Hydrothermal Treatment of Digested Sludge for Nutrient Recovery

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The constant increase of global population is directly associated to the necessity of a large amount of food, which has a direct impact on an agri-food industry that will require million tons of fertilizers to guarantee the necessary food production. To face this challenge, biomass waste appears as an undervalued natural source of nutrients from which alternative fertilizers could be developed. Within these wastes, sludges from wastewater treatment plants stands out for their high content of N (> 60 g/kg), P (> 20 g/kg) and K (> 40 g/kg) and its annually large generation (> 10 million tonnes (d.b) in Europe) (Sengupta et al., 2015). Digested sludge (digestate) from anaerobic digestion stage concentrates the organic matter and nutrients from the previous sewage sludge.

Hydrothermal carbonization (HTC) allows treating organic matter with high moisture content at temperatures between 170 and 260 ºC and autogenous pressure. Depending on the operating conditions and the composition of the reaction medium, the HTC can favour the realising of nutrients from the waste to the process water (PW) or their concentration on the solid product known as hydrochar (HC) (Ekpo et al., 2016). This work presents the results on the recovery of nutrients (N, P and K) from HTC of digestate.

A digestate with 56 g N/kg, 28 g P/kg and 31 g K/kg (d.b.), and a moisture, carbon and ash content of 90, 30.5 and 30 %, respectively, was selected as raw material. HTC runs were carried out in a ZipperClave stirred pressure vessel (4 L) at 170, 200 and 230 ºC for 1 h, and after reaction the reactor was cooled at room temperature. The slurry was vacuum filtered to separate the resultant phases and the solid phase was dried at 105 ºC for 24 h. The process water and the hydrochar were labelled as PW-T and HC-T, respectively, where T represents HCT temperature. Extraction of nutrients from hydrochar were carried out by means of a 5 M HCl washing (1g HC with 10 mL of acid water) for 2 h in an orbital shaker. The resultant leachate (L-T) and the washed hydrochar (WHC-T) were separated by vacuum filtration. Moreover, an acid-mediated HTC using 0.1, 0.3 and 0.5 M HCl were carried out under the abovementioned reaction conditions. Hydrochar and process water were labelled as HC-T-[HCl] and PW-T-[HCl], respectively. A fractional factorial experimental design was carried out with the aim to study the fate of nutrients depending on the temperature and HCl concentration. Characterization of the hydrochar, process water and leachate was carried out in terms of C and N content by a CHNS analyzer and P and K, together with Cd, Cr, Hg, Ni, Pb, As and Cu concentration, using an ICP-OES. Speciation of N and P compounds was determined with a Hach cuvette test system. A calorimetric bomb was used for the determination of the higher heating values (HHV), according to the technical specification UNE-EN 5400.

The distribution of N, P and K in the HTC products is shown in Table 1. The fate of P along plain HTC was controlled by temperature, being mainly retained in the hydrochar at higher temperatures (65.5 % at 230 ºC) due to the formation of phosphatometallic complexes which inhibited its solubilization (Zhao et al., 2018). An increase of the reaction temperature favoured the release of N (from the hydrolysis of proteins and amino acids) and K (mainly in form of soluble salts) directly to process water (69.8 and 51.4 %, respectively, at 230 ºC). The HCl washing of hydrochar promoted an extra releasing of N, P and K to liquid phase, which together with the nutrients amount concentrated in the process water, allowing a recovery of 82 %, 83 % and 78 % of the N, P and K of the digestate from HTC products obtained to 230 ºC.

