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Valorization of Agroindustrial Waste from Chestnut Production

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In recent years, the consumption of fruits of European chestnut has considerably enhanced due to their positive health effects. However, the chestnut peeling process generates solid residues (inner and outer shells), which account for about 10–15% of the whole chestnut weight. In the present study, an integration between a chemical and a thermochemical process is proposed as a valorization route for the chestnut residues: the extraction of polyphenols, a class of strong natural antioxidants, and the slow pyrolysis for biochar production. The chestnut residues after the polyphenols extraction are used as pyrolysis feedstock, and the produced biochars are applied as adsorbing materials to simplify the recovery of the extracted polyphenols.
The aim of this study is to evaluate how the physical and chemical characteristics of biochar from chestnut residues influence the adsorption of polyphenols. The biochar production was carried out in a slow pyrolysis reactor using two feedstocks (as received and post-extraction chestnut residues) and three pyrolysis temperatures (500 °C, 600 °C and 700 °C), thus resulting in six different biochars. Each biochar was used as an adsorbent material for the polyphenols in the aqueous extracting solution obtained from chestnut residues. Specific classes of polyphenols were considered, such as non-tannin polyphenols, hydrolysable tannins and condensed tannins. The adsorption efficiency of biochar increases in the char produced at 700 °C for both the considered feedstocks. The analysis of the specific polyphenols groups shows that, despite having an overall adsorption capacity much lower than activated carbon, biochars have a great selectivity for the adsorption of non-tannin polyphenols.

1. Introduction

The agro-industrial sector produces a large amount of waste, whose disposal represents both an environmental and an economic issue. However, the agro-industrial wastes often contain significant percentages of potentially active biomolecules, such as polyphenols (Ignat et al., 2011), that can be recovered and used in the pharmaceutical, nutraceutical or cosmetic sector for their antioxidant, antimicrobial and anticarcinogenic properties (Boots et al., 2008).
Hot water extraction can be adopted as an environmentally and economically sustainable method for extracting these compounds. However, the product of the extraction process consists of a dilute aqueous mixture of various types of biomolecules. A further step is required to purify the extract and separate the polyphenols from the undesired molecules (i.e. carbohydrates, proteins). Filtration and/or adsorption/desorption (Pérez-Larrán et al., 2018) are the most applied techniques for the purification step and biochar can be identified as a very promising adsorbing matrix (Rosales et al., 2017), even though its characteristics (surface area, porosity and surface functional groups) should be properly tuned for enhancing the adsorption efficiency and selectivity.
Biochar properties, as well as the characteristics of the adsorbate solution, contribute to define the adsorption mechanisms involved in the process; moreover, more than a single adsorption mechanism can occur at the same time, making the process difficult to be controlled (Tan et al., 2015). Adsorption of simple and substituted phenols have been studied both for biochar (Oh and Seo, 2019) and activated carbon (Liu et al., 2010); the main parameters affecting the phenols adsorption are the surface area and pore size distribution of the biochar and, to a less extent, its surface chemistry (Han et al., 2013). However, the knowledge on simple

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and substituted phenols adsorption is not sufficient to predict the adsorption mechanisms of polyphenols, since they typically have much higher molecular weight and more complex chemical composition. The comprehension of such mechanisms could allow a fine tuning of the char properties relevant for the adsorption process through the proper choice of the pyrolysis experimental conditions.
In this work, chestnut shells were chosen for polyphenols extraction (Aires et al., 2016) and as received and extracted shells were used for the production of six biochar samples under slow pyrolysis conditions at three different temperatures (500, 600 and 700 °C). The biochar samples were applied for the purification of the extracting solution and their adsorption efficiency and selectivity were evaluated and compared with the performances of a commercial activated carbon.

