Hydrothermal Carbonization as an Efficient Tool for Sewage Sludge Valorization and Phosphorous Recovery

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Hydrothermal carbonization (HTC) of sewage sludge has been investigated in this study to demonstrate its capability to segregate phosphorous element and produce a solid energy dense material, i.e. hydrochar, which could find application as solid bio-fuel and/or soil amendment. In this study, centrifuged anaerobically digested sewage sludge (total solid content: 21 wt.%) from Trento North (Italy) waste water treatment plant was hydrothermally carbonized at 190 and 210 °C at 1 and 3 h of residence time. Hydrochars, recovered via filtration, were leached using 4 M HCl solution at room temperature to transfer phosphorous (P) and inorganic elements into the aqueous solution. Recovery of P was achieved via phosphate salt precipitation by alkalinisation, up to pH 9, of the acidic leachate using a 5 M NaOH solution. Sewage sludge and the corresponding hydrochars, before and after acid leaching, were characterized in terms of energy properties (HHV) by calorimetric analysis, P and inorganic elements content via ICP-OES. Results showed that HTC promotes segregation of P element in the hydrochar (up to 90 wt.% of the initial content on a dry basis at 190 °C, 1 h). The study demonstrated that P can be effectively recovered via precipitation via acidic leaching and subsequent alkalization with total recovery yields higher than 70 wt.%. The hydrochar residues, after leaching, showed inorganic elements content and energy properties compatible with their possible use as soil amendment in agriculture and/or as solid biofuel.

1. Introduction

In the last decades the continuous growth of urban population together with a more stringent legislation on sewage sludge effluent quality standards have risen the need to investigate new technologies to reduce the quantity of sludge to be disposed of and improve safety of sewage sludge management (Ferrentino et al., 2016). The high nutrients content, particularly nitrogen and phosphorous, and sludge heavy metal contamination (Al, Cd, Cu, Fe, Pb, Zn etc.) have indeed led the regional governments and municipalities to forbid or drastically reduce the use of such residue in agriculture due to the high environmental risks. Raw wastewater contains relevant amount of phosphorous (P), averagely 1.8 g per capita per day, and this element concentrates in residual sludge (Cornel and Schaum, 2009). P is listed as a critical raw material for Europe (EU Report 2017 – list of Critical Raw Materials for the EU) and its recovery from such residues is of strategic importance for its application as fertilizer in agriculture and it is essential to human life and vital for food production. Today, P is mainly obtained from mined phosphate rock, but natural reserves of P rock are limited and mostly concentrated in Morocco, USA and China (Van Kauwenbergh, 2010). Wet thermochemical process at subcritical water condition, named hydrothermal carbonization (HTC), was extensively investigated in the last few years for energy densification of wet agro-industrial waste as olive mill waste (Volpe et al. 2018), olive trimmings (Makela et al. 2018), corn stover (Reza et al. 2015), grape marc (Lucian et al. 2019), organic fraction of municipal solid waste (Lucian et al., 2018), food and paper waste (Gupta et al. 2019). HTC was also recently found to reduce efficiently the volume of the excess sludge, enhancing dewaterability and reducing environmental risks connected with its disposal while sensibly affecting the company management costs (Wilk et al., 2019; Wang et al., 2019). The aim of this study is to demonstrate that HTC of sewage

sludge, coupled with acid leaching of hydrochars, is a valid and efficient process for high yield phosphorous recovery while producing high value-added products, such as solid biofuel and/or organic fertilizer.

2. Materials and methods

2.1 Material

Approximately 20 kg of centrifuged digested sewage sludge was provided by a civil sewage sludge treatment plant, located in Trento, Italy. The material was carefully homogenized, portioned in 2 litres plastic containers and frozen at -30 °C to preserve its characteristics. The sludge was left to defrost overnight before each HTC experiment.

2.2 Feedstock and hydrochars analytical characterization

The total solid (TS) of the sludge was measured by drying samples in an oven at 105 °C until constant weight, volatile solid (VS) was evaluated by heating samples in a muffle at 550 °C for 6 h. Ash content was measured according to UNI EN 14775:2010 standard method. Total phosphorous (P) content of the starting material and hydrochars was evaluated following the APHA (2012) standard methods for the examination of water and wastewater; samples were first digested in H_2SO_4, forming molybdophosphoric acid, which was then reduced by stannous chloride to molybdenum blue. The concentration was measured photometrically at 690 nm and compared against a calibration curve. Higher heating value (HHV) of raw sample and hydrochars was evaluated according to the CEN/TS 14918 standard by means of IKA C-200 calorimeter. The inorganic elements and heavy metals content of sewage sludge and hydrochars was measured, after digestion in aqua regia, by means of inductively coupled plasma optical emission spectrometry in an ICP-OES Spectrometer (Agilent Technologies, Santa Clara, USA).

