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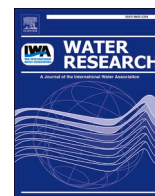
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Integrated resource recovery from aerobic granular sludge plants

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ABSTRACT

The study evaluated the combined phosphorus, nitrogen, methane, and extracellular polymeric substances (EPS) recovery from aerobic granular sludge (AGS) wastewater treatment plants. About 30% of sludge organics are recovered as EPS and 25–30% as methane (≈ 260 ml methane/g VS) by integrating alkaline anaerobic digestion (AD). It was shown that 20% of excess sludge total phosphorus (TP) ends in the EPS. Further, 20–30% ends in an acidic liquid waste stream (≈ 600 mg $\text{PO}_4\text{-P/L}$), and 15% in the AD centrate (≈ 800 mg $\text{PO}_4\text{-P/L}$) as orthophosphates in both streams and is recoverable via chemical precipitation. 30% of sludge total nitrogen (TN) is recovered as organic nitrogen in the EPS. Ammonium recovery from the alkaline high-temperature liquid stream is attractive, but it is not feasible for existing large-scale technologies because of low ammonium concentration. However, ammonium concentration in the AD centrate was calculated to be 2600 mg $\text{NH}_4\text{-N/L}$ – and $\approx 20\%$ of TN, making it feasible for recovery. The methodology used in this study consisted of three main steps. The first step was to develop a laboratory protocol mimicking demonstration-scale EPS extraction conditions. The second step was to establish mass balances over the EPS extraction process on laboratory and demonstration scales within a full-scale AGS WWTP. Finally, the feasibility of resource recovery was evaluated based on concentrations, loads, and integration of existing technologies for resource recovery.

1. Introduction

Wastewater is considered a valuable resource rather than a waste due to resource scarcity, market demand, and economic interests. Therefore, the transition of conventional wastewater plants into resource recovery plants has become of interest recently (van Loosdrecht and Brdjanovic, 2014). Wastewater provides opportunities to recover energy, biosolids, reusable water, and other valuable nutrients such as nitrogen, phosphorus, and other elements (Kehrein et al., 2020; Hao et al., 2019b).

A Dutch public-private partnership led to the development of the full-scale aerobic granular sludge technology, also known as “Nereda technology” for wastewater treatment. Aerobic granular sludge (AGS) is a promising technology as it offers key advantages compared to conventional activated sludge technologies (Pronk et al., 2015; de Kreuk et al., 2005). These advantages include a 75% reduction in footprint, a 30% reduction in energy, and less operating costs associated with phosphorus removal. The study of AGS not only opened a door for a more resource-efficient wastewater treatment technology but also created new opportunities for resource recovery, with the recovery of extracellular polymeric substances (EPS) as a successful example (Lin

et al., 2018; Sam and Dulekgurgen, 2016; Seviour et al., 2009).

EPS is a polymeric gel material produced by bacteria during cell metabolism that consists of proteins, polysaccharides, DNA, lipids, glycoproteins, and humic substances that form the matrix in which the cells are immobilized as granular particles (Seviour et al., 2019). EPS from aerobic granular sludge offers various applications in agriculture, building, textile, and paper industries (van der Knaap, 2019; Henze et al., 2020). It also showed unique properties as a composite material, bio-stimulant, and flame retardant (Kim et al., 2020; Feng et al., 2019; Lin et al., 2015). The Netherlands has the world’s first two demonstration-scale installations to extract EPS from Nereda® granules under the product name Kaumera. The EPS extraction process involves elevated temperature and pH conditions to dissolve the biofilm matrix in granules and target structural EPS, as reported by Felz, 2019. EPS recovery introduces an innovative concept to valorize the COD instead of converting COD into energy. According to the bio-based recovery value pyramid, biomass should ideally be first delegated as a material (higher value) before it is delegated to final energetic use (lower value) (Stegmann et al., 2020). COD has a relatively large exergy content that should be preserved and converted into carbonaceous materials. Moreover,

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there has always been a perception that chemical energy is the only source of recoverable energy in wastewater; however, studies showed that the potential of thermal energy recovery is around ten times larger than chemical energy recovery as biogas (X. Hao, Li et al., 2019). For these reasons, it is argued that COD recovery should be in the form of materials (i.e., EPS) rather than energy. The EPS extraction process under elevated pH and temperature conditions might also offer recovery opportunities for other elements, such as phosphorus, nitrogen, or methane, which could create a new generation of AGS WWTPs with integrated resource recovery. However, EPS yield should not be affected by resource recovery since it is likely the main driver for a recovery facility.

Phosphorus is on the list of critical raw materials issued by the EU because its supply security is at risk and its economic importance is high. Phosphorus is considered a bottleneck due to its life-essential nature and low abundance. Phosphorus recovery from wastewater is experiencing increased interest as sewage is one of the richest streams of phosphorus (Childers et al., 2011; ESPP webinar, 2020; Eynard et al., 2020). According to van Dijk et al., 2016, phosphorus in wastewater accounts for 15% of total imported phosphorus in Europe. In AGS WWTPs, phosphorus removal relies on phosphorus-accumulating organisms (PAOs) taking phosphate in wastewater as intracellular phosphorus during the alternation of anaerobic and aerobic phases in the Nereda tank (de Kreuk et al., 2005). High pH and temperature extraction conditions could potentially change phosphorus speciation or mineralogy in sludge, enabling or exacerbating recovery. Nitrogen is another essential nutrient found in wastewater. In AGS WWTP, ammonium-nitrogen is removed in the form of nitrogen gas through simultaneous nitrification and denitrification, and a small part of it ends in the sludge (de Kreuk et al., 2005; Henze et al., 2020). During the EPS extraction process, the AGS undergoes thermo-alkaline conditions, potentially releasing organic and inorganic nitrogen into the liquid streams (Siarni et al., 2020; Toutian et al., 2020). Evaluating the nitrogen fate over the process is to be considered to assess its recovery potential. Anaerobic digestion could also be integrated into the EPS extraction process as a secondary technology to recover further COD as methane from the alkaline sludge residuals by-product stream from the EPS extraction process. This integration is interesting as alkaline pre-treatment of sludge increases the anaerobic degradability of organics and biogas yields (Fang et al., 2014; Li et al., 2012). Evaluating the potential of phosphate and ammonium recovery from digestate liquid fraction is also to be considered as they are released during organics digestion (Uysal et al., 2010). Nitrogen and phosphorus recovery from the EPS extraction process by-product streams is also crucial to prevent operational issues due to their recirculation to the WWTP influent. Due to all these reasons, investigating the status of organics, phosphorus, and nitrogen over the EPS extraction process is of interest.

The fate of nutrients through the EPS extraction process is unknown.

A careful analysis of the EPS production process is vital to identify the best synergies to combine these elements' recovery within the EPS extraction process. Mass balances can provide insight into how and what to expect from integrated recovery technologies to evaluate these synergies. They are a robust decision tool to estimate quantities of elements of interest in all relevant streams, recovery potential, make value chains, and evaluate market potential (Kehrein et al., 2020; Solon et al., 2019). However, the existing laboratory-scale EPS extraction protocol by Felz et al., 2016 shows differences compared to large/demonstration-scale extractions which are relevant for resource recovery as summarized in Table 1. The most significant difference is the dilution factor during the extraction, as dilution affects concentrations and saturation conditions, so it does not allow for accurate judging of the potential of combined nutrient recovery. A representative translation of large-scale conditions to laboratory scale is essential for a realistic evaluation of concentrations and quantities.

