Sustainable valorization of digestate and polluted phytomass through hydrothermal carbonization to produce hydrogen peroxide

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In recent years, the increasing emissions of green-house gasses (GHGs) and their associated effects of increasing the frequency and intensity of natural calamities (floods, forest fires, storm precipitations, glacial melting, etc) have been confirmed as a sad reality. In this line, EU environmental regulations (UNEP, 2020) have advocated for a transition to renewable-based energy generation and simultaneously slashing fossil fuel composition by at least 6% within the year 2030 to reduce emissions significantly. Then, although all renewables have pross and cons, green technologies and valorization of resources have a pivotal role on efficient waste management strategies to move towards the circular economy objectives.

In this context, two sustainable strategies to generate a value-added material were considered. To start with, the re-use of phytomass (herbaceous biomass used in environmental remediation processes) to avoid their management. This material would require some complex treatment because of the presence of heavy metals (or other toxic compounds) in their composition. Their origin commonly comes from a phytoremediation treatment which is a low-energetic technology to extract pollutants (mostly heavy metals) from contaminated soils using the growing of an hyperaccumulator plant. The other feedstock considered is a digestate which is obtained from anaerobic digestion (AD) which is a recommended technique with a multifaceted applicability for two major by-products: biogas (consisting predominantly of CH_4, CO_2, hydrogen sulfide and many micronutrients) and the previously mentioned digestate (solid rich in N_2, phosphorous, potassium and several micronutrients). To avoid further process of waste management, considered substrate of AD can be sewage sludge that can be obtained in Municipal Wastewater treatment plant. The aim with this technology is not only to promote biogas for thermal and electrical applications but also to recover and use digestates to obtain an electro-active material (EAM) essential for environmental applications.

To treat both solids generated, hydrothermal carbonization (HTC) emerges as a thermochemical process able to valorize wet organic and solid wastes within the temperature range of 180 ºC to 250 ºC that do not require a drying pretreatment to obtain an EAM. Some important parameters according to their further uses are higher specific area, surface functional groups, electrical conductivity and structural defects that can make them good candidates for be employed in electrochemical and environmental processes as H_2O_2 electrogeneration.

H_2O_2 is an oxidant widely used in various sectors as industrial bleaching, chemical synthesis, and disinfection. Although initially it was obtained with an energy-intensive anthraquinone process with many drawbacks, in last decades the electrochemical production with $2e^-$ oxygen reduction reaction ($2e^-$ORR) has been widely studied (Moreira FC, 2017). Production with this method depends in large extend on the cathode material to avoid competitive reactions and mass-transfer limitations. In this point several types of carbon materials have been used (graphite felts, carbon paper, carbon felts…) applying a surface modification using materials as carbon blacks (CB) to improve their electrical properties and electrode's stability (Fangke, Yu, 2015). Looking for circular economy processes, the replacement of CB (fossil fuel derivate) seems to be a good starting point. Then, hydrochars obtained by hydrothermal carbonization (HTC) of both biomass wastes mentioned are great alternatives that avoid the use of fossil fuels and allow the valorization of wastes.

Thus, in this work it was explored the behavior of hydrochars obtained from both origins (phytomass and digestate) to be used as electrocatalysts of cathodes to replace CBs in the production of H_2O_2 through $2e^-$ORR. Digestate from AD of sewage sludge and *Phragmites Australis* phytomass were used and obtained from WWTP of Ciudad Real and from a Wetland National Park (Daimiel, Spain), respectively. In both cases their recovery is interesting due to their structural changes promoted by their different composition and because they represent environmental problems that are necessary to treat: in the case of digestate, it is a waste and in the case of phytomass, it can increase the fire hazard or eutrophication problems because of the accumulation of bigger amounts of biomass in natural wetlands.

Related to the experimental procedure, hydrothermal carbonization was carried out in an autoclave with a solid-water ratio of 150 $g \cdot L^{-1}$ at different temperatures and times with autogenerated pressure. Solids used are phytomass and digestate and also mixtures with different ratios of digestate and phytomass with the aim to improve the surface functional groups, the high electrical conductivity and porosity generated in both materials. Results indicate different proximate analysis of both wastes, low humidity for phytomass and high humidity for digestate, however their derivate hydrochars seems not to have good electrocatalytic properties to enhance the production of H_2O_2 thought 2e-ORR. In figure 1a, it was shown their low electric intensity measured so it would be necessary improve their porous structure and surface functional groups. Nevertheless, preliminary data indicated that the mixture of both materials showed synergic effect in the electrochemical parameters because of their heterogeneous composition, porous structure and surface functional groups that produce an electrochemical response of -37.6 mA at -0.9V vs Ag/AgCl (3KCl)) and H_2O_2 production of 123.72 mg L^{-1} at 120 min (Figure 1).

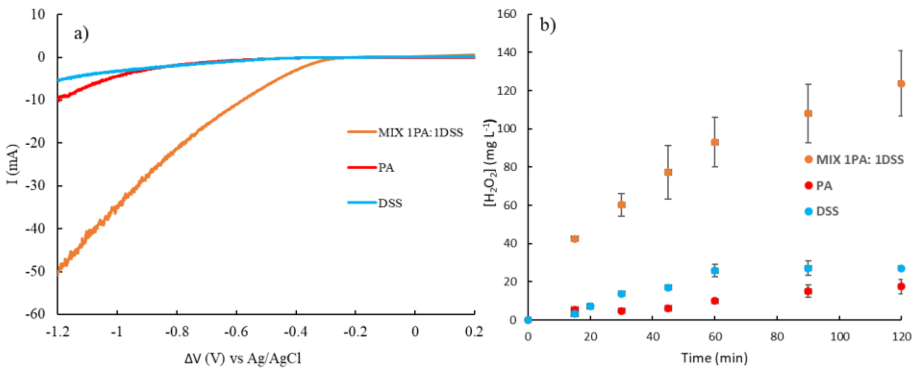

Figure 1. a) Linear sweep voltametries and b) electrochemical generation of hydrochars synthesized (PA: Phragmites Australis; DSS: Digestate from sewage sludge and MIX 1PA:1DSS: mixture of PA and DSS in % w/w) Electrolyte: Na_2SO_4 0.05 M. Potential: -0.9 V. Reference electrode: Ag/AgCl (KCl 3M). Constant air flow and stirring

In conclusion, this study underscores the viability of utilizing EAMs for electrochemical H_2O_2 production, emphasizing the importance of activation procedures and comprehensive understanding of physico-chemical properties. Finally, the evaluation of the synergetic effect of the mixture of heterogeneous materials would make more sustainable and cost-efficient this process that not only validates the circular economy concept but also exemplifies the transformation of wastes into valuable chemicals, thereby enhancing the economic feasibility of these environmental technologies.

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