

# Methanation Chemical Reaction-Based Management and Valuation of Wastewater from Oil Mills

**Gopal Arora<sup>1\*</sup>, Sainu Baliayn<sup>2</sup>, Krishan Kumar<sup>3</sup>**

<sup>1</sup>Department of Chemistry, Sanskriti University, Mathura, Uttar Pradesh, India

<sup>2</sup>Department of basic sciences, IIMT University Meerut, Uttar Pradesh, India

<sup>3</sup>Department of Biotechnology, Parul University, PO Limda, Vadodara, Gujarat, India

## Abstract

In this study, we looked at an integrated technique for the recovery and reuse of water for agricultural use while treating the refractory pollutants in olive mill wastewater (OMW). There is a significant standard of OMW produced during the olive oil extraction process. Due to the significant environmental concern posed by the high concentration of organic phenolic chemicals in these effluents. The goal of this article is to completely characterize the physicochemical makeup of raw OMWs before treating them with anaerobic digestion (AD) to release methane and lessen their toxicants. At mesophilic temperature, an AD was run semi-continuously. The outcome of the physicochemical study reveals that the substrate under study is characterized by a substantial rise in volatile solid (VS), which indicated a buildup of organic compounds, a considerable rise in the suspended matter (SM), a methane production that achieved a value of 250 ml/g of solid, and a high acidity (pH = 5.8). It is possible to use the digestate that has not yet left the digester as fertilizer for farming or as an inoculum to make it simple to start even more AD operations. To assess its agricultural quality, the digestate from the digester used to handle waste from the olive mill was characterized as NH<sub>4</sub>, P, K, Mg.

**Keywords:** Methane, Polyphenol, Methanogenic potential (MP), Olive wastewaters, and Meknes

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## 1. Introduction

The cultivation of olives is widespread across the Mediterranean region, which is also home to 98% of the world's olive trees. According to estimates from the International Olive Council, 3.67 million tons of olive oil will be produced all around the world in the 2019–2020 growing season, illustrating the significance of olive oil due to the many health advantages that have been shown [1]. Olive oil manufacturing has a significant socioeconomic impact, but it also produces a lot of waste, including liquid effluent and solid waste in the form of olive pomace, which must be managed to avoid pollution issues. In general, the following estimations are made for OMW: Depending on the extraction technology used, 1 kg of olives yields between 1 and 1.5 liters of OMWs. There are lipids and polyphenolic chemicals in OMWS, which contribute to its phytotoxicity [2, 3]. One of the primary methods for treating OMW is anaerobic fermentation, which also produces it possible to use biogas as an energy supply to produce power and heat while lowering the content of the wastewater. The inhibition because of polyphenol and the acidity of OMW appears to make this process unpredictable [4]. The valorization of organic waste has the potential to

provide considerable amounts of renewable energy in addition to lowering the amount of pollution that is caused to the environment. The application of the process of AD to OMW has been seen to be fraught with several challenges; these challenges are mostly attributable to OMW's high concentration of organic chemicals. In addition, OMW is an acid effluent with a pH of 5, and it lacks nitrogen and alkalinity in the range of 0.2...0.5 g N/l and 1...2 g CaCO<sub>3</sub>/l, respectively. Several other pretreatments, such as dilution pretreatment by aerobic culture, have been used to eradicate this issue [5].

The technique developed by the Intergovernmental Panel on Climate Change may be used to compute greenhouse gas emissions. The largest contributor to emissions in the palm oil mill sector is the Palm Oil Mill Effluent, which may be mitigated by the collection of the gaseous byproduct, methane. It will be possible to determine the overall amount of emissions that were cut down on if one first determines the number of greenhouse gases that were created by the functioning of the methane capture system [6]. There is no way to tell how much methane is released into the atmosphere. Using closed static chambers

