Report on Evaluation of NPK recovery potential from TORWASH®-treated paper sludge, waste olive pomace and fruit & vegetable waste

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Executive Summary

This report presents selected results from the different Torwash® campaigns of the F-CUBED project, the derived materials and the assessment of the nutrient recovery strategy developed by University of Hohenheim (UHOH). Including the key findings of the deliverables D2.4, D3.4 and from Task 4.8, this report summarizes the NPK recovery potential for paper sludge, waste olive pomace, and orange peels processed by Torwash® at the 3 different industrial sites throughout Europe.

The paper sludge derived Torwash® products proved to be promising for the production of the mineral fertilizer struvite, while economic considerations are still needed to clarify if the recycling of these nutrients (N and P) on-site in the wastewater treatment plant itself (where the sludge originates) might be beneficial, as it could save otherwise needed additives (urea, phosphoric acid) in the aerobic treatment step of the wastewater treatment facility.

The nutrients coming from orange peels and waste olive pomace are almost solely found in the Torwash® liquid effluents after filtration. A forced struvite precipitation from these effluents can easily recover 50% of the phosphate content, while ammonia recovery is relatively minor via this approach. Also, the overall yield of mineral fertilizer from these residues is very low because the concentration of nutrients, especially phosphate, in the biomass is low from the beginning. The high organic loading and the good biodegradability of these effluents seems promising for anerobic co-digestion. The recovery of nutrients in the resulting digestate enables the complete utilisation of NPK in the form of an organic fertilizer and might be superior to otherwise arduously-produced mineral fertilizer from low nutrient containing biomass.

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1. Introduction

The main objective of the F-Cubed project is to develop an advanced process concept for the hydrothermal conversion of a broad range of low-quality biogenic residues to intermediate bioenergy carriers. The F-Cubed approach combines mild-hydrothermal conversion of wet organic streams via TORWASH® reactor technology with advanced mechanical dewatering and anaerobic effluent treatment. To build a complete value chain from the feedstock to the end products, the F-Cubed approach includes also parallel recovery of the specific value-added co-products, including nutrients (NPK).

The main aim of the nutrient recovery tasks is to find and optimize an effective nutrient recovery depending on the treated biogenic residues. After the first assessment of all feedstock-dependant streams and a prescription of the fate of relevant nutrients like NPK, the options for their flexible recovery need to be evaluated. An effective approach to recover phosphate and nitrogen (as ammonium) in form of the slow-release fertilizer struvite ($MgNH_4PO_4 \cdot 6H_2O$) was already developed for the related process of the hydrothermal carbonisation (HTC) of urban sludge and manure-based digestates, reaching a phosphate recovery of more than 80%. F-Cubed conditions are more moderate than the HTC conditions (e.g., a lower temperature range is used, from 180 to 200 ℃). Testing phosphate recovery as struvite at these novel conditions for varying feedstock by this approach is addressed. This investigation aimed to provide data for the value chain assessment.

1.1. Description of the document

This document presents the combined results on the evaluation of NPK recovery potential from the TORWASH treated paper sludge, waste olive pomace and fruit & vegetable waste. Special focus is on the potential to recover phosphorus in the form of struvite and nitrogen in the form of ammonia. Moreover, the potential for potassium recovery and the use of treated product streams directly as fertilizer is discussed.
The obtained results will inform subsequent sustainability and value chain assessments of the F-Cubed process.

1.2. WPs and Tasks related with the deliverable

WP	Task	Relation to deliverable D4.4
WP2	T2.4	Dewatered solid and Liquid effluent from the treated paper sludge from this task used for the estimation on the NPK recovery potential
	T2.7	Anaerobically pre-treated filtrate samples from treated paper sludge were used for the estimation of NPK recovery
	T2.8 D2.4	Results on Evaluation of NPK recovery potential from TORWASH® treated paper sludge from this task (D2.4 summarizes the main results) used as input for D4.4
WP3	T3.4	Dewatered solid and Liquid effluent from the treated waste olive pomace from this task used for the estimation on the NPK recovery potential
	T3.7	Anaerobically pre-treated filtrate samples from waste olive pomace were used for the estimation of NPK recovery
	T3.8 D3.4	Results on Evaluation of NPK recovery potential from TORWASH® treated waste olive pomace from this task (D3.4 summarizes the main results) used as input for D4.4
WP4	T4.4	Dewatered solid and Liquid effluent from the treated orange peels from this task used for the estimation on the NPK recovery potential
	T4.7	Anaerobically pre-treated filtrate samples from orange peels were used for the estimation of NPK recovery
	T4.8	Results on Evaluation of NPK recovery potential from TORWASH® treated orange peels from this task used as input for D4.4
WP5	T1,2,3,4,5	Output from D4.4. will be used as input for WP5

2. Materials and Methods

This chapter describes the materials and methods used for evaluating the potential to recover primary nutrients such as N, P and K, from the TORWASH® treated paper sludge, waste olive pomace and orange peels.

2.1 Description of the received samples

The TORWASH® process is a hydrothermal process for the treatment of wet biomass streams. In brief, the TORWASH® process operates at relatively mild temperatures (150 - 250 °C) and results in fibers in the wet residues becoming brittle. This allows for more efficient dewatering, as well as a "washing out" of salts that have dissolved in the process. During dewatering of TORWASH® effluent, pressed cakes can be produced with a dry matter content ranging from 30 – 65 % (depending on feedstock and pressing equipment), and these cakes can be agglomerated to form intermediate energy carriers. Organic material which is dissolved in the liquid effluent is biodegradable and can be converted to biogas (Figure 1).