Therefore, this study involved the development of a modified laboratory protocol to simulate large/demonstration-scale conditions. This was crucial for conducting future experiments to test resource recovery technologies on sludge from various sources and seasons, and to make predictions about large-scale impacts in later stages. This study aims to set the foundation for a new generation of AGS WWTPs with integrated resource recovery by answering two main research questions. The first question relates to the recovery potential of combined phosphorus, nitrogen, EPS, and methane from AGS WWTP. So, mass balances were established on laboratory and demonstration scales EPS extractions and extrapolated to a full-scale Nereda AGS WWTP to address this question. The second question is about the possible existing technologies that can be applied to recover these elements to reach a fully integrated AGS WWTP. To address this, concentrations, stream composition, speciation of nutrients, and loads were used to qualitatively evaluate the feasibility of existing technologies.

2. Materials and methods

2.1. Laboratory extractions

Laboratory extractions were performed using AGS surplus sludge samples collected after belt thickening from Epe AGS WWTP. The sludge samples are a mix of flocs and small granules so-called "selection spill" which is the sludge removed after every cycle. Sludge samples had the following average composition: 5%TS, 4.3%VS, 30 g P/Kg TS, and 60 g N/Kg TS. Extractions were performed based on a newly developed modified protocol adapted from demonstration-scale practices in Epe and Zutphen. Table 1 summarizes how the modified laboratory protocol mimics Zutphen/Epe demonstration-scale EPS extractions. The detailed laboratory protocol steps are listed in Section 3 of the supplementary material.

Table 1

Differences between Felz et al., 2016 laboratory extraction, Epe&Zutphen demonstration extractions (other steps not mentioned in the table were similar), and the established new modified protocol.

Parameters	Original (diluted) laboratory protocol (Felz et al., 2016)	Epe/Zutphen demonstration scale practice	New modified (undiluted) laboratory protocol in this study
Sludge used	Granules $\geq 2\text{mm}$	Excess granular sludge (small granules + flocs)	Excess granular sludge (small granules + flocs)
Sludge concentration	$< 0.8 \text{ w/v\%}$	5 w/v\%	5 w/v\%
Base used	$0.5\% \text{ (w/v)}$ Sodium carbonate	$25\% \text{ (w/v)}$ Potassium hydroxide	$25\% \text{ (w/v)}$ Potassium hydroxide
Base addition	No pH control	pH-controlled 9–11	pH-controlled 9–11
Alkaline extraction	80°C , 30 min	80°C , 2 h	80°C , 2 h
Acid used	1 M Hydrochloric acid-pH 2–4	9.5 M hydrochloric acid- pH 2–4	9.5 M hydrochloric acid- pH 2–4
Centrifugation	4 Celsius (4000xg, 20 mins)	30 Celsius -Decanter (3300xg, HRT= 5mins) -Disc (9000xg, HRT=1 min)	30 Celsius (4000xg, 20 mins)
Mixing	- 400 rpm during alkaline extraction -100 rpm during acidification	-3 kW in the first two compartments of the alkaline reactor -0.55 kW in the acidification tank	-400 rpm during alkaline extraction -100 rpm during acidification

2.2. Epe demonstration extractions

The resemblances and differences between the modified laboratory and Epe demonstration extractions were assessed in this study. Epe AGS WWTP is the first full-scale domestic wastewater treatment plant in the Netherlands to install the innovative Nereda sewage treatment technology, operated by the water authority Waterschap Vallei en Veluwe. The WWTP treats wastewater produced by the town of Epe with an average daily influent equal to 6200 m³, and 37,167 p.e. At the time of this sampling campaign, the Nereda® reactors had a sludge concentration of 8 g MLSS/L and were operated with process cycles of approximately 6 h: 3 h of aeration, 1 h of settling, and 2 h of anaerobic feeding/simultaneous effluent withdrawal (these data are site-specific and vary between different WWTP's). The excess sludge was stored in an aerated sludge buffer tank before being transported to the belt thickener in the EPS extraction installation. The EPS extraction installation in Epe is the second installation in the Netherlands. Before our investigation, many extraction runs had been performed at the site, and in general, extraction runs in the demonstration plant are for a few days only. Sampling for this study was performed on a continuous EPS extraction process treating 0.5 m³ spill sludge/hour. KOH and HCl dosing rates were 11 and 7 L/ hour, respectively. 20th June 2021 was the starting day of the campaign to run the system and ensure steady-state conditions. Then, samples were collected two days after the start of the operational run. So, two-time samples were collected on the 22nd and 23rd of June 2021.

Fig. 1 shows the process flow in the Epe demonstration with sampling points:

- Stream B, which is the initial thickened sludge stream,
- D, which is the alkaline liquid stream containing the hydrolyzed EPS,
- G, which is the alkaline liquid residue stream that remains after EPS hydrolysis and separation,
- F, which is the EPS production stream,
- and H is the acidic liquid stream after EPS production and separation.

To confirm that our sampling days are representative, we compared results from our study with earlier results from Epe (E. van der Knaap, 2019) and other unpublished measurements performed by RHDHV as described in section (2) in the supplementary material in detail. This comparison showed that the measurements of 23rd June 2021 were more typical for the normal operation of the plant than the results of 22nd. On this first day especially the operation of the alkaline centrifuge was different than normal. Therefore, we focus in the result section on the results of June 23rd. The results of the 22nd can be found in the supplemental information. The differences between the 22nd and 23rd are interesting and discussed in Sections 4.2.1 and 4.2.2.

Correspondingly, sludge samples from the 22nd and 23rd were collected to perform laboratory extractions as described in Table 1 at a similar pH as Epe. For all laboratory and Epe demonstration-scale samples, measurements were done in triplets, and average values and their standard deviation were calculated.

2.3. Mass balance calculations

Regarding laboratory-scale mass balances, concentrations, masses, and volumes of different fractions were measured experimentally. Regarding demonstration-scale mass balances, concentrations were measured experimentally for collected samples. D, G, F, and H flow rates were calculated using measured concentrations instead of using flow meters data logger to ensure the accuracy of these flows using B (sludge feed) as the initial condition, as shown in Section 1 of the supplementary material. Epe demonstration installation does not treat the full sludge flow from Epe Nereda WWTP, but the results were extrapolated to give the effect if it would be full scale. The mass balances over Nereda WWTP were evaluated based on the 2021 one-year average measured flows and the composition of influent, effluent, and sludge data were collected from the plant database. The plant has the following average wastewater influent composition: 835 mg COD/L, 81 mg N/L, and 7.2 mg P/L, and a daily load of 4174 Kg COD/day, 497 kg N/day and 44 kg P/day. Sankey diagrams depicted mass flows, where flow sizes are proportional to the influent mass flow expressed in%.

2.4. Analysis

2.4.1. Total solids (TS) and volatile solids (VS)

TS and VS were analyzed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1999)

2.4.2. Total chemical oxygen demand (TCOD) and total nitrogen (TN)

Both TCOD and TN were measured using Hach Lange test kits (LCK514,338,238, Hach Lange, UK), heated in a thermostat (HT200S, Hach Lange) to 170 Celsius, and then analyzed using a spectrophotometer (DR. 3900 VIS spectral photometer, wavelength range 320–750 nm). Carbon and nitrogen fate through the EPS extraction process was further confirmed by analyzing total carbon and total nitrogen using an Elemental analyzer (Mettler Toledo, America).

