Revalorization of solid waste microalgae biomass from pig manure water treatment towards fertilizers production

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The use of microalgae is growing in different applications in the last decades. Pharmaceuticals, cosmetics, animal feed, biofuels, chemicals, wastewaters treatment and fertilizers production are several fields that they are being applied. This is not only due to the current oil crisis, but also to the necessity of new energy sources with the aim of having feasible and environmental friendly processes. The microalgae seem to be an effective option for the agro-food wastewater treatment with high nutrient contents. The wastewater is treated and converted into an effluent that could be returned with minimal environmental issues or reused. The nutrients accumulation (N and P) in the biomass, which was produced in this process of treatment, becomes an attractive residue for its possible valorization (Singh et al., 2016).

The production of biogas is one of the tendency for this biomass, and the maximum theoretical yield is 0.40L CH_4/g SV, considering the whole microalgae biomass. This reduced digestibility is attributed to the strong structure of its cell wall and to the presence of recalcitrant compounds, hence, it is necessary to apply different pretreatments to break the cell wall and increase the biomass biodegradability. The use of obtained digestate solid (after the anaerobic digestion) as a fertilizer is an interesting alternative. Europe requires annually of 11 Mton N, 2.8 Mton phosphorus and 2.6 Mton of potassium, of which a significant percentage is imported. The use of microalgae for the fertilizers production could generate new business opportunities and would be an important advantage for the European economic sector (BBI, 2016).

Therefore, this work aims at implementing the biorefinery concept by valorizing the microalgae biomass produced from pig manure wastewater treatment as a substrate for biogas production through anaerobic digestion. Furthermore, several pretreatments are applied to improve the CH_4 methane production. The obtained digestate solid is used in a new subsequent revalorization for fertilizer production.

The microalgae biomass was obtained from pig manure treatment in thin layer reactor and *Scenedesmus sp.* was the principal microalgae specie. The biomass content was 47% C, 7% N and 0.5% P. The pretreatments that are used for the sugars release and cell wall rupture are: ball mill (three ball sizes, 5 to 60 min), alkaline (1M a 5M de NaOH, 5 to 60 min in autoclave), peroxide-alkaline (1 a 5% H_2O_2, pH 11.5 adjusted with 2M NaOH, 50ºC, 120 rpm, 60 min) and steam explosion (130 to 170ºC, 5 to 30 min, in 5L reactor and another tank to perform the decompression suddenly). All experiments were performed with 5% dry weight of algal biomass. The pretreated biomass is cooled to room temperature and the solid fraction is separated by centrifugation (10 min, 10000 rpm). The liquid and the solid are maintained at 4 °C. The mass loss of solids by solubilization and the composition in terms of sugars, alcohols, organic acids, furfural, hemifurfural and acetone of the liquid pretreatment fraction are analyzed. Humidity, ash, carbohydrates, lipids and proteins are also analyzed in the pretreated solid phase.

Methane production tests have been carried out with the pretreated solid fraction and pretreated solid and liquid fractions under the same conditions at 35 °C in a laboratory thermostatic chamber, maintaining a ratio of 0.5 g $VS_{substrate}$/g $VS_{inoculum}$. The serum bottles used for this tests were 160 mL with a useful volume of approximately 100 mL (adding water if necessary). The digestate of the wastewater plant of Valladolid was used as inoculum. The bottles were passed through helium and incubated at 35 °C until the biogas production remained constant. The biogas production is periodically determined by measuring the increment in pressure through a PN 5007 manometer (IFM, Germany), after each measurement the bottles are left at atmospheric pressure. To determine the biogas composition, head space volumes are sampled by gas chromatography using Varian CP-177 3800 GC-TCD equipped with CP-Molsieve 5A and CP-Pora BOND Q columns using helium as gas. A blank is made using only inoculum to quantify the amount of methane produced by endogenous respiration.

The kinetics of the anaerobic digestion provides relevant information about the effect of the inhibitory compounds generated by the pretreatment on the biodegradability, and to determine if the hydrolysis is the limiting step. There are several models of the kinetic analysis of biogas production process; it all depends on the types of substrate used for anaerobic digestion and the controlling step. The Gompertz model considers inhibition behavior of the anaerobic digestion process, and estimates the kinetic parameters; biogas yield potential, duration of the lag phase, and maximum biogas production rate. Nevertheless, the first order model is used when the hydrolysis reaction is the rate limiting step of the overall process, and estimate the extent of the reaction, and the hydrolysis constant. Moreover, the model parameters are calculated by minimizing the least square difference between observed and predicted values (Passos et al., 2015).

$$B = B_0 \cdot [1 - \exp(-k_H \cdot t)] \qquad \text{(Eq. 1)}$$

$$B = B_0 \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{B_0}(\lambda - t) + 1\right]\right\} \qquad \text{(Eq. 2)}$$

In these equations, B represents the cumulative methane production (mL CH_4/gVS) and t is the assay length of the assay (d). These models estimate the methane production potential B_0 (mL CH_4/g VS, related to the substrate biodegradability), the hydrolysis coefficient k_H (d^{-1}), the maximum biogas production rate R_m (mL CH_4/g VS·d), and the lag time λ (d).

The results are reporting an increase of the biodegradability up to 60% when the pretreatments are applied compared with the control (untreated biomass) and around 400 mL CH_4/g VS $_{microalgae}$. The obtained digestate solid has approximately 70-80% dry solid content and humidity between 20-30%. The main parameters that determine its quality are pH, TOC, humidity, total solids, total nitrogen, total phosphorus, Mg and K content, heavy metals (Ni, Cd, Hg, Pb), biuret ($C_2H_5N_3O_2$), polychlorinated biphenyls (PBCs) and the pathogen content (*Escherichia coli*, *Salmonella*) (Dogan-Subasi E. and Demirer G.N.).

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