

## Article

# Industrial-Scale Hydrothermal Carbonization of Agro-Industrial Digested Sludge: Filterability Enhancement and Phosphorus Recovery

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**Abstract:** Hydrothermal carbonization (HTC) provides an attractive alternative method for the treatment of high-moisture waste and, in particular, digested sludge. HTC could reduce the costs and environmental risks associated with sludge handling and management. Although it is recognized that the dewaterability of hydrochars produced from digested sludge, even at mild temperatures (180–190 °C), is highly improved with respect to the starting material, the filterability of HTC slurries for the recovery of the solid material (hydrochar) still represents a challenge. This study presents the results of an investigation into the filterability of agro-industrial digested sludge HTC slurries produced by a C-700 Carborem™ HTC industrial-scale plant. The filterability of HTC slurries, produced at 190 °C for 1 h, with the use of acid solutions of hydrochloric acid, sulfuric acid or citric acids, was investigated by using a semi-industrial filter press. The use of sulfuric acid or citric acid solutions, in particular, significantly improved the filterability of HTC slurries, reducing the time of filtration and residual moisture content. The acid treatment also promoted the migration of heavy metals and phosphorus (P) in the HTC filtrate solution. This study demonstrates that P can be recovered via the precipitation of struvite in high yields, recovering up to 85 wt% by mass of its initial P content.

**Keywords:** hydrothermal carbonization; digested sludge; citric acid; hydrochar filterability; phosphorus recovery; struvite; heavy metals removal; dewaterability



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## 1. Introduction

The recent development of the agro-industry to satisfy increased demand for processed food and beverages requires new and sustainable technologies for agro-industrial waste management [1]. During agro-industrial processing—used in, for example, the sugar [2], winery [3] dairy [4] and meat processing [5] industries—large quantities of organic waste such as agro-industrial sludge is produced, which needs to be correctly processed, valorized and/or disposed of. Among the different strategies for the valorization of agro-industrial sludge, direct soil application, sludge drying, composting and the use of anaerobic digestion to produce energy are the most often used [6]. Even if the direct soil application of the sludge could be economical, and the characteristics of agri-food sludge make their direct use in agriculture somewhat suitable, application rates should take into account the characteristics of the soil and the nutritional requirements of crops [6]. Due to the high environmental risks associated with heavy metal accumulation in soil [7], the direct soil application of sludge is a practice which is severely restricted in many European countries nowadays. Sludge drying reduces transportation costs, leading to the easier storage and distribution of the material [8], but the high energy demands and investment costs associated with this technology, even when solar energy is used [9], make it a less

popular technology. Composting is a thermophilic aerobic process where organic matter in sludge is stabilized, eliminating pathogens, and the resulting material, named compost, can be applied as a soil amendment. To produce valuable compost, the reacting material should maintain an optimum pH, a correct C/N ratio, moisture, airflow, a certain particle density and a mechanical structure. Bulking agents, such as wood chips and sawdust, are commonly used as structuring materials [10]. Due to the low economic value of the compost, the composting of agro-industrial sludge is a long and often not economically viable process. Moreover, when the starting material is contaminated by heavy metals, the resulting compost does not meet the specifications to qualify as a soil amendment, and thus needs further treatment before its use [11]. The anaerobic digestion (AD) of sludge is without doubt the most popular conversion technology for agro-industrial waste valorization, leading to the partial conversion of organic carbon into a bio-methane rich biogas [12]. Due to the high residual organic carbon content, the AD of solid and liquid agro-industrial wastes alone or in co-digestion with sewage sludge can produce high bio-methane yields [13,14]. AD is, in fact, an attractive strategy for meeting the growing need for renewable energy sources, as it produces a biogas rich in bio-methane that contributes to sustainable and renewable energy production [15].

As a result of the AD of agro-industrial sludge, great quantities of digested sludge are produced as by-products. Agro-industrial digested sludge is a high-moisture residue, typically showing total solid content (also referred to as dry matter content) between 1.5 and 8 wt% [16–18], a significant amount of residual carbon (up to 40 wt%), and nutrients such as nitrogen and phosphorus (up to 0.2–14 wt% [17–19] and 1.7 wt% [19] respectively, on a dry basis (db)). Together with residual C and nutrients, anaerobically digested sludge, depending on its specific origin, can contain variable quantities of heavy metals such as lead, cadmium, chromium, copper, lead, mercury, nickel and zinc [20], together with pathogens such as *Salmonella* and *Escherichia coli* [6]. As stated above, the sustainable processing of agro-industrial waste, which offers the opportunity to recover and valorize residual carbon, and to retrieve valuable nutrients such as phosphorus, which is considered a critical element in Europe [21], must include appropriate treatment of the waste products before disposal, in order to avoid sanitary problems and the risk of environmental pollution [22,23]. The recovery of nutrients and the safe disposal and/or volume reduction and use of such high-moisture residues represent challenges due to increasingly strict regulations regarding the possible agronomic use of such residues as soil amendments. Recently, environmental regulations have limited the direct landfilling of digested sludge. European waste management policy states that reducing the quantity of waste landfilled and re-using and recycling waste through other recovery methods (energy recovery for instance) are priority objectives [24]. Among the emerging technologies capable of valorizing such residues, hydrothermal carbonization (HTC) treatment has attracted increasing attention in the last few years. HTC involves the thermochemical treatment of high-moisture organic residues (moisture content typically higher than 60 wt%) used to carbonize wet residual biomass under subcritical water conditions at autogenous water saturated pressure [25,26]. During HTC, which is commonly carried out in a closed vessel at temperatures ranging between 180–250 °C and at corresponding pressures of 10–40 bars, biomass undergoes a progressive decomposition via dehydration, decarboxylation and aromatization reactions [27]. This leads to a high-energy, dense solid carbonaceous residue with enhanced hydrophobic character, known as hydrochar, and a liquid phase rich in organics [28,29], together with small amounts of gas, mainly composed of CO<sub>2</sub> [30]. The use of HTC technology to upgrade several different types of waste organic materials, such as agro-waste [31–36], dairy wastes [37,38], paper mill waste [39,40], and the organic fraction of municipal solid waste [41–44], has been widely investigated. More recently, the HTC literature has focused also on the upgrading of sewage sludge and anaerobically digested sewage sludge, with the aim of reducing the amount of residue to dispose, and enhancing the dewaterability [45–47] and filterability of the sludge [48], and phosphorous recovery [49–52]. Although HTC studies on sewage sludge are numerous, very few stud-

