thus, can lead to reductions in greenhouse gas emissions. The treatment of OMWW is still a major challenge facing this industry, so anaerobic digestion has become an established and proven technology for the treatment of this effluent.

2. Materials and methods

Anaerobic digestion was carried out in 3L at mesophilic conditions (35-40°C). The reactor is provided with two suitable devices for taking samples for analysis and the production of biogas, it is fully stirred by means of an electromagnetic stirrer connected to a motor [10]. the digester was connected to a gasometer, system consisting of to calculate methane production, a bubbler containing a solution of NaOH (6N) is installed between the digester and the gasometer, it is used to capture CO_2 from biogas.

2.1. Substrate and Inoculum

OMW used in this study were collected from extraction unit olive oil works with the three-phase processes by the press system in the industrial area at Meknes city in Morocco (site 1). Their main physicochemical compositions are summarized in Table 1. The inoculum was made from a mesophilic anaerobic reactor of wastewater plant in Marrakech. it was selected on the basis of their high methanogenic activity [11].

2.2. Procedure and Chemical analysis

Starting digester takes 2 phases: the inoculation in which the digester is fed by the inoculum with a organic loading rate of 8 gVS / L. Inoculation digesters is very important for the startup acceleration because it ensures sustainable biogas production by methanogenic bacteria and introduce the addition of an inoculum provides an active microbial mass, it is essential to find a suitable inoculum containing methane producing microorganisms. After this phase the digester is fed with the substrate treated (OMWW) with the organic loading rates 0.5, 1, 1.5, 2 and 2.5 g SV/l and the volume of methane produced was measured using the gasometer by the water displacement method.

The metal elements including BP, Cu, Fe and Zn were analyzed by the technique of atomic absorption spectroscopy to flame, the apparatus is of type Analytik Jena NONAA350 programmed by a computer guided by the software Aspect LS Version 1.3.2.0 Palo Alto, USA). Suspended matter was determined by filtration on a cellulose filter (0.40 μm), it is the difference of the filter weight before and after drying in the oven (105 ° C). Determining concentration of total phenols in the different samples was performed by the Folin Ciocalteu method described by [12]. The alkalinity is measured by adding an acid standard solution (sulfuric acid) in the presence of a pH meter. The total solid is obtained after drying the sample in an oven at 105 ° C for 24 hours and weighing the residue, the mineral solid after drying the sample in a muffle furnace at 550°C for 2 hours and the volatile solid is obtained by the difference between the total solid and the mineral solid [10].

3. Results and discussion

3.1. Methane productivity

Figure 2 shows the variation of methane productivity with the load added in the digester, methane production volumes are respectively 108, 247, 320, 333 and 400 ml/L digester for the loads 0.5, 1, 1.5, 2 and 2.5 g VS/L. We can note that the methane productivity increase with the increase of load added.

3.2. Stability of digester

During this experiment we followed the evolution of pH and alkalinity; they represent the parameters of anaerobic digestion stability control. Several experiments have shown that they exist a number of factors that influence the process of anaerobic digestion, for this it is necessary to ensure that the experiment is performed under stable conditions, it is very important in order to obtain a highest biogas yield [13]. Figure 4 shows the variations of the alkalinity in the digester. The alkalinity caused by bicarbonates of calcium must be relatively high to function properly. One considers in general; it is necessary to have at least 1000 mg/L of alkalinity (expressed in mg of $CaCO_3$ per liter) in a reactor that works in good condition [14]. It is noted that the alkalinity in the digester is on average 1400 mg/L, the value is optimal because it is necessary that the alkalinity is comprised between 1000 and 3000 mg/L for proper functioning of the anaerobic digestion, thus, the measure of alkalinity enables us to assess the stability of anaerobic digestion and its resistance to acid attack and when the digester has a high alkalinity it can have a good buffer capacity which is actually the neutralizing capacity a sudden acidity of the middle. Figure (4) shows changes in pH in the digester during the entire period of the process of anaerobic digestion. The process of anaerobic degradation is strongly dependent on pH as each microbial groups implicated in the reaction has a specific pH range for optimum growth. The optimal pH range for mesophilic anaerobic digestion is close to neutrality, varying for each type of bacteria between 6.5 and 7.5 [15].