and CH<sub>4</sub> metre systems based on TGS2611 sensors, SHT11, and microcontrollers, this study sought to estimate the wastewater treatment facilities for use on land that feed anaerobic lakes, which produce methane emissions. Contrarily, if the C/N ratio is large, suggesting a deficiency in nitrogen on the substrate, this has a detrimental effect on the synthesis of proteins required by microorganisms for growth [7]. Biochemical methane potential studies were performed on three-phase olive mill solid waste at temperatures of 37.5 °C and 55 °C to assess its methane potential. It has two distinct reaction rates for the enzyme mixes with 3POMSW, 0.130 d1 from t = 0 to 14 days and 0.034 d1 from t = 28 to 63 days, respectively. The established straightforward analytical calculations may be used to determine the current biogas output and to improve the biological nutrient removal process via process optimization [8]. Biochemical methane potential tests are used to calculate the generation of biogas and bio-methane from olive mill effluent. Hence, experiments were conducted in mesophilic environments using mixes comprising 0%, 20%, and 30% of the volume of olive mill effluent. Olive mill effluent may be AD to produce renewable energy, which is a viable method of resolving managerial and environmental problems brought on by traditional disposal [9]. For the detoxification of wastewater from olive mills and their use in the generation of energy, a laboratory-scale investigation into the execution of an integrated process plan that combines oxidation and AD technique was conducted. The TPC is initially marked reduced, and then substrate biodegradability is improved as the suggested pretreatment approach dramatically boosts the value of AD, making the Fenton's oxidation combined with the AD viable strategy for processing 3-phase OMW [10]. The ideal operating conditions for a lot of OMW compositions, which correspond to actual or assumed effluents from various locations, were established; this is a crucial step that enables one to predict the potential for such waste to be valorized for the generation of green hydrogen. Coke production, which occurs when the temperature of the supply is reduced, was also taken into consideration [11]. In a closed-loop method, they assess the thorough enhancement of the consequences obtained from the two-step elaboration process of olive oil. The OWW and OOWW combination used to cultivate the microalga *Raphidocelis subcapitata* allowed for the elimination of sugars, nitrate, phosphate, and soluble chemical oxygen requirement. These nutrient elimination procedures are necessary to maintain the standard of water found at the surface, although they are expensive and sometimes challenging to administer [12]. To compile and evaluate newly released studies on wastewater treatment methods used in olive mills, both conventional and sustainable. On the other hand, environmentally friendly treatment methods try to recover the valuable components using various techniques before treating the leftover wastewater [13]. To identify the general benefits and potential applications of both systems, the operational and design characteristics of each were examined. OMW is anticipated to become a sustainable resource for ingredients with high economic value via a valorization-treatment technique, which might result in a successful company [14]. It gives a broad overview of the potential for liquid by-products of olive oil to serve as a source of nutrients for the development of

novel additions or constituents with specific functions. Olive by-products were formerly solely thought of as a significant environmental problem, but in recent decades, a large number of researchers have thoroughly examined their antibacterial properties [15].

The primary benefit of the result may be utilized as fuel for vehicles or for the simultaneous creation of heat and power due to this method, and as a result, can result in a decrease in the radiation of greenhouse gases. The contribution of this work is to treat the unprocessed OMW performing possible pre-processed to determine its methane production through AD. Because the process of OMW is not yet a key problem for this sector, AD has developed into a well-stable and trustworthy process of this wastewater.

The rest of the portion of the research was organized in the following manner: The study's materials and methods are presented in Section II. The performance analysis is provided in Section III. Section IV contains the conclusion and suggestions for further research.

## 2. Materials and methods

In 3L, AD took place under mesophilic conditions (35–40°C). Between the digester and the gasometer, a bubbler filled with a Naoh (6N) is set up to extract CO<sub>2</sub> from the biogas. Two efficient tools are installed in the reactor to collect samples for both biogas generation and evaluation. The digester was linked to a gasometer, and it is fully agitated using an electromagnetic stirrer coupled to a motor.

### 2.1. Inoculums and Substrate

OMW was obtained from olive oil works' extraction units during the study's data analysis region of the city of Meknes in Morocco. These works employ three-phase processes and press systems (site 1).

**Table 1.** Common features of OMW

Parameters	Values	Units
Moisture	90	%
Totalsolids	102.8	g/l
pH	5.4	
Suspendedmatter	15.6	g/l
Redox potential	146	mV
Chemicaloxygendemand	144	g/l
Dissolvedoxygen	1.2	mg/l
Lead	5.26	mg/l
Copper	9.66	mg/l
Phenols	1.2	g/l
Alkalinity	300	mgCaCO <sub>3</sub> /l
Electricalconductivity	10.7	ms/cm
Turbidity	320	NTU
Salinity	8	mg/l
iron	78.01	mg/l
Zinc	15.61	mg/l
VS	61.12	g/l

The primary physicochemical constituents of these substances are outlined in Table I. Mesophilic anaerobic reactors housed in a Marrakech wastewater treatment plant was used to manufacture the inoculum. It was chosen because of its strong methanogenic activity, which led to its selection.

