Nutrient recovery and subsequent sludge pyrolysis – a future solution for municipal waste water management?

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As most of the phosphorus (P) reservoirs are located only in few countries, it is important to find different sources to guarantee national food security. Nitrogen (N) recovery, on the other hand, is interesting in energy saving point of view as production of nitrogen fertilizers by Haber-Bosch synthesis is very energy intensive. Wastewaters contain much P and N and are locally produced so they are very interesting source for nutrient recovery. They also contain organic carbon, that could be captured and utilized in soil conditioning instead of emitting it into the atmosphere as CO_2. However, the heavy metals, pathogens and organic contaminants in wastewater treatment sludge are affecting its use in agriculture and soil conditioning.

Since 2014, Helsinki region environmental services authority (HSY) has developed a nutrient recovery process called RAVITA™. The process enables P recovery directly from as phosphoric acid. The process can be divided into two steps. First, P is removed from wastewater by effective post-precipitation and chemical sludge with high P content is produced. In the second step, P is recovered from the chemical sludge by dissolution and solvent-solvent extraction processes. Besides P recovery, the process enables precipitation chemical recovery. In addition, the process can be combined with N recovery from reject waters. Hence, the resulting end product is ammonium phosphate which is suitable as such for NP fertilizers. The recovered phosphoric acid is a valuable and multipurpose chemical for various industrial fields besides fertiliser industry. (Rossi *et al.*, 2018).

Wastewater sludge processing has been studied at HSY since 2016. Pyrolysis was chosen as the most interesting technology in 2017 and is currently studied in more detail in a joint research project with the Natural Resource Institute Finland and Gasum Ltd, a biogas company operating in the Nordic countries. Pyrolysis is seen as a possible solution for eliminating organic pollutants. It produces energy while preserving some of the carbon and nutrients in the sludge, thus acting as a carbon sink and being a better solution compared to sludge incineration.

This paper present results from the analysis of organic contaminants in the end products of the combined process shown in detail in Figure 1.

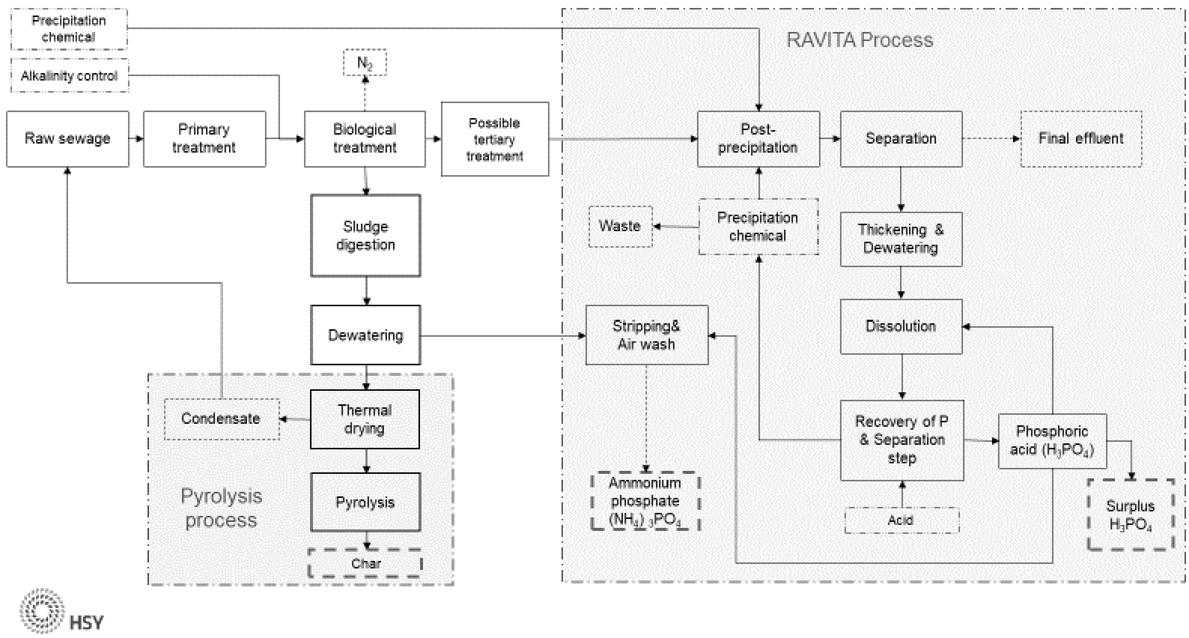

Figure 1. The process combination of RAVITA™ nutrient recovery and sludge pyrolysis