3.4. Methanogenic potential and Biodegradability

The methanogenic potential represents the maximum amount of methane produced per liter of effluent or per kg of waste when they are treated in an anaerobic digestion reactor. The methanogenic potential differs depending on the treated substrate and also the pretreatment which was undergoes, it increases with the percentage of dry matter. in this experiment, the methanogenic potential of different loads 0.5, 1, 1.5, 2 and 2.5 g VS/L are respectively 216, 247, 213, 166.7 and 160 ml/g VS. Figure 6 shows the biodegradability in the digester, this is the organic matter degraded relative to that added, this figure shows the evolution of VS eliminated in relation to VS added. The Biodegradability is in the order of 64%, which is the degradation rate of the waste treated in the digester (r = 0.9705).

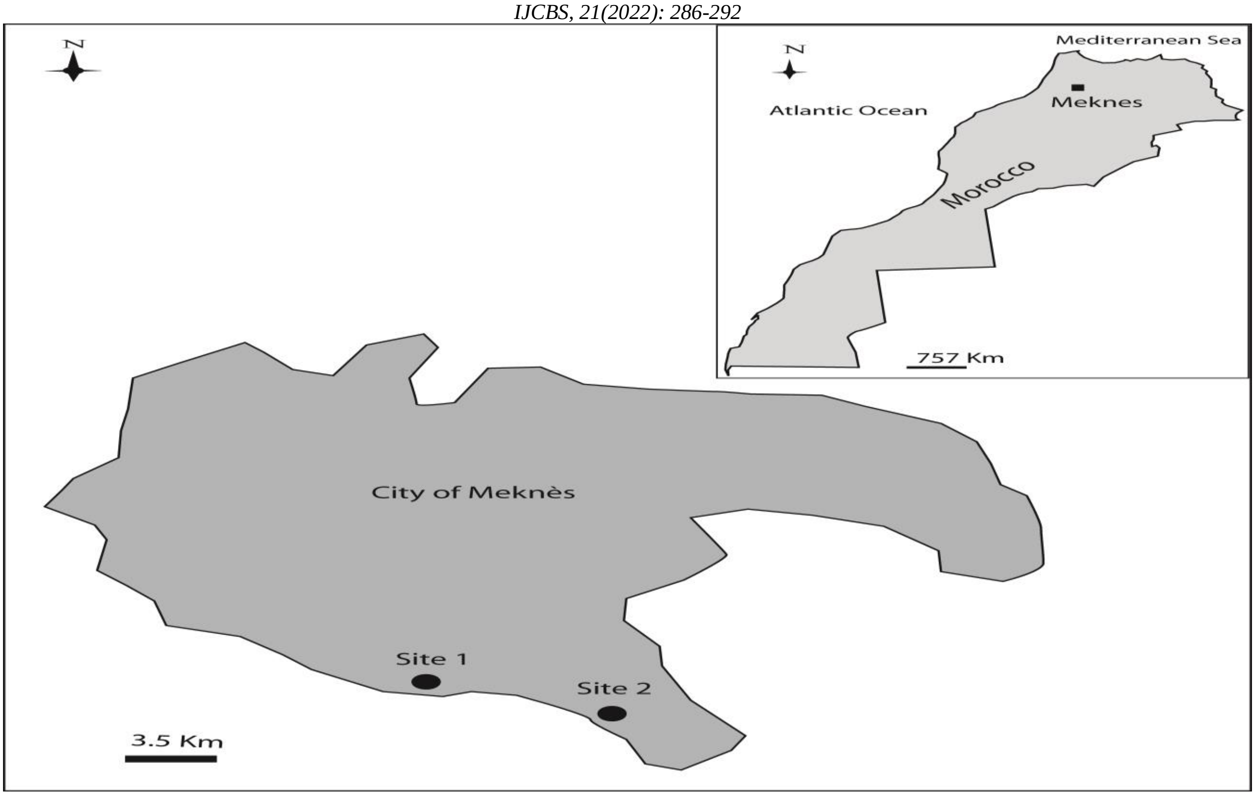

Figure 1: Localization of the trituration unit of olive oil [16].

