Resource project
Energimyndigheten 42483-1

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OBJECTIVE

Determination of the potential to recover phosphorous from hydrochar produced from hydrothermally treated sludge from wastewater treatment plants (WWTP). Additional objectives are to determine the dewaterability of the produced hydrochars and to compare the behaviour of digested and undigested sludge in the processes studied.

EXPERIMENTAL SECTION

Both digested and undigested sewage sludge was used in the study, the characteristics of the sludge are given in Table 1. Both sludges were obtained from a waste water treatment plant (WWTP) located near Halle a. d. Saale, Germany and used for the experiments both at DBFZ (Leipzig) and ATB (Potsdam). Excess sludge is dewatered with a centrifuge and then anaerobically stabilized, recovering some energy by means of methane.

Table 1: Chemical composition of the sludges used in the study, together with their dry substance (DS) contents.

	Undigested	Digested
DS (%)	5.5	21.3
C (% DS)	38.6	34.1
H (% DS)	5.4	5.0
N (% DS)	2.6	5.4
S (% DS)	0.5	1.1
P (mg/g_{DS})	12.7	42.6
Al (mg/g_{DS})	10.2	15.6
Ca (mg/g_{DS})	23.5	35.1
Fe (mg/g_{DS})	23.7	56.1
Mg (mg/g_{DS})	3.5	6.4

Experiments performed at Deutsches Biomasseforschungszentrum gemeinnützige GmbH (DBFZ) at Leipzig, Germany

Both digested and undigested sludge were hydrothermally carbonised at pH 6, 7 and 8. H_2SO_4 and NaOH (both 1 molar) were used to adjust the pH. To obtain comparable results, the digested sludge was diluted with deionised water to the DS of the undigested and dewatered sludge (5.5 %) before the HTC runs. In all experiments approximately 400 g of the slurry was added to a batch reactor (Berghof, 500 mL total volume) heated with thermal oil. The experiments were carried out at 200 °C with a holding time of 4 hours and thereafter cooled to ambient temperature. After the reaction, the resulting slurries were filtered with a screw press. A more detailed description of the experimental design is given in Table 2.

Table 2: The experimental parameters used for the HTC runs at DBFZ (Leipzig).

	Sludge		Water	Additive		pH	
	Amount (g)	DS (%)	Amount (g)	Type	Amount (g)	Before HTC	After HTC
Undigested	403.8	5.5	–	–	–	6.2	4.9
Undigested	395.8	5.5	–	NaOH	2.0	6.9	5.0
Undigested	399.3	5.5	–	NaOH	5.0	8.1	5.2
Digested	103.5	21.3	296.5	H_2SO_4	4.7	6.1	5.8
Digested	103.4	21.3	297.7	H_2SO_4	0.3	7.1	6.0
Digested	103.4	21.3	296.7	NaOH	2.6	8.1	6.1

In the subsequent leaching experiments approximately 220 mL of 4 M HCl were added to 10 g of hydrochar and shaken for 30 minutes. The obtained slurries were filtered with vacuum filtration through 15 µm cellulose paper. The extracted hydrochar was washed 3 times with 500 mL of distilled water and shaken for 30 minutes during each washing cycle. 5 M NaOH was added to the leachates to adjust the pH to around 9 and the final adjustment of pH to 9.2 was made by 0.1 M NaOH and 0.1 M HCl. The precipitate that was formed in the leachates was recovered with a centrifuge and dried. The hydrochar, the leached hydrochar, the leachate and the precipitate were analysed on their P content.[1]

The determination of P, Al, Ca, Fe and Mg was done via ICP-OES (all solids were microwave digested with aqua regia prior to analysis), while C, H, N and S were determined with an elemental analyser after drying.

Experiments at Leibniz Institute for Agricultural Engineering and Bioeconomy (ATB) at Potsdam, Germany

In these HTC runs 8 kg of sludge (both undigested and the diluted digested) were placed in a 5 gallon (18.6 L) Parr reactor equipped with a stirrer. The experiments were carried out in the exact same way as those in the smaller scale at DBFZ. The reactor was heated to 200 °C with a heating rate of 2 °C/min. Temperature was held for 4 hours and the whole mixture was stirred continuously at 90 rpm. After the reaction was finished, the reactor cooled down to ambient temperature overnight. When cooled off, the process water was separated from the hydrochar by a screw press with a filter towel and further filtered through a mesh with a defined pore size of 100 µm. Additional details of the experimental design are given in Table 3.

Table 3: The experimental parameters used for the HTC runs at ATB (Potsdam).

	Sludge		Water
	Amount (g)	DS (%)	Amount (g)
Undigested	8007.1	5.6	–
Digested	1702.9	20.7	6343.1

[1] The leaching procedure is in accordance to Heilmann et al. "*Phosphorous reclamation through hydrothermal carbonisation of animal manures*" Environmental Science and Technology 48 (2014) 10323–10329.