**2.2. Process and chemical evaluation**

The process of starting the digester consists of two stages: the inoculated, which involves supplying an organic inoculum to the digester at a loading ratio of Eight gVS / Land the loading phase. It is essential to locate an appropriate inoculum that contains methane-producing microorganisms. Inoculation digesters are very valuable for innovation acceleration since it makes sure methanogenic bacteria are responsible for the generation of biogas in a sustainable manner and introduces by including an inoculated, which creates a productive microbiological mass. Following this stage, the substrate-treated OMW is added to the digester, along with organic loading rates of 0.5, 1, 2, 2.5, and 1.5 g SV/l. The Methane concentration generated is then calculated using a gasometer using the water displacement technique. The method of atomic absorption spectroscopy was used to investigate the metallic components Zn, BP, Fe, and Cu. The apparatus that was used was of the kind Analytik Jena NONAA350, and it was designed by a computer utilizing Version 1.3.2.0 of the software Aspect LS Palo Alto. The weight of the filter both before and after it was dried in the oven at 105 degrees Celsius was used to estimating the quantity of SM, which was measured by filtering using a cellulose filter with a pore size of 0.40 micrometers. The Folin-Ciocalteu technique, which was described, was used to calculate the levels of total phenols present in each of the several data. When an acid standard solution, such as sulfuric acid, is added to a sample in the current of a pH meter, the alkalinity of the solution may be determined. The sample may be dried at 105 ° C for one day before the residue is weighed to determine the total solid. The mineral solid can be produced by heat the sample at 550 ° C for two hours in a muffle furnace, and the VS may be derived by subtracting the mineral solid from the total solid.

**3. Performance Analysis**

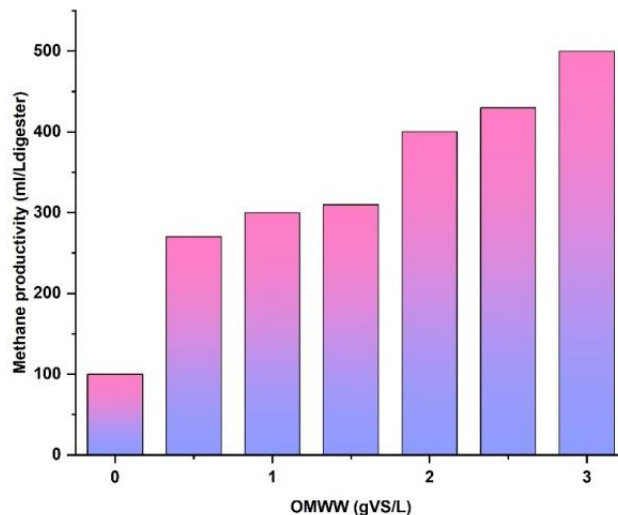
**3.1. Methane productivity**

Figure 1 displays the fluctuation in methane productivity that occurs due to the addition of the load in the digester. It is clear to see that the amount of load applied contributes directly to the level of methane production.

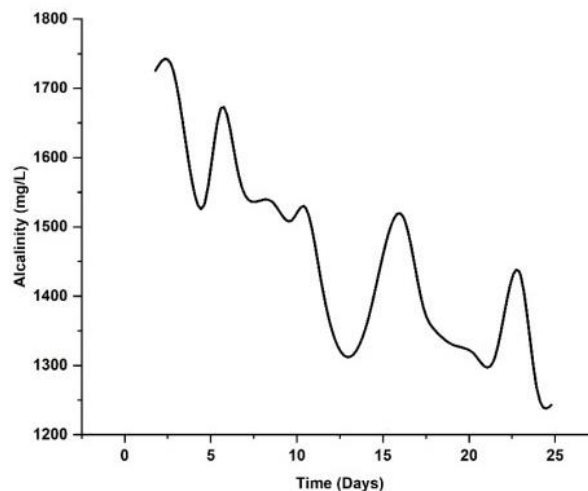
**3.2. Digester stability**

In this experiment, we tracked the changes in pH and alkalinity, which stand in for the stability control parameters of AD. For this reason, it's crucial to make sure the study is carried out below steady settings to get the largest biogas production feasible. AD may be influenced by a variety of circumstances, as shown by several tests. The different levels of alkalinity found in the digester are shown Arora et al., 2023

in figure 2. For the system to operate as intended, the alkalinity that is produced by calcium bicarbonates must be relatively high. It is important to keep in mind, on a more general level, that a reactor in proper operating condition has to have an alkalinity level of at least 1000 mg/L, which is stated as mg of CaCO<sub>3</sub> per liter.



**Figure 1.** Methane production varies for various organic loading rates.



**Figure 2.** Alkalinity varies in the digester.

The digester's alkalinity has been measured to be 1400 mg/L on average. This figure is optimal because the AD must operate well, and it has to have an alkalinity of between 1000 and 3000 mg/L. As a consequence, Alkalinity testing allows us to measure the robustness of Acid-attack resistance of AD. In addition to this, when the digester has strong alkalinity, it can have variations that occur in the pH level of the digester over the whole of the AD process are shown in figure 3. The anaerobic degradation process is very sensitive to changes in pH because each microbial group that is involved in the reaction needs a particular pH level to achieve optimal growth conditions. The pH level that is suitable for mesophilic AD is anywhere near neutral

and ranges anywhere from 6.5 to 7.5, depending on the kind of bacteria present.

