1st Conference on Green Chemistry and Sustainable Coatings

Pisa, Italy, 17th -18th June 2022

New exploitation strategies of the by-products deriving from the hazelnut supply chain

Domenico Licursi[1], Claudia Antonetti[1], Nicola Di Fidio[1], Sara Fulignati[1], Marco Martinelli[1], Monica Puccini[2], Sandra Vitolo[2], Anna Maria Raspolli Galletti[1]

Affiliation: [1]Department of Chemistry and Industrial Chemistry, University of Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy; [2]Department of Civil and Industrial Engineering, University of Pisa, Largo Lucio Lazzarino, 56122 Pisa, Italy. claudia.antonetti@unipi.it, nicola.difidio@unipi.it, sara.fulignati@dcci.unipi.it, marco.martinelli@unipi.it, monica.puccini@unipi.it, sandra.vitolo@unipi.it, anna.maria.raspolli.galletti@unipi.it
Telephone: +390502219350, domenico.licursi@unipi.it

Keywords: Hydrochar, active carbons, hazelnut shells, hydrothermal processing, levulinic acid

Introduction

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 used in the pharmaceutical and cosmetic industry (Mattonai et al., 2017). Focusing on the shell fraction, this represents ~50 % of the total nut weight (about 273 thousand metric tons, based on the 2021-2022 worldwide data on hazelnut production) (Statista, 2022). Differently from cuticles, shells are rich in recalcitrant lignin (~38 wt%), in addition to cellulose and hemicellulose (each component accounting for ~23 wt%) (Mattonai et al., 2017). 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, these both fractions of hazelnut shells can be successfully valorized and, in this perspective, we have proposed a new cascade approach, converting its cellulosic fraction into levulinic acid (~9-12 wt%), and recovering an abundant carbonaceous hydrochar as the final waste (~45 wt%), mainly composed of aromatic and furanic units (Licursi et al., 2017). In this work, the exploitation of this waste biomass-derived hydrochar for environmental applications has been investigated, after its pyrolysis and chemical activation treatments (H_3PO_4, $ZnCl_2$, KOH, NaOH). The synthesized new active carbons (ACs) have been properly characterized and used as adsorbents for CO_2 and methylene blue removal. This proposed

Horizon 2020 European Union Funding for Research & Innovation

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integrated approach makes possible to fully exploit the hazelnut shell feedstock, smartly closing the biorefinery cycle of the hazelnut wastes, in a sustainable and circular perspective.

Experimental

Hydrochar was synthesized from hazelnut shells, according to our previous work (Licursi et al., 2017), then pyrolyzed, and finally chemically activated by H_3PO_4, $ZnCl_2$, KOH or NaOH treatments. Different characterization techniques (SEM, FT-IR, ultimate and proximate analysis, specific surface area, pore volume and size distribution) were used to screen the most interesting ACs and perform the subsequent adsorption study. Adsorption tests of methylene blue were carried out by UV-Vis spectroscopy (at 657 nm), whilst CO_2 adsorption was determined by thermogravimetric analysis, evaluating the uptake in sample weight (mg/g) as a function of the time.

Results and Discussion

A preliminary characterization of the synthetized ACs 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), thanks 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) by adsorption involving the external surface of the porous carbon, and further assisted by its surface functional groups.

Conclusions

New active carbons have been synthesized starting from hazelnut shells-hydrochar, recovered downstream of the optimized levulinic acid production. KOH treatment of the pyrolyzed hydrochar is highly required for the selective development of microporosities, and the resulting active carbon is recoverable in good yield (~65 wt%). CO_2 and methylene blue adsorption tests have highlighted the promising performances of the pyrolyzed hydrochar-KOH activated carbon, opening the way to possible hydrochar uses for new environmental applications.

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