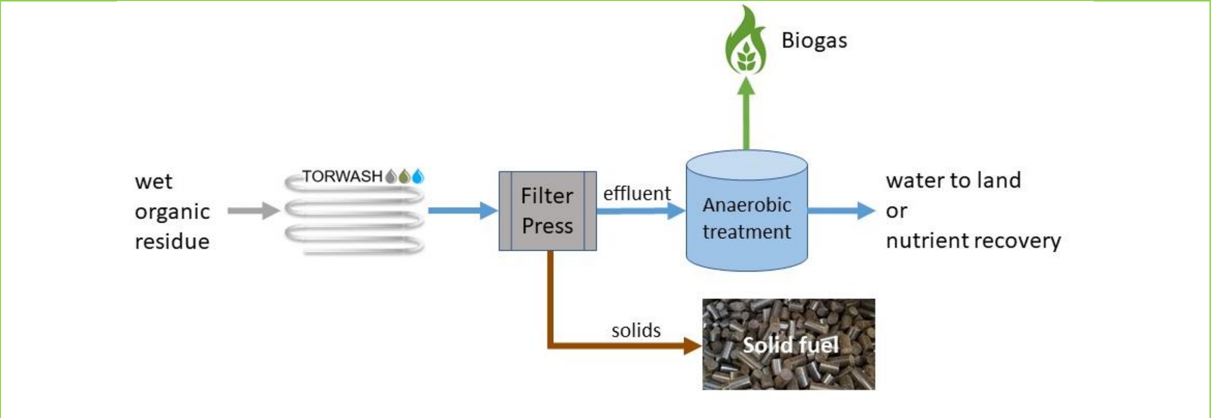


Figure 1. Block diagram of the TORWASH® concept

The wet organic residue treated in the TORWASH® process during the F-CUBED project included paper sludge, olive pomace and orange peels. The paper sludge is a by-product of the biological wastewater treatment process at the Smurfit Kappa (Piteå, Sweden) paper mill. Olive pomace is the solid material (without stones) obtained after the first mechanical oil extraction of olives. It was provided by Frantoio Oleario Chimienti (Bari, Italy). Orange peels, the solid residue after pressing for orange juice production, was provided by Delafruit (Reus, Spain).

The feedstocks were processed on-site by TORWASH® continuous flow pilot plant. The typical flow during the long-duration test was ~25 kg/hr. The treatment temperature was set between 190-200 °C. The feedstock dry matter varied depending of the feedstock between 1.7-5 %. The slurry produced during long-duration TORWASH® tests was subsequent dewatered by a pilot-plant membrane filter press of Limburg Filter which was set at a (adjustable) pressure. The part of the dewatered solids collected (or filter press cake) and liquid effluent (or filter press effluent after filter press) were distributed to University of Hohenheim (UHOH) for further investigation on NPK recovery. To estimate the potential of the NPK recovery after the anaerobic treatment of the liquid effluent, the post-digested effluent originating from anaerobic biodegradability tests was provided by project partner PAQUES as well. An overview of the received samples are shown in Table 2.

Table 1: Overview of the samples that were used for estimation of NPK recovery

Work package	Feedstock	Description of received samples	Project partner
WP2	paper sludge	- 2 L and 4 L of press liquor (collected at 08-09-2021 and 21-09-2021, respectively) - 2 x 1 kg of dried filter cake (collected 10-09-2021 and 21-09-2021, respectively)	TNO
		- 1L of post-digested effluent	PAQUES
WP3	olive pomace	- 4 L of press liquor (sample of 11-11-2021); - 2 x 1 kg of dry filter cake (11-11-2021 and 12-11-2021)	TNO
		- 1L of post-digested effluent	PAQUES
WP4	orange peels	- 1 L of press liquor (sample of 25-04-2022) and - 1 kg of dry filter cake (29-04-2022)	TNO
		- 1L of post-digested effluent	PAQUES

The pre-dried filter cakes received were dried at 105 °C until at a constant weight and ground up (<1mm) for future analysis. These solids were stored at room temperature, while effluents were stored at 3 °C. No specific pre-treatment was performed prior to the processing of effluents.

2.2 Analytical methods for the characterization of the received samples

Total content of the nutrient elements

To evaluate the inorganic elemental composition of the dewatered solids, liquid effluent, post-digested effluent samples as well of recovery product streams, optical emission spectroscopy with inductively coupled plasma (ICP-OES; Agilent 715) was used. In this way, the elemental content of P, K, Ca, Mg, S and Fe were evaluated. The spectrometer was calibrated using a blank solution and an internal multi-element standard solution with a 1% HNO_3 matrix. The solid samples were prepared in accordance with the procedure described in a former publication (Ovsyannikova et al. 2019). Liquid samples were diluted with 1% HNO_3 at a defined ratio depending on the concentration of the elements before injection into the spectrometer. The reported values of the elements are the average value of three sample injections.

The content of the micronutrients (Cu, Mn, Mo, Ni and Zn) was evaluated by ICP-MS (Perkin Elmer NexION) according to (Janßen 2011).

Total carbon (C), and total nitrogen (N) content in the solid samples

The content of C and N in the solid samples was evaluated by means of elemental analysis (HekaTech, Euro EA). To determine the CN content, a two-point calibration was performed.

Total nitrogen content (TNb), ammonium nitrogen content (NH_4-N) and chemical oxygen demand (COD) in the liquid samples

The liquid samples underwent analysis for TNb, NH_4-N and COD. These were evaluated with Hach-Lange cuvette tests LCK 338, LCK 304 and LCK 114, respectively, after corresponding dilution with Milli-Q water. The pH of the liquid samples was determined directly (HACH HQ40d).

Main DOC constituents in liquid

Liquid samples were analysed by means of HPLC for several carbohydrates (Metrohm, amperometric), organic acids (Merck Hitachi Primade, DAD210nm/RI), furfurals (Merck Hitachi, UV) and phenols (Merck Hitachi DAD 210nm) which are known as main constituents of hydrothermal process water by in-house methods which are described elsewhere (Wuest 2020).

Content of organic pollutants (PAH and phenols) and heavy metal content

To evaluate the possibility of using the received effluents as fertilizer, the content of the organic pollutants (PAH: sum of the polycyclic aromatic hydrocarbons) and heavy metals was determined. The 16 EPA-PAH (as selected by US-Environmental Protection Agency) were measured according to DIN 38407-39 (F39): 2011-09. The content of the heavy metals (As, Cd, Cr, Pb, V and Hg) was evaluated by ICP-MS (Perkin Elmer NexION) according to (Janßen 2011).

2.3 Tests for the recovery phosphorus and nitrogen as struvite ($NH_4MgPO_4 \cdot 6H_2O$)

To assess the option for recovery of phosphate and nitrogen (as ammonium) in the form of struvite, laboratory scale experiments were conducted. Phosphate was extracted and precipitated by means of pH-stat automatic titration (SI Analytics, TitroLine 7000, Figure 2).

