Comparison of hydrothermal carbonization and low-temperature pyrolysis for nutrients recovery from the milk/dairy processing sludge

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Milk (dairy) processing plants have to deal with high volumes of sludge after treatment of effluents. The dairy processing sludge (DPS) is rich in macro and micro-nutrients, which facilitates in its application in agriculture as fertilizer (as biosolids in line with current regulations). Due to high moisture content (90%) and associated high transport cost its application is limited to farmlands near the wastewater treatment plants. This practice is becoming unsustainable, since on the one hand it leads to local oversupply and accumulation of certain substances in soil and the other to uncontrolled nutrient losses. Moreover, DPS has to be stored for most of the year as its application is limited to the growing season (Hu et al., 2021). There is a need to find a way of concentrating nutrients in an easy to store and transport form. Thermal processes, such as hydrothermal carbonization and pyrolysis, of DPS may be a possible solution as they result in pathogen removal, nutrient enrichment, especially phosphorous, in the solid products, hydro-chars/bio-chars. This study compares nutrient content and its transformation in hydro-chars/bio-chars after hydrothermal carbonization and pyrolysis of DPS.

Laboratory scale hydrothermal carbonization (HTC) and low-temperature pyrolysis (LTP) were carried out. HTC experiments were conducted in an electrically heated 1L Parr reactor with a glass liner at three different temperatures (180, 200 and 220 °C) and two residence times (1 and 2 hours) with replicate runs. For the HTC tests DPS as received was used. After the HTC process, the reactor was air-cooled and the solid product (hydro-char/biochar) was separated from the liquid by vacuum filtration, air-dried at ambient temperature, ground and, stored in air-tight plastic containers. The mass of DPS used for each experiment and masses of both products were recorded.

The experimental campaign of LTP is in progress at the time of abstract submission. For LTP tests sludge was dried at ambient temperature. Pyrolysis was carried out in laboratory-scale reactor consisting of a quartz cylinder whose exterior was wrapped with heating tape and insulation, connected to a rubber stopper with thermocouple and gas inlet on the one side, and condenser with twin-neck round-bottom flask on the other (for cooling and collection of liquid and gaseous products). Temperature was regulated with an electrothermal power regulator connected to the heating tape. Before each experiment, the reactor was flushed with nitrogen. LTP was conducted at three different temperatures (350, 450 and 550 °C) and two residence times (30 and 60 minutes) with replicate runs. Dried DPS was placed in a cylindrical steel basket and put into the pre-heated reactor for a specified time. After LTP the reactor was cooled to room temperature for 2 hours. The solid product (bio-char) was stored in closed air-tight plastic containers.

This study examines the content of phosphorus (P), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na) and inorganic sulfur (S) in DPS and bio-chars obtained from HTC and LPT as a function of process conditions. The content of total nutrients was measured with inductively coupled plasma optical emission spectrometry after acid digestion of ashed samples in a microwave oven (CEN/TS 15290:2006). The content of water-soluble nutrients was also determined. The different forms of P in DPS and hydrochar/bio-chars were determined: organic P, inorganic P, apatite P and non-apatite inorganic P and quantified following extraction using HCl and NaOH as extractants (García-Albacete et al., 2012; Pardo et al., 2003). Mass balances on the HTC and LTP processes were performed and were used as a basis for nutrient mass balances. The study will compare and contrast the transformation of nutrients during HTC and LTP. The results of P, Ca, K, Mg, Na and S content and recovery in hydro-char/bio-char obtained from HTC are presented in Table 1, Figure 1 and Figure 2. Similar results for LTP bio-chars will be included in the conference paper together with a comparison of both processes.