ies have reported information regarding the HTC upgrading of agro-industrial digested sludge and, to the best of our knowledge, none have reported experiments carried out at an industrial scale. This study reports novel findings on the HTC upgrading of digested agro-industrial sludge at an industrial-scale level, investigating the influence of acid leaching HTC slurry pre-treatments on HTC residues' filterability, while assessing HTC's ability to sensibly reduce heavy metal concentrations in solid phases and to promote high rates of phosphorous recovery as microcrystalline struvite.

## 2. Materials and Methods

### 2.1. C-700 Continuous Operating HTC Plant of Carborem Srl

HTC slurry and corresponding hydrochars were produced and supplied by Carborem Srl (Rovereto, Italy). HTC residues were obtained using a Carborem HTC continuous operating plant, named C-700, as shown in Figure 1.



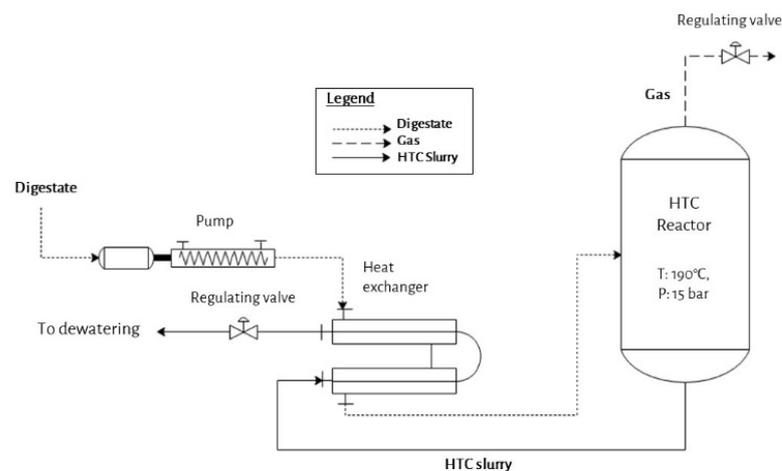
**Figure 1.** C-700—HTC plant, Carborem, fully operative at a waste water treatment plant.

The C-700 HTC plant operating at Mezzocorona (Trentino Alto Adige, Italy) treats 700 L/h of thickened agro-industrial sludge at temperatures up to 200 °C and a corresponding pressure of 15 bars. The containerized plant includes a stainless-steel HTC plug flow reactor, a PLC, a diathermic oil boiler for thermal energy supply, a heat exchanger and two storage tanks, one for the digested sludge and one for the produced HTC slurry.

The digestate is fed by a pump, which has to overcome the pressure generated in the HTC reactor and the head losses due to the frictional resistance of the piping system (especially the heat exchanger, placed before the HTC reactor). The pressure inside the reactor is maintained by the pump and by two regulating valves: one is placed on the HTC slurry pipe, and the other is placed in the upper part, on the HTC gas pipe, as shown in Figure 2.

The heat exchanger is provided to recover the heat from the hot fluid stream (i.e., the HTC slurry exiting the HTC reactor at 190 °C), and thus pre-heat the cold stream (i.e., the entering sludge fed by the pump at a temperature of approximately 20 °C). The valve on the HTC slurry pipe regulates the flow rate leaving the reactor while maintaining the pressure in the HTC reactor.

Thermal energy for the HTC process is provided by a diathermic oil boiler fed with methane, provided by the municipal network or biogas produced by the anaerobic digester located in the waste treatment plant in Mezzocorona. When continuously operated, at 190 °C with a residence time of 1 h, the mean value of electricity and gas consumption is  $4.6 \pm 0.1$  kWh, and  $8.5 \pm 0.3$  m<sup>3</sup> of methane per ton of digested sludge treated.



**Figure 2.** Simplified scheme of the C-700—Carborem HTC plant.

During the HTC process, a fraction of the biomass is also converted into a gas that is mainly composed of  $\text{CO}_2$  [30]. As a consequence, the amount of SL produced is lower than the treated sludge: from each ton of digested sludge (DS) treated, 0.933 tons of SL is produced. In order to compute the slurry mass yield ( $MY_{SL}$ ) of the process, Equation (1) is reported:

$$MY_{SL} = (V_{SL} \times TS_{SL}) / (V_{DS} \times TS_{DS}) \times 100 \quad (1)$$

where  $V_{SL}$  is the volume of produced slurry by means of HTC treatment (L),  $TS_{SL}$  is the total solid content of SL (%),  $V_{DS}$  is the volume of treated DS (L) and  $TS_{DS}$  is the total solid content of DS (%).