2.4.3. Microwave digestion

All solid samples were destructed by microwave digestion to convert them to liquid analyses. Samples were digested in an Ethos Easy from Milestone with an SK-15 High-Pressure Rotor. Around 50 mg of solids were put in a Teflon vessel in which 10 mL of ultrapure HNO₃ (64.5–70.5% from VWR Chemicals) was poured. The digester is set to reach 200 Celsius in 15 min, run at this temperature for 15 min, and cool down for 1 hour.

2.4.4. ICP-OES

The inorganic elemental composition was measured via Inductively Coupled Plasma (Perkin Elmer, type Optima 5300 DV) with an Optical Emission Spectroscopy as a detector. The device was equipped with an Autosampler, Perkin Elmer, type ESI-SC-4 DX fast, and the data were processed with the software Perkin Elmer WinLab32. The rinse and internal standard solutions were 2%HNO₃ and 10 mg/L of Yttrium.

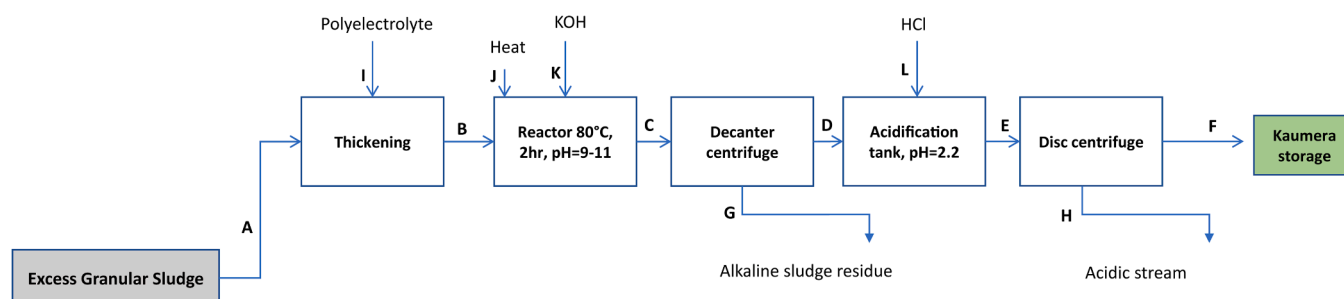


Fig. 1. EPS extraction process from excess aerobic granular sludge in Epe installation.

2.4.5. IC

Liquid samples were pre-treated first by filtering the samples through 0.45 μm followed by 0.22 μm membrane filters before analysis. Anions and cations (free dissolved ions) were measured by Metrohm Compact ion chromatograph Flex 930. To confirm these measurements and to avoid small colloidal particles squeezed through the filters, ultrafiltration was used. Liquid samples were filtered using ultrafiltration centrifugal tubes with polyethersulfone (PES) members with a molecular weight cutoff (MWCO) of 3 K (ThermoFisher, UK).

2.4.6. X-Ray diffraction (XRD)

Room-temperature dried samples were used for XRD analysis. The sample was filled in a 0.7 mm glass capillary and tamped so the solid settled. The capillaries were sealed with a burner and mounted in a sample holder. The device used was a Bruker D8 Advance diffractometer with Cu K α radiation (Coupled θ – 2θ scan 10° - 110° , step size 0.030° 2θ , counting time per step 2 s). The data evaluation was performed using Burker software DiffracSuite.EVA vs. 6

3. Results

3.1. Concentrations in laboratory and Epe demonstration extractions

Table 2 shows the total solids, TCOD, total nitrogen, total phosphorus, and dissolved species relevant for nutrient recovery as phosphate, ammonium, calcium, and magnesium ions in the alkaline and acidic liquid streams. Table 3 shows the EPS-Kaumera and alkaline sludge residue composition in laboratory and Epe extractions. Unlike the original laboratory protocol, the new modified laboratory protocol concentrations are comparable and have the same order of magnitude as the demonstration-scale concentrations. It was also observed that the concentrations of Ca^{2+} and Mg^{2+} in the alkaline stream are (6–10) times lower than in the acidic liquid stream both in the modified laboratory protocol and Epe demonstration scale, which could be due to the EPS nature as discussed, in Section 4.4.2.

3.2. The appearance of an alkaline gel layer

After the thermal-alkaline hydrolysis step and centrifugation, there was a stratification of the granular matrix into a residue part (lower layer), a gel layer (middle layer), and a soluble layer (upper layer) shown in Fig. 2. Despite the appearance of the alkaline gel layer, it was

Table 2

Alkaline and acidic liquid streams concentrations comparison between laboratory protocols and Epe demonstration.

	Original laboratory protocol		Modified laboratory protocol		Epe demonstration-scale	
	Alkaline stream	Acidic stream	Alkaline stream	Acidic stream	Alkaline stream (D)	Acidic stream (H)
TS%	0.7 \pm 0.01	0.8 \pm 0.10	3.4 \pm 0.03	1.9 \pm 0.05	3.5 \pm 0.04	1.9 \pm 0.05
mg/L						
TP	94 \pm 0.5	71 \pm 0.4	879 \pm 6.0	680 \pm 7.0	960 \pm 15	702 \pm 7.0
TN	339 \pm 2.0	229 \pm 8.0	2230 \pm 160	1000 \pm 3.0	2475 \pm 15	1248 \pm 5.0
TCOD	4600 \pm 10	2400 \pm 30	38,000 \pm 500	11,400 \pm 240	33,000 \pm 1500	12,400 \pm 30
PO_4^{3-} -P	40 \pm 0.6	48 \pm 0.3	615 \pm 3.0	630 \pm 2.6	572 \pm 8.0	604 \pm 10
NH_4^+ -N	18 \pm 0.4	22 \pm 0.1	105 \pm 0.2	110 \pm 1.0	85 \pm 0.5	82 \pm 1.2
Ca^{2+}	13 \pm 0.3	6 \pm 0.1	35 \pm 0.8	204 \pm 8.0	30 \pm 0.5	267 \pm 1.9
Mg^{2+}	<5.00	6 \pm 0.1	10 \pm 1.0	105 \pm 0.8	11 \pm 0.2	110 \pm 0.8

Table 3

Alkaline sludge residue and Kaumera-EPS concentrations comparison between laboratory protocol and Epe demonstration.

	Modified laboratory protocol		Epe demonstration-scale	
	Alkaline sludge residue	Kaumera-EPS	Alkaline sludge residue (G)	Kaumera-EPS (F)
TS% g/Kg TS	9.7 \pm 0.1	8.3 \pm 0.7	8 \pm 0.1	8.6 \pm 0.1
TCOD	1170 \pm 70	1260 \pm 90	1210 \pm 20	1260 \pm 20
TN	50 \pm 1.0	65 \pm 1.0	56 \pm 2.0	70 \pm 4.0
TP	25 \pm 0.1	20 \pm 0.2	23 \pm 0.1	23 \pm 0.2

observed that the Kaumera yield is \approx 30% of TCOD (or volatile solids) of sludge both in the original (diluted) and modified (undiluted) laboratory extraction protocol when this alkaline gel layer is not included in the EPS soluble fraction. Understanding the fate of this alkaline gel layer in both laboratory and Epe demonstration scales is discussed in Sections 4.2.1 and 4.2.2. Table 4 shows the average composition of this alkaline gel layer compared to the Kaumera-EPS on the laboratory scale. The gel layer has higher inorganic content than Kaumera as it has a higher P, Ca, and Fe content. XRD analysis also showed that the alkaline gel layer contains vivianite; however, no crystalline P-mineral was detected in Kaumera, which shows that P speciation in both fractions is different. The presence of vivianite can be explained by the fact that Fe precipitates in neutral to alkaline conditions, and there is always Fe in the raw sewage (Wilfert et al., 2015). There is also a slaughterhouse discharge to Epe WWTP, which contains most likely high levels of Fe. Spectra are shown in Section 5 of the supplementary material.