After the first assessment, the suitable feedstocks were used in a scalable, semitechnical unit (Figure 2, mini-plant). The main part of the mini-plant is a phosphate salt precipitation unit. It is an air-agitated reactor, which allows high flexibility of the precipitation process and is promising to harvest larger particles. In brief, the air-agitated reactor consists of the operating zone (~4.8 L) and settling zone (~1.5 L). The operating zone includes two tubes, one inside the other. The settling zone is a cone collector. The influents are fed into the inner tube by means of a peristaltic pump. To mix the solution and induce circular liquid movement in the reactor, air is injected into the inner tube through an air-sparger. The extraction unit is a mechanically stirred reactor (~8 L). To separate the derived liquid fraction during the extraction product streams, a laboratory filter press was used.

The phosphate recovery process was evaluated in terms of P extraction efficiency from solids (Eq. 1), P recovery by precipitation from solution (Eq. 2), purity of the precipitate (Eq. 3), total yield of precipitate (Eq. 4) and total phosphate recovery via extraction and precipitation(Eq. 5). All recovery rates were calculated based on the total P content determined by ICP-OES.

$$P\ extraction, [\%] = \frac{amount\ of\ P\ in\ dewatered\ solid - amount\ of\ P\ in\ the\ solid\ residue}{amount\ of\ P\ in\ the\ dewatered\ solids} \cdot 100 \tag{Eq. 1}$$

$$P(NH_4 - N)\ recovery, [\%] = \frac{amount\ of\ P(NH_4 - N) in\ the\ inlet\ solution - amount\ of\ P(NH_4 - N)\ in\ the\ residue\ solution}{amount\ of\ P(NH_4 - N) in\ the\ inlet\ solution} \tag{Eq. 2}$$

$$stuvite\ content, [\%] = \frac{n_{N\ in\ precipitate} \cdot M_{struvite}}{m_{precipitate}} \cdot 100 \tag{Eq. 3}$$

where m is the mass, n_N is the molar amount of nitrogen, and M is the molar mass.

$$total\ precipitate\ yield, [g \cdot L^{-1}] = \frac{m_{precipitate}}{V_{extarct} + V_{liquid\ effluent}} \tag{Eq. 4}$$

$$total\ P\ recovery, [\%] = \frac{P_{extracted\ from\ solids} \cdot P_{recovered\ via\ preciputation}}{100} \tag{Eq. 5}$$

	
laboratory scale	**mini-plant**

Figure 2: Key equipment for recovery phosphorus and nitrogen as struvite

3. Results and Discussion

3.1 Characterization of the TORWASH® product streams

3.1.1 Dewatered solid (dry filter cake)

Elemental analysis of the TORWASH® dewatered solids (filter press cakes) (Table 2) shows different trends for each feedstock. While the dewatered solids from the paper sludge contain a considerable amount of macronutrients (especially P) and may be considered as a secondary source of these, the composition of the dewatered solids from the waste olive pomace and orange peels is not considered a phosphate source. The content of P in the solids from paper sludge is around 20 mg/g, as for waste olive pomace and orange peels only 0.2 mg/g. Nonetheless, the solid phase from paper sludge contains a high amount of Ca and Mn, which is affecting the subsequent phosphate recovery and needs to be considered.

The TORWASH® dewatered solids differ not only in the nutrient contents but also in content of heavy metals. The content in the dewatered solids from the paper sludge is several orders of magnitude higher that from waste olive pomace and orange peels.

The high carbon content and low heavy metals content in the dewatered solids from the waster olive pomace and orange peels may be beneficial for its application in agricultural production as soil amendment. The ratio of C:N shows already beneficial values for a possible composting treatment to enhance agricultural value.

Table 2: Elemental composition of the TORWASH® dewatered solids

			paper sludge		**waste olive pomace**		**orange peels**
			10.09.21	21.09.21	11.11.21	12.11.21	29.04.22
macronutrients	C	%	46.2	46.8	66.1	65.3	56.1
	N	%	4.3	4.6	1.5	1.5	2.2
	P	mg/g	21.2	23.4	0.2	0.2	0.2
	K	mg/g	0.9	0.5	1.1	1.4	1.2
	Ca	mg/g	21.3	22.2	4.3	4.5	11.2
	Mg	mg/g	3.0	2.7	0.1	0.1	0.2

	S	mg/g	8.8	9.4	1.2	1.0	1.4
micronutrients	Fe	mg/g	6.7	6.8	0.2	0.2	0.4
	Mn	mg/kg	11500	14400	2.78	1.95	3.63
	Zn	mg/kg	1125	1199	26.1	19.7	12.9
	Cu	mg/kg	64.9	65.6	37.0	42.2	21.0
	Mo	mg/kg	7.97	10.7	0.55	0.53	0.25
	Ni	mg/kg	10.5	9.3	1.45	1.14	3.95
heavy metals	Cd	mg/kg	11.2	10.2	<0.025	0.032	<0.100
	Cr	mg/kg	32.3	32.8	3.97	1.67	2.31
	Pb	mg/kg	39.3	38.7	0.282	0.272	3.03
	V	mg/kg	22.2	23.3	0.408	0.500	<0.100
	As	mg/kg	3.16	3.13	<0.025	<0.025	<0.100
	Hg	mg/kg	0.135	0.143	<0.025	<0.025	<0.100

3.1.2 Liquid fraction separated in the dewatering step (filter press effluent)

Phosphorus was found in relatively low concentrations in the filter press effluents from all three feedstocks (30-80 mg P/L). In contrast, the K concentration show clear dependency on the feedstock type. The effluent from the waste olive pomace was the richest in K (~1600 mg K/L), followed by effluent from the orange peels (~3 time less) and from paper sludge (~15 time less). The analyses also showed that the content of the nitrogen compounds in the effluents is reflective of that in the feedstock. The Torwashing of the protein-rich paper sludge results in a high content of nitrogen compounds in the effluent compared to the treatment of the waste olive pomace and orange peels. Moreover, the analyses identified that after Torwashing, 8-20% of the nitrogen was in the available inorganic form of ammonium-nitrogen (Table 3).