## 2.2. HTC Slurries Preparation and Conditioning

### 2.2.1. HTC Slurries Preparation

In this study, agro-industrial thickened digested sludge (containing approximately  $5 \pm 0.5$  wt% of total solid content), produced by the anaerobic digestion of a mixture of sludge from distilleries and dairies, was carbonized at  $190^\circ\text{C}$  for 1 h using the C-700 plant operating in a continuous mode (700 L/h). The produced HTC slurry (named SL), with a total solid content on average of  $3.9 \pm 0.1$  wt%, was collected and stored as produced in 5 L plastic containers at  $4^\circ\text{C}$  or sent to a  $11.5\text{ m}^3$  storage tank. Then, SL was centrifuged at 2800 rpm by a CBB Decanter model CD 50 SIV industrial centrifuge (Figure 3) working at a flow of  $7\text{ m}^3/\text{h}$  of SL with the addition of  $2.8\text{ m}^3/\text{h}$  of a diluted (0.25% by mass in water) medium, a cationic polyelectrolyte solution, namely HIDROFLOC CL1808™. The centrifuged material named SLHC (slurry hydrochar), showing a total solid content on average of  $27.7 \pm 0.5$  wt.%, was also stored in 5 L plastic containers and kept at  $4^\circ\text{C}$  before further treatments and analysis.

### 2.2.2. Conditioning of HTC Residues

In order to enhance filterability and promote phosphorus and heavy metals migration into the liquid phase, SL and SLHC residues were treated with a mineral acid (HCl or  $\text{H}_2\text{SO}_4$ ) or with a citric acid solution. To promote cake formation in the case of SL residues, inert filtration additives, such as waste cellulose powder or granular perlite, were also used. Preliminary laboratory tests, carried out at the Carborem lab facility, had indeed already demonstrated the effectiveness of such treatments in increasing the dewaterability of the HTC samples when leached with acid solutions.

SL residues were conditioned by adding 30 g/L of citric acid or concentrated sulfuric acid to 7.5 L of SL, corresponding to a dose of acid to total solids (TS) of SL of about 0.77 by mass. The obtained solutions were left mixing using an electrical stirrer (a Kacssoo model ES-60M) at 800 rpm for 1 h. Filtration additives, cellulose powder (40 g/L) or expanded

perlite (20 g/L) were added after 60 min of mixing and were left to be stirred for 15 min before the filtration tests.

SLHC-conditioned samples were prepared by adding 2 L of 0.5 molar solution of citric acid or hydrochloric acid or sulfuric acid, respectively, to 1.6 kg of SLHC residue. The dose of acid to total solid content was kept equal to 4.5. The as-obtained mixture (named SLS) was left to be stirred at 800 rpm for 60 min before filtration. The conditioned hydrochars and the conditioned HTC liquids were obtained by liquid–solid separation with a filter press. The schematic diagram of HTC-conditioned sample production is illustrated in Figure 4.

The SL-conditioned samples were named using the abbreviation X\_ACID\_CONC\_ADD\_CONC (where X stands for the type of residues: SL = mixture before filter press; HC= hydrochars, i.e., solid residues after filter press; L = conditioned liquids after filter press; ACID stands for the type of acid: CIT= citric acid, SOLF = sulfuric acid; CONC stands for concentration (g/L); ADD stands for additive: CELL = cellulose, PERL = perlite). To clarify, SL samples are listed in Figure 4.

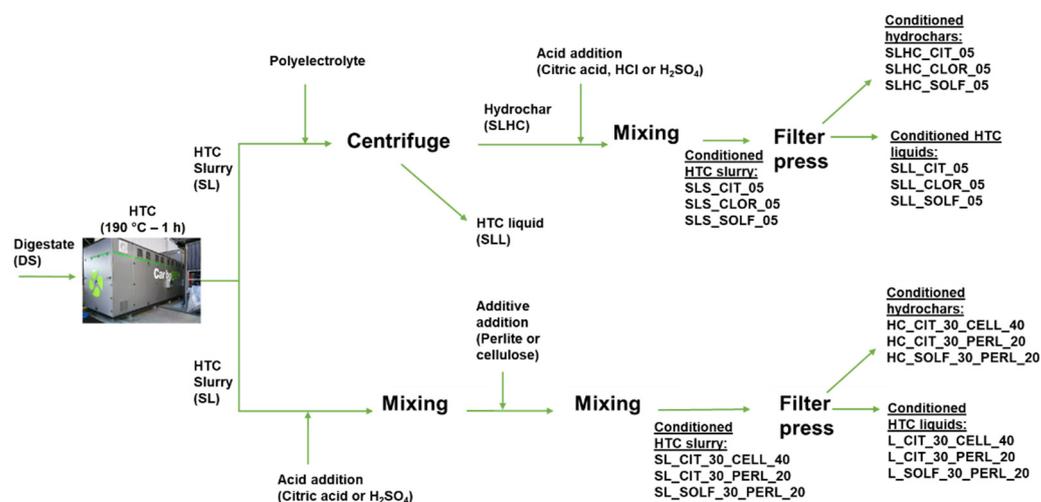
The SLHC-conditioned samples were named using the following abbreviation: X\_ACID\_05 (where X stands for the type of residues: SLS = mixture before filter press; SLHC = hydrochars; SLL = liquids; ACID stands for the type of acid: CLOR = hydrochloric acid); 05 stands for solution molar concentration (0.5 M). For more details on the nomenclature, please see Figure 4.

Hydrochloric acid (HCl, P.A. grade 37%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, P.A. grade 96–98%) and citric acid monohydrate (reagent grade > 99%) were purchased by Sigma Aldrich (St. Louis, MO, USA) and used as received. Granular (2–6 mm) expanded perlite (AGRLIT<sup>®</sup> 3) was purchased in a local market and used as received, and cellulose waste powder (granular size 1 mm) was provided by SPI Srl and used as received.



