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The case of study of hazelnut shells biorefinery: Synthesis of active carbons from the hydrochar recovered downstream of levulinic acid production

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Abstract

Hazelnut processing industry generates significant waste streams, in particular cuticles and shells. Extractives are the main components of the cuticle fraction (~36 wt%), mainly including polyphenols and fatty acids, which can be advantageously employed in the pharmaceutical and cosmetic industry. Focusing on the shell fraction, this represents ~50 % of the total nut weight. Differently from cuticles, shells are rich in recalcitrant lignin (~38 wt%), in addition to cellulose and hemicellulose (each component accounting for ~23 wt%). Up to now, this waste, which is preponderantly produced in Italy and Turkey, is mostly underutilized, being limitedly used as a boiler fuel for domestic heating and for landscaping. On the other hand, both these fractions of hazelnut shells can be successfully valorized and, in agreement with the objectives of the project PRIN 2020 LEVANTE "LEvulinic acid Valorization through Advanced Novel Technologies" (2020CZCJN7), we have proposed a new cascade approach, converting its cellulosic fraction into levulinic acid (~9-12 wt%), recovering as final waste an abundant carbonaceous hydrochar (~45 wt%), mainly composed of aromatic (from lignin) and furanic (from degradation of C5/C6 sugars) units. In the LEVANTE project, this hydrochar was activated by pyrolysis and chemical treatments (H_3PO_4, $ZnCl_2$, KOH, NaOH), and the synthesized new active carbons (ACs) have been properly characterized (ultimate and proximate analysis, FT-IR, surface properties and SEM microscopy). This preliminary screening allowed us to select the KOH-AC as the most interesting one, as further confirmed by the highest CO_2 adsorption capacity (~90 mg/g), due to its well-developed microporous texture. This new AC was also effective for the removal of the bulkier methylene blue (complete removal, corresponding to ~250 mg/g). This proposed integrated approach makes possible to fully exploit the hazelnut shell feedstock, smartly closing the biorefinery cycle of the hazelnut wastes, in a circular economy perspective. In addition, the selective fractionation of soluble C5 and C6 sugars of shell fraction is currently under investigation and this will enable us to obtain an hydrochar with a less-degraded lignin fraction, thus moving towards progressively more sustainable hydrothermal and activation reaction conditions.
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Keywords: *hazelnut shells, levulinic acid, hydrochar, active carbons*

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