Table 3: Elemental composition, pH and of the TORWASH® liquid effluent

			paper sludge		**waste olive pomace**		**orange peels**
			08.09.21	21.09.21	11.11.21	12.11.21	25.04.22
	pH		6.3	6.1	4.4	4.4	4.1
macronutrients	TNb	mg/L	900	1060	142	127	291
	NH_4-N	mg/L	244	177	11.8	8.5	21.4
	P	mg/L	81.1	38.2	85.7	87.8	32.7
	K	mg/L	104	81.0	1590	1672	481
	Ca	mg/L	60.1	74.0	73.3	49.8	144
	Mg	mg/L	48.8	24.5	76.9	64.0	48.9
	S	mg/L	313	243	44.8	45.2	33.1
micronutrients	Fe	mg/L	12.1	4.2	0.6	0.7	0.6
	Mn	µg/L	16400	21100	930	560	41
	Zn	µg/L	186	167	1210	790	<5.0
	Cu	µg/L	2.5	1.7	5.54	3.12	67
	Mo	µg/L	45.0	63.0	<0.50	<0.50	<5.0
	Ni	µg/L	37.0	34.0	9.97	10.9	6.0
heavy metals	Cd	µg/L	<1.0	<1.0	<0.50	<0.50	<5.0
	Cr	µg/L	32.0	24.0	2.78	2.4	<5.0
	Pb	µg/L	1.3	<1.0	5.97	4.38	<5.0
	V	µg/L	13.0	12.0	<0.50	<0.50	<5.0
	As	µg/L	24.0	25.0	2.3	3.1	<5.0
	Hg	µg/L	0.076	0.092	<0.25	<0.25	<5.0

Table 4 shows the description of the main organic components as well as the resulting COD.

While the paper sludge-derived material had a low COD of 7.9 to 9.8 g/L, the effluents from waste olive pomace as well as from orange peels show considerable higher amounts of COD of 27.9 and 43.3 g/L, respectively. As the COD for paper sludge effluent was described quite well by the detection of compounds from the hydrothermal degradation of carbohydrates, it is suspected that mainly nitrogen-containing compounds (melanoidinic structures) are contributing to the COD of waste olive pomace and orange peel effluents.

In addition, a screening for the most common Phenols was performed together with trace analytics for the most environmental harmful PAHs (16 EPA-PAH) to assess its applicability of the liquid product in agricultural production; the results showed no concerning contents for further application.

Anaerobic digestion, especially interesting for the high COD effluents, was carried out by partner Paques (description in 3.1.3).

Table 4: Content of the organic compounds in TORWASH® liquid effluent

		paper sludge		**waste olive pomace**		**orange peels**
		08.09.21	21.09.21	11.11.21	12.11.21	25.04.22
COD	g/LO$_2$	9.8	7.9	27.9	27.8	43.4
Sucrose	mg/L	1590	-	650	618	320
Glyceraldehyde	mg/L	166	156	563	546	379
Levulinic acid	mg/L	175	123	152	149	62.0
Furfuryl alcohol	mg/L	252	323	249	300	164
1,2,4-Benzenetriol	mg/L	-	56.0	170	215	50.0
Hydroxymethylfurfural	mg/L	64.5	99.3	294	205	218
Furfural	mg/L	42.7	187	307	346	140
Glucose/Galacturans	mg/L	1090	1360	440	201	1240
Fructose (Malic acid)	mg/L	201	214	1310	922	-
Pyruvaldehyde	mg/L	93.8	46.0	582	474	109
Formaldehyde/ (Dihydroxyacetone)	mg/L	-	97.4	447	428	617
Formic acid	mg/L	356	84.6	1290	1540	772
Acetic acid	mg/L	298	371	2210	2580	663
MeOH	mg/L	-	-	1510	1540	898
Acetaldehyde	mg/L	-	257	-	-	-
Et/OH (Benzoic acid)	mg/L	510	272	1640	2600	5200
Resorcinol	mg/L	112	79.1	na	na	196
Catechol	mg/L	134	56.4	na	na	12.3
Phenol	mg/L	3.40	-	na	na	15.8
PAH*	µg/L	na	na	bql**	bql**	bgl**

*PAH (sum of 16 polycyclic aromatic hydrocarbons) as organic pollutants; **content of all of the polycyclic aromatic hydrocarbons analyzed was less than quantification limit
na=not analyzed

3.1.3 Post-digested effluent (from anaerobic degradation test)

Liquid samples (post-dewatering) were processed by project partner Paques to test and quantify the biodegradability of the organic content. For highly concentrated wastewaters, it is necessary to dilute the sample to reach a COD concentration that is not inhibiting the anaerobic biomass used in the biodegradability test.

The dilution does not change the anaerobic biodegradability of the waste water. Such a dilution is necessary since the anaerobic biodegradability test is a batch test in which the COD concentration at the start is high but decreases in time. In a full scale continuous anaerobic reactor, the balance between continuous feeding and continuous conversion ensures that the biomass is not exposed to high COD concentrations.

The added NH_4 and PO_4 in the tests with Olive pomace were only needed to start the test, but will not be needed in a full-scale application, as sufficient N & P are released as NH_4 and PO_4 during the anaerobic conversions. This is confirmed, e.g., by the measured NH_4 concentration at the end of the olive pomace test being higher than the initial added amount.

For further discussion the dilution and addition of these starter nutrients are considered (Table 5 and 6).

Table 5: Dilution factors for anaerobic biodegradability test

	substrate	applied dilution factor	Added NH4-N (to diluted start sample) (mg N/L)	Added PO4-P (to diluted start sample) (mg P/L)	Measured NH4-N concentration in diluted end sample (mg NH4-N/L)
WP2	paper sludge	2.25	0	0	n.d.
WP3	olive pomace	8.4	72	44	97.2
WP4	orange peels	12.5	0	0	62.8

Table 6: Elemental composition of the post-digested effluent

			paper sludge		**waste olive pomace**		**orange peels**	
				x 2.25		x 8.4		x 12.5
	pH		8.1		7.5		7.5	
macronutrients	TNb	mg/L	412	927	103	862	49.4	618
	NH_4-N	mg/L	317	713	75.3	632	31.2	390
	P	mg/L	23.9	54	39.9	335	4.7	59
	K	mg/L	40.2	90.5	311	2610	50.9	636

3.2 Analyses of the potential for NPK recovery

3.2.1 Mass flow of NPK

This section addresses the evaluation of the nutrient flows through the value chain and the identification of appropriate points for their recovery.