**Figure 3.** Industrial centrifuge to recover SLHC residue.

Figure 4 reports a scheme of the HTC residue conditioning and the procedure before and after filtration using the semi-industrial filter press.



**Figure 4.** Schematic diagram of HTC residues production.

### 2.3. Filtration Tests

Filtration experiments for SL- and SLHC-conditioned samples were carried out using a semi-industrial filter press. The semi-industrial filter press used in this study was the AUTEMI filter press (model LAB200), using 25  $\mu\text{m}$  pore size synthetic filter fabric with an air permeability of 100 L/(min·dm<sup>2</sup>) at 200 Pa. The filtration pressure was set at 10 bar and the total time of filtration was no longer than 80 min. Filtration experiments were carried out by charging approximately 3 L of sample into the filter press loading tank and registering the volume of filtrate every 10 min. The permeability, amount of liquid filtered out over time and the surface of filtration, (filtration area equal to 0.0232 m<sup>2</sup>) was plotted in order to evaluate and compare the filterability of the sample when compared to the untreated starter material.

The residual moisture content of the filtration cake was also evaluated via a thermo-balance KERN DAB 100-3 60. The filtration cake was then carefully rinsed with DI water to remove the mother liquids and a portion of the solid was dried in a ventilated oven at 105 °C and stored in a sealed flask before analytical characterizations. Solid mass yields of the filtration residues were determined as the mass ratio of the recovered solid material over the starting mass, excluding the mass of the inert filtration additive when used (cellulose powder or granular perlite).

A portion of the filtrate solution of each sample was collected and stored in a plastic sealed flask at 4 °C before analytical characterization. Another portion of the selected samples was also recovered for phosphorus recovery experiments.

### 2.4. Phosphorus Recovery

Liquid fractions of SL and SLHC residues obtained after filtration using the filter press, named SLL\_CIT\_05\_HC, SLL\_CLOR\_05\_HC, SLL\_SOLF\_05\_HC, L\_CIT\_10\_CELL\_40, L\_CIT\_30\_PERL\_20 and L\_SOLF\_30\_PERL\_20, were investigated for potential P recovery. Phosphorus was recovered via the precipitation of microcrystalline struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O).

A total of 0.1 L of each filtrate solution was left to be stirred after the addition of magnesium chloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O) using approximately a 20 wt% molar excess with respect to the stoichiometric amount of initial P content in the liquid fractions. After the complete dissolution of the magnesium salt, the pH of the resulting solutions was slowly increased up to 9.15 with the addition, drop by drop, of 4 M sodium hydroxide (NaOH) solution. Before increasing the pH, in the filtrates obtained when conditioning SL or SLHC without citric acid, an additional 0.5 mol/L of citric acid was used to avoid the precipitation of metal hydroxides upon the addition of NaOH solution. Once the desired pH was reached, a white micro-crystalline powder was promptly produced, evidencing the

formation of struvite. The solution was kept stirring for two hours to ensure the complete precipitation of struvite. The struvite was recovered via Büchner filtration, rinsed a few times with DI water to eliminate the mother liquor, and dried in a ventilated oven at 105 °C for at least 12 h before analytical characterizations.

In order to compute the P recovery after centrifugation, Equation (2) is reported:

$$P_{rec} = (V_x \times TS_x \times P_x) / (V_{DS} \times TS_{DS} \times P_{DS}) \times 100 \quad (2)$$

where  $V_x$  is the volume of produced slurry by means of HTC treatment or the mass of hydrochar produced after dewatering (L or kg),  $TS_x$  is the total solid content of SL or HC (%),  $P_x$  is the P content of SL or HC (%),  $V_{DS}$  is the volume of treated DS (L),  $TS_{DS}$  is the total solid content of DS (%) and  $P_{DS}$  is the P content of DS (%). In order to compute the P losses after centrifugation, Equation (3) is reported:

$$P_{losses} = (V_{LIQ} \times P_{LIQ} \times 10^{-6}) / (V_{DS} \times TS_{DS} \times P_{DS}) \times 100 \quad (3)$$

where  $V_{LIQ}$  is the volume of HTC liquid produced after dewatering, also considering the addition of polyelectrolyte (L),  $P_{LIQ}$  is the P content of HTC liquor (mg/L),  $V_{DS}$  is the volume of treated DS (L),  $TS_{DS}$  is the total solid content of DS (%) and  $P_{DS}$  is the P content of DS (%).

### 2.5. Analytical Characterization of Digestate, HTC Residues and Struvite

The heavy metal (Cd, Hg, Ni, Pb, Cu, Zn), phosphorus and magnesium concentrations of all samples (raw sludge, HTC slurry, hydrochars, HTC liquids after filtration) were evaluated by means of an ICP 8300 DV Optima Perkin Elmer spectrometer equipped with a high-performance SCD detector using EPA 6010D: 2018 + EPA 3051A: 2007 standard methods. Leaching of the samples was carried out via microwave-assisted digestion using a 10 wt% nitric and hydrochloric solution in water at a temperature of 175 °C. All analyses were performed at least in duplicate, ensuring a  $\leq 5\%$  maximum deviation. Total organic carbon (TOC) determination of the samples was carried out by a TOC analyzer (model PRIMACS SNC-100) following the UNI EN 15936:2012 standard method. The total solid content was measured by the moisture analyzer DAB 100-3 60. The total nitrogen and the total organic nitrogen were determined following the CNR IRSA 6 Q64 Vol.3 1985 and ANPA 3/2001 Met. 14.2 methods, respectively. The pH of hydrochar was measured according to the CNR IRSA 1 Q 64 Vol 3 1985 + APAT CNR IRSA 2060 Man 29 2003 method, while the pH value of the liquid/slurry samples was measured with a portable LLG-pH meter 5. The total chemical oxygen demand (COD) and soluble COD (sCOD) of the HTC liquids were determined following the ISO 15705:2002 standard method. Proximate analyses were carried out by a LECO Thermogravimetric Analyzer TGA 701. Moisture content (M), volatile matter (VM), fixed carbon (FC) and ashes were determined following a thermal program modified from the ASTM D-3175-89 standard. Higher heating values (HHVs) were evaluated according to the CEN/TS 14918 standard by means of a LECO AC-500 calorimeter.