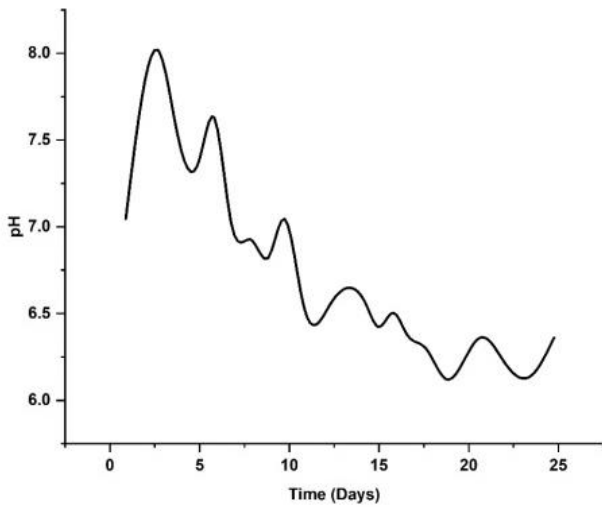


Figure 3. PH change during OMW AD

### 3.3. Biodegradability and Methanogenic Potential

Figure 4 depicts the MP, which is the highest number of methane that may be created per liter of the effluent of trash when these materials are processed in an AD reactor. The MP varies with the processed substrate as well as the preprocessing that was undergone, and it increases as the percentage of dry materials in the substrate increases. In this study, the MP of different load is determined to be 218, 249, 215, 165.6, and 162 ml/g VS correspondingly.

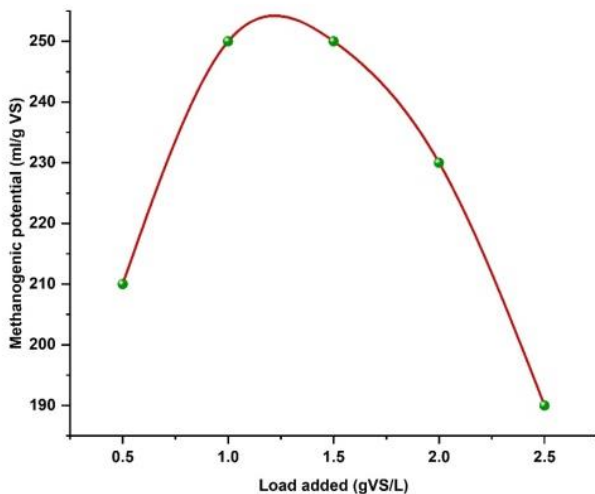


Figure 4. OMW's methanogenic potential at various loads

This is the organic matter that was decomposed concerning that which was introduced, and this figure illustrates the progression of VS that was removed concerning those that were added. Figure 5 displays the biodegradability in the digester. The biodegradability, or degradation value, of the waste that was digested in the digester, is somewhere about 64% ( $r = 0.9705$ ).

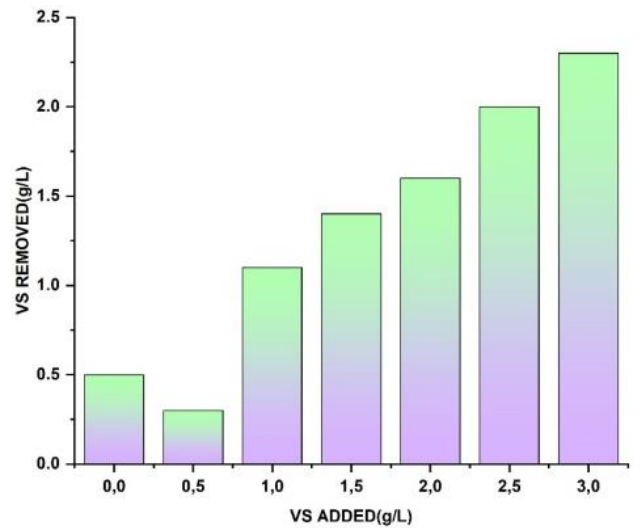


Figure5.VS added and VS removed concerning one another

### 4. Conclusions

The importance of anaerobic ferment is addressed in this study of OMW as a means of mitigating the deleterious effects of olive mills on the surrounding environment. This is accomplished by the fermentation process's capacity to break down potentially harmful organic matter through the activity of bacteria that are present in biomass, and it also generates energy in the form of biogas. The digestate that is left over in the digester may be put to use as fertilizer in farming or as an inoculum to facilitate the beginning of new processes of AD in other environments. The generation of a large quantity of waste, both liquid and solid, in a relatively short amount of time is one of the most significant drawbacks associated with the extraction of olive oil. The trash created by the olive oil industry will likewise increase proportionally in the future. Olive Oil Mill Effluent, the wastewater generated by olive oil mills, comprises organic material that, when subjected to microbial activity, will create methane and carbon dioxide.

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