Feedstock composition is the key factor influencing the fate of nutrients and nutrient recovery options. To identify options for nutrient recovery, the overall mass balances of most the important nutrient elements (P, N, and K) for long-duration TORWASH® testing were derived (Figure 3). These were based on the dataset from Section 3.1 (additional data in Table A 1). While the derived mass balance for treated paper sludge was closed relatively well, the mass balance for treated olive pomace and orange peels shows strong underestimation. The fouling and deposition in the reactors may be one of the reasons for the underestimation of elemental mass balances. The mass balances identified the tendencies for nutrient flows and options for their recovery.

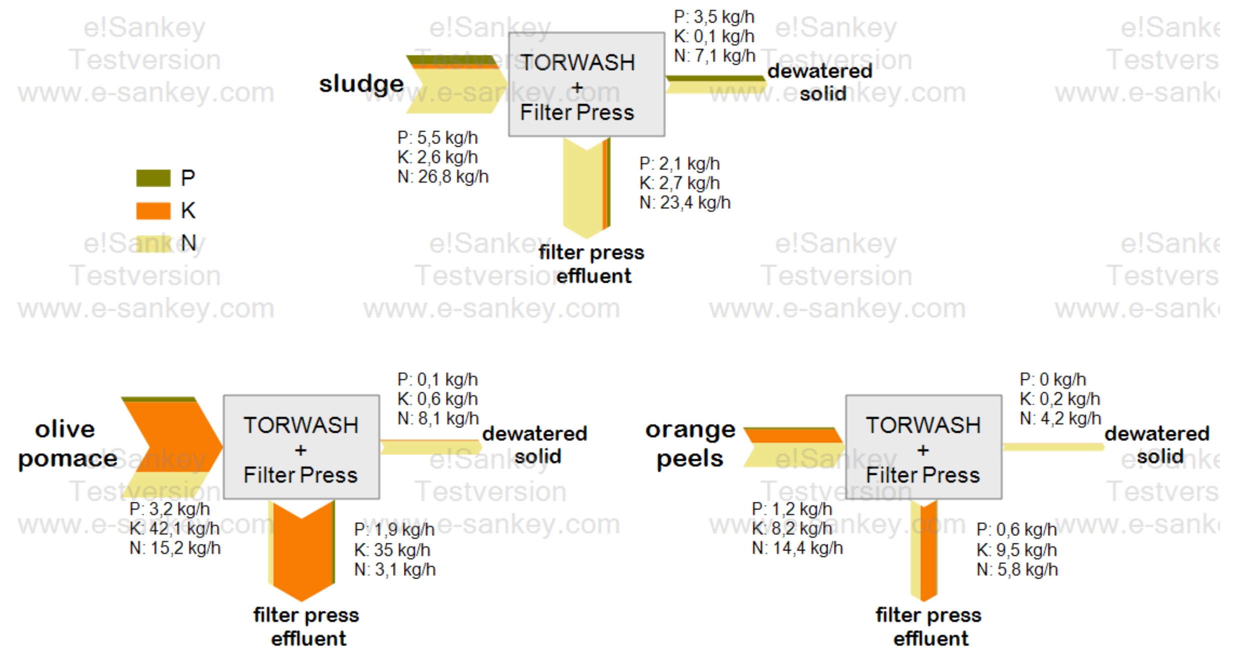


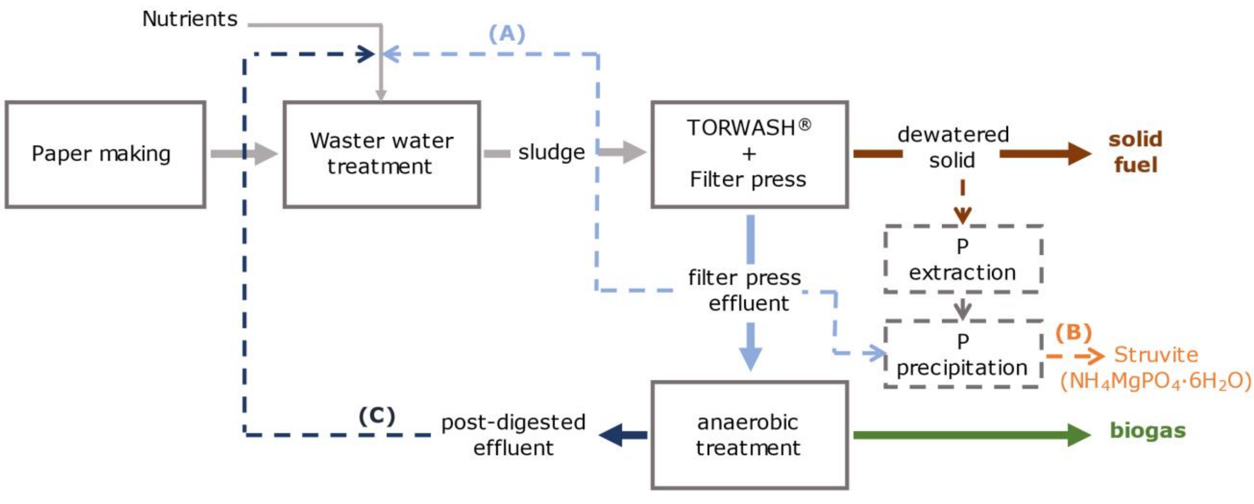
Figure 3: Estimated mass flow of the most relevant nutrient (NPK) through the value chain

The distribution of PN after treatment of the paper sludge differ from the treatment of the waste olive pomace and orange peels. The mass balances of P for paper sludge suggested that it was distributed between the dewatered solid (~63%) and filter press effluent (~37%). In comparison to the paper sludge, a higher mobility for P for the filter press effluent was identified for waste olive pomace and orange peels. This can be explained by higher content of the metal ions such as Ca, Al, Fe, Mg in the paper sludge that tended to be precipitated as phosphate salts under applied hydrothermal conditions. While the initial N was primarily distributed to the effluent in the case of the paper sludge (~87%), its percentage in the effluent in the case of the olive pomace and orange peels was ~20% and 40 %, respectively. Potassium salts usually show a high solubility in water and for all feedstocks; therefore, K primary recovery with the filter press effluent was expected.