Hydrothermal carbonization led to increased contents of total P (36.72 - 44.20 mg/g) in hydrochars/bio-chars compared to DPS (25.50 mg/g). Total content of Ca in hydro-chars was higher (35.72 – 53.71 mg/g) than in in DPS (29.50 mg/g). Magnesium content increased from 1.81 mg/g in DPS to 2.29 – 3.58 in chars. The observed increase in P, Ca and Mg was due to a concentration effect. In contrast, total K (2,10 – 2.61 mg/g) and Na (2.80 – 3.54 mg/g) content in hydrochars/bio-chars were lower than in DPS, 4.36 and 6.62 mg/g respectively, which have been released from solid matter into process water during HTC. The content of inorganic S in solid (hydrochar/bio-char) changed only slightly after HTC, from 5.86 mg/g in DPS to 5.13 – 5.93 mg/g.

Table 1. Effect of HTC process conditions on total nutrients contents in solid material hydro-char/bio-char.

	Total nutrient contents mg/g ± SD					
	P	S (inorganic)	Ca	K	Mg	Na
DPS	25.50 ± 0.59	5.86 ± 0.06	29.52 ± 3.43	4.36 ± 0.01	1.81 ± 0.06	6.62 ± 0.10
180-1	38.30 ± 0.54	5.13 ± 0.06	35.72 ± 0.27	2.32 ± 0.05	2.29 ± 0.03	3.19 ± 0.05
180-2	36.72 ± 0.74	5.30 ± 0.12	42.89 ± 0.00	2.61 ± 0.00	2.82 ± 0.00	3.54 ± 0.00
200-1	42.07 ± 1.9	5.74 ± 0.20	34.09 ± 5.09	2.20 ± 0.01	2.38 ± 0.25	2.95 ± 0.02
200-2	42.05 ± 1.18	5.66 ± 0.13	38.59 ± 4.79	2.10 ± 0.02	2.75 ± 0.14	2.88 ± 0.15
220-1	44.20 ± 0.74	5.92 ± 0.10	53.71 ± 8.54	2.26 ± 0.44	3.48 ± 0.33	2.90 ± 0.72
220-2	44.02 ± 1.50	5.88 ± 0.21	42.88 ± 5.66	2.12 ± 0.01	3.10 ± 0.25	2.80 ± 0.03

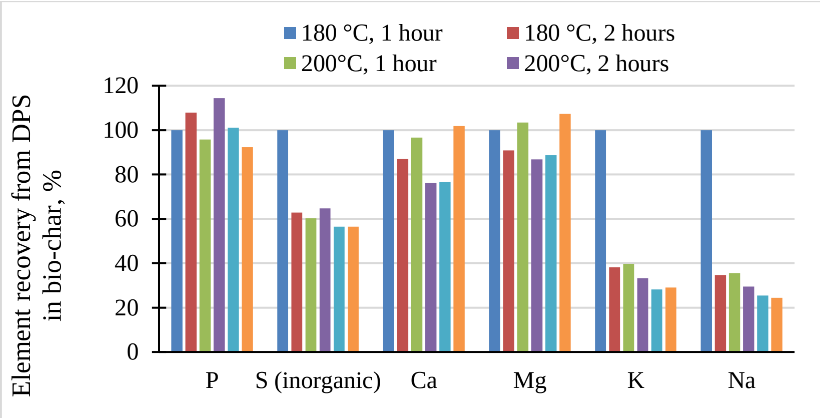

Figure 1 – Recovery of nutrients in hydro-chars/bio-chars after HTC.

High recovery of P, Mg and Ca in solids (hydro-char/bio-char) (80 - 100 %) was observed for all HTC process conditions. About 60% of inorganic S remained in hydro-chars/bio-chars. In contrast, only 25-40% of K and Na was recovered in hydro-char/bio-char due to the high solubility of their salts in process water. The recovery of K and Na decreased with process temperature and residence time increase.

Transformation of P during HTC (wet process) and LTP (dry process) was investigated.

This study will give an indication of which of the two investigated process HTC or LTP would provide a better alternative for concentration of micro and macro-nutrients in solid products hydro-char/bio-char from potential valuable feedstock with a very low heavy metal content, dairy processing sludge.

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