2.3 HTC experiments

HTC experiments were carried out in a 2 L stainless-steel AISI 316 batch unstirred reactor. General assembly of the reactor and HTC procedure were previously reported (Merzari et al., 2018). For each experiment, 600 ±0.1 g of sewage sludge (about 126 g on a dry basis, d.b.) were mixed with 365 ±0.1 g of DI water (biomass to water ratio b/w equal to 15 wt% on a dry basis) and placed in the reactor. Once sealed, the reactor was purged by flushing it with pure nitrogen (N_2, AirliquideAlphagaz1^{TM}) and the system heated up to the set temperature, 190 or 210 °C (temperature gradient up to 10 °C/min) and kept reacting for a fixed residence time of 1 or 3 hours for all the experiments. After the end of the residence time, the reactor was quenched by means of a cold stainless-steel mass at -30 °C placed at its bottom. In the meanwhile, compressed air was blown into the reactor to speed up the cooling process. At a temperature lower than 100 °C further cooling, down to room temperature, was achieved by immerging the reactor in a flowing water bath. Once at room temperature, the reactor outlet gas valve was opened and reaction gases collected in a plastic graduated cylinder previously filled with water to evaluate the evolved gas volume and calculate gas mass yield. The reactor was disassembled, thus solid and liquid residues recovered by filtration. The solid residues, hydrochars, labelled HC_T_t (being T the temperature in Celsius and t residence time in hours) were dried in a ventilated oven at 105 °C overnight while the liquid fraction stored for analytical characterization. HTC runs were repeated at least three times to ensure reproducibility of the results. After drying and weighing, the hydrochar yield (solid yield, SY) was computed as the ratio between the mass of hydrochar produced and the initial mass of the feedstock ($g_{hydrochar}/g_{feedstock}$, both on dry basis). The hydrochars were characterized in terms of total phosphorous, heavy metal content and higher heating value (HHV). Gas yield (GY, $g_{gas}/g_{feedstock}$, both on dry basis) was computed by means of the ideal gas law, considering CO_2 as the sole gaseous product (Hitzl et al., 2015). The liquid yield (LY, $g_{liquid}/g_{feedstock}$, both on dry basis), due to species dissolved in the HTC liquor owing to feedstock decomposition, was calculated by difference (LY = 1 − SY − GY).

2.4 Phosphorous recovery and quantification

The procedure of P recovery involved two successive steps. The first step was extraction using 4 M hydrochloric acid prepared by dilution of high purity HCl (Sigma Aldrich, ACS reagent grade 37%). For each trial of acid extraction, 50 ± 0.1 g of dried hydrochar were treated with 250 ml of a 4 M HCl solution with stirring at room temperature for 1 h. After extraction, the residual solid material (non-extractable hydrochar) was recovered via vacuum filtration and washed with distilled water, until the filtrate was neutralized to pH 7. All the aqueous filtrate was recovered for phosphorus isolation. The extracted hydrochars were dried in an oven at 105 °C overnight, and are labelled HC_{Ext}_T_t similarly to the raw hydrochars. The second step in the phosphorus recovery was phosphate salt precipitation by alkalinisation of the acid extracted hydrochar solution. A 5 M sodium hydroxide solution was prepared by dissolution of solid NaOH pellets (Sigma Aldrich –

ACS reagent grade 97%) in deionized water. Alkalinisation was carried out at room temperature, under constant stirring, by slow addition of the 5 M NaOH solution, until the solution reached pH 9.0. The orange material, precipitated from the initially clear solution, was recovered by vacuum filtration and rinsed with water, until the filtrate reached neutral pH. The solid residue was dried overnight at 105 °C in a ventilated oven. The orange solid residue was characterized in terms of total phosphorous content via ICP-OES analysis.

3. Results and discussion

3.1 Feedstock properties and characterization

Tables 1 and 2 show the properties of the feedstock in terms of TS, VS, Ash, HHV (Table 1) and heavy metal content (Table 2).

Table 1: Sewage sludge properties.

TS	VS*	ASH*	P*	HHV* [MJ/kg]
21.0	69.3	29.5	3.1	16.25

*wt% on dry basis

Table 2: Heavy metal concentration in sewage sludge (ppm, dry basis).

Cd	Cu	Hg	Ni	Pb	Zn
10	222	0	5	51	955

Notably, the raw sludge shows a HHV of 16.25 MJ/kg, comparable to those of ligno-cellulosic biomass (Volpe et al., 2016) but also considerable quantities of inert material (ashes 29.5 wt%) suggesting that the raw material is not a good candidate as solid bio-fuel The high amount of ashes is indeed not desirable due to the high risk of slagging and fouling phenomena during combustion (Reza et al., 2013; Reza et al. 2015). The not negligible amount of heavy metals found in the raw material (Table 2) makes impossible to use this substrate, although rich in nutrients such as nitrogen and phosphorus, as soil amendment. The high amount of P (3.1 wt%) confirms the importance of such a residue as a P source and thus the need of develop an efficient route for its recovery.