The nutrient flows suggest that any nutrient recovery strategy should be based on the liquid effluents. Only paper sludge showed considerable amounts of P in the solid residue which would make it suitable for enhanced nutrient recovery as struvite, as described in the following chapter.

3.2.2 NPK recovery options for treated sludge

Figure 4 illustrates the option for nutrient recovery for the treated paper sludge.



(A) Recycling liquid effluent as nutrient -rich medium in wastewater treatment

(B) Recovery of P and part of N (as ammonium) in the form of ready -to-use fertilizer such as struvite

(C) Recycling post-digested effluent as nutrient-rich medium in wastewater treatment

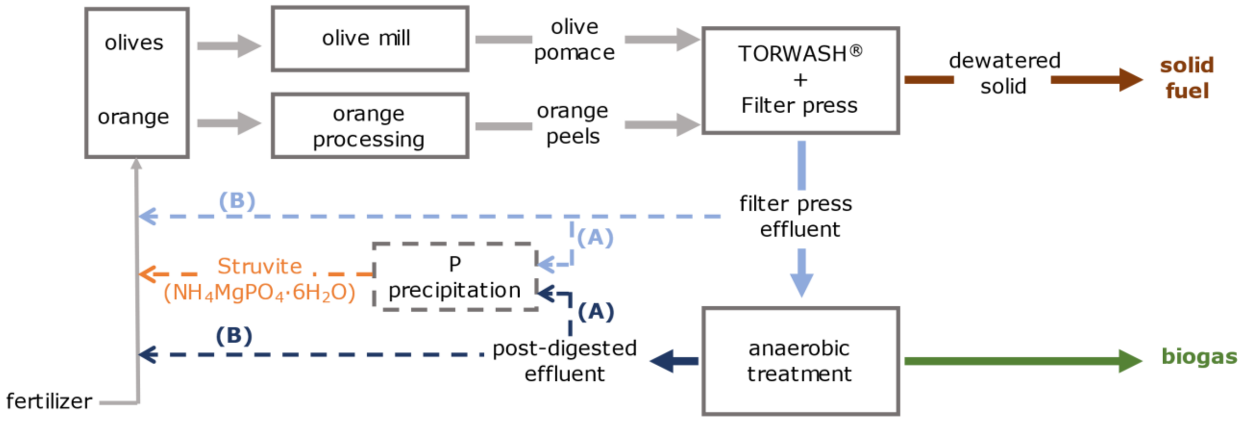
Figure 4: Options for nutrient recovery for treated paper sludge

Due to the high retrieval of phosphate in the dewatered solid and the high content of it, dewatered paper sludge solids are shown to be an appropriate point for phosphate recovery. To produce an already marketable fertilizer, phosphate needs to solubilized by means of extraction, in this case acidic leaching. By combining the soluble phosphates with the NH_4-N, which is released from biomass into filter press effluent, struvite ($MgNH_4PO_4{\cdot}6H_2O$) precipitates (Scenario B). This scenario for phosphate and nitrogen (as ammonium) recovery as struvite was investigated in detail. After an initial proof of concept and optimization at laboratory scale, the main data/results was derived by trials in a technical scale mini-plant (Figure 2).

Inorganic nitrogen (as ammonium) and P in the filter press and post-digested effluent could replace the nutrient elements that are supplied for the support of the aerobic stage at the wastewater treatment plant at the paper mill of Smurfit Kappa *(Scenario A and C).* This may be beneficial in terms of economics because it may reduce the current use of additives like urea and phosphoric acid. However, the presence of phenolic compounds (Table 4) in the effluents can have a negative effect on the bacteria used in this wastewater treatment process, even in low concentrations. Given this fact, the post-digested effluent may be more beneficial for nutrient recovery because it is less concentrated with respect to organic compounds than filter press effluent. Moreover, the organic nitrogen compounds present in the filter press effluent mineralize during digestion, which increases the content of available nitrogen for bacterial activity. In view of recycling effluents in wastewater treatment, future investigations regarding ecotoxicology and possible consumption of effluents (dilution factor) are needed.

3.2.3 NPK recovery options for treated olive pomace and orange peels

The measured concentrations of primary, secondary and micronutrients in the filter press and post-digested effluent from olive pomace and orange peels show that these could potentially facilitate plant growth by application as liquid fertilizer (Figure 5, Scenario B). The evaluation of its ecotoxicology towards soil bacteria and terrestrial plants is usually necessary to establish their potential use as fertilizer. Also limiting for direct agricultural use is the low pH of the effluents. Neutralization by liming seems therefore necessary. To avoid problems in direct application of effluents, the soluble phosphate and ammonia may be concentrated and precipitated in form of a solid mineral fertilizer such as struvite (Scenario A). The potential to recover struvite was therefore investigated in more detail.



(A) Recovery of P and part of N (as ammonium) in the form of ready -to-use fertilizer such as struvite from effluents

(B) Recycling effluents as liquid fertilizer

Figure 5: Options for nutrient recovery for treated waste olive pomace and orange peels

3.3 Investigation of the potential to recover struvite ($NH_4MgPO_4 \cdot 6H_2O$)

In this section, the results of experimental work on struvite precipitation are presented. The experiments in laboratory- and in technical scale are highlighted separately.

3.3.1. Phosphate-rich feedstock (paper sludge)

Laboratory scale

To solubilize the phosphate from the dewatered solid, extraction tests were performed with solutions of 1M sulphuric and 1M oxalic acids and a mixture of citric (30%) and sulphuric acid (70%). While the choice of sulphuric acid application is explained by its strength and low cost, organic acids were selected for their reduction properties (especially oxalic acid), ability to form complexes with metal ions in the extract and subsequently improve the quality of phosphate fertilizer (especially citric acid). The main parameter controlled during the extraction tests was the pH of the slurry made up from pre-milled dewatered dry solids and water. The pH value was adjusted with acid solution. The pre-test showed that for all acid solutions, P content in the supernatant increased significantly starting from pH 3; lowering the pH from 1.5 to 0.5 did not significantly affect the P extraction. The highest P extraction was achieved with oxalic acid, followed by a mixture of citric and sulphuric acid (Figure 6). At a pH value of 1.8, P extraction was 86% with oxalic acid, 77% with a mixture of citric and sulphuric acid, and 68% with sulphuric acid.