RESULTS AND DISCUSSION

Mass balances and dewaterability of the hydrochar

The results showed that nor pH (within the range examined here) nor the type of sludge affected the amount of hydrochar produced during the hydrothermal carbonisation, see Table 4. Changing pH within the small range of 6-8 showed no significant effect on the dewaterability of the resulting hydrochars all ranging from 26.4 to 28.6 % DS.

When the HTC experiments were performed in a bigger scale, around 8 kg of sludge instead of 400 g, the hydrochars had a higher DS content (Table 4), which could be a result of different filtering procedures in the two laboratories.

It should be noted that the undigested sludge produced a hydrochar with a DS content of 44 % by a small scale screw press, while the DS was 28.4 % for the hydrochar from the digested sludge (Table 4). These values are confirmed by the fact that the process water produced from the digested sludge had a higher DS content (1.1 %) compared to the corresponding value for the undigested sludge (0.7 %).

Table 4. Material balances of the HTC experiments performed at DBFZ (Leipzig) and ATB (Potsdam)

	Slurry		Hydrochar		Process water	
Sludge	**pH**	**(g)**	**(g)**	**DS (% FM)**	**(g)**	**DS (% FM)**
Runs at DBFZ, Leipzig						
Undigested	6.2	400.3	64.8	28.1	332.6	
Undigested	6.9	394.9	86.1	26.8	309.6	
Undigested	8.1	399.0	68.9	28.3	327.9	
Digested	6.1	397.3	88.5	25.7	310.2	
Digested	7.1	387.5	59.7	26.5	325.1	
Digested	8.1	394.2	60.4	26.9	331.6	
Runs at ATB, Potsdam						
Undigested		8007.1	629.2	44.4	7203.2	0.7
Digested		8046.0	627.7	28.4	7317.7	1.1

The concentration of some elements in the sludges, hydrochars and process waters are given in Table 5. The results showed that more than 90 % of carbon, hydrogen, nitrogen and sulphur were found in the hydrochar, and less than 10 % in the process water. Additionally, there were no significant differences between the two hydrochars.

The distributions of the studied metals are given in Figure 1. It shows that the hydrochar from the undigested sludge retained almost all aluminium (Al) and phosphorous (P), while the alkali earth metals (Ca and Mg) have a higher solubility. 85 % of iron (Fe) was found in the hydrochar. While the figure shows that the hydrochar from the digested sludge retained the metals better as compared to the hydrochar from the undigested sludge, this could be a result from the fact that the dewaterability of the hydrochar from the digested sludge was lower, it contained 71.6 % process water, compared to 55.6 % for the undigested hydrochar. Since the process waters also contained metals, the metal contribution from the remaining process waters in the hydrochars is not insignificant.

Table 5: The concentration of some elements in sludge, hydrochar and process water (PW) produced when digested and undigested sludge were hydrothermally carbonised at ATB (Potsdam).

	Undigested			**Digested**		
	Sludge	**Hydrochar**	**PW**	**Sludge**	**Hydrochar**	**PW**
Carbon (C, % DS)	38.6	38.2	46.3	34.1	29.5	48.1
Hydrogen (H, % DS)	5.4	4.8	5.4	5.0	3.5	6.2
Nitrogen (N, % DS)	2.6	1.3	7.8	5.4	1.3	1.9
Sulphur (S, % DS)	0.5	0.6	1.3	1.1	1.4	1.9
Phosphorous (P)	12.7 *(mg/g$_{DS}$)*	15.6 *(mg/g$_{DS}$)*	44.4 *(mg/L)*	42.6 *(mg/g$_{DS}$)*	61.6 *(mg/g$_{DS}$)*	146.0 *(mg/L)*
Aluminium (Al)	10.2 *(mg/g$_{DS}$)*	14.5 *(mg/g$_{DS}$)*	2.8 *(mg/L)*	15.6 *(mg/g$_{DS}$)*	23.6 *(mg/g$_{DS}$)*	0.2 *(mg/L)*
Calcium (Ca)	23.5 *(mg/g$_{DS}$)*	26.4 *(mg/g$_{DS}$)*	295.0 *(mg/L)*	35.1 *(mg/g$_{DS}$)*	54.1 *(mg/g$_{DS}$)*	36.2 *(mg/L)*
Iron (Fe)	23.7 *(mg/g$_{DS}$)*	28.5 *(mg/g$_{DS}$)*	186.0 *(mg/L)*	56.1 *(mg/g$_{DS}$)*	90.5 *(mg/g$_{DS}$)*	49.7 *(mg/L)*
Magnesium (Mg)	3.5 *(mg/g$_{DS}$)*	3.5 *(mg/g$_{DS}$)*	65.7 *(mg/L)*	6.4 *(mg/g$_{DS}$)*	9.2 *(mg/g$_{DS}$)*	27.9 *(mg/L)*
Amount (g)	8007.1	629.2	7203.2	1702.9	627.7	7317.7
DS (%)	5.5	44.4		21.3	28.4	