3.2 HTC residues mass yields and hydrochars characterization

Table 3 shows, as commonly reported in the literature (Volpe et al., 2018; Sabio et al., 2016), that the hydrochar yield decreased at increasing process severity, while gas and liquid yields showed an opposite trend. HHV of hydrochars did not significantly change with HTC process conditions showing a value close to that of the starting materials. The slight increase in ash content of hydrochars in respect to the raw sludge together with the constancy of the HHV values suggest that the increase in hydrochars carbonization is compensated by the increase in inorganic material content.

Table 4 reports the amount of P (wt,% on a dry basis d.b.) segregated in the HTC solid residue at different reaction conditions. In particular, between 74 and 90 wt.%$_{d.b.}$ of the P initially present in the raw feedstock was recovered in the hydrochars. Hydrochar obtained at the less severe condition, 190 °C and 1 h, showed best P segregation while the amount of recovery decreased at higher HTC temperatures and longer times of reaction.

Table 3: Hydrochar, liquid and gas mass yields and hydrochars HHV and ash content.

Sample	Solid Yield (wt.%$_{d.b.}$)	Liquid Yield (wt.%$_{d.b.}$)	Gas Yield (wt.%$_{d.b.}$)	HHV [MJ/kg]	Ash (wt.%$_{d.b.}$)
HC_190_1	90.5	5.0	4.5	16.26	39.1
HC_190_3	76.2	18.5	5.3	16.50	38.5
HC_210_1	76.4	17.9	5.7	16.50	41.0
HC_210_3	68.5	25.2	6.3	16.12	44.6

Table 4: P segregation in raw hydrochars.

Sample	P (wt.%$_{d.b.}$)
HC_190_1	90.4
HC_190_3	79.1
HC_210_1	80.5
HC_210_3	74.0

3.3 Hydrochars HCl leaching and phosphorous recovery

Upon treatment of raw hydrochars with 5 HCl solution, the remaining solid residues (hydrochars after extraction HC_{Ext}) showed solid mass yields (SY) ranging between 55 and 58 wt.% $_{d.b.}$ in respect to the raw hydrochar and overall solid yields between 40 and 52 wt.%$_{d.b.}$ in respect to the raw sludge (Figure 1).
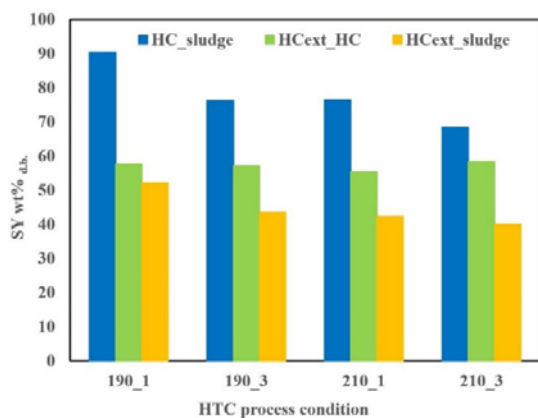

Figure 1: Hydrochar mass yields before and after HCl leaching.

Table 5 shows the HHVs and ash content of the solid residues after HCl extraction. We observe an increase of HHV of the extracted hydrochars (HC_{Ext}) of about 40 wt.% in respect to the feedstock and the raw hydrochars before HCl treatment. The HC_{Ext} HHV values are slightly dependent on HTC severity while ash content ranged between 15 and 20 wt.%$_{d.b.}$ The increase of the HHV and the lower ash content suggest that extracted hydrochar could find application as solid bio-fuel.

Table 5: HHV and ash of raw and HCl extracted hydrochars.

Sample	HHV [MJ/kg]	Ash (wt.% $_{d.b.}$)
$HC_{Ext\_}190\_1$	22.23	14.6
$HC_{Ext\_}190\_3$	23.66	19.7
$HC_{Ext\_}210\_1$	23.96	17.3
$HC_{Ext\_}210\_3$	23.37	18.0

Upon treatment of the HCl leaching solution with a 5 M NaOH solution up to pH = 9, a brown solid residue was precipitated thus recovered by vacuum filtration and dried in a ventilated oven at 105 °C overnight.

