

Case Report

Available Treatment Methods for the Development of a Sustainable Solution for the Pollution Caused in Air, Soil and Water by the Olive Mill Wastewaters

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Submitted: 10 September, 2015

Accepted: 28 September, 2015

Published: 30 September, 2015

ISSN: 2333-7141

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OPEN ACCESS**Keywords**

- Olive mill wastewater
- Pollution
- Treatment methods
- High added value constituents

Abstract

The current study summarizes the available methods and techniques for the effective management of Olive Mill Wastewaters (OMW) that is the main by-product from the process of olive oil production. OMW is characterized by the very high organic and phenolic content that inhibits its biodegradation rendering it responsible for many severe environmental phenomena. Despite the fact that to a large extent OMW is considered as a waste, this work is related with the concept that the olive mill by-products are resources and not waste, aiming to the development of innovative available techniques. Specifically, OMW contains high added value constituents which can be isolated by different treatment methods and then exploited into different scientific fields such as the food industry, pharmaceuticals, etc. As a matter of fact, the paper is associated with the description of all the available treatment methods of OMW in order to combat the extent of OMW pollution, experienced mainly in the Mediterranean countries. As an ultimate purpose, the development of an integrated treatment process of OMW is proposed aiming to the fully exploitation of the by-product.

ABBREVIATIONS

OMW: Olive Mill Wastewater; CWA: Constructed Wetlands Applications; COD: Chemical Oxygen Demand; BTF: Biological Trickling Filters; TSS: Total Suspended Solids; AOP: Advance Oxidation Processes; MF: Micro-Filtration; UF: Ultra-Filtration; NF: Nano-Filtration; RO: Reverse-Osmosis.

INTRODUCTION

Olive oil production is associated with the co-production of a large amount of residual wastewater, practically equal to the weight of milled olives, due to the addition of high quantities of water during the processing of oil production. Nevertheless, as olive oil industry has a significant contribution to the financial development of the Mediterranean countries (95% of the world olive oil production [1]), the co-produced OMW has to be efficiently treated as its uncontrolled disposal into aquatic

receptors is responsible for water contamination, eutrophication and aesthetic deterioration of the ecosystems [2]. As a matter of fact, it is of profound importance for all the Mediterranean countries to develop cost effective treatment methods for the OMW management.

Advantages and Drawbacks of Available Techniques

Many available techniques have been reported concerning the treatment of OMW taking into account the environmental impact of the direct disposal of the untreated by-product. Apart from disposal practices, the other developed treatment methods are the biological and physicochemical treatment methods.

Disposal practices

Disposal of OMW to lagoons: Calcium oxide is initially used as a flocculant for the treatment of OMW. Disposal of the treated supernatant to lagoons allows natural evaporation of the

liquids [3]. The main disadvantage arisen from this method is the aesthetic deterioration of the surrounding areas, along with the bad odors and the growth of insects as well.

Controlled disposal of OMW to cultivated or uncultivated fields: OMW is transported and disposed in certain fields (e.g. olive tree fields). Studies have demonstrated that the controlled disposal of OMW to specific areas can have beneficial effects as it enriches soil with nutrients [4].

Constructed Wetlands Application (CWA): CWA is an environmentally friendly, low cost treatment method employed for the exploitation of agricultural wastewaters and for the removal of their initial organic matter [5]. This particular process involves the implementation of different substrates and plants aiming to achieve higher removals of the organic loading and the total suspended solids. In addition, CWA has been proposed as a pretreatment process for the more efficient treatment of many by-products such as OMW [6].

Biological methods

Biological methods can be applied on the condition that the phenolic compounds are previously removed or sufficiently reduced, because phenolics are toxic for the microorganisms that control biodegradation.

Aerobic digestion: In this method, aerobic microorganisms (bacteria[7] or fungi) are implemented for the degradation of organic fraction contained in the waste [8]. One of the main arisen disadvantages is the high Chemical Oxygen Demand (COD) that increases the energy consumption rendering the respective operational cost very high.