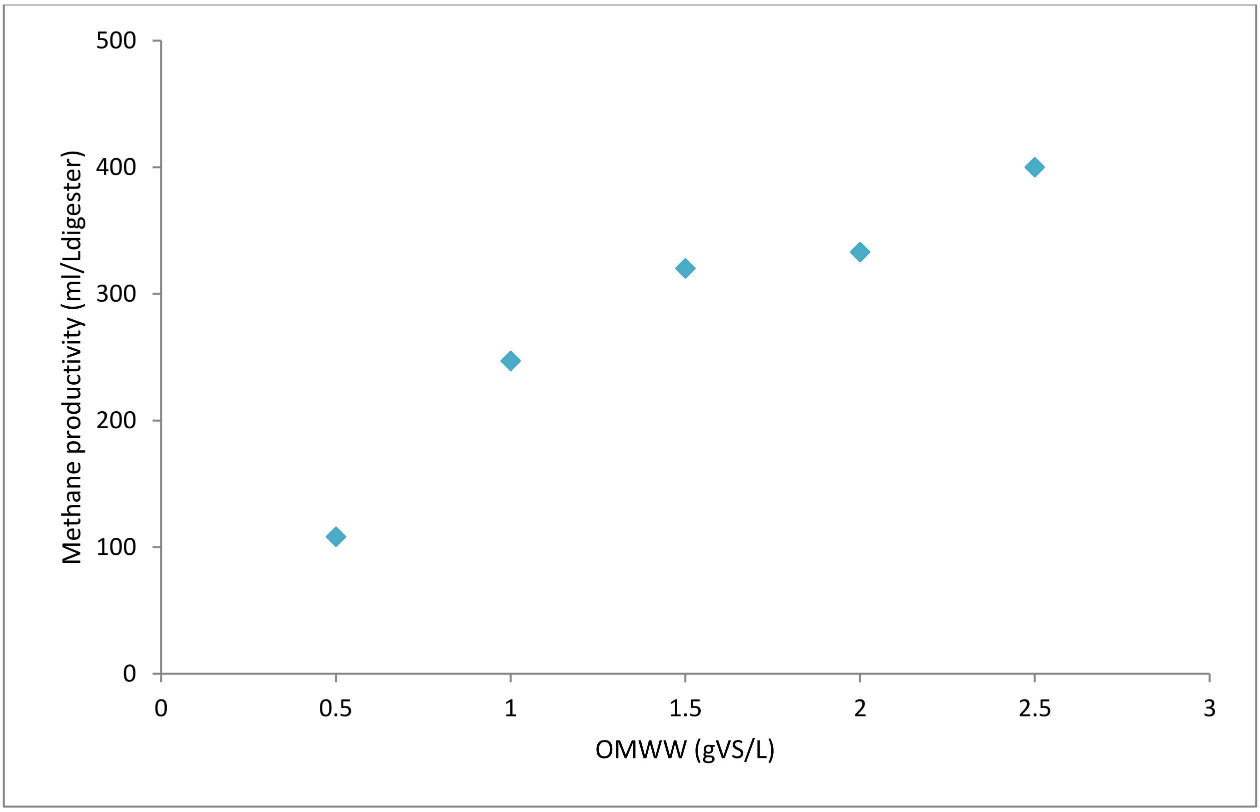

Figure 2: Variation of methane productivity for different organic loading rate.