Figure 2 shows the P recovery on a dry basis (wt.%$_{d.b.}$) in the raw hydrochar sludge (P_HC_sludge, blue histogram), in the precipitate to respect to raw hydrochars (P_prec_HC, green histogram), and the total phosphorous recovered in the precipitated residues in respect to the raw sludge (P_prec_sludge, yellow histogram). The results evidence that the best overall P recovery of 71 wt.%$_{d.b.}$ was obtained at 190 °C 1 h, while at the most severe condition of 210 °C and 3 h the P recovery decreased to approximately 58 wt.%$_{d.b.}$
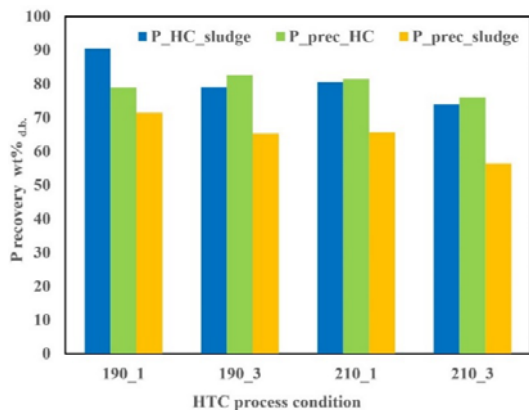

Figure 2: Phosphorous percentage recovery in hydrochars before HCl treatment (P_HC_sludge); P percentage recovery in the precipitate in respect to raw hydrochar (P_prec_HC) and sludge (P_prec_sludge).

3.4 Heavy metal content evaluation in the extracted hydrochars characterization

Table 6 reports the concentration (ppm on a dry basis, $ppm_{d.b.}$) of heavy metal detected in sewage sludge and its extracted hydrochars. In order to establish if the sludge hydrochars could be possibly used as soil amendments, their heavy metals concentrations are compared to the limits reported in the Italian national decree law 75/2010 for fertilizers.

Table 6: Heavy metals concentration in sludge and extracted hydrochars, compared to the upper limits reported in Italian decree law 75/2010 for fertilizers.

Sample	Cd ($ppm_{d.b.}$)	Cu ($ppm_{d.b.}$)	Ni ($ppm_{d.b.}$)	Pb ($ppm_{d.b.}$)	Zn ($ppm_{d.b.}$)
Limits*	**1.5**	**230**	**100**	**140**	**500**
Sludge	*10*	222	5	51	*955*
HCExt_190_1	0	195	0	0	442
HCExt_190_3	0	159	0	0	395
HCExt_210_1	0	*299*	0	12	*974*
HCExt_210_3	0	205	0	11	*763*

From the values reported in Table 6, we note that raw sludge does not respect the limits of the decree law 75/2010 for Cd and Zn element concentrations, but the sludge hydrochars obtained at 190 °C 1 and 3 hours after hydrochloric acid treatment show heavy metal concentrations slightly lower than the limit values.   For what stated above, sludge hydrochars obtained at 190 °C after HCl treatment, due to their relatively high carbon content, higher than 35 wt% absence of bacteria (i.e. salmonella and Escherichia coli) and low heavy metals content could be used as mixed composted soil amendments.

Digested sewage sludge disposal costs in Northern Italy are about 100 €/t but are expected to rise rapidly up to 200 €/t. According to Merzari and co-workers (Merzari et al., 2019), HTC reduces the costs involved in sludge treatment and disposal with values as low as 42 € per ton of sewage sludge. Recycling back the HTC liquor to the anaerobic digester improves methane production during anaerobic digestion providing about one third of the thermal energy requirement of HTC process, thus significantly reducing its operational costs. The operative costs of P removal could be estimated around 100 €/t of digested sludge, but the recovery of P and energy and/or agricultural valorization of the produced solid hydrochar is expected to cover the entire expenses while significantly reducing the amount of waste material to be disposed.

4. Conclusions

Hydrothermal carbonization of centrifuged digested sewage sludge showed to be able to segregate, in the solid residues, up to 90 wt.% of phosphorous (HTC at 190 °C and 1 h). Recovery of P was carried out by HCl leaching of sludge hydrochars and subsequent precipitation of a phosphate rich precipitate by alkalinisation (pH=9) of the resulting leachate using a 5 M NaOH solution. Best total P recovery rate of about 71 wt.% was obtained starting from hydrochar produced at 190 °C and 1 h. Although both the starting material and the raw hydrochars cannot be used as solid bio-fuels due to the high ash content (39-45 wt.%) and low HHV (16.3 – 16.6 MJ/kg), the hydrochloric acid treated hydrochars showed better energy properties (HHV in the range 22.2 – 24.0 MJ/kg) and slightly lower ash content (between 15-20 wt.%). Upon extraction with HCl, the hydrochars showed also a reduced heavy metal concentration, respecting the limits fixed by the Italian national law for fertilizers 75/2010. In conclusion, the hydrochar residues, after acidic leaching, showed inorganic element content and energy properties compatible with their use as soil amendment in agriculture and/or as solid biofuel.

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