A new modern process based on aerobic digestion has been reported recently, for full-scale system treatment of OMW, namely Biological Trickling Filters (BTF). BTF have been employed in order to achieve higher efficiencies concerning the treatment of OMW. The trickling filter is composed of an open air cylindrical tank, containing polyethylene short open cylinders as packing material, and a perforated disk at the bottom of the filter in order the treated by-product to be collected. The final results seem to be very encouraging achieving a sufficient reduction of the initial COD (exceeding 50%) [9].

Anaerobic digestion: The main feature of anaerobic digestion is that biodegradation of the organic load takes place in the absence of oxygen. The produced methane compensates the energy demands for the operation of the process [10].

Co-composting methods for the production of an excellent quality of bio-compost: This is mainly an aerobic composting procedure under controlled conditions, where OMW can be mixed with olive kernels, chicken or sheep manure or horse manure, branches of olive trees, branches of vineyards, leaves, grapes, whey (dairies), winery waste, etc. The idea is to exploit other residuals (solids or liquids) which are produced by other agro industrial processes operating in the same area with the olive mills [11, 12].

Physicochemical methods

Treatment with calcium oxide: Lime treatment has been proposed as a pretreatment procedure for the reduction of the

polluting effect of OMW [13]. During this process, calcium oxide is employed as a flocculant resulting in a sufficient reduction of the initial organic load. Furthermore, the treatment with calcium oxide is proposed because of its low operational cost.

Coagulation/flocculation: Coagulation and flocculation is a relatively low cost process in which many flocculants (ferric chloride and polyelectrolytes) are employed in order to reduce both COD and Total Suspended Solids (TSS) [14, 15].

Electro-coagulation: In this process coagulation is inaugurated after the application of a electrical current in the solution. The electrodes employed, are mainly made of metals such as Al and Fe causing the release of ions and as a result the forming of nuclei for the onset of the coagulation [16]. This particular treatment method shows sufficiently high reduction of the phenolic content (exceeding 70%) rendering the by-product appropriate for further treatment [17, 18].

Acid Cracking pre-treatment: Acid cracking pre-treatment involves the addition of an acid (usually sulfuric acid) for the pre-treatment of the by-products. The acid addition results in a sufficient reduction of the pH (pH<2) enhancing the precipitation of the formed flocks and the reduction of the initial organic load (COD) [19]. Despite the fact that the COD removal is sufficiently lower in compare to the electro-coagulation process, Acid Cracking pre-treatment requires lower energy consumption rendering the operational cost more affordable [20].

Advance Oxidation Processes (AOP): Through this procedure, OMW is oxidized at conditions of room temperature and air pressure. Oxidation is achieved through electrolysis, ozonation, Fenton, Photo-Fenton and supercritical water oxidation.

The Electrolysis involves the oxidation of the organic load that takes place either directly on the anode or through the agents formed in the solution. The electrical voltage is the driving force for the onset of oxidation and as a matter of fact the operational cost of the process is very high [21]. During the ozonation process, O₃ is used as oxidant and a sufficient reduction of phenolic content is achieved despite the rather low reduction of organic loading [22]. Fenton oxidation employs Fenton's reagent, which consists of hydrogen peroxide (H₂O₂) and ferric ions (Fe (II)), for the waste's oxidation through a series of reactions [23]. As it is not an electrically driven method, it requires low energy supply but the extensive need for H₂O₂ increases the operational cost. During the Photo-Fenton oxidation, the efficiency of the method is enhanced due to the use of ultraviolet radiation which accelerates the regeneration of ferric ions [15, 24, 25]. The supercritical water oxidation involves the oxidation of the initial organic load that takes place at higher values of the critical water's temperature and also in the presence of sufficient high values of pressure (25-35MPa) [16].

Membrane filtration: This method implements membranes of Micro-Filtration (MF), Ultra-Filtration (UF), Nano-Filtration (NF) and Reverse Osmosis (RO) for the fractionation of compounds from liquid solutions. This method has been successfully applied for the purification of OMW stream [26]. In a recent work, membrane filtration was implemented for the fractionation of phenolic compounds and mono or disaccharides

in the concentrate stream of RO process. For further isolation of the phenolic content from the carbohydrates, the adsorption/desorption in resins followed resulting in the formation of solutions substantially enriched in phenolic content [27].