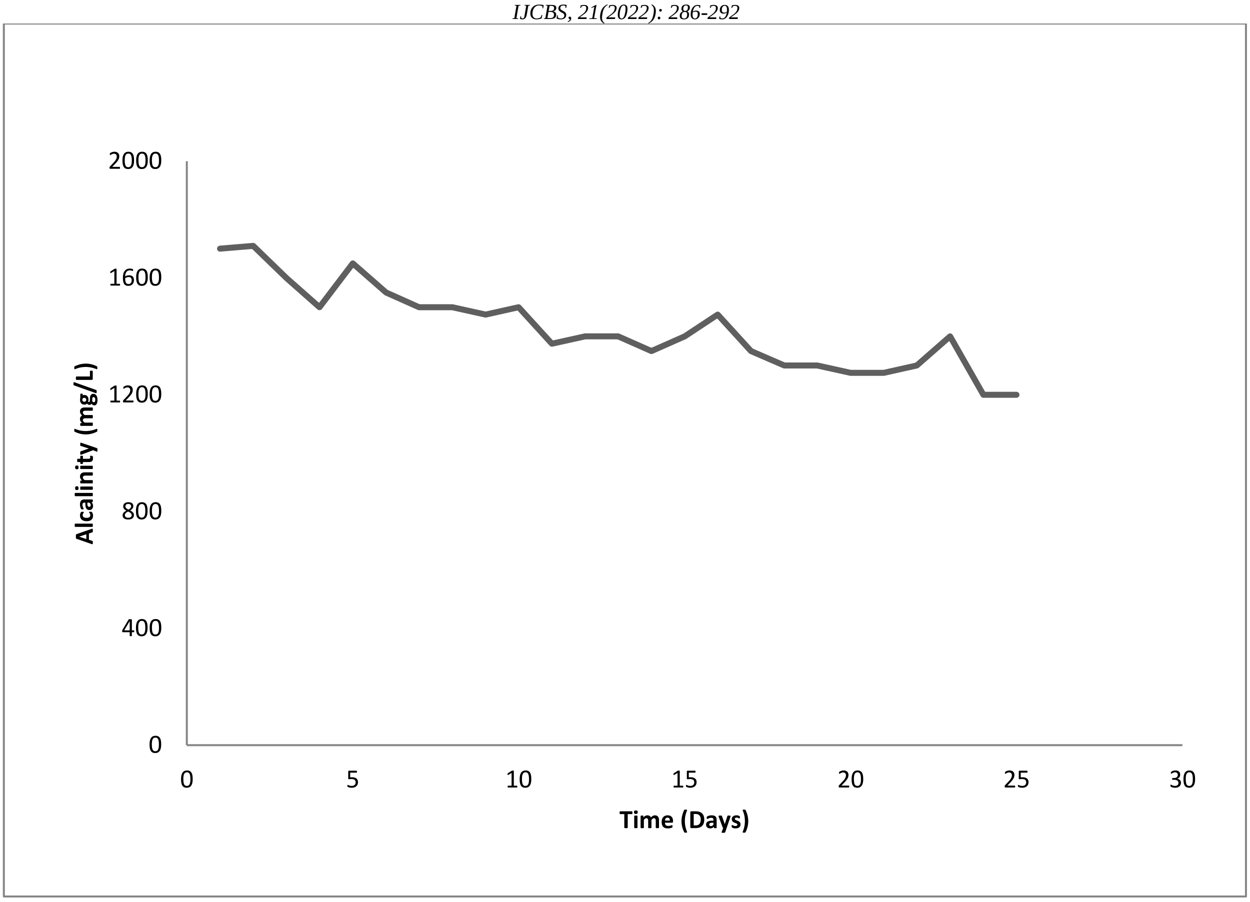

Figure 3: Variation of alkalinity in the digester.