3.3. The potential of carbon recovery (laboratory scale extractions)

The TCOD mass balance over the EPS extraction using the modified laboratory protocol (undiluted) was established, as shown in Fig. 3a. TCOD balances were confirmed by the fate of volatile solids along the process, data shown in table (4) of the supplementary material. During the alkaline step, the high pH enriches the negative charges of the EPS, causing its repulsion and solubilization (Lotti et al., 2019), and around 40% of sludge TCOD ended in the alkaline liquid stream. Then, during the acidification step, the low pH reduces the negative charge of the EPS, causing its precipitation as a hydrogel with a yield of 30% of excess granular sludge TCOD. It was estimated that 35% of the initial COD was present in the alkaline gel layer, 25% in the alkaline sludge residue, and only 10% ended in the acidic liquid stream, possibly a fraction of organics that cannot precipitate at low pH conditions. By comparing the TCOD (volatile solids) fate in original (diluted) and modified (undiluted) laboratory protocols, it was observed that the gel layer ended in the acidic liquid stream in diluted conditions, increasing the TCOD percentage to 45% instead of 10%, as indicated by the shaded gray arrow in Fig. 3a. Instead, the modified laboratory protocol shows this layer as an independent fraction on top of alkaline sludge residue.

The alkaline sludge residue by-product stream could function as an input for an alkaline mesophilic anaerobic digester (AD). The alkaline sludge residue theoretical composition was calculated as described in Kleerebezem, 2014 based on its dry organic matter, TCOD, and TN content. From these measurements, the elemental substrate composition $\text{C}_c\text{H}_h\text{O}_o\text{N}_n$ and the stoichiometry of the anaerobic digestion are estimated as shown in Table 5. The model predicts the maximum methane production to be 516 ml/g VS, assuming 100% degradation. However, in practice, around 50% degradation of organics occurs at maximum, as discussed in Section 4.3, which makes the potential of methane production \approx 260 ml/g VS, recovering 30% of sludge TCOD as methane.

3.4. The potential of phosphorus recovery (laboratory scale extractions)

A phosphorus mass balance over laboratory scale using the modified protocol (undiluted) was established, as shown in Fig. 3b, including the

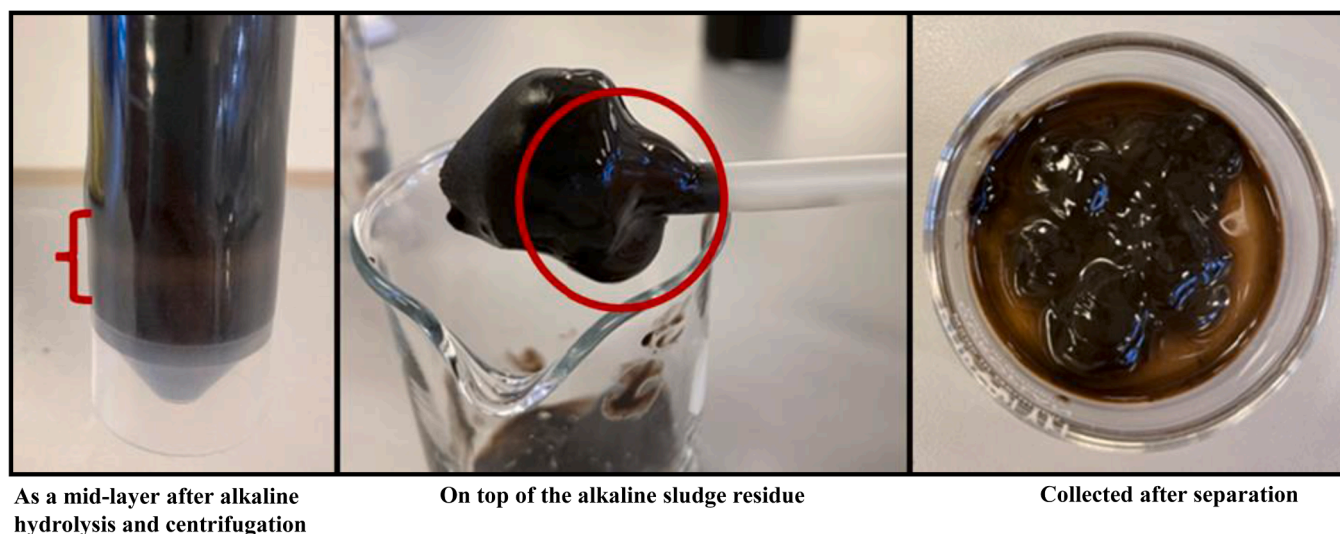


Fig. 2. The alkaline gel appearance with the modified laboratory protocol.

Table 4

Average composition of Kaumera-EPS and alkaline gel layer in the laboratory extraction.

	Alkaline Gel layer	Kaumera-EPS
g TCOD/ Kg TS	1260 ± 25	1260±90
g TP/ Kg TS	30± 0.3	20±0.15
g TN/ Kg TS	65 ± 2	65±0.6
g Ca/ Kg TS	12 ± 0.1	2.5 ± 0.1
g Fe/ Kg TS	16± 0.2	5.6 ± 0.1

bound and free dissolved ortho-phosphate species. 20% of excess sludge total phosphorus ends in the EPS fraction. Bound phosphorus in liquid streams was calculated as the difference between the measured values of total phosphorus and free ortho-phosphates. Total phosphorus in EPS was estimated to be divided into a 3:1 ratio of bound phosphorus to free dissolved phosphorus, assuming that the subtraction of P species in the alkaline and acidic liquid streams calculates the P fraction in EPS. However, this should be measured directly to be confirmed in future research.

Since most of the current phosphorus recovery systems recover ortho-phosphates from liquid streams, ortho-phosphate fractions in alkaline and acidic liquid streams were measured. The ortho-phosphate % in the spill sludge was initially measured as 10% of sludge TP. 25% of sludge TP was released to the alkaline stream during the alkaline hydrolysis step as ortho-phosphate and 20% in the acidic liquid stream. The concentrations of ortho-phosphates in alkaline and acidic liquid streams were 615 and 630 mg PO₄-P/L, respectively.

Ortho-phosphate in the anaerobic digestion centrate was also assessed. It was calculated using the laboratory measurements of alkaline sludge residue as the influent and some basic assumptions from literature research, as shown in section 7 in the supplementary material. 15% of sludge TP would end in effluent with a concentration of 900 mg PO₄-P/L.

3.5. The potential of nitrogen recovery (laboratory scale extractions)

The nitrogen mass balance for modified laboratory scale extractions of Epe sludge was established, as shown in Fig. 3c, including the organic and inorganic dissolved species. In spill sludge, nitrate and nitrite concentrations were negligible, ammonium was less than 2% of sludge TN, and the rest was organic nitrogen. So, the nitrogen mass balance was dominated by organic nitrogen. 30% of excess sludge TN ends in the EPS fraction, primarily as organic nitrogen. The nitrate and nitrite species

concentrations were negligible in the liquid streams, and ammonium concentrations in the alkaline and acidic liquid streams were low. The fraction of ammonium-nitrogen was around 2% of sludge TN, with 105 and 110 mg NH₄-N/L for alkaline and acidic streams, respectively. The ammonium fraction possibly ending in the digestate liquid effluent of the anaerobic digestion (centrate) was also calculated using the laboratory measurements of the alkaline sludge residue and some basic assumptions from literature research, as shown in section 6 of the supplementary material. It was estimated that around 25% of TN in sludge would end in the effluent with a concentration equal to 2600 mg NH₄-N/L.