1000 population equivalent (PE) RAVITA™ pilot plant is operated at Viikinmäki wastewater treatment plant (1,1 million PE) in Helsinki. Currently the pilot plant consists the chemical sludge production. In 2020, the phosphoric acid production will be in 1000 PE pilot scale. This enables more accurate mass balance calculations of the process. Furthermore, product and side stream quality will be analysed. Energy and cost calculations will be done.

Pyrolysis of sludge was conducted with a pilot scale plant owned by Gasum Ltd in Turku, Finland. Wastewater treatment sludge was digested in mesophilic conditions and dried to 83 % TS before pyrolysis at 500 °C for 1 hour and 30 minutes. Organic contaminants were analyzed from three replicate samples. The analyzed compound groups were: pharmaceutical substances, hormones, phthalates, bisphenol-A, polybrominated diphenyl ethers, triclosan and methyl triclosan, perfluorinated compounds (PFCs), HBCDD and TBPA, alkyl phenols and ethoxylates, PCDD/Fs and PAHs.

Results from both the RAVITA™ and pyrolysis pilots have been positive. It has been possible to transfer more than 80 % of the P entering the RAVITA™'s first step to the recovery part. Recovered products, phosphoric acid, precipitation chemical and pyrolyzed sludge have low organic micropollutant concentrations. Analysis results of organic contaminants deemed most relevant in land applications by the Finnish Environment Institute (Fjäder 2016) are shown in Table 1.

Table 1. Organic contaminants in end products

	recovered H_3PO_4	recovered $Al_2(SO_4)_3$	pyrolysed sludge		recovered H_3PO_4	recovered $Al_2(SO_4)_3$	pyrolysed sludge
	ug/l	ug/l	mg/kgTS		ug/l	ug/l	mg/kgTS
DEPH	34	<0,3	1,933	sum PAH EPA 16	--	--	1,87
PFOS	<0,010	<0,010	0,00067	Acenaphthene	<0,050	<0,005	0,047
PFBA	<0,050	<0,050	<0,001	Acenaphthylene	<0,050	<0,005	<0,02
BDE-209	<0,10	<0,10	<10	Anthracene	<0,050	<0,005	0,06
ofloxacin	<5,0	<5,0	<0,1	Benzo[a]anthracene	<0,010	<0,001	0,04
siprofloxacin	<10	<10	<0,5	Benzo[b]fluoranthene	<0,010	<0,001	0,05
diclofenac	<0,50	<0,50	<0,01	Benzo[k]fluoranthene	<0,010	<0,001	<0,02
estrone	<0,5	<0,5	<0,01	Benzo[a]pyrene	<0,0017	<0,00017	0,05
tetracycline	<1,0	<1,0	<0,01	Benzo[g,h,i]perylene	<0,0050	<0,00050	<0,03
triclosan	<0,050	<0,050	0,0057	Dibenz[a,h]anthracene	<0,0050	<0,00050	<0,03
bisphenol A	<1,0	<1,0	<0,5	Fenantreeni	<0,050	<0,005	0,28
				Fluorene	<0,050	<0,005	0,18
				Fluoranthene	<0,050	<0,005	0,14
				Chrysene	<0,010	<0,001	0,12
				Indeno[1,2,3-c,d]pyrene	<0,0050	<0,0005	0,06
				Naphthalene	<0,1	<0,01	0,67
				Pyrene	<0,050	<0,005	<0,02

When pyrolysis and RAVITA™ are combined, nutrients, P and N, and carbon are utilized efficiently. Implementing the RAVITA™ process will affect the quality of the sludge. As phosphorous and the precipitation chemical will be recovered, the sludge will have a higher carbon content and the phosphorous remaining in the sludge will be more readily plant available. This will make the pyrolyzed sludge a more appealing product. HSY is investing in a pilot scale (3000 tonnes/year) sludge pyrolysis unit which will be in operation in Dec 2020. Results presented in this paper represent the pyrolysis of conventional sludge. Testing the pyrolysis of the biological sludge from the RAVITA™ process will be done in the near future.

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