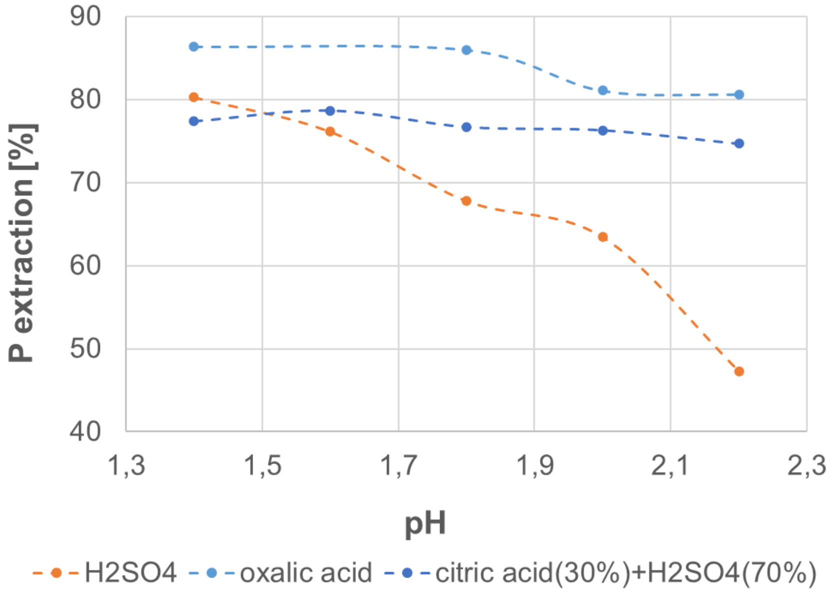


Figure 6: Phosphate extraction from dewatered solids due to pH adjustment

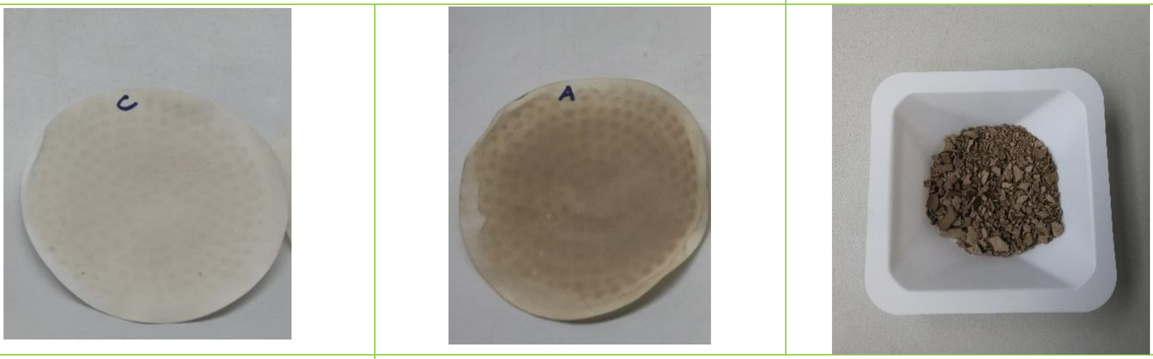
To precipitate struvite, the phosphate-rich extract produced at pH 1.8 were mixed with a pre-determined amount of filter press effluent and $MgCl_2 \cdot 6H_2O$ as a magnesium source to achieve favorable stoichiometric ratios for struvite precipitation. Afterwards, its pH value was adjusted to 9.0 to induce precipitation of phosphate salts. The pH was held constant for 1 hour.

Phosphate precipitation from the P-rich extract produced with oxalic acid resulted in higher P recovery (91%) and higher mass of derived precipitate (4 g/L) but lower content of struvite in the precipitate (41%) than from the extract produced with citric and sulphuric acids (45%, 1 g/L; 84%, respectively). The main impurities in the precipitate from the P-rich extract produced with oxalic acid were Mn, Al, and Ca (Table A 3). The fertilizing value of the derived products requires a future detailed investigation. Content of impurities in the precipitate from extract produced with sulphuric and citric acid was low, which is also reflected in the color of the precipitate (Figure 7) and it was characterized as high purity struvite; however, in this case the yield and the total P recovery were low. Nitrogen recovery (as ammonia) was around 40-50% in both cases. More detail about the performance of phosphate recovery as struvite at lab scale and the derived precipitates can be found in Appendix (Table A 2).

Overall, 78% of the initial phosphate from biomass was recovered in the struvite-based precipitate by using oxalic acid for P extraction from dewatered solid. And in the case of mixture citric and sulphuric acid 35%. The overall difference in performance of these two experiments are summarized in Table 7.

Lab scale

Mini-plant



from P-rich extract produced with citric and sulphuric acid

from P-rich extract produced with oxalic acid

Figure 7: Derived precipitate from treated paper sludge

Table 7: Performance of phosphate precipitation from P-rich extract produced with oxalic acid and mixture of citric and sulphuric acid

acid	precipitate yield	precipitate purity	direct use precipitate as fertilizer	P recovery	NH4-N recovery
Oxalic acid	+	0	0	+	0
Citric+H_2SO_4	-	+	+	0	0

+, 0, - are performance indicators by the subjective perception of the author ranging from positive, neutral to negative respectively

Mini-plant operation

Phosphate recovery as struvite from the dewatered solid was demonstrated in the mini plant (Figure 2). For P extraction from the solids in the mini plant, oxalic acid was used as it proved to be beneficial in the previous lab-scale trials. The total P recovery rate in the mini-plant was 38% and therefore below expectations based on the lab trials (Table A 3). The design of the extraction unit and the applied mixing conditions were identified as the main reason for this. To reach the phosphate release rate demonstrated at lab scale it is crucial to ensure a sufficient wetting and resuspension of the dry filter press cakes during acid leaching. This will be included in further development of the unit operation.
The results of subsequent precipitation of struvite in the air-agitated reactor (P recovery from solution, total yield of precipitate and precipitate composition) were consistent with the results from lab scale tests.