3.6. Recovery potential in perspective to Epe AGS WWTP+ Eps extraction plant

Fig. 4 shows TCOD, total phosphorus, and total nitrogen over Epe Nereda WWTP and its large-scale EPS extraction installation. TCOD balance showed that 40% of the plant TCOD daily load ends in excess aerobic granular sludge. The excess sludge goes into the EPS extraction process, in which the final EPS yield is 30% of excess sludge TCOD. With the potential integration of biogas production into the process, 25% of sludge TCOD is calculated to be recovered by AD technology. Methane production was estimated, as explained earlier (Kleerebezem, 2014), as shown in Table 6, assuming

Table 6, assuming 50% organic degradation occurs at max at practice. Potential methane production from Epe is around 260 ml/g VS and 64 m³/day.

Total phosphorus balance revealed that 90% of the daily phosphorus load of Epe Nereda WWTP ends in the excess sludge and is removed from the system. The phosphorus ends in the EPS fraction represent 20% of the excess sludge TP. Ortho-phosphate fractions in the alkaline and acidic liquid streams are 35% and 30% of excess sludge TP, respectively, with ≈ 600 mg PO₄-P/L. The ortho-phosphate fraction potentially present in the AD centrate was calculated as ≈15% of sludge TP with ≈800 mg PO₄-P/L.

Total nitrogen balance showed that 67% of the WWTP daily nitrogen load is removed from the system as nitrogen gas through the simultaneous nitrification-denitrification process, and around 24% enters the EPS extraction process. 30% of excess sludge TN is recovered in the EPS fraction as organic nitrogen. The ammonium concentration in alkaline and acidic streams is ≈ 80–100 mg NH₄-N/L. Ammonium concentration in the AD centrate was also calculated to be ≈ 2600 mg NH₄-N/L— and represents 17% of sludge TN. Sections 8 and 9 in the supplementary material provide detailed calculations over the AD.

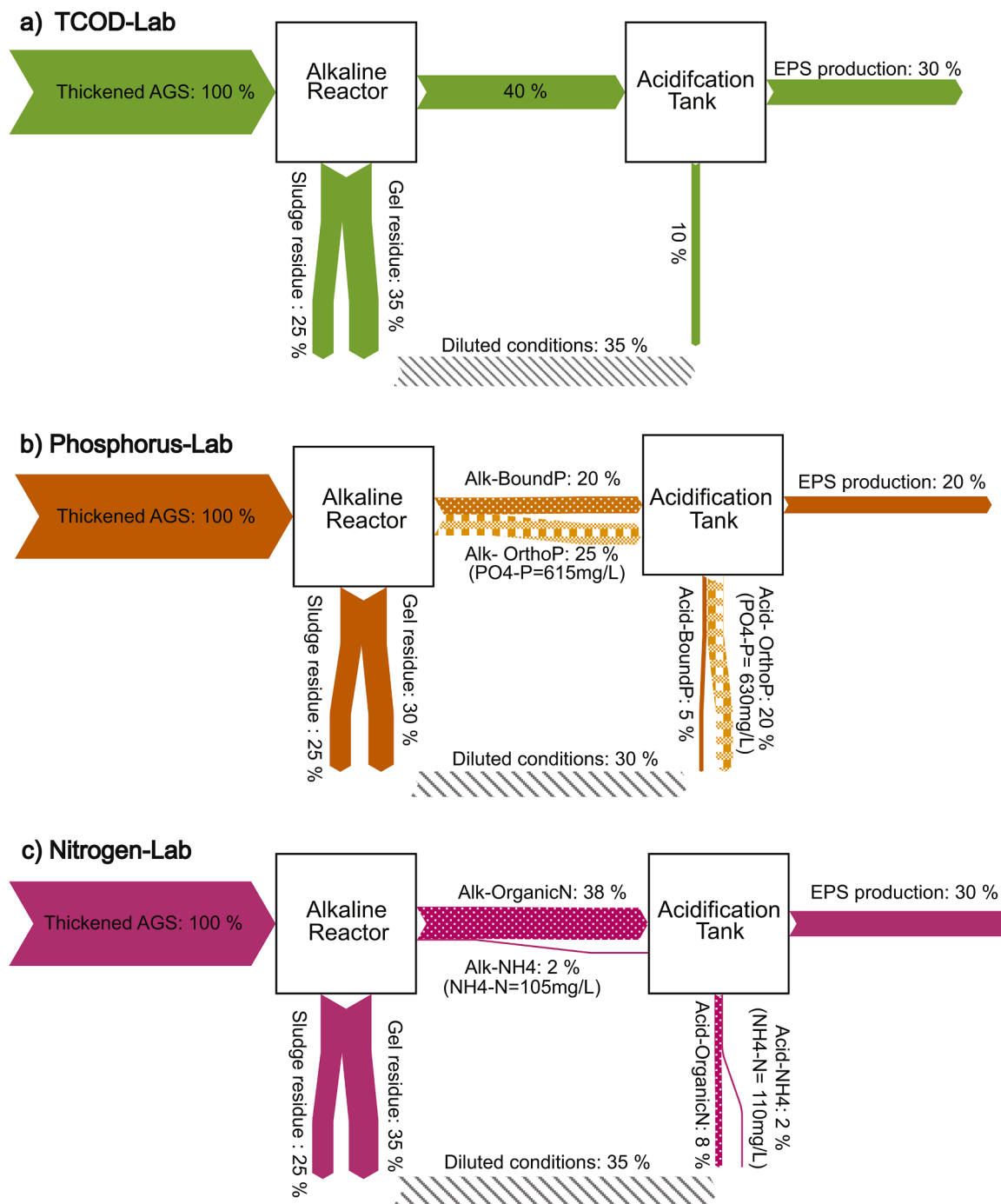


Fig. 3. Mass balances for laboratory scale undiluted extractions performed on AGS samples from Epe WWTP. Results are average from triplicates measurements. All percentages express% of the original sludge sample. The shaded gray arrow shows the amount of C, P, or N going to the acidic stream in the case of the diluted protocol. a) TCOD (organic solids), b) The dotted orange arrow shows the amount of bound phosphorus, and the shaded orange arrow shows the amount of free ortho-phosphate, c) The dotted arrow shows the amount of organic nitrogen.

Table 5

Theoretical substrate composition and degradation equation of alkaline sludge residue (lab), calculated as described in (Kleerebezem, 2014).

