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**Abstract**

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## Abstract

The development of the direct biomass utilization for diverse industrial applications is turning the organic solid waste into one of the most promising feedstocks for the production of wide spectrum of competitive bio-based products with great market significance. The bioconversion of organic waste into value added bio-chemicals supply chain as a waste management strategy should be a viable method towards the implementation of the circular economy principles. This approach is an important challenge from the technological, economic and environmental perspectives.

The organic fraction of municipal solid waste (OFMSW) is globally produced in large amounts and the low cost availability of this substance makes it attractive to reduce the negative environmental impact of the fossil resource utilization. One of the most relevant advantages in the consideration of the sustainable management of organic waste is the generation of valuable products from low-value streams that are generated continuously. The production of the multiple targets required a highly efficient conversion process of organic waste. Currently, the anaerobic digestion (AD) is one of the preferred treatments for the intensive biodegradation of OFMSW and it is considered as well-established waste to energy technology.

To date, the main product considered in AD processes is biogas, consisting of a mixture of methane and carbon dioxide. However, hydrogen gas (H<sub>2</sub>) and soluble metabolites, which are intermediate products of this process have a higher added value than biogas, could potentially be extracted prior to their conversion into methane. The fractionation of substrate composition (carbohydrates, proteins and lipids) by means of pretreatments is a necessary step to improve the efficiency of bioconversion. Suitable pretreatments for the anaerobic processes can be used to overcome the process limitation of the substrate bioconversion and to promote the modification of the internal structure of the biomass.

The chemical pretreatments with organic solvents seems to be one of the most effective pretreatment to fractionate the organic substrates into its major components. These pretreatments have already been applied to the lignocellulosic fraction (LF) of organic solid waste to improve enzymatic accessibility and to fractionate lignocellulosic biomass in high purity cellulose, lignin and hemicellulose, but their application to OFMSW is still limited. The OFMSW pretreatment through organic solvent could increase, via substrate fractionation, the highest valorisation of its potential to generate both bioenergy and value-added chemical, so as to ensure the recovery of the main components of OFMSW in a sustainable perspective. The organic solvent is indeed expected to improve the hydrolysis as well as to increase the available substrate-carbon.

The analysis of scientific literature highlighted that formic acid applications represent innovative chemical pretreatment options for OFMSW to be converted into high-quality intermediates by means anaerobic processes. Furthermore, research development has recently pointed out that the wide range of molecules accumulated during anaerobic processes represent new opportunity for recycling waste into added-value molecules, such as short chain carboxylic acids and alcohols.

The research project aimed to study the applicability of formic acid pretreatment in order to propose alternative and suitable uses of pretreated organic waste. The capacity of the operating conditions of the pretreatment to improve the quality of useful components of the substrate were studied in order to assess the technical and economic feasibility of the pretreatment for the anaerobic processes; the production of the building blocks of the value added chemicals was evaluated as well.

The experimental activity was divided in two main steps. In the first experimental phase, various combinations of the different operating conditions of the pretreatment were studied according to a factorial design and the relation between pretreatment effects and organic matter composition was assessed and statistically explored by means of an analysis of variance. This experimental phase was also characterized by the Biochemical Methane Potential (BMP) test of the different solid pretreated substrates as well as the estimation of the soluble metabolic products in order to evaluate the effectiveness of the pretreatment on both the bio-methane production and the conversion of the chemical structure of the soluble biomass.

In the last step of the experimental activity, the combination of the organic solvent pretreatments and the dark fermentation tests of the organic waste was performed in order to promote the simultaneous recovery of valuable streams of biochemicals.

The first phase of research activity were conducted at the Sanitary Environmental Engineering Division (SEED) of Salerno University (Italy). This part of the research was focused on the evaluation of the effect of the formic acid pretreatment on organic waste conversion using differently composed OFMSW substrates. Different operating conditions of the pretreatment were applied to the substrates according to a specific factorial design. The individual and combined effect of the operating parameters on the solubilisation, the biochemical properties and chemical conversion of the pretreated substrates were statistically quantified. Results showed that specific combinations of the operating conditions of the formic acid pretreatment induce the disintegration of the biomass and the increase of the soluble compounds. These effects result in improved biodegradability and, consequently, in higher bio-methane production from the BMP tests of the pretreated substrates. Conversely, some pretreatment combinations induced a stronger disintegration of the biomass and the formation of by-products which are less biodegradable than the other pretreated substrate. However, these pretreatment combinations involved the production of liquid substrates rich in volatile fatty acid and other metabolites which could be used as building blocks for different kinds of bio-chemical products.

The second phase of the research activity was performed at the Laboratory of the Environmental Biotechnology (LBE) of the National Institute for Agricultural Research (INRA – France).

The aim of the research activity at LBE was to evaluate the feasibility of the combination of the formic acid pretreatment of OFMSW substrates with the dark fermentation tests in order to promote the recovery of carbon sources as well as hydrogen production. Detailed evaluation of the hydrogen production was carried out. The combination of formic acid pretreatments and dark fermentation tests promoted the simultaneous production of the hydrogen and the other biomolecules. Conversely, when the hydrogen production was inhibited by specific pretreatment conditions, the results showed a significant production of the metabolic products like lactate and ethanol which are characterized by a world market as larger as that of hydrogen.

The results of the experimental activity showed that the application of the formic acid pretreatment prior to the anaerobic processes to organic solid waste allow the simultaneous production of the energy and the value added biomolecules carrier.

The research activity proved that the formic acid pretreatment to the organic solid waste represents an innovative and promising method in recovering and adding value to waste, possibly through a multi-product approach of environmental biorefinery.