3.3.2. Feedstock with low phosphate content (Waste olive pomace and fruit & vegetable waste)

For the feedstocks waste olive pomace and orange peels, classified as feedstocks with overall low phosphate content and high mobility of phosphate towards the liquid effluent, an approach of direct struvite precipitation was investigated at laboratory scale similar to that described in 3.3.1. While orange peel effluent had an already beneficial stoichiometric relationship between phosphate, ammonia and magnesium (1.4:1.9:1) to reach supersaturation for struvite precipitation, certain amounts of $MgCl_2$ and ammonia needed to be added to olive pomace effluents to reach supersaturation. After adjusting the pH to a value of 9 and keeping it constant for 60 minutes, 50% of P could be recovered as mixtures of struvite and different Ca-phosphate salts for olive pomace, as well as 60% of P for orange peel effluents. As ammonia was present in excess, the ammonia recovery was not complete, but due to the fact that phosphate precipitated not exclusively as struvite, the recovery rates were only 13 % for olive pomace and 15 % for orange peels. The high amount of impurities, especially of an organic nature, can be seen the dark coloring of the precipitates (Figure 8). The overall performance of this nutrient recovery approach is summarized in Table 9.

Precipitate from olive pomace effluent

Precipitate from Orange peel effluent

Figure 8: Derived precipitates from treated effluents

Table 9: Performance of direct phosphate precipitation from liquid effluents

effluent	P content	Balanced content NH_4-N:P	Balanced content Mg:P	NaOH consumption	P recovery	Precipitate purity
Olive pomace	-	-	0	-	0	0
Orange peels	-	+	+	0	0	-

+, 0, - are performance indicators by the subjective perception of the author ranging from positive, neutral to negative respectively

4. Conclusions

The different feedstocks treated in the F-cubed project show specific nutrient (i.e., NPK) contents, mobilities and availabilities, leading to different possible approaches for their recovery. Paper sludge, with the highest nutrient but also heavy metal content, proved to be most suitable for struvite recovery. Even so, the acid leaching approach to mobilize bound phosphate needs to be improved with respect to acid consumption, avoiding of impurities by chemical complexation and improved resuspension of Torwash press cakes. The leaching might be improved by integration with the filtration step itself, avoiding the handling of already pressed solids. While the production of a struvite based mineral fertilizer is already feasible, the integration of nutrient recovery to the waste water treatment process seems very beneficial but the feasibility, cost effectiveness and other benefits need to be examined in detail in follow-up studies.

The Torwash process provided a good separation of nutrients from orange peels and olive pomace to the respective liquid fraction of the effluent. An immediate struvite precipitation is possible with these materials, but the expected yields and the purity of the fertilizers will be rather low. This will have negative impact on the marketability and the expected economic performance of this approach. The high organic content of the effluents makes them rather interesting for anaerobic co-digestion, yielding additional energy, while recovering all nutrients (NPK) in the anerobic digestate, which can be used as organic fertilizers.

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Appendix

Table A 1: Input data from the TORWASH® testing

		Paper Sludge	**Olive pomace**	**Orange peels**
throughput	kg/h	26.6	25.4	22.8
dry matter of feed	%	1.6	4.6	3
solid yield*	%	39	46	28
effluent yield**	%	99.2	90.9	89.7
feed content				
P	mg/g	13	2.7	1.8
K	mg/g	6.1	36	12
N	%	6.3	1.3	2.1
*(as percentage of total initial solid) **(of initial water)				

Table A 2: Performance of phosphate recovery as struvite from treated paper sludge

		Lab 1	Lab 2	Mini-plant
Extraction of P from dewatered solids				
Operating parameter				
Used acid		citric+H_2SO_4	oxalic	oxalic
pH		1.8	1.8	1.8
time	min	60	60	60
Solid-to H2O	g/L	0.2	0.2	0.2
Perfomance				
acid consumption	mL/g_{solids}	1.5	1.5	1.3
P extraction	%	77	86	41
Content of solid residue:				
C	%	47.9	50.1	48.8
N	%	4.5	4.5	4.3
P	mg/g	5.5	3.3	12.9
K	mg/g	0.3	0.2	0.4
Mg	mg/g	0.9	0.8	1.8
Ca	mg/g	20.1	21.9	18.6
S	mg/g	26.6	8.7	8.4
Fe	mg/g	4.1	3.9	5.3
Al	mg/g	11.4	10.0	13.5
Mn	mg/g	2.1	3.2	7.2
Precipitation of P from mixed solution				
Operating parameter				
Initial NH_4-N:Mg:P	mol:mol:mol	1:1:1	1:1:1	1:1:1
pH		9.0	9.0	9.0
time		60	60	60

aeration	$m^3/(h \cdot m_2)$	-	-	56
Perfomance				
$MgCl_2 \cdot 6H_2O$ consumption	g/L	2.3	2.2	1.6
1M NaOH consumption	mL/L	91	53	73
Precipitate yield	g/L	1.0	4.0	2.6
Precipitate purity	%	84	41	45
P recovery from the solution	%	45	91	92
NH_4-N recovery from solution	%	38	52	41
Content of liquid residue:				
COD	g/L O_2	NA	NA	7.8
NH4-N	mg/L	119	98	101
P	mg/L	218	39.3	23.3
K	mg/L	56.9	87.9	67.4
Mg	mg/L	173.2	138.2	98.8
Ca	mg/L	91.6	8.1	2.3
S	mg/L	382.7	224.2	211.2
Fe	mg/L	45.3	10.2	6.2
Al	mg/L	100.8	9.5	2.5
Mn	mg/L	180.1	26.6	18.4
Total P recovery via extraction and precipitation	%	35	78	38

Table A 3: Composition of precipitate derived from treated paper sludge

		Lab 1	Lab 2	Mini-plant
		citric acid +H_2SO_4	*oxalic acid*	*oxalic acid*
N	%	4.8	2.4	2.6
P	mg/g	111.2	117.8	86.3
Mg	mg/g	88.0	61.1	42.8
K	mg/g	4.3	4.6	3.0
Ca	mg/g	2.8	21.0	23.4
Al	mg/g	<8	43.6	29.7
Fe	mg/g	<2	16.7	11.1
Na	mg/g	4.2	16.3	11.6
S	mg/kg	30.8	3.1	2.0
Mn	mg/kg	8.4	62.3	48.9
C	%	1.7	4.4	5.4