Struvite microcrystals were characterized via XRD analysis, using a Siemens D5000 X-Ray Powder diffractometer, Co X-ray radiation,  $\theta$ -2 $\theta$ ; 10–60: step 2 $\theta$ : 0.02, time per step: 0.5 s.

## 3. Results

### 3.1. Digested Sludge and HTC Slurry Properties and Characteristics

Table 1 reports the total solid (TS) and phosphorus (P) content of digested sludge (DS) and HTC residues: HTC slurry (SL) and HTC centrifuged hydrochar (SLHC).

**Table 1.** Total solid content (TS), pH, TOC, total N, and P content and P recovery of HTC residues.

| Sample             | Total Mass (kg) | TS %  | TS (kg) | pH  | TOC wt% db | N Tot wt% db        | P wt% db            | P (kg) | P Rec. wt%            |
|--------------------|-----------------|-------|---------|-----|------------|---------------------|---------------------|--------|-----------------------|
| DS                 | 1000            | 5.1   | 51.0    | 7.0 | 26.0       | 3.6                 | 2.3                 | 1.17   | -                     |
| SL                 | 933             | 3.9   | 36.4    | 7.0 | 24.5       | 3.1                 | 3.1                 | 1.14   | 97.3                  |
| SLHC               | 131             | 27.7  | 36.3    | 7.1 | 29.3       | 2.8                 | 3.1                 | 1.10   | 94.0                  |
| HTC<br>Liq-<br>uid | 1175            | <0.01 | 0       | 7.0 | -          | 1370 <sup>(1)</sup> | 76.5 <sup>(1)</sup> | 0.09   | -7.7 <sup>(2,3)</sup> |

(1). Data expressed in terms of mg/L. (2). Negative value means *p* losses. (3). The value was computed following Equation (3).

DS (5.1 wt% of TS), once carbonized in the C-700 plant, operating in a continuous mode at 190 °C for 1 h, is converted into SL with a 67 wt% mass yield on a dry basis (db) computed by means of Equation (1). The P concentration (uncertainty of the data in brackets), initially 2.3 ( $\pm 0.5$ ) wt% db in the DS, increased in the SL sample, reaching a value of about 3.1 ( $\pm 0.8$ ) wt%, thus demonstrating that the HTC process is able to concentrate P in the slurry SL residue. Following Equation (2), it was possible to compute a P recovery of about 94.0% into hydrochar (SLHC). When subjected to centrifugation, the HTC residue SLHC showed a total solid content of 27.7 wt% and a P content of about 3.1 ( $\pm 1.1$ ) wt% db. Following Equation (2), it was possible to compute a P recovery of more than 96 wt% of the initial P content. The segregation of P in the solid phase during the HTC of sewage sludge has been recently reported [49,50]. In order to confirm these data, the P concentration was also measured in the HTC liquid and showed a concentration of 76.5 mgP/L allowing the computation of the P losses calculated in 7.7%. Considering the high uncertainty of the P data, the P balance could be considered consistent.

Table 2 reports the heavy metal content (data reported are the average of two analyses, standard deviation <5%) of the DS and HTC residues before (SL) and after centrifugation (SLHC).

**Table 2.** DS, SL and SLHC heavy metal content (on db).

| Sample | Cd (mg/kg) | Hg (mg/kg) | Ni (mg/kg) | Pb (mg/kg) | Cu (mg/kg) | Zn (mg/kg) |
|--------|------------|------------|------------|------------|------------|------------|
| DS     | <0.12      | <0.20      | 17.2       | 6.4        | 440        | 232        |
| SL     | 0.18       | 0.21       | 22.8       | 11.7       | 830        | 301        |
| SLHC   | <0.12      | 0.32       | 10.3       | 19.4       | 650        | 309        |

As observed for P element, heavy metals also concentrate in the SL and SLHC residues during HTC. In particular, not surprisingly, copper and zinc elements are found in high concentrations. Copper and zinc compounds are in fact extensively used in agriculture as micronutrients [53].

### 3.2. SL and SLS Residues Filtration Experiment Results

Figures 5 and 6 show the permeability of SL- and SLS-acid-conditioned samples, respectively.

From Figure 5, it can be seen that acidic treatments of SL and the addition of a filtration agent drastically improve the permeability of the HTC slurries. Filtration tests on SL run with the sole use of a filtration agent or after the acidic leaching, without the addition of the filtration agent, which did not improve the filtration performance of SL. The SL sample obtained by adding 30 g/L of sulfuric acid and 20 g/L of micro-granular perlite, SL\_SOL\_F\_30\_PERL\_20, showed the best performance, reaching a permeability value about 400 L/h m<sup>2</sup> after 10 min of filtration, a value eight times higher than the untreated SL sample. The SL samples obtained using citric acid (30 g/L) and perlite or cellulose, SL\_CIT\_30\_PERL\_20 and SL\_CIT\_30\_CELL\_40, showed an increase in the permeability of about five and three times, respectively, when compared to the starting SL material. The results show that perlite gives a higher filtration efficiency when compared

to that of cellulose. Preliminary Büchner filtration tests showed that leaching of SL using hydrochloric acid did not appreciably promote the permeability of SL; thus, conditioning of SL with hydrochloric acid was not taken into consideration.

