Valorization of Sludge Digestate and Biomass Wastes for the Electro-Generation of Hydrogen Peroxide

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The initiative promoted by the European Commission through the REPowerEU plan in 2022 aims to accelerate the energy transition by reducing direct dependence on fossil fuels (European Commission, 2022). In this context, biomethane obtained through anaerobic digestion plays a fundamental role, with production expected to increase to 35 billion cubic meters by 2030. However, the growing utilization of biomethane is expected to result in an exponential increase in digestate generation, a byproduct of biogas production. The current annual digestate production within the EU28 is projected to reach 180 million metric tons. While this byproduct can serve as soil fertilizer, its high nitrogen content and the risk of emitting nitrous oxide and carbon dioxide greatly restrict its usability (Mariappan et al., 2024). Another alternative would be to treat it thermally to harness its energy potential or to produce a treated material with potential applications.

In this line, many researching groups have recently focused on the treatment of biomass waste through hydrothermal carbonization (HTC), followed by different activation procedures to enhance the surface properties. HTC is a treatment process that involves applying mild temperatures (180 – 240ºC) and self-generated pressure to the materials being treated. The resulting product is called hydrochar. The goal was to find a material derived from lignocellulosic waste to replace fossil fuel-based carbons as catalysts in the electrochemical generation of hydrogen peroxide (H_2O_2). Among the biomass residues studied, *Phragmites australis*, a plant waste material from natural wetlands, showed the best H_2O_2 accumulation capabilities (Ramírez et al., 2024). It exhibited several important properties that enhanced the 2e- Oxygen Reduction Reaction (2e-ORR), which leads to H_2O_2 production (Eq. 1). Some of these properties included a high specific surface area, an optimal ratio of oxygen-containing functional groups and an appropriate level of structural defects.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

In this context, the main objective of the research was to investigate the feasibility of using digestate as a catalyst for the 2e-ORR in H_2O_2 accumulation. To achieve this, real digestate from the Ciudad Real urban wastewater treatment plant was thermally treated with HTC and subsequently subjected to chemical activation or pyrolysis. Additionally, its combination with *Phragmites australis* was studied to determine whether any synergy between the materials could enhance this application. Thus, the aim is to close the loop of the circular economy, viewing these materials not as waste, but as new raw materials with the potential to be valorized in this electrochemical application.

This study analyzed the behaviour of hydrochar obtained from digestate at 200 ºC (D200), hydrochar from *Phragmites australis* at 200 ºC (PhA200), hydrochar from digestate subjected to subsequent chemical activation with KOH at 600 ºC (D200-KOH), hydrochar from a 50 % digestate and 50 % *Phragmites australis* (H1:1), its chemically activated hydrochar with KOH (H1:1-KOH) and its hydrochar treated with pyrolysis at 1000 ºC (H1:1-1000). All thermal treatments after HTC were conducted in a N_2 atmosphere.

Firstly, the physicochemical characterization of all materials studied was conducted. A proximate analysis was performed to determine the exact atomic percentages of C, H, N, O and S in the materials. Thermogravimetric analysis (TGAs) was carried out to evaluate the thermal stability of each material. Raman analysis was used to determine the structural order of the materials. Fourier-transform infrared (FTIR) spectroscopy was employed to identify the various functional groups present on the surface of the materials. Surface area and porosity were calculated using N_2 adsorption-desorption isotherms. Finally, surface images of the materials were captured using scanning electron microscopy (SEM).

Once the physicochemical properties of the materials were characterized, an electrochemical study was conducted to evaluate their viability as carbon-based catalysts for the 2e-ORR. To assess the electrocatalytic capacity and study the onset potential, linear sweep voltammetries (LSVs) were performed. For the H_2O_2 accumulation tests, chronoamperometries (CA) at -0.9 V vs Ag/AgCl (3M) were conducted. H_2O_2 was measured

using the titanium (IV) oxysulfate method. Additionally, Faradaic efficiencies (FE) and energy consumption (EC) were calculated. Figure 1 shows the results of H_2O_2 accumulation from two-hour experiments.

