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## Doctoral Dissertation Doctoral Program in Civil and Environmental Engineering (34<sup>th</sup> Cycle)

## Application of biochar as additive in Anaerobic Digestion

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## Abstract

Anaerobic digestion (AD) is an established technology able to treat many organic wastes and wastewater while producing bioenergy. However, some critical issues continue to occur in digesters, including process instabilities and inhibition phenomena. Biochar (BC) is an attractive material with heterogeneous properties that can be customized for new applications. Among them, BC has been proposed as additive to AD to improve and stabilize biomethane production from many substrates. However, a deep understanding of the complex mechanisms of BC intervention and their correlation with BC physico-chemical properties need to be further explored. A wide range of BCs has been employed in literature inducing diverse responses of AD system. Therefore, the definition of the optimal characteristics and dose of BC to maximize AD performances is highly needed. Lastly, the long-term effects of BC on the AD in continuous mode and the economic feasibility of BC addition still need to be assessed.

To contribute filling these gaps, the main purpose of this doctoral dissertation is to investigate the impact of BC addition to AD. In detail, the objectives are as follows: (1) to revise the main mechanisms of BC intervention in AD (Chapter 2); (2) to investigate the role of the physico-chemical properties of BC on the AD of representative substrates through multiple AD tests in batch mode (Chapter 3 and 4); (3) to verify the role of BC under more realistic feeding conditions, through lab-scale semi-continuous AD experiments (Chapter 5); (4) to assess the correlation of BC physico-chemical properties and AD performances through a meta-analysis (Chapter 6); (5) to analyse the economic feasibility of the application of BC to AD (Chapter 6).

In Chapter 2, the main mechanisms of BC intervention in AD were exposed and correlated to its main properties. The contribution of BC seems to be linked to its adsorption capacity of many compounds, but also to its roles as support media and accelerant of microbial activity. Both physical and chemical properties of BC control these mechanisms.

Chapter 3 explored the impact of BCs with diverse physico-chemical features on biomethane production from waste activated sludge (WAS) and mixed sludge (MS) through AD batch tests. The addition of BCs enhanced and accelerated methane production to different extents. The most

promising was the activated BC derived from sewage sludge (SS550a), increasing methane yield by 17 % for WAS and by 22 % for MS, thus selected for the subsequent semi-continuous AD test. Principal component analysis (PCA) identified some key BC properties correlated to the performance of AD of sewage sludge.

Chapter 4 assessed the biomethane production of wine lees (WL) during AD batch tests. WL were identified as a promising substrate for AD, with high methane yields (up to  $1.257 \text{ Nm}^3 \text{ kgvs}^{-1}$ ) and high removals of sCOD (up to 92-96 %), but relevant risks of instabilities. The inhibition of methanogenesis due to the accumulation organic acids also occurred, where the addition of BCs did not mitigate the inhibition phenomena.

Chapter 5 investigated the impact of SS550a to the mesophilic AD of MS under semi-continuous feeding in a lab-scale digester, obtaining typical biogas yields (0.163-0.286 Nm<sup>3</sup>  $g_{VS}$ -1d<sup>-1</sup>) with 67-69 % of methane. Except to contribute to the buffering capacity of AD, the addition of SS550a did not affect the performance of AD of MS in semi-continuous mode. Further research is needed to better clarify the role of BC addition to AD under continuous mode over the long-term.

Chapter 6 focused on the correlation of BC physico-chemical features with AD performances, through a systematic meta-analysis of current literature studies. Overall, BC addition to AD was proved to increase and accelerate biomethane production. In the subset of studies in batch mode (408 case, 76 articles), BC addition increased the CH<sub>4</sub> yield and the maximum CH<sub>4</sub> production rate (R<sub>max</sub>), while shortening the lag-phase ( $\lambda$ ). On the other hand, from the subset of studies in semi-continuous mode (83 cases, 18 articles), the addition of BC significantly enhanced CH<sub>4</sub> production rate. Based on the subgroups meta-analysis, an optimal range of BC physico-chemical maximizing AD performances was identified as follows: high ash ( $\geq$  20 %) and low C content (< 50 %), large O/C molar ratio ( $\geq$  0.3), high contents of O ( $\geq$  20 %) and N ( $\geq$  0.6 %), acidic pH (< 7.0), and moderate SA (< 10 m<sup>2</sup> g<sup>-1</sup>). The economic evaluation identified a wide range of maximum sustainable BC unit cost (C<sub>BC,max</sub>), in the range 0-7,500 \$ ton<sub>BC</sub><sup>-1</sup>, that matches the higher revenues from energy production. The reduction of BC dose (below 0.45-0.76 g<sub>BC</sub> g<sub>VS</sub><sup>-1</sup>) was shown as a crucial step towards the cost-effectiveness of the practical application of BC to full-scale digesters.

This doctoral dissertation provides some significant contributions to scientific literature regarding the role of BC additive to improve AD performances. Furthermore, the optimization of BC features targeting this application may address further research studies and provide some practical indications towards the production of customized BCs.