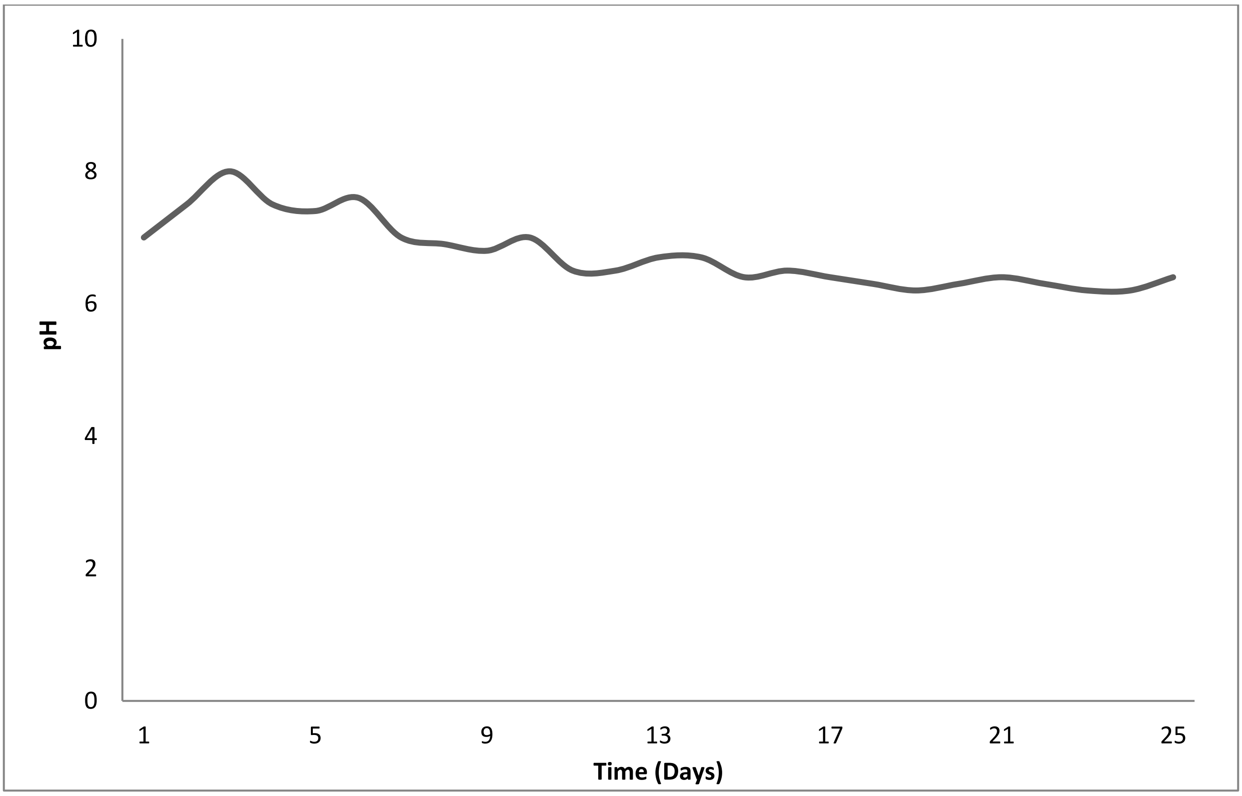

Figure 4: Evolution of pH during anaerobic digestion of OMWW.

