Interaction of cold plasma with different chemical reagents for improved fractionation of lignocellulose

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Agricultural residues are a feedstock but are often treated as waste. In total, over 70% of agricultural residues are disposed of by landfilling or thrown away in open dumps, contributing to the environmental pollution and sometimes are even burnt. Therefore, agricultural residues are also an emerging environmental pollutant, with a nearly five times higher volume than municipal solid waste (Kaza et al., 2018). Strategies aimed at recovering most of the resources from agricultural residues are preferred and needed, particularly if they are scalable and suitable for developing or remote regions. Developed treatments for the decomposition and fractionation of lignocellulose-rich agricultural residues should also follow the zero-waste approach and principles expressed in different SDGs.

Cold plasma enables the continuous forming of different reactive species through an electrical field at ambient conditions. Thanks to their high reactivity and low selectivity, these species are an excellent precursor to the conversion of recalcitrant lignocellulose biomass. Their impact on lignocellulose degradation is even more pronounced in combination with different chemicals. When cold plasma treatment (CPT) is complemented with chemical reagents, ions deriving from acids, alkalis, or inorganic salts are accelerated due to a strong electrical field, and their collision with reactive species originating from plasma is more prominent, providing a synergistic effect (Zhang et al., 2021). We combined CPT with an alkaline hydrogen peroxide solution and an acidic Fenton reagent for improved delignification and facilitated enzymatic hydrolysis of corn stalks. Lignin content was determined spectrophotometrically, by its solubilization in acetyl bromide. Structural alterations in treated samples were determined by FTIR and Raman spectroscopy to estimate the contribution of CPT in biomass degradation.

We proved that combined CPT/alkaline and CPT/Fenton treatments reduced lignin content by up to 85 and 53%, respectively, in a significantly shorter time than conventional alkaline and Fenton reagent treatments. Thanks to a higher delignification rate, treated biomass was more susceptible to enzymatic hydrolysis. The digestibility of the obtained carbohydrate-rich fraction was either preserved or enhanced, depending on the process conditions. FTIR spectra confirmed the treated biomass delignification while retaining the carbohydrate fraction almost intact for further valorization. Raman spectroscopy showed that lignin was not only depolymerized but also oxidized during the treatments. Residual lignin-rich fractions are important precursors, e.g. to produce pharmaceuticals and bio-based chemicals, suitable for the removal of heavy metals or even precursors for bio-based supercapacitors (Liu et al., 2019; Thielke et al., 2022).

Employment of CPT contributed mostly to obtaining cellulose-, hemicellulose-, and lignin-rich fractions transformed to a greater extent. Lignin-rich fraction, often undervalued, was oxidized during the treatment, becoming more suitable for further application in biotech processes. Moreover, cold plasma could reduce the number of microorganisms present in the treated biomass, making it acceptable for open fermentation without additional sterilization steps. Obtained results have shown the potential of a hurdle approach with cold plasma in fine-tuning the properties of obtained fractions. However, further optimization of the process could enhance yields of each isolated fraction and enable better understanding of the complex interactions of cold plasma and lignocellulose substrates which are needed for advancements of treatment.

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