Substrate composition	Degradation Equation
C _{2.8} O _{0.66} N _{0.13}	-1 C _{2.8} O _{0.66} N _{0.13} -0.25 H ₂ O + 0.66 CH ₄ + 0.26 CO ₂ + 0.13 NH ₄ HCO ₃

4. Discussion

The fate of the alkaline gel layer is first discussed to provide a basic understanding required for the following discussions on the observed differences between the mass balances in Epe demonstration plant on the 22nd and 23rd of June and laboratory extractions in Section 4.2.1 and 4.2.2. This gel layer has implications on the recovery% reported and later sections discuss how the layer distributes over either the liquid or the solid phase depending on the decanter operation and design. The focus of this study is to evaluate the potential of carbon, phosphorus, and

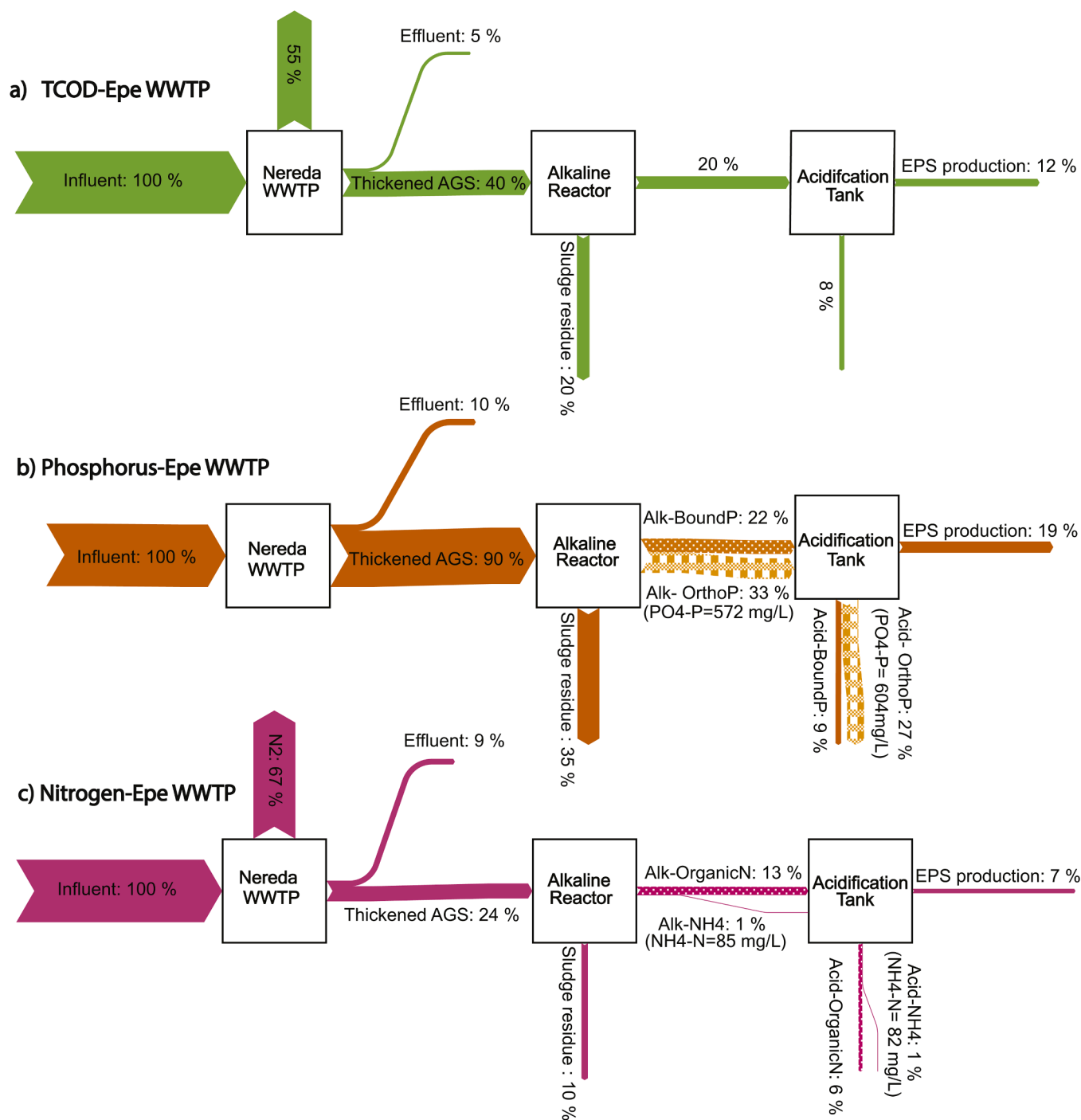


Fig. 4. a) TCOD, b) phosphorus, c) nitrogen balances for Epe Nereda WWTP+ EPS extraction process. Results are average from triplicates measurements. All mass flows are expressed in% of WWTP daily load.

Table 6
Theoretical substrate composition and degradation equation of alkaline sludge residue (Epe), calculated as described in (Kleerebezem, 2014).

Substrate composition	Degradation Equation
$C_{2.8}H_{2.8}O_{0.65}N_{0.11}$	$-1 C_{2.8}H_{2.8}O_{0.65}N_{0.11} - 0.16 H_2O$ $+ 0.65 CH_4 + 0.25 CO_2 + 0.11 NH_4HCO_3$

nitrogen recovery from the EPS extraction process as discussed in Sections 4.3, 4.4, and 4.5.

4.1. Alkaline gel layer formation

The modified laboratory protocol revealed a new alkaline gel layer as a middle layer between the sludge residue and the hydrolyzed EPS supernatant. This layer was not observed with the earlier laboratory protocol as the gel layer probably ended in the acidic liquid stream after separation, as indicated by gray arrows in Fig. 3. On the demonstration scale, due to inefficient solid-liquid separation, it was only easy to observe it once the current work pointed it out. There are several

possible explanations for the appearance of this layer: 1) dilution affects the supersaturation and solubility of organics and polymers, similar to inorganic systems, so EPS might precipitate due to higher concentration in the new laboratory protocol/on demo scale; 2) polymers differentiate into different polymer fractions based on molecular weight, higher molecular weight precipitates, and lower molecular weight dissolves, or 3) this fraction has less negative charge density compared to the rest of the dissolved EPS, so it is not readily soluble (Lotti et al., 2019). The exact reason for this layer's appearance has yet to be explored, and further characterization is needed. Fractionation of EPS samples and using advanced analytical methods can help with more accurate EPS characterization. Pre-treatments can achieve this by enriching targeted compounds, followed by purification steps. The purification can be based on solubility using different solvents, charge using chromatography, or size exclusion chromatography (Felz, 2019; Seviour et al., 2019). Such advanced analytical methods can be applied to reveal the differences between Kaamera and the alkaline gel layer in terms of quality and the reason for its appearance. Understanding the mechanism of this gel layer formation could also open a new direction to separate EPS into different polymer fractions, and each fraction is oriented to specific applications.

4.2. Epe demonstration-scale extractions

4.2.1. Fate of the alkaline gel layer in Epe

Comparing the 22nd results to the 23rd showed that the 22nd had a much larger Kaamera VS% yield, reaching around 50%. That revealed two implications: 1) that there is a potential to increase the yield of Kaamera by recovering this alkaline gel layer as well, or 2) insufficient solid/liquid separation leads to higher yield but quality deterioration of Kaamera (i.e., a lower fraction of gel-forming polymer). This observation shows that optimizing the decanter separation is crucial in the EPS extraction process and needs further attention. Further research is required to identify the quality difference between the 30%VS Kaamera yield (no alkaline gel layer) and the 50% VS Kaamera yield (including alkaline gel layer + undiluted conditions) to assess if this gel layer can be combined with Kaamera for higher recovery without deteriorating the quality. The fate of this gel layer affects the elemental mass distribution over the process.