2. Experimental setup

2.1 Feedstock

Chestnut shells were used for the polyphenols extraction process. They were provided by a small cooperative located in Avellino province, in Italy. Chestnut shells as received and after the extraction process were used as feedstock for biochar production. Both the pyrolysis feedstocks were ground and tableted in pills whit a diameter of 13 mm and a height of 2 mm. The two feedstocks were characterized through ultimate analysis for their CHNO content with a LECO CHN628 analyzer (LECO) and through incineration at 600 °C for their ash content; the results of both analyses are reported in Table 1 on a dry basis. A full compositional analysis was conducted and the results were also reported in Table 1: the extractive content was determined following the NREL/TP-510-42619 procedure, after drying the samples at 105 °C for 2 hours; the extractive-free sample was then used to obtain the holocellulose content according to the sodium chlorite method (Rowell, 2012) and the lignin content was calculated by difference.

Table 1: Biomasses ultimate analysis results, ash content and compositional analysis results

Biomass	C	H	N	O[(a)]	Ash	Extractive	Lignin[(a)]	Holocellulose
Chestnut Shells	51.92 (3.4)	5.18 (0.6)	0.96 (0.2)	40.98 (4.4)	0.96 (0.2)	36.13	28.77	34.14
Chestnut Shell after extraction	46.71 (1.0)	5.00 (0.2)	0.52 (0.1)	47.29 (0.4)	0.48 (n.a.)	21.80	34.22	39.84

(a) obtained by difference

After the extraction, the oxygen content of chestnut shells increased at the expense of the carbon content. The ash content of chestnut shells was halved after the extraction process.
Accordingly, also the results of the compositional analysis were affected by the extraction process; in fact, after the extraction, the extractive content was reduced while lignin and holocellulose contents increased.

2.2 Extraction

The extraction of polyphenols and other organic macromolecules from chestnut shells was carried out using distilled water as solvent, with the procedure described by Squillaci et al. (2018). The biomass to solvent ratio was 5% wt/vol.: in particular 25 g of biomass were kept in 500 mL of boiling distilled water for 1 hour under continuous stirring. The mixture was then cooled in ice and centrifuged for 30 minutes at 4 °C (Centrifuge RC 6+, SORVALL), in order to separate the solid residue from the liquid phase named in the following 'extract'. The obtained solid residue was rinsed with 225 mL of distilled water and centrifuged again as described above. The rinsing procedure was conducted twice, and all of the retrieved supernatants were added to the extract. The extract was characterized as described below and then stored at -20 °C before the adsorption tests, while the solid residue was dried and then used as feedstock for the pyrolysis experiments.
The characterization of the extract was conducted with a spectrophotometer (Varian Cary 100 Scan) using chemicals purchased from Sigma-Aldrich. The determination of the sugar content was based on the procedure described in Miller (1959) using 3,5-Dinitrosalicylic acid, while the protein content was determined by Bradford assay (Bradford, 1976). The total polyphenols content and their distribution among the different classes (hydrolysable tannins, condensed tannins and non-tannin polyphenols) were evaluated through Folin-Ciocalteau assay (Singleton e Rossi, 1965) following the procedures described by Squillaci et al. (2018).

2.3 Biochar production

The pyrolysis reactor employed for this work consists of a jacketed chamber (L=0.024 m, W=0.04 m, H=0.052 m): the carrier gas flows into the jacket and then its flow is reversed towards the pyrolysis chamber, passing through a ceramic flow straightener before entering the chamber. More details can be found in Ragucci et al.