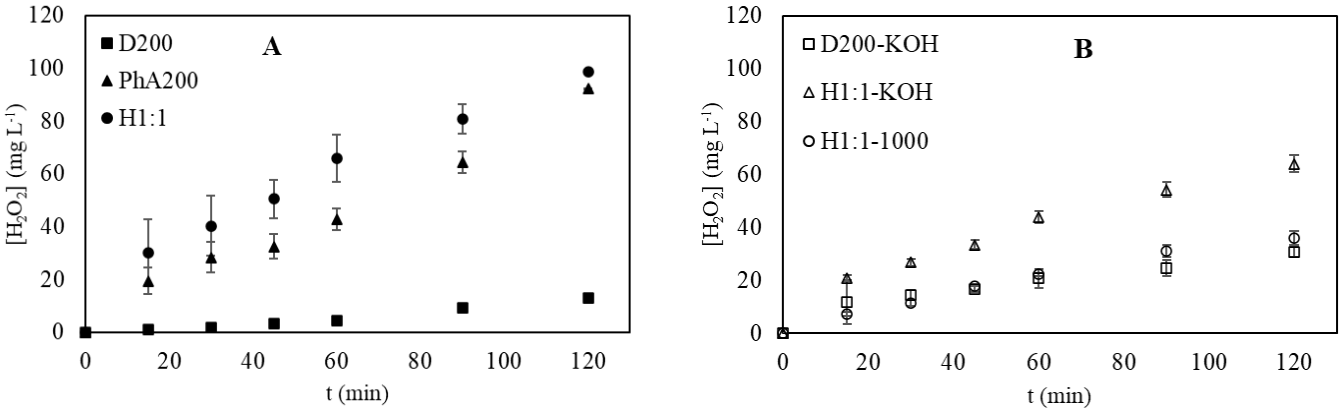

Figure 1. Hydrogen peroxide production assays for the synthesized materials (A) at HTC stage: D200, PhA200 and H1:1 and (B) with chemical activation and pyrolysis: D200-KOH, H1:1-KOH and H1:1-1000. The electrolyte employed for all experiments was 100 ml of 0.05 M Na_2SO_4 with constant aeration and stirring.

As shown in Figure 1 (A) and (B), the best H_2O_2 accumulation results were obtained with the hydrochar from the digestate and *Phragmites australis* mixture (H1:1), although there was little difference compared to the hydrochar from *Phragmites australis* (PhA200), with 100 mg L^{-1} and 92 mg L^{-1} H_2O_2, respectively. Far behind, with just 13 mg L^{-1}, was D200, the hydrochar derived solely from the digestate. This demonstrated that, on its own, it was not capable of serving as an effective electrocatalyst for this reaction. On the other hand, the three materials chemically activated or pyrolyzed after HTC achieved lower results compared to H1:1 and PhA200. H1-1KOH, H1:1-1000 and D200-KOH achieved 64, 36 and 31 mg L^{-1} respectively.

The physicochemical properties of selected materials could explain these results. The hydrochar derived from digestate (D200) has a negligible surface area, which has been shown to be a key parameter for optimizing the reaction and this may explain its poor performance. On the other hand, the activations of materials containing digestate lost most of the functional groups containing oxygen molecules, which has been shown to also benefit the H_2O_2 formation mechanism. However, the hydrochars derived from *Phragmites australis* (PhA200) or the *Phragmites australis*-digestate mixture (H1:1) achieved intermediate values of these properties, which favoured the accumulation of H_2O_2, explaining why they achieved the best results.

With all of this, it can be concluded that, although the accumulation results were not excessively high, digestate can be valorized for this application avoiding their treatment as waste. Furthermore, the H1:1 mixture, which achieved the best results, only required HTC as thermal treatment, avoiding the need for high temperatures or chemical agents afterward, which is a significant outcome.

Acknowledgments

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