4.2.2. Epe demonstration versus laboratory extractions

Epe mass balances showed that the potential of TCOD, TP, and TN recovery% by the EPS fraction is similar to the laboratory scale. The concentrations have the same order of magnitude on both scales, as shown in Table 2. However, there is a difference in the mass% distribution of nutrients at the decanter separation step following the alkaline hydrolysis, causing a larger fraction of elements to end in the alkaline liquid stream in Epe demonstration and eventually the acidic liquid stream. The TCOD, TP, ortho-phosphate, and TN in the alkaline liquid stream in Epe are 10%, 15%, 10%, and 20%, respectively, higher than the laboratory scale. These observations are explained by two main differences: the decanter solid/liquid separation efficiency and steam injection for heating up sludge to 80 Celsius. The solid/liquid separation efficiency of the decanter would affect the fate of the alkaline gel layer and consequently make a difference in the mass distribution. Steam injection is used in Epe to increase the temperature of the excess sludge before alkaline hydrolysis, and it accounts for 20% of the inlet flow to the alkaline reactor (dilution factor =1.2). Since the concentrations of Epe demonstration and laboratory extractions are in the same order of magnitude, and the dilution effect of steam injection is not significant enough to change that magnitude, it is concluded that a small fraction of the alkaline gel layer ends in the alkaline liquid stream. However, the solid/liquid separation at the laboratory scale is fully controlled and efficient, so the alkaline gel layer ends on top of the alkaline sludge residue fraction.

The steam injection is an Epe-specific case. For instance, in Zutphen,

the first EPS-Kaamera extraction demonstration-scale installation, heating is done through a heat exchanger. Also, decanter centrifuge settings could differ from one extraction plant to another. The comparison showed that the modified laboratory protocol gives results comparable to the demonstration scale installation in Epe. The laboratory protocol can be tailored to specific conditions to predict full-scale mass balances reasonably well in later stages, i.e., for other sludges from different installations or seasons without the need to realize a pilot installation. It also showed that the operators should be aware that the gel layer fate at full scale will depend on the alkaline solid-liquid separation efficiency.

4.3. Carbon recovery

COD balances showed a 30% EPS yield in the laboratory and Epe demonstration scales. It was reported that the amount of Kaamera extracted is approx. 25–35% of the organic matter in the waste sludge in e in an earlier study (van der Knaap et al., 2019). Calculations also showed that 25–30% of sludge TCOD can be recovered as methane by anaerobically digesting the alkaline sludge residue. The AD is proposed to be mesophilic (35 °C) and alkaline (pH=9–11), similar to the characteristics of the alkaline sludge residue after solid-liquid separation. Alkaline conditions are commonly used as an effective sludge pre-treatment step for better degradability, higher biogas production, and methane content. In neutral pH digestion systems, 25–60% CO₂ and 40–75% CH₄ ratios are usually obtained (Ryckebosch et al., 2011). According to CO₂/HCO₃ speciation against pH, the vapor pressure of CO₂ is minimal at pH 9–11, as most CO₂ stays in solution as (bi)carbonate. In high pH digestion systems, CO₂ remains in solution, yielding biogas predominantly composed of methane (>95%) (Nolla-Ardevol et al., 2015). The potential of methane production using the alkaline sludge residue is calculated to be ≈260 ml/g VS, according to (Kleerebezem, 2014), and the degradation of around 50% of organics based on Literature and industrial practice (van Nieuwenhuijzen et al., 2011; Roš and Zupančič, 2002). The first proof of principle batch experiments on digestion of this residue under mesophilic alkaline conditions (pH=9.5) showed that the methane content was around 98%, with 2% CO₂ as expected. The same experiments also showed methane yield equal to 200–240 ml/g VS; the substrate recovered as methane was about 40–50% (V.Sels, MSc, TU Delft, 2019)(unpublished results), which is in line with the calculations in this study. However, some crucial points still need to be investigated in future anaerobic digestion research of this residue, such as the need for pH adjustment during digestion because of CO₂ solubility and VFA production, the evaluation of ammonia toxicity, microbial community, and media composition.

4.4. Phosphorus recovery

According to the established mass balances, phosphorus recovery is realized in two ways during the EPS chemical extraction process. The first one is phosphorus present in the EPS fraction, which is potentially considered recovered phosphorus after understanding the role of phosphorus in polymer properties and its industrial applications. The second way is ortho-phosphate recovery from alkaline or acidic and digestate liquid streams.

4.4.1. Phosphorus recovery in the EPS fraction

Market competition is one of the problems facing phosphorus recovery implementation because phosphate rock is still cheap. Phosphorus recovery costs from wastewater on a large scale are estimated at €2 per kg P as a bare minimum and could be more than €10 per kg P (Egle et al., 2016; Molinos-Senante et al., 2011). However, the value of phosphorus in phosphate rock is less than €1 per Kg P. It is argued that upcycling P-recovery products with higher value and quality than fertilizer phosphates is a way to accelerate the P- recovery market. The production of P₄ derivatives from waste streams has gained interest

recently (ESPP webinar, 2020; Jupp et al., 2021). P₄ derivatives are P compounds that are cost-intensive as they must be produced via the thermal route of phosphate rock and used in specific industrial applications. EPS-Kaamera from AGS is a potential example of upcycling P-recovery products as it can substitute some P₄ derivatives, i.e., as a flame retardant. Kim et al., 2020 reported that EPS-Kaamera acts as a high-performance bio-based flame retardant as it shows self-extinguishing properties. It also meets the flame retardancy requirements in US Federal Aviation Regulation standards. In addition, EPS from granules has the advantage that it can be produced at a large scale as flame retardants, unlike other biomacromolecules such as DNA, whey proteins, or caseins (Alongi et al., 2014), as sufficient waste granular streams can be provided from Nereda® WWTPs.

Future research focused on understanding the phosphorus speciation in EPS is needed to establish the role of phosphorus for Kaamera properties, which can be manipulated to enhance and change its properties to maximize the usage of recovered phosphorus in EPS in more comprehensive industrial applications. Mass balances showed some assumptions about P-speciation in Kaamera, which will be measured directly in future research for a properly confirmed speciation. According to these assumptions in the results in Sections 3.4 3.6, around 70–75% of phosphorus in EPS is bound phosphorus, and 30–25% is free ortho-phosphates. Free ortho-phosphate is not an integral part of the polymer, and it is present since EPS is precipitated in the acidic stream, which contains high amounts of free ortho-phosphates. Bound phosphorus in EPS could be organic, inorganic, or ortho-phosphate loosely bound by electrostatic interactions. Organically bound phosphorus and loosely-bound ortho-phosphate are expected to be the most dominant fractions. EPS is expected to have phosphorylated proteins, phospholipids, and phosphosugars due to the extracellular and intracellular components released during alkaline hydrolysis (García Becerra et al., 2010). Also, EPS hydrogel is precipitated at around pH=2–4, which is very low to expect any mineral inorganic phosphorus present, as they would dissolve.