(2013). The biomass was loaded onto the sample holder trays; about 10 pills of biomass were loaded on each tray, for a total weight ranging between 12 and 16 g. Pyrolysis tests were carried out using nitrogen as a pyrolyzing agent under slow pyrolysis conditions (heating rate=5 °C/min). A total of six different biochars were produced, three for each feedstock, as received and extracted (indicated with the prefixes C and CE, respectively) at different pyrolysis temperatures (500, 600 and 700 °C).
All the produced biochars and a commercial activated carbon (AC) from Sigma-Aldrich were characterized through ultimate analysis for CHNO content and incineration for ash content as described for the feedstock in section 2.1. In addition, pH was determined following the procedure described in IBI protocol (2012) using a digital pH-meter (pH50+, XS Instruments). The porosity of the biochars was investigated using an Autosorb iQ porosimeter (Quantachrome) with liquid nitrogen as the adsorbate.
Measurements of -OH groups on biochar surface were performed employing the Boehm titration (Boehm, 1994) according to the procedure described by Schönherr et al. (2018). Only the determination of the total acidic groups was possible, mostly because of the partial hydrophobicity of the produced biochars and the probable release of acidic/basic species. (Fidel et al., 2013)

2.4 Adsorption tests

To evaluate the adsorption capacity of the produced biochars towards polyphenols, 250 mg of biochar or activated carbon were suspended in 5 mL of the extract obtained from chestnut shells for 1 hour under continuous stirring at room temperature. The char was then separated from the liquid phase through centrifugation for 20 minutes at 4 °C (Megafuge 1.0R, Heraeus); moreover, in order to ensure a total separation, the supernatants were also processed with a syringe filter (0.22 μm).
The supernatants were characterized as described in section 2.2 for the extract; moreover, the pH of each supernatant and of the extract was determined using a digital pH-meter (SevenEasy, Mettler Toledo).
The adsorption efficiencies of each biochar sample toward the various classes of molecules were calculated by difference between the content of each class in the extracts before and after the adsorption tests.

3. Results and Discussion

3.1 Extraction

The concentrations of the identified biomolecules contained in the extract are reported in Table 2.

Table 2: Content of biomolecules classes in the extract. GAE = Gallic Acid Equivalents, BSAE = Bovine Serum Albumin Equivalents, GE = Glucose Equivalents

Total polyphenols (μg GAE/mL)	Proteins (μg BSAE/mL)	Reducing sugars (μg GE/mL)	Non-tannin polyphenols (μg GAE/mL)	Total tannins (μg GAE/mL)	Hydrolyzable tannins (μg GAE/mL)	Condesed tannins (μg GAE/mL)
2385.27	813.00	6009.45	632.19	1753.08	59.86	1693.22

The percentage composition of the quantified biomolecules classes is shown in Figure 1a, while Figure 1b represents the distribution of the polyphenols classes:

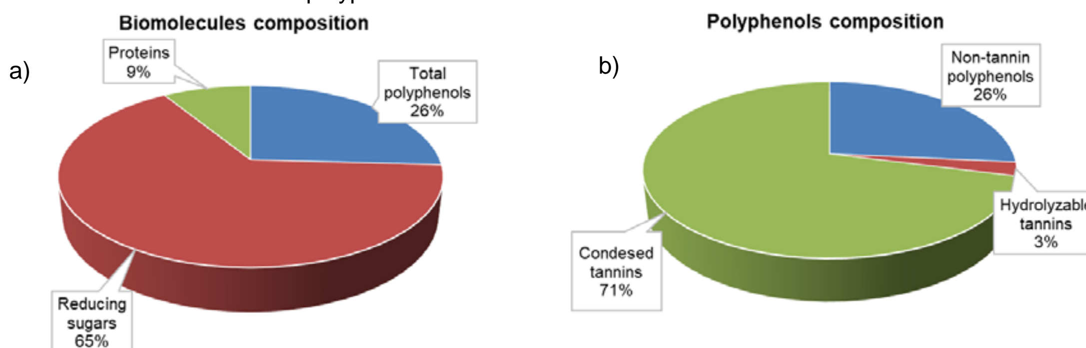

Figure 1: Biomolecules (a) and polyphenols composition (b)

The most abundant biomolecules class in the extract, among the considered ones, consists in the reducing sugars, which accounts for 65% of the total extracted biomolecules; the polyphenol content is still relevant, accounting for 26% of the quantified biomolecules. As shown in Figure 1b, the total polyphenols are mainly

made up of condensed tannins followed by non-tannin polyphenols characterized by a lower molecular weight. Only 3% of the total polyphenols is represented by hydrolysable tannins.