As shown in Figure 6, during filtration experiments starting from SLS leached samples, the treatment with a 0.5 molar citric acid solution led to the best permeability results. The highest permeability rates were reached after 10 min of filtration. The permeability values of SLHC-conditioned samples, when treated with 0.5 M citric acid, H<sub>2</sub>SO<sub>4</sub> or HCl treatment, were found to be 225, 155 and 70 L/h m<sup>2</sup>, respectively. Due to its high TS content, the SLHC sample cannot be filtered, thus its permeability is considered equal to zero. The higher permeability of the SL samples, when compared to SLS ones, can be mainly related to the differences in the TS content. Indeed, SL samples show a TS content between 5.9 and 7.9 wt%, while the SLS samples show a TS content higher than 12 wt%. Moreover, the use of perlite or cellulose led to the formation of a stable cake.

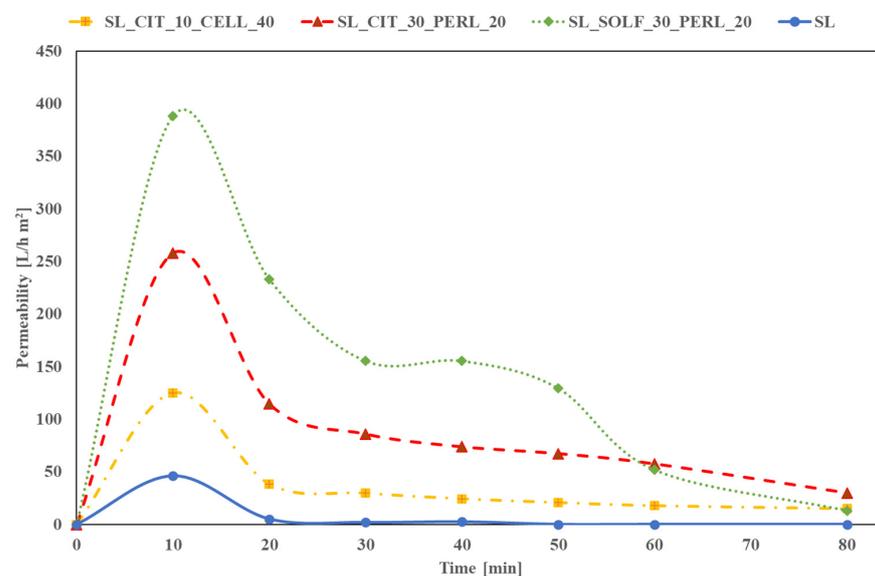


Figure 5. Permeability of SL- and SL-conditioned samples.

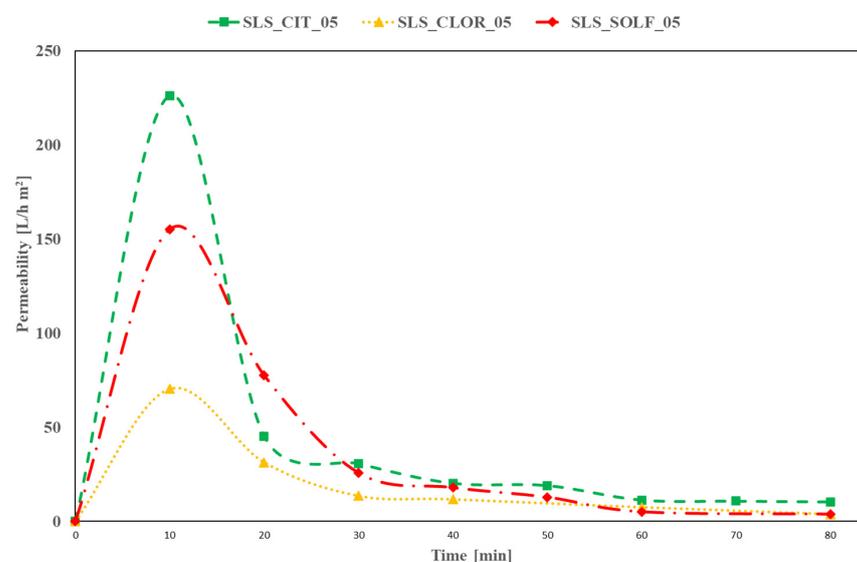


Figure 6. Permeability of SLS conditioned samples.

### 3.3. SL and SLHC Conditioned Solid Characteristics

Table 3 shows the total solid (TS) content, solid mass yields percentage (MY), P and heavy metals content on db of the solid residues obtained upon filtration of SL- and SLHC-conditioned samples. Cd concentration was not included because it was always lower than the detection limit.