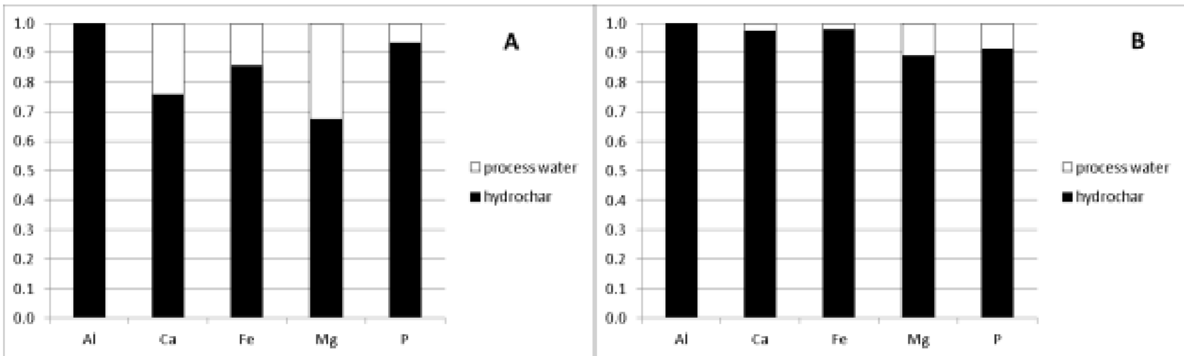

Figure 1. Distribution of aluminium (Al), calcium (Ca), iron (Fe), magnesium (Mg) and phosphorous (P) between hydrochar and process water produced when undigested (A) and digested (B) were hydrothermally carbonised at ATB, Potsdam.

Retention of phosphorous in the hydrochar

Changing pH within the small range of 6-8 had also no effect on the retention of phosphorous, see Table 6. In all cases, more than 90 % of phosphorous was retained in the hydrochar during the hydrothermal carbonisation.

Table 6. The measured distribution of phosphorous (P) between hydrochar and process water (PW) when digested and undigested sludge were hydrothermally carbonised at different pH at DBFZ (Leipzig) and ATB (Potsdam). Note that at DBFZ the dependence of pH on the distribution of phosphorous was studied while at ATB the material balances were determined.

	Sludge			Hydrochar			PW		
Sludge	**pH**	**P (mg/g_{DS})**	**P (mg)**	**P (mg/g_{DS})**	**P (mg)**	**Share of total (%)**	**P (mg/L)**	**P (mg)**	**Share of total (%)**
Runs at DBFZ, Leipzig									
Undigested	6.2			15.0	279.3	98.7	11.3	3.8	1.3
Undigested	6.9			14.6	339.8	98.1	21.5	6.6	1.9
Undigested	8.1			15.7	311.4	98.2	17.7	5.8	1.8
Digested	6.1			49.2	1145.1	98.7	49.0	15.1	1.3
Digested	7.1			56.4	911.2	95.2	139.0	45.5	4.8
Digested	8.1			61.2	1015.6	95.1	157.0	52.4	4.9
Runs at ATB, Potsdam									
Undigested		12.7	5491	15.5	4360	93.1	44.4	322	6.9
Digested		42.6	15307	61.0	10974	91.1	146.0	1077	8.9

Recovery of phosphorous

It was possible to recover around 90 % of the phosphorous in the hydrochars by leaching with acid followed by precipitation in high pH, see Table 7. There was no significant difference between the hydrochars from the undigested and digested sludge. Taking account that around 92 % of the P was retained in the hydrochars during the hydrothermal carbonisation (Table 6) a leaching recovery of ≈90 % points to the possibility of recovering 83 % of the phosphorous in the sludge from WWTP by hydrothermally carbonisation followed by leaching of the hydrochars.

Table 7. Recovery of phosphorous (P) by leaching hydrochar from thermally carbonised undigested and digested sludge as described before

	Undigested	Digested
Amount P in the starting hydrochar (mg)	154	605
Amount P in leached hydrochar (mg)	2.6	4.8
Amount P in the precipitate (mg)	135	545
Recovered P (%)	89	90

How the phosphorous is bound in the final high-pH precipitate has not been studied within this preliminary study, but most probably it consists of an inorganic phosphate salt which should be characterised it in the future.

SUMMARY

The main results from this study can be summarised as follows:

- In total, 90 % of the phosphorous in hydrochar from undigested and digested sludge from a WWTP can be recovered by acid leaching followed by precipitation at high pH.
- 92 % or more of the phosphorous are retained in the hydrochar when undigested and digested sludge were hydrothermally carbonised.
- During HTC, no significant difference could be detected for the retention of phosphorous in the hydrochar in the pH range from 6 to 8.
- The dewaterability for hydrochar from undigested sludge (44.4 % DS) was higher than the corresponding value for digested sludge (28.4 % DS).
- More than 90 % of the carbon, nitrogen, and sulphur could be found in the hydrochar from both undigested and digested sludge.
- Calcium and magnesium a higher solubility than aluminium and iron within the tested range.