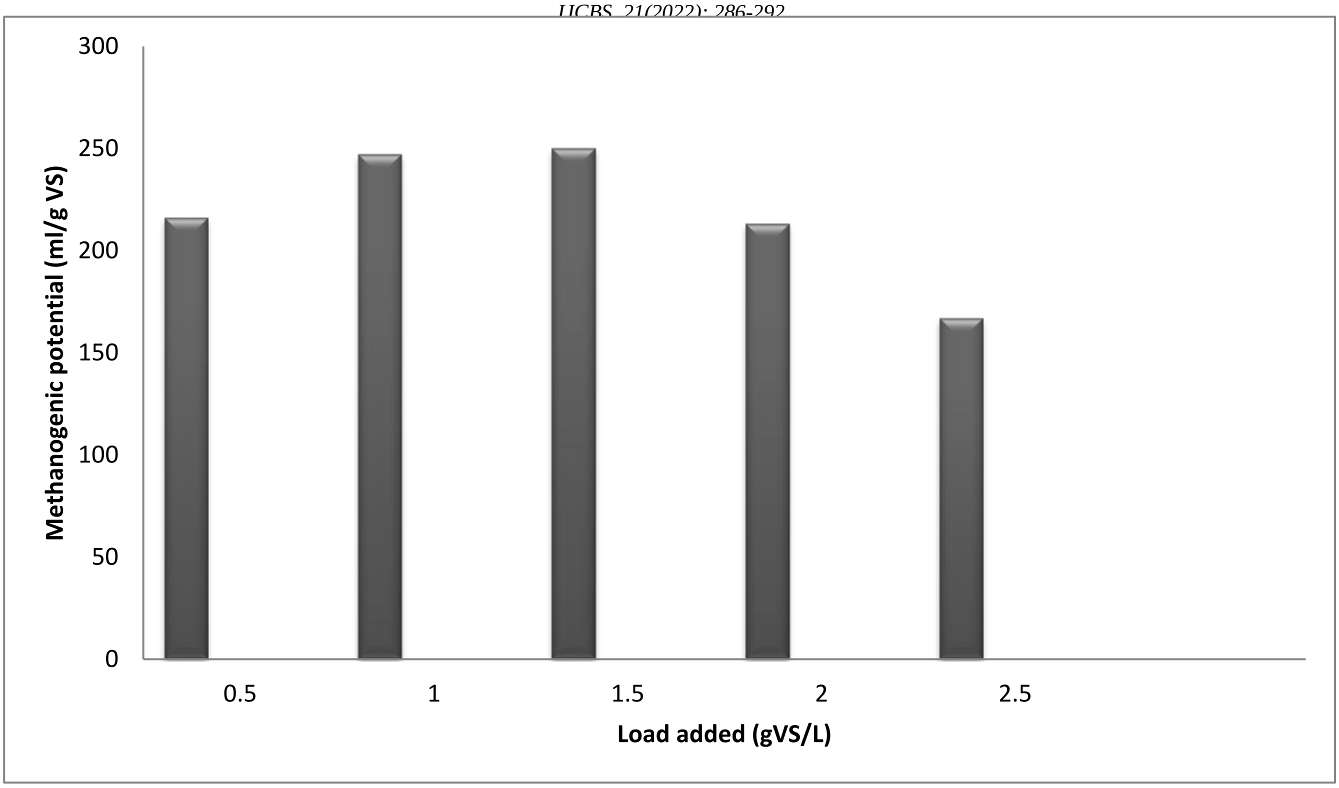

Figure 5: Methanogenic potential of OMWW for different loads (from 0.5 to 2.5 gVS/L)

