Bio-valorization of olive mill wastewater: balancing the carbon to nitrogen ratio with high protein substrates

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Introduction: Energy security and waste management are two interrelated issues faced by modern society. Throughout the years the natural environment has been shaped by human activity and the quest for low cost resources that have to be sacrificed into an unsustainable economic model. Large scale food production is among the main waste producing operations generating significant volumes of solid and liquid waste.

Fats and oils are significant food sources for humans, backed up by a multibillion industry, specialized in extracting and refining oils ready for human consumption. One of the first plant derived oils extracted and used by humans was olive oil. Olive oil is extracted from the olive fruit with the worldwide production up to 3 million tons annually (La Cara et al., 2012) whereas, the volume of the wastewater generated by this operation is calculated at 30 million m^3 per annum (Morillo et al., 2008). Olive mill wastewater (OMWW) is a brown to black colored effluent containing carbohydrates and oils and it is rich in phenols and other compounds presenting toxic activity toward living organisms.

OMWW management is a challenging process as the economics of the mills combined with the seasonality, the organic content and the phytotoxic properties of this wastewater, obstructing its sustainable valorization. Another significant problem of OMWW is its unbalanced nature, characterized by very high carbon concentrations and very low nitrogen content,thus diminishing the effectiveness of biological treatment processes and their overall applicability.

On the other hand, anaerobic digestion (AD)is a method that can be applied to this waste stream, offering the opportunity for resource recovery and economic sustainability. AD is offering the opportunity for bio-converting high strength wastewater into biogas and digestate, both of which can be readily utilized, either as a fuel source or a fertilizer respectively. While the process is not very demanding, as no aeration is required, a number of basic process parameters must be met for it to be efficient and effective. The three most important parameters include (a) the heating of the reactors to mesophilic or thermophilic levels, (b) exclusion of oxygen from the reactors as it is toxic toward the methanogenic archaea and (c) regulation of the carbon to nitrogen ratio to 20 and 30:1.

In this study, the anaerobic digestion of OMWW with the application of different nitrogen rich additives was investigated. These additives were utilized in order to balance the influent streams and improve the efficiency of the process. The co-substrates used were four animal derived byproducts namely: a) bone and meat meal (BMM), b) blood meal (BM), c) feather meal (FETH) and mixture of feather and blood meal (F&BM), two plant derived products a) soybean meal (SM) and b) corn gluten (GLUT) and one fish derived product, namely fish meal (FM).

Materials and methods:

<u>Substrates and inoculum</u>

The OMWW was collected from a three phase olive mill. This production unit is a low intensity family run facility producing approximately 40 tons of olive oil per year. The mill employs the three phase extraction process coupled to the generation of significant volumes of wastewaters.

The inoculum used was collected from four, six litre digesters operating under steady state with cattle manure as substrate and an OLR of approximately 3kg/VSm^3-d. Prior to the application of the digesters the inoculum was drained from the reactors, mixed in a 25 L plastic container and then returned back to the digesters. This step was undertaken to minimize problems related to the possible differences of the initial seed.

The protein rich substrates were collected from a pet food manufacturer. The animal derived substrates utilized were blood meal, bone and meat meal, feather meal, mixture of blood and feather meal and fish meal. The plant derived protein sources were the soybean meal and the gluten. The animal derived high protein substrate was produced through the rendering of slaughterhouse or aquaculture waste. The steps of this process include milling, cooking, dehydration and fine milling, with the products being of powdery consistency. Soy meal is the byproduct of vegetable oil production and is composed by the defatted soybeans. Gluten is one of the products generated during the wet milling of corn and for its production the stages of fine milling, agglomeration and washing are employed. All substrates after collection were stored in a freezer at -20°C until further utilization.

Batches and digesters

250mL Duran bottles were used as batch digesters and for assessing the biomethane potential and biodegradability of the different substrates. In order to evaluate the batch process and generate comparable results two loading rates were evaluated. These were 10 and 20kgVS/m^3.These loading rates were selected based on the available literature as these have been shown to be sufficient in terms of ensuring a robust process and minimizing the likelihood of process overload by accumulation of intermediate products (Boulanger et al., 2012). In the second stage of the experiment, four identical stainless steel reactors were used. The reactors were heated through the recirculation of hot water within the water jacket, feeding and removal of the substrates was taking place manually, while the mixing of the reactors was achieved with the application of immersed propellers and direct current mixing motors.

Results and discussion:

Mono digestion of each substrate

The highest production was derived by the BMM with a value of 511mLCH_4/gVS_{added}, which is approximately 16% higher compared to the production of the BM&FM with a production of 427mLCH_4/gVS_{added}. Related to the plant derived substrates, specific methane production was found at 495mLCH_4/gVS_{added} and 460mLCH_4/g$VS_{added}$for the GLUT and SOY respectively. The OMWW assessed in this study produced a specific methane yield of 384mLCH4/gVSadded, which is significantly lower compared to the protein rich substrates assessed and approximately 56% of its theoretical biomethane potential.

Batch Co-digestion

The highest production was derived by the OMWW&FM with a yield of 482mLCH_4/gVS_{added} corresponding to the 80% of the ultimate production for this mixture. The digestion of the other mixtures were also very positive with the mixture of OMWW&BM and of OMWW&SOY offering yields of 454 and 446mLCH_4/gVS_{added}corresponding to the 72 and 70% of the ultimate production for the two mixtures respectively. The lowest production was registered for the mixture containing OMWW&BMM with a yield of 418mLCH_4/g$VS_{added,}$ equal to the 63% of the ultimate production which on the other hand is only 17% lower to that offered by the mixture containing OMWW&FM. When the OLR was increased to 20kgVS the specific production of all substrate mixtures was reduced. The highest reduction was registered for the mixture containing BM with approximately 120mLCH_4/gVS_{added} corresponding to a reduction of 26%. For all other substrates the reduction was lower than 20%.

Conclusions:OMWW, a heavily polluted effluent can be valorized through anaerobic digestion into biogas and digestate. The addition of nitrogen-rich substrates offers the opportunity to attain a steady process with high bioconversion efficiencies. The type of co-substrate seems to be an insignificant process parameter with no substantial differences registered when fish, animal or plant derived proteins were used as nitrogen carrying additives. Our work outlines a framework paving the way towards the possibility to valorize OMWW in treatment plants in the vicinity of olive mills without the requirement of manure addition. This results in the minimization of bacterial contamination risk from transportation of manure near the olive mills. According to our results, one ton of nitrogen rich substrate can be used for the treatment of more than 50m^3 of OMWW, while at the end of the process, the recovered effluent presents significantly better characteristics as a soil improver when compared to the raw OMWW.

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