Ecotoxicity of hydrochar from hydrothermal carbonization of biomass waste

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In recent years, new processes for the management of biomass waste in a circular economy framework are being considered. Hydrothermal carbonization (HTC) is a thermochemical technology of growing interest for the treatment of biomass waste with high moisture content. The main product of HTC is a carbonaceous material commonly called hydrochar, which has applications as biofuel, as activated carbon precursor for adsorbents and catalytic supports, and soil amendment, among others. Understanding the correlation between the composition of biomass waste and the carbonization process is essential for discerning its influence on hydrochar properties and, consequently, its potential application. The main objective of this investigation is to evaluate the ecotoxicity of hydrochar produced through HTC using diverse biomass wastes, with a particular emphasis on their applicability as soil amendment.

Four biomass wastes were used as raw materials: food waste (FW), sewage sludge (SS), swine manure (SM), and garden and park waste (GPW). Thermochemical experiments were conducted in high-pressure steel reactors at various reaction temperatures (180, 210, and 240 ºC) for 1 h, using 1 kg of wet feedstock. The resulting hydrochar (HC) were labeled according to each carbonized waste, followed by the reaction temperature (T) (e.g., HCFWT, for FW-based hydrochar). Each hydrochar was subjected to sequential washing with water (5 cycles, each lasting 24 h) using a v/w ratio of 6:1 (water:hydrochar) to simulate the impact of irrigation on the potential leaching of ecotoxic compounds. These washed hydrochars (WHC) and the associated leachants (L) were identified based on each feedstock and reaction temperature (e.g., WHCSST and LSST, for SS-based products). Hydrochars (HC and WHC) and leachants were analyzed by pH, electrical conductivity, elemental analysis (C, N, S, and H), and metallic composition (ICP-OES). The proximate composition of hydrochars (ash, volatile matter, and fixed carbon) was also analyzed. Chemical oxygen demand (COD), total organic carbon (TOC), and the chemical species in leachants were also evaluated (GC-MS). The ecotoxicity of leachants was analyzed by acute toxicity bioassays through Toxi-ChromoTest (*Escherichia coli*) and Microtox (*Vibrio fischeri*).

Washed hydrochars showed an elevated fixed carbon content, a pH ranging from 5 to 6, and a significant reduction in conductivity, which could mitigate soil salt stress, and a favorable nutrient availability for soil fertilization (with the retention of most magnesium (81%) and phosphorus (76%) in the hydrochar). Significant leaching (even higher than 80%) of various inorganic elements, such as Al, Ca, Fe, and Na, was determined. However, concentrations lower than 0.01 mg/L were detected in the leachants related to heavy metals (As, Cd, Cr (VI), Cu, Ni and Pb) except for Zn.

Sequential washing of the hydrochars showed that potentially phytotoxic elements present in the solids were not solubilized in the leachant. Washed hydrochars derived from food waste (WHCFWT), swine manure (WHCSMT), and garden and park waste (WHCGPWT) exhibited the potential to preserve, improve, and safeguard the physical, chemical, structural, and biological properties of soil. However, for washed hydrochar from sewage sludge (WHCSST), sequential washing did not effectively reduce the concentration of Cu, Ni, Pb, and Zn, which remained above the limit values established by Regulation (EU) 2019/1009 [1]. Although direct application of these hydrochars to soil is not feasible, it can be blended with other chars with lower heavy metal content to fulfill regulatory requirements.

Figure 1 shows the evolution of the leachant toxicity derived from the sequential washing of hydrochar. Regarding *Escherichia coli* assays, the toxicity of leachants obtained at low HTC temperature exhibited elevated toxicity levels. Conversely, LSS and LGPW240 showed reduced toxicity, with values below 10%. Sequential washing induced a decrease in leachant toxicity, yielding values below 25% threshold, considered as non-toxic. A similar toxicity trend was observed in *Vibrio fischeri* assays.