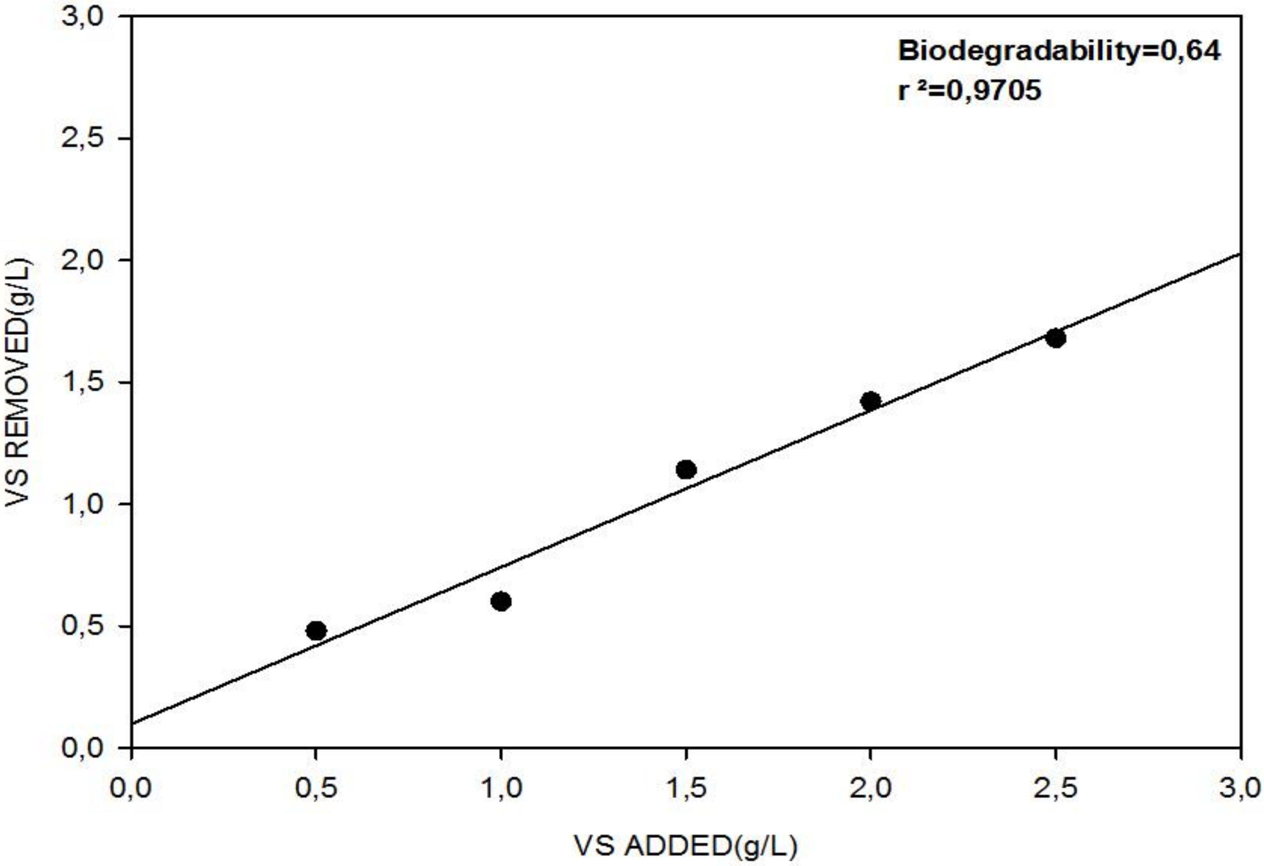

Figure 6: The relation between VS added and VS removed

Table 1: Main characteristics of olive mill wasters

Parameters	**Units**	**Values**
pH		5.4
Moisture	%	90
Total solids	g/l	102.8
Volatile solids	g/l	61.12
Phenols	g/l	1.2
Alkalinity	mg CaCO3/l	300
Chemical oxygen demand	g/l	144
Redox potetial	mV	146
suspended matter	g/l	15.6
dissolved oxygen	mg/l	1.2
Electrical conductivity	ms/cm	10.7
Turbidity	NTU	320
Salinity	mg/l	8
iron	mg/l	78.01
Zinc	mg/l	15.61
Lead	mg/l	5.26
Copper	mg/l	9.66

4. Conclusions

This study reveals the importance of the anaerobic fermentation of olive mill waste waters because it reduces their adverse effects on the environment; by its ability to degrade harmful organic matter under the action of bacterial activity of biomass, and also to produce energy as a biogas. the digestate remaining in the digester can be used as fertilizer in agriculture or as inoculum to make easy starting other experiences of anaerobic digestion.

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