Table 1. Distribution of nutrients in the resulting phases after HTC of digestate ($g/kg_{digestate}$, in dry basis)

Sample	N	P	K	Sample	N	P	K
HC-170	28.4	14.1	18.4	PW-170	27.9	13.9	13.0
HC-200	18.8	18.2	15.2	PW-200	37.3	10.2	15.9
HC-230	16.9	18.6	14.5	PW-230	39.2	9.7	16.8
WHC-170	20.6	4.3	12.0	L-170	7.8	9.8	6.4
WHC-200	11.8	5.5	8.4	L-200	7.0	12.7	6.8
WHC-230	10.0	4.8	5.7	L-230	6.9	13.8	8.8
HC-170-0.1	19.8	11.0	18.3	PW-170-0.1	36.5	17.0	13.4
HC-170-0.5	8.7	3.6	10.9	PW-170-0.5	47.4	24.9	20.7
HC-200-0.3	11.0	9.5	12.1	PW-200-0.3	45.1	19.0	19.2
HC-230-0.1	11.7	10.9	13.9	PW-230-0.1	44.5	17.1	17.3
HC-230-0.5	0.9	3.3	11.2	PW-230-0.5	55.4	25.5	21.2

In order to improve the direct recovery of nutrients from the process water, the HTC of the digestate was performed with the addition of HCl. As can be seen in Table 1, an increase of the reaction temperature had a remarkable effect on the extraction of the nutrients to the process water independently of the HCl concentration. Moreover, high HCl concentration (0.5 M) favoured the leaching of N, P and K, being this variable more significant in the case of the N. A study of three-dimension based response surface allows to optimize the operating conditions (temperature and HCl concentration) that maximize the recovery of nutrients (Fig. 1). Around 98 % of initial N was released to the process water after HTC at 230 ºC and 0.5 M HCl, establishing the following speciation: ammonium (47 %), organic nitrogen (36 %) and nitrates (17 %). In addition, increasing HCl concentration (0.5 M) was also crucial to improve the P realising (in form of ortho-phosphate) (≈ 87 %) and K (≈ 69 %) leaching to PW, being not decisive the selected HTC temperature.

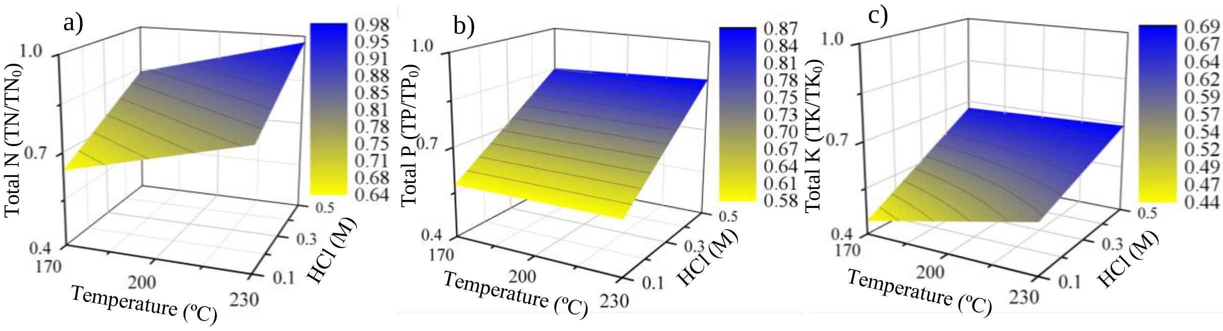

Fig.1. a) Nitrogen, b) phosphorus and c) potassium recovery in the process water by HCl-mediated HTC.

The acid washing of the hydrochar obtained in plain HTC was crucial to improve its properties in terms of N (< 2 %), S (< 0.2 %) and ash (< 10 %) content and to achieve a HHV above 17 MJ/k, requirements of ISO 17225-8 for their possible use as solid biofuel, while hydrochar from HCl-mediated HTC was not suitable for energy valorization (N (> 3%), S (> 0.8 %) and ash (> 35 %) content, together with a HHV < 14 MJ/kg). The inorganic composition of these hydrochars in mg/kg (Cd < 1.5, Cr < 2, Hg < 1, Ni < 50, Pb < 120, As < 40 and Cu < 200), fits within the established limits by the Regulation (EU) 2019/1009 in terms of growing subtract and soil amendment.

In conclusion, the fate of nutrients along the HTC of digestate is dependent of temperature and acid conditions. The results suggested that HCl-mediated HTC of digestate could facilitate nutrient recovery, allowing to improve the N, P and K extraction directly to process water at 230 ºC and 0.5 M HCl and to obtain a resulting hydrochar with suitable properties to be valorised for soil purposes.

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