Cooling Crystallization: Cooling crystallization is an alternative, low cost treatment method which was implemented because of the increasing need for selective recovery of high added value constituents, present in OMW. During this process, it is possible to recover high added value components of interest from the respective solution based on their freezing point [2, 28].

Conversion of 3-phase to 2-phase decanters and disposal of the solid-liquid to core mill plants: There are two types of extraction processes: the continuous three-phase centrifugation process which produces 20% oil, 50% three-phase liquid waste and 30% three-phase olive mill solid waste [29]. The two-phase uses a more effective centrifugation technology and produces oil as the liquid phase and a very wet, plastic olive cake as the solid phase [30, 31]. In the first case, solid waste (pomace) is completely dried and the oil is extracted by using hexane as solvent, while in the second case the two-phase olive mill waste (also called alperujo, olive wet husk, olive wet pomace or olive wet cake) consists of olive cake which contains the olive vegetation water in addition to the olive solids. This is doubling the amount of cake that is produced and rendering it unsuitable from the environmental point of view [31]. Specifically, on the one hand, core mill plants 'adopt' the treatment problem and pollution created before by olive mill enterprises. On the other hand, the new drying process that is used for the removal of humidity from semi-solid waste is responsible for air pollution causing extremely severe problem to the atmosphere.

Combination of the available treatment techniques

A stand-alone treatment solution for the efficient treatment of this effluent is not feasible because of the complex composition of OMW. For this reason, many researchers suggest the combination of different treatment techniques in order to contribute to the confrontation of this serious environmental phenomenon. For instance, the combination of the constructed wetland and electrochemical oxidation process was developed in the work of P. Grafias et al. [6]. The final results were very promising, denoting that for some experimental results a final removal of 95% was achieved for the case of color and COD removal rendering the final waste non toxic.

Furthermore in the work of Papaphilippou et al. [15], an innovative process for the exploitation of OMW effluent was adopted. As a first step, the coagulation/flocculation process was employed for the removal of the organic load and the phenolic content present in OMW. Solvent extraction with ethyl acetate followed for the recovery of the remaining phenolic content. As a final treatment method, the photo-Fenton oxidation was applied, achieving a reduction of the remaining COD and phenolic content by 73% and 87% respectively.

The combination of the available treatment methods is also proposed in the work of Zagklis et al. [27]. Initially, membrane filtration has been used for the fractionation of high added value phenolic compounds. Specifically, the reverse osmosis concentrate, containing the low molecular weight compounds,

was further treated with non ionic XAD4, XAD16 and XAD 7HP resins for the isolation of phenols from carbohydrates. The final results were very promising, reaching a final concentration of 378 g/L in gallic acid equivalents. To further research the possibility of extracting phenolic compounds, Kontos et al. [28] suggested the implementation of cooling crystallization process for the selective recovery of phenolic compounds from OMW.

CONCLUSION

As olive oil production is highly increased, the environmental consequence of the uncontrolled disposal of OMW is an issue of vital importance especially for the Mediterranean countries. The management of produced OMW constitutes a chronic and particularly unsolved problem, because of their high organic load and the very high concentration of phenolic compounds that classify OMW as hardly degradable. This is ascribed to the polyphenols resistance to biodegradation that turns OMW into phototoxic and hazardous material towards bacteria, plants and animals. Furthermore, the presence of these compounds in OMW makes the treatment of this wastewater problematic preventing OMW discharge to sewer systems or uncontrolled land application. As a matter of fact, the rapid increase of olive planted area in European countries; the lack of economically-viable solutions and the uncontrolled disposal of OMW are the main factors contributing to severe risks for water and soil quality. It is a very important issue for all the Mediterranean countries to follow the European Union's regulation and develop alternative financial affordable techniques by combining different treatment methods. For instance, the implementation of membrane filtration, the resins adsorption/desorption and cooling crystallization may be the starting point for the development of a lab scale process aiming to the fully exploitation of the produced by-product. However for the development of an industrial pilot plant, the cooperation between university, industry and local authorities is required.

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Cite this article

Kontos SS, Iakovides IC, Pantziaros AG, Paraskeva CA (2015) Available Treatment Methods for the Development of a Sustainable Solution for the Pollution Caused in Air, Soil and Water by the Olive Mill Wastewaters. *JSM Environ Sci Ecol* 3(1): 1016.