**Table 3.** Filtration residues, TS, TOC, MY, and heavy metals concentration (db).

| Sample             | TS wt% | TOC wt% | MY * wt% | P wt% | Hg (mg/kg) | Ni (mg/kg) | Pb (mg/kg) | Cu (mg/kg) | Zn (mg/kg) |
|--------------------|--------|---------|----------|-------|------------|------------|------------|------------|------------|
| SL                 | 5.1    | 26.0    | -        | 3.10  | 0.21       | 22.8       | 11.7       | 830.0      | 301.0      |
| HC_CIT_30_CELL_40  | 41.0   | 26.1    | 89.3     | 0.10  | 0.10       | 6.7        | 0.9        | 24.6       | 13.6       |
| HC_CIT_30_PERL_20  | 54.7   | 20.3    | 85.5     | 0.06  | 0.34       | 3.1        | 1.2        | 57.0       | 20.6       |
| HC_SOLF_30_PERL_20 | 42.9   | 18.3    | 87.3     | 0.24  | 0.12       | 11.4       | 1.4        | 34.1       | 24.8       |
| SLHC               | 27.7   | 29.3    | -        | 3.10  | 0.32       | 10.3       | 19.4       | 650.0      | 309.0      |
| SLHC_SOLF_05       | 42.8   | 24.4    | 87.5     | 0.14  | 0.11       | 4.1        | 2.2        | 91.2       | 22.0       |
| SLHC_CLOR_05       | 38.8   | 26.8    | 80.0     | 0.39  | 0.16       | 3.7        | 2.0        | 97.1       | 37.9       |
| SLHC_CIT_05        | 44.0   | 35.8    | 83.3     | 0.13  | 0.18       | 8.4        | 1.9        | 93.8       | 36.3       |

\* Evaluated by subtracting the mass of additives from the total mass of the SLHC samples.

The results reported in Table 3 show that, upon acidic conditioning and filtration, the solid residues present solid mass yields between 80 and 89 wt% db. The HC residues show significant increases in total solid content and an important reduction phosphorus and heavy metal concentrations when compared to the corresponding starting materials. In fact, the results show that acidic leaching was able to move most heavy metals and P, initially present in the SL and SLHC residues, in the acidic liquid phases recovered via filtration; similar results were recently reported in the literature [45,49,50].

Table 4 reports the P mass balance upon SL and SLHC acidic conditioning before and after filtration. Following the conditioning treatment, reported in the methodology section, the mass balances consider 7.5 kg of SL starting solution and 1.6 kg of SLHC material.

**Table 4.** P mass balance.

| Sample             | M <sub>sample</sub> (g) | P (g) | TS wt% | P <sub>cake</sub> wt% db | P <sub>cake</sub> (g) | P <sub>Filtrate</sub> (g) | P <sub>rec-Filtrate</sub> wt% |
|--------------------|-------------------------|-------|--------|--------------------------|-----------------------|---------------------------|-------------------------------|
| SL                 | 7500                    | 9.1   | 3.9    | -                        | -                     | -                         | -                             |
| SL_CIT_30_CELL_40  | 8025                    | 9.1   | 10.2   | 0.10                     | 0.56                  | 8.51                      | 93.8                          |
| SL_CIT_30_Perl_20  | 7875                    | 9.1   | 8.5    | 0.06                     | 0.24                  | 8.83                      | 97.4                          |
| SL_SOLF_30_Perl_20 | 7875                    | 9.1   | 8.5    | 0.24                     | 0.97                  | 8.09                      | 89.3                          |
| SLHC               | 1600                    | 13.7  | 27.7   | -                        | -                     | -                         | -                             |
| SLS_SOLF_05        | 3650                    | 13.7  | 12.1   | 0.39                     | 1.51                  | 12.23                     | 89.0                          |
| SLS_CLOR_05        | 3640                    | 13.7  | 12.2   | 0.14                     | 0.50                  | 13.24                     | 96.4                          |
| SLS_CIT_05         | 3715                    | 13.7  | 11.9   | 0.13                     | 0.48                  | 13.26                     | 96.5                          |

P<sub>cake</sub> and P<sub>Filtrate</sub> stand for the phosphorus remaining in the solid residue and the liquid fraction after filtration, respectively.

Data reported in Table 4 show that up to about 97 wt% of the P initially found in SL and SLHC residues can be recovered in the liquid fraction upon acidic conditioning and filtration. Considering the recovery rates of P in SL and SLHC residues, the results show that up to 94 and 93 wt% of the initial P content in DS can be recovered, respectively.

In order to evaluate the possible use of the solid residues obtained upon filtration, they were also characterized in terms of fixed carbon (FC), volatile mass (VM) and ashes (ash). Table 5 shows proximate analysis data (db) of the digestate and hydrochars.

**Table 5.** Proximate analysis of digestate and hydrochars.

| Sample             | VM wt% | FC wt% | Ash wt% | HHV (MJ/kg) |
|--------------------|--------|--------|---------|-------------|
| DS                 | 41.7   | 9.9    | 48.4    | 11.33       |
| SLHC               | 39.6   | 10.6   | 49.8    | 11.27       |
| HC_CIT_30_CELL_40  | 52.0   | 9.5    | 38.5    | 11.32       |
| HC_CIT_30_PERL_20  | 31.5   | 9.4    | 59.1    | 9.38        |
| HC_SOLF_30_PERL_20 | 28.0   | 5.1    | 66.9    | 7.20        |
| SLHC_SOLF_05       | 46.1   | 6.0    | 47.9    | 11.19       |
| SLHC_CLOR_05       | 40.2   | 13.1   | 46.7    | 12.20       |
| SLHC_CIT_05        | 50.7   | 16.8   | 32.5    | 17.59       |

The proximate analysis data show that acidic treatment, as expected, when compared with the DS and SLHC materials, led to a significant decrease in the ash content for all the samples [54,55], except for the residues where perlite was added as filtration additive, with perlite being an inert material. The relative low ash content of HC\_CIT\_30\_CELL\_40 sample can be also attributed to the addition of cellulose, a material virtually devoid of ash. Between all the samples, SLHC\_CIT\_05 showed the lowest ash content (32.5 wt%), while it had the highest values of FC (16.8 wt%) and HHV (17.59 MJ/kg). Although the solid residues, evidently, are not good candidates, for solid biofuels, due to the relatively low HHVs and in particular due to the high ash content that could promote slagging and fouling during combustion [56–58], the low heavy metal content and the relatively high carbon content make these residues suitable candidates for soil amendment materials.