3.2 Biochar production

As expected, biochar yield decreased with the increase of the pyrolysis temperature (from ~38% at 500°C to ~33% at 700°C), while, despite of the differences in the chemical CHNO content, the effect of the feedstock pre-treatment on the biochar yields was negligible. Table 3 shows the results of the biochars chemical characterization. The results of the elemental analysis are expressed in terms of H/C and O/C ratios.

Table 3: Biochars ultimate analysis results, ash contents, pH values and concentrations of -OH groups

Sample	H/C	O/C	Ash [%wt. d.b].	pH	Total -OH [mmol/g]
C500	0.029	0.255	3.09	8.896	0.0605
C600	0.020	0.157	3.45	9.410	0.0000
C700	0.010	0.126	3.76	10.245	0.0000
CE500	0.031	0.240	2.09	7.628	0.0731
CE600	0.021	0.181	1.34	8.200	0.0000
CE700	0.011	0.120	2.04	9.665	0.0023
AC	0.000	0.133	2.39	8.034	n.a.

All of the above biochar properties, except for the ash content, depend mostly on pyrolysis temperature and showed little or no variation for the employed feedstock.
In general, with the rising of the pyrolysis temperature both the H/C and O/C ratios decreased from ~0.03 to ~0.01 and from ~0.25 to ~0.12 respectively, with C700 and CE700 having a similar composition to the activated carbon. The two biochars series had different ash content, varying between 3-3.8% for the C-series biochars and ~2% for the CE-series biochars except for CE600 that showed an anomalous lower value. The pH of the biochars increased with the pyrolysis temperature for both the feedstocks, although the CE-series results in slightly more acidic pH values probably due to the lower ash content (Yuan et al., 2011). The presence of -OH surface functional groups was detected only for biochars produced at 500 °C.
The results of the porosimetric analysis are reported in Table 4.

Table 4: Results of the porosimetric analyses on biochars and activated carbon

Sample	BET specific surface [m^2/g]	Mesopore surface [m^2/g]	Micropore volume [cm^3/g]	Mesopore volume [cm^3/g]	Pore total volume [cm^3/g]
C500	32.9	6.9	n.d.	0.019	0.0334
C600	387.7	7.8	0.144	0.020	0.1699
C700	385.1	5.7	0.140	0.018	0.1654
CE500	44.3	6.8	n.d.	0.016	0.0359
CE600	335.4	6.8	0.126	0.015	0.1436
CE700	313.3	6.5	0.120	0.012	0.1424
AC	974.2	107.7	0.326	0.366	0.7105

The porosity of the produced biochars depended greatly on the pyrolysis temperature, while the type of feedstock had a less relevant influence. It is worth noticing that biochars produced at 600 and 700 °C had similar porosity characteristics, while biochars produced at 500 °C were characterized by less developed porous structures. In particular, both the BET specific surface and the pore total volume are one order of magnitude smaller for C500 and CE500 than for the other biochars. Since the mesopore surface and volume exhibited slight variations among all the biochars, it can be assumed that this difference is due to the lack of micropores in C500 and CE500. The activated carbon, on the other hand, showed higher values than biochars for every considered feature; this difference is particularly relevant for the mesoporous fraction that increased from 6.8 and 6.5 m^2/g for the biochars to 107.7 m^2/g for the activated carbon.

3.3 Adsorption tests

Table 5 reports the pH measured for the extract and of each extract-biochar combination at the end of the adsorption test.

Table 5: pH values for the extract and the extract-biochar combinations

Sample	pH
Extract	4.27
Extract + C500	6.87
Extract + C600	6.98
Extract + C700	7.37
Extract + CE500	6.23
Extract + CE600	5.71
Extract + CE700	6.58
Extract + AC	4.32

The extract had a pH of 4.27 and the addition of the biochar caused an increase of its value, that is more consistent as temperatures rises (excluding CE600 that showed an anomalous behavior). The addition of activated carbon did not change the pH value of the extract.
Figures 2a and 2b show the adsorption efficiencies for the different biomolecules classes and for the specific polyphenols classes, respectively.

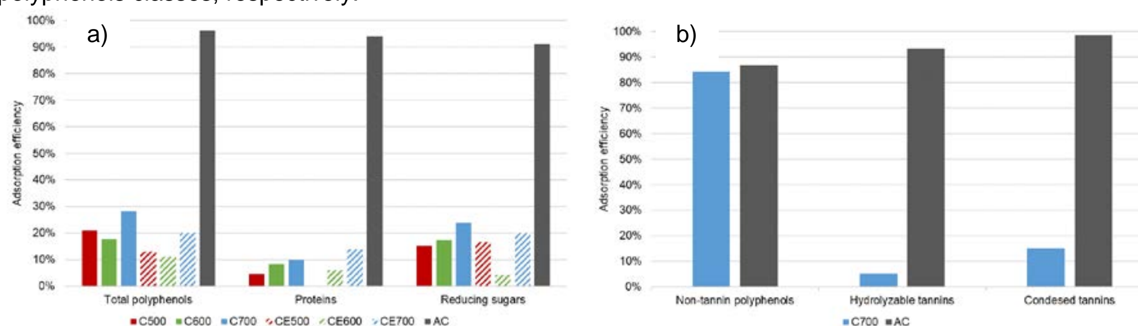

Figure 2: Adsorption efficiencies towards different macromolecules classes (a) and polyphenols classes (b)

As can be seen in Figure 2a, in general C-series biochars have slightly higher adsorption efficiencies than CE-series biochars for each class of biomolecules. The adsorption efficiencies for proteins are the lowest; the total polyphenols adsorption efficiency ranges from ~10% for CE600 to ~28% for C700, with the lowest adsorption efficiency registered for the biochars produced at 500 and 600 °C for both the biochar series.
The differences between the adsorption efficiencies of biochars produced at 500 and 600 °C are small, despite the different porous structures and surface chemistry (-OH surface functional groups). On the other hand, the increase of the adsorption efficiency observed for the biochars produced at 600 and 700 °C is apparently in contrast with their very similar porosity and surface chemistry; moreover, the reported differences between the adsorption efficiencies were not consistent with the pH of the extract-biochar systems since in the case of phenols adsorption on biochars it was observed that the lower is the pH the higher is the adsorption efficiency (Mohammed et al., 2018). The net charge on the biochar surface could be relevant in the adsorption mechanism since it affects the dissociation of the polyphenols in the aqueous solution and their propensity to be adsorbed on the biochar surface. The activated carbon AC had a very high adsorption efficiency, higher than 90% towards each class of biomolecules. In this case, the low pH as well as the high BET surface can be responsible of this behavior.
C700 biochar, which had the highest values of adsorption efficiency for total polyphenols, was further investigated for its selectivity towards different polyphenols classes. Figure 2b shows that C700 had high selectivity towards the smaller molecules, the non-tannin polyphenols, reaching an adsorption efficiency similar to the one of AC. On the other hand, the AC had a scarce selectivity among the three considered classes; this is likely due to its more developed porosity that allow the adsorption also of the bigger molecules like tannins.

4. Conclusions

Biochar was studied as cheap alternative to the purification of polyphenols in the extract from chestnut peeling residue. It was observed that:

- Biochar shows a certain adsorption efficiency towards polyphenols, even if it results less efficient than AC;
- Biochar shows a great selectivity towards the non-tannin polyphenols;

- Biochars produced at higher temperatures has a higher adsorption efficiency;

The preliminary results obtained in this work indicated that further studies are needed to elucidates the role of the biochar surface chemistry, especially the surface charge distribution, in the adsorption mechanism.

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