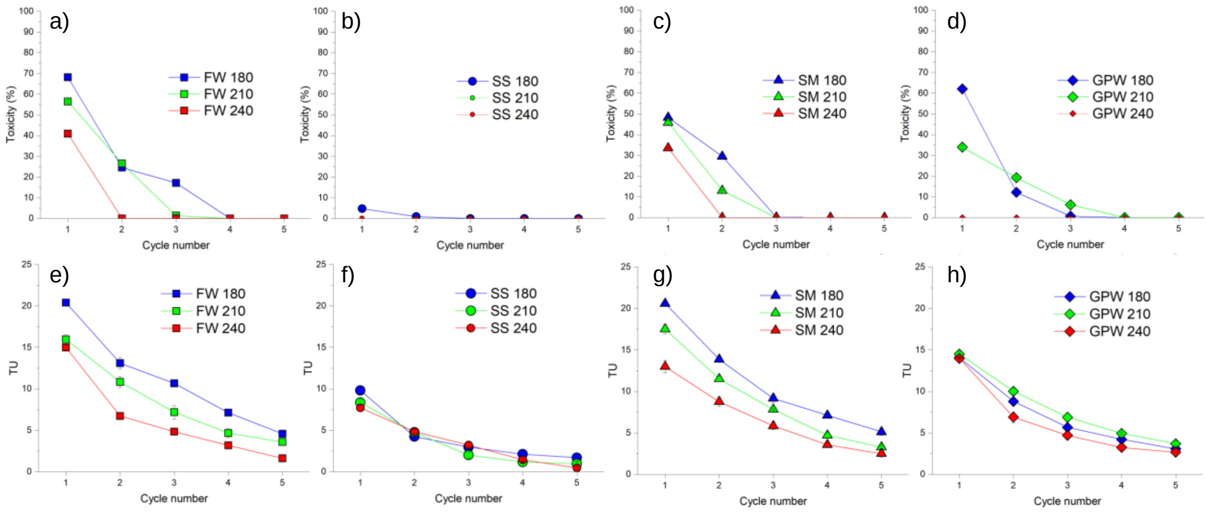

Figure 1. Ecotoxicity of leachants obtained from washed biomass-derived hydrochars by *Escherichia coli* (a, b, c, and d) and *Vibrio fischeri* (e, f, g, and h) assays.

Increasing both the carbonization temperature and the number of washing cycles significantly decreased the ecotoxicity of the leachants. Finally, the values dropped below 10% for the Toxi-ChromoTest and reached 10 toxicity units for the Microtox test, after the third washing cycle. The ecotoxicity sequence resulted in LFWT > LSMT > LGPWT > LSST. Consequently, it can be concluded that LFWT exhibited a higher ecotoxicity level when compared to LSMT, LGPWT, and LSST, in ascending order of ecotoxicity. **Table 1** shows the EC_{50} values for the hydrochars calculated according to the 24-h protocol described by Council Regulation (EC) 440/2008 [2].

Table 1. Ecotoxicity (EC_{50}) of hydrochars-derived from food waste, sewage sludge, swine manure, and garden and park waste.

Sample	EC_{50} (mg/L)	Sample	EC_{50} (mg/L)	Sample	EC_{50} (mg/L)	Sample	EC_{50} (mg/L)
HCFW180	8,171.8 (0.4)	HCSS180	17,002.0 (0.0)	HCSM180	8,092.6 (0.2)	HCGPW180	11,854.0 (1.3)
HCFW210	10,436.3 (0.6)	HCSS210	19,965.1 (0.1)	HCSM210	9,521.1 (1.3)	HCGPW210	10,548.5 (1.2)
HCFW240	11,120.1 (1.1)	HCSS240	21,603.7 (0.8)	HCSM240	12,845.2 (1.2)	HCGPW240	11,913.3 (0.1)

Standard deviation is reported in brackets

According to Council Regulation (EC) 440/2008, all hydrochars can be classified as non-ecotoxic (with EC_{50} values above 3,000 mg/L). The sequential washing process facilitated the leaching of nitrogen-bearing organic compounds such as pyridines, amines, and amides present in the hydrochar. The results suggest a relationship between HTC operating conditions and the waste composition, which influences the characteristics of hydrochar and, consequently, its potential applications as soil amendment. The results obtained from this study can provide valuable information for the effective valorization of biomass waste, leading the way towards sustainable utilization of this resource.

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References

[1] EUROPEAN PARLIAMENT, 2019. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003.

[2] COUNCIL REGULATION (EC) No 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). OJL 142, 31.5, pp. 1–739.