4.4.2. Ortho-phosphates recovery from alkaline, acidic, and AD centrate

The potential of ortho-phosphate recovery from alkaline or acidic liquid streams is attractive. According to laboratory extractions, 25%–20% of sludge TP, and 35%–30%, according to Epe demonstration, end in these two fractions as ortho-phosphates. The ortho-phosphate% increase from 10% of sludge TP initially in spill sludge to 25–35% of sludge TP in the alkaline liquid stream could be attributed to polyphosphate hydrolysis. The phosphate concentration is 600 mg PO₄-P/L, comparable to concentrations reported for mature technologies of the full-scale phosphate recovery processes for municipal and industrial wastewater (Desmidt et al., 2015). There are possible technologies to consider for phosphorus recovery from these two streams. For example:

- 1- nanofiltration on the alkaline stream can bleed off the phosphate (and other salts) to the permeate and keep the EPS in the retentate. That would concentrate the EPS and might reduce acid consumption in the later step. However, organic fouling of the membrane could be challenging (Wang et al., 2009).
- 2- the acidic stream has a low pH, meaning that most phosphate is present as H₃PO₄/H₂PO₄⁻. Further lowering the pH to <1 would get all the phosphate to the unionized form as H₃PO₄, and this could create a way to separate phosphoric acid from other salts via ion-selective membranes. However, this would require an extra acid dosage and is cost intensive.
- 3- chemical precipitation by metal addition as magnesium and calcium is the most common straightforward technology for ortho-phosphate recovery from liquid streams. Alkaline and acidic liquid streams are expected to have pros and cons for chemical phosphorus precipitation. For instance, the alkaline liquid stream has an advantage as it has a high pH value, making it suitable for calcium phosphate and struvite recovery. Struvite consists of equimolar amounts of

magnesium, ammonium, and phosphate and forms at pH=8–9 (Desmidt et al., 2015; Doyle and Parsons, 2002), calcium phosphate forms at pH ≥ 9 when the concentrations of phosphorus and calcium are high (Jupp et al., 2021). So, there will be no need to adjust the pH of the alkaline stream to form these minerals. However, this stream also contains solubilized EPS. Metal addition could interfere with its solubilization as it might get complexed or trapped by the polymer, causing the soluble polymers to co-precipitate, affecting the final EPS yield. Table 2 shows that soluble Ca²⁺ and Mg²⁺ in the alkaline stream are significantly lower than in the acidic stream. This suggests that the highly negatively charged polymers trapped these ions at high pH conditions. Similar observations were reported in soil literature that EPS contains metal binders, such as phosphate, amine, carboxyl, and hydroxyl groups, that trap divalent cations such as Ca²⁺ and Mg²⁺ and inhibit the precipitation of calcium carbonate as it reduces the saturation of calcium (Dittrich and Sibling, 2010; Kremer et al., 2008). The second reason is that visual Minteq modeling showed that the calcium phosphates and struvite are to be formed in the alkaline supernatant; saturation indexes are shown in Section 4 of the supplementary material. So, the alkaline liquid stream is already supersaturated; however, no precipitation is seen. That reflects the possible complexity of phosphorus recovery from this stream. On the other hand, the acidic stream has a low pH=2–4, requiring intensive chemical addition for pH adjustment and extra costs to precipitate struvite or calcium phosphate (Cichy et al., 2019). The acidic by-product stream would not interfere with the EPS production as it is already precipitated and removed, and the organics interference would be minimal. It seems that the acidic stream is more promising, so current research is ongoing to validate the possibility of phosphorus recovery in the acidic stream through chemical precipitation.

Ortho-phosphate fraction in the AD centrate was calculated based on our measurements and assumptions from Literature. Phosphorus remains in solution after digesting EBPR excess sludge as reported by Jardin and Popel, 1994 is 38% of the total phosphorus brought to the digester. No data is available for granular sludge. The calculations showed that this centrate would contain 12% (Epe)–15% (laboratory) of sludge TP with concentrations ≈700–900 mg PO₄-P/L, showing promising feasible recovery.

4.5. Nitrogen recovery

Figs. 3 and 4 show the fate of nitrogen through the EPS extraction process. 30% of sludge TN is recovered in the EPS mainly as organic nitrogen, which fits with its composition of proteins, and complex glycoconjugates as glycoprotein (Felz, 2019). The concept of recovering ammonium from the alkaline liquid stream is attractive since it has high pH and high temperature, which are required for commercial ammonium recovery technologies. Air stripping and membrane stripping are the most advanced applied technologies on a large scale for ammonium recovery. Both technologies require high pH of about 9–10 and high temperatures of 70–80 °C (van der Hoek et al., 2018). The energy efficiency of the recovery depends highly on the ammonium concentration. Ammonium recovery should not require more energy than ammonium production by the Haber-Bosch process. Ammonium concentration in the alkaline supernatant is 105 mg NH₄-N/L— which is too low to be efficiently recovered (Maurer et al., 2006; Ye et al., 2020) as reported in the recent STOWA report on mature ammonium recovery technologies (Elbersen et al., 2021). So, ammonium recovery from the alkaline liquid stream would be a no-go. However, the ammonium fraction in the anaerobic digestion centrate was calculated to be 17% (Epe) and 25% (laboratory) of sludge TN with a concentration of around 2600 mg NH₄-N/L →, which would make it feasible for ammonium recovery. These numbers were calculated assuming digestion releases 55% of the sludge nitrogen content (Soerensen et al., 1999; Suschka and Grübel,

2014).

4.6. Practical implications

Resource recovery from wastewater is still in its infancy but the consensus is that it should be developed in the context of a more sustainable society (Kehrein et al., 2020a, 2020b). This paper is taking the first steps towards this and setting a base for decision-makers. Several aspects are relevant to consider for a smooth implementation in the future. Firstly, the technologies used are quite different from operating a standard WWTP, and the goals are different. Utilities will have to consider how they can manage resource recovery at the WWTP, either by adaptation or by partly outsourcing the resource recovery operations. Secondly, the EPS extraction process is the primary process, and other integrated recovery technologies are associated with its by-product streams, so there should be a substantial market demand for Kaumera for such a treatment scheme to make sense. The EPS from AGS forms an interesting new resource for gel-forming biopolymers with much higher market potential and new applications than i.e. alginate or carrageenan. Kaumera could comprise 50% of the turnover Energy & Raw Materials Factory (ERMF) of the Dutch Water Authorities (van Leeuwen et al., 2018). It can be used in agricultural, horticulture, paper, coatings, and construction industries and can be applied as a gel, foam, or fiber. In 2022, Koppert Biological Systems, Chaincraft, and RHDHV signed a long-term contract for collaboration in applying Kaumera as a bio-stimulant. Another promising application is flame retardancy, as described in Section 4.4.1, so it can be used to produce materials and coatings (Kim et al., 2020). EPS can also be used in composite material production as it can hold up to 80% of inorganic filler material, and clay-Kaumera composites were tested. Using Kaumera in composite materials makes it an excellent option to replace many of the current applications of oil-based plastics (Henze et al., 2020).

5. Conclusion

Mass balances allowed the quantification of loads and concentrations of carbon, phosphorus, and nitrogen species relevant for recovery to set the foundation for a new generation of AGS WWTP with integrated resource recovery. It was shown that combined EPS, methane, phosphorus, and nitrogen recovery is promising. 30% of sludge TCOD is recovered as EPS, which has wide possible applications, and 25–30% of sludge TCOD could be recovered as biomethane by integrating alkaline anaerobic digestion (AD). 20% of sludge TP is recovered in the EPS. About 20–30% of TP ends in the acidic liquid waste stream and, 15% in the AD centrate as ortho-phosphates. These ortho-phosphate fractions are recoverable by integrating chemical precipitation. 30% of sludge TN ends in the EPS mainly as organic nitrogen and 20% in the AD centrate as ammonium which membrane or air stripping technologies can feasibly recover.

This study showed that the developed modified laboratory protocol is an excellent tool for predicting large-scale EPS extractions. It can be used for future experimental work focused on nutrient recovery or to test the effect of sludge from different installations or seasons and predict the consequences on a large scale. With the new laboratory protocol, a gel layer was discovered. Comparing the demonstration and laboratory extractions revealed that the fate of the alkaline gel layer depends on the solid/liquid separation efficiency of the decanter centrifuge. This layer could offer additional EPS recovery however its formation, character, and effect on the quality of the recovered EPS need further research.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Data availability

Data will be made available on request.

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Supplementary materials

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