#### 3.4. Phosphorus Recovery from HTC Liquid Residues

Table 6 reports the pH, the amount of ammonium and P per liter of the liquid sample obtained upon leaching and filtration in the filter press.

**Table 6.** pH, mass of  $\text{NH}_4^+$  and P per liter of filtrate solution.

| Sample            | pH  | N ( $\text{NH}_4^+$ ) (g/L) | P (g/L) |
|-------------------|-----|-----------------------------|---------|
| L_CIT_30_CELL_40  | 4.0 | 0.60                        | 1.278   |
| L_CIT_30_PERL_20  | 3.4 | 0.72                        | 1.236   |
| L_SOLF_30_PERL_20 | 4.4 | 0.73                        | 1.168   |
| SLL_SOLF_05       | 2.3 | 3.78                        | 4.954   |
| SLL_CLOR_05       | 2.6 | 3.21                        | 4.858   |
| SLL_CIT_05        | 3.2 | 3.36                        | 4.611   |

Table 7 reports the data of struvite production per liter of treated filtrate solution, and corresponding P recovery percentages. The data show that between 51 and 58 wt% of the P found in the SL sample and between 86 and 98 wt% of the initial P content found in the SLHC residue can be recovered as struvite.

**Table 7.** Solid mass yields of struvite recovered via precipitation.

| Sample            | P (mol/L) | Struvite (g/L) | Struvite (mol/L) | P Rec Struvite wt% |
|-------------------|-----------|----------------|------------------|--------------------|
| L_CIT_30_CELL_40  | 0.041     | 5.15           | 0.021            | 50.8%              |
| L_CIT_30_PERL_20  | 0.040     | 5.64           | 0.023            | 57.5%              |
| L_SOLF_30_PERL_20 | 0.038     | 5.15           | 0.021            | 55.6%              |
| SLL_SOLF_05       | 0.160     | 38.53          | 0.157            | 97.9%              |
| SLL_CLOR_05       | 0.157     | 33.13          | 0.135            | 85.9%              |
| SLL_CIT_05        | 0.149     | 33.30          | 0.136            | 90.9%              |

Data show that phosphorus element was successfully recovered via the precipitation of struvite micro-crystals with a recovery mass yield between 51 and 98 wt% with respect to the P initially contained in the HTC filtrates. Best recovery yields were achieved starting from SLHC residue treated with 0.5 M citric acid (90.9 wt%) and 0.5 M sulfuric acid

97.9 wt%), leading to, respectively, total P recovery rates of approximately 84.6 and 91.0 wt% when referring to the initial content of P in the DS starting material.

Recently, Becker et al. reported a phosphorus recovery rate from sewage-digested sludge for struvite as high as 82.4 wt% with respect to the initial P content [50].

XRD analysis of the recovered material demonstrated it, when compared with the available spectra database [59], to be struvite.

Figure 7 shows XRD spectrum of struvite recovered from the SLL\_CIT\_05 sample.

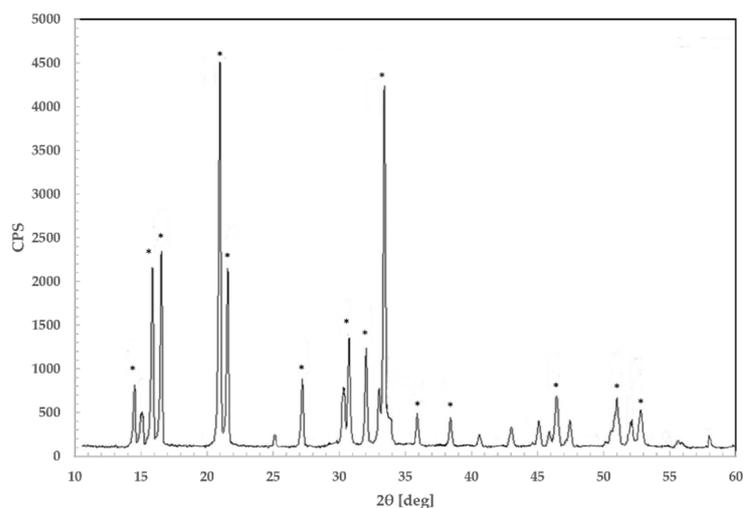


Figure 7. XRD spectrum of struvite recovered from of SLL\_CIT\_05 sample (\* struvite peaks).

#### 4. Conclusions

The present study demonstrates that HTC is an efficient and industrially promising technology for the treatment of digested agro-industrial sludge. HTC slurries of digested agro-industrial sludge produced by the C-700 Carborem™ HTC industrial-scale plant were conditioned with different acidic solutions. Acid leaching, using HCl, H<sub>2</sub>SO<sub>4</sub> or citric acids solutions, and the use of perlite and/or cellulose powder, were showed to enhance the filterability and thus the dewaterability of the HTC slurry residues while leading to the almost quantitative migration of P and heavy metals into the liquid phase. The solid phase, showing low heavy metal residual content, and relatively high carbon concentration, can be a good candidate as a soil amendment. Approximately 96 wt% of the P initially present in the DS residue is segregated into SLHC (hydrochar). Upon acid treatment, between 3 and 11 wt% of the P is lost in the solid phase and the remaining 89–97 wt% is moved to the liquid fraction. Struvite precipitation led to a recovery of P up to 91 wt% when referring to the initial DS phosphorus content.

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