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ORIGINAL PAPER

Nutrient Recovery from Biogas Digestate by Optimised Membrane Treatment

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Abstract

Biogas plants produce nutrient rich digestates as side products, which are usually used as local fertilisers. Yet the large amount and regional gradients of biogas plants in Germany necessitate management, conditioning, and transportation of digestates, in order to follow good fertilising procedure and prohibit local over-fertilisation. With a membrane-based treatment chain, i.e. centrifugation, ultrafiltration, and reverse osmosis, digestates can be separated into a solid N,P-fertiliser, a liquid N,K-fertiliser, and dischargeable water. Up to now, the high energy demand of the process chain, in particular the ultrafiltration step, limits the economical market launch of the treatment chain. A reduction of the energy demand is challenging, as digestates exhibit a high fouling potential and ultrafiltration fluxes differ considerably for digestates from different biogas plants. In a systematic screening of 28 digestate samples from agricultural biogas plants and 6 samples from bio-waste biogas plants, ultrafiltration performance could be successfully linked to the rheological properties of the digestate's liquid phase and to its macromolecular biopolymer concentration. By modification of the fluid characteristics through enzymatic treatment, ultrafiltration performance was considerably increased by factor 2.8 on average, which equals energy savings in the ultrafiltration step of approximately 45%. Consequently, the energy demand of the total treatment chain decreases, which offers potential for further rollout of the membrane-based digestate treatment.

Keywords Biogas · Ultrafiltration · Nutrient recovery · Rheology · Energy demand

Abbreviations

AGRI	Agricultural biogas plant
BIO-WASTE	Bio-waste biogas plant
CHP	Combined heat and power
EPS	Extracellular polymeric substances
k	Consistency factor
n	Power-law index
R_c	Cake layer resistance
R_m	Membrane resistance
RO	Reverse osmosis
UF	Ultrafiltration

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Introduction

In the last years, the number of biogas plants in Germany increased to more than 9300 plants with a total installed capacity of 4500 MW_e in 2017 [1]. Biomethane, electrical, and thermal energy produced in biogas plants play an important role in the ambitious targets of Germany's "Energiewende" (energy transition). Biogas plants produce highly nutritious digestates as side products—about 10,000–30,000 $t_{digestate}$ per MW_e and year [2]. The total amount of digestate produced by German biogas plants in 2017 can be estimated to 80 million tons [3]. Digestate is a good agricultural fertiliser with remarkable contents of phosphorus, nitrogen and potassium. Table 1 gives the range of nutrient concentrations and cumulated nutrient mass from raw digestate in Germany [4].

Digestate is usually used to manure local fields and cover nitrogen, phosphorus, and potassium demand of the crops. Additionally, digestate can contribute to humus production in the soil because of its high organic load [5]. According to the German fertiliser ordinance [6], nitrogen application on agricultural fields is limited to 170 $kg_N \cdot ha^{-1} \cdot a^{-1}$ and phosphorus to 20 $kg_{P2O5}·ha^{-1}·a^{-1}$. These limitations ensure a proper manuring procedure and protect drinking water quality. The latest revision (DüV 2017) includes the balance of nutrients from biogas plants and increases the cut-off time for manuring on agricultural fields in the winter period.

Some German federal states like Lower Saxony and North Rhine-Westphalia locally exceed the maximum amount of total nitrogen (170 $kg_N·ha^{-1}·a^{-1}$) in certain rural districts. In general, there is no mean nutrient excess for the entire federal states (e.g. Lower Saxony $N_{average}$ = 124 $kg_N·ha^{-1}·a^{-1}$). Local nutrient gradients induce manure and digestate transportation of 100–200 km from fertiliser excess regions to fertiliser demand regions [7]. Primarily, digestate and manure thus need to be converted into storable and transportable nutrient fractions. Different separation techniques for partial conditioning and total conditioning of digestates are available and discussed in literature. When partial conditioning is applied, the separation focuses on solid fertiliser production. Decanter centrifuges realise high separation efficiencies regarding phosphorus of about 60–90% towards the solid phase [8, 9]. The ratio of the readily soluble phosphorus amounted to 70% in digestates [10]. The liquid fraction is enriched in nitrogen (dissolved ammonia) and potassium. Total conditioning further treats the liquid fertiliser phase to achieve a mostly organic-free concentrate of ammonia and potassium and dischargeable water. The used equipment often depends on the infrastructure and availability of heat and energy. Evaporators [11], stripping units [12] and membrane processes [13–16] are applied.

The total conditioning process investigated in this study is based on a separator, a decanter centrifuge, an ultrafiltration unit, and a reverse osmosis unit (see Fig. 1). The permeate of the reverse osmosis step is particle-free and contains very low nutrient concentrations. When applying a multi-stage reverse osmosis unit, the water reaches discharge quality.

The achievable nutrient concentration of the fertiliser products strongly depends on the input material (Table 2) [14–16]. The solid fertiliser is characterised by high concentrations of dry matter, total nitrogen, and phosphorus. The liquid fertiliser is lean in phosphorus but represents an inorganic nitrogen and potassium fertiliser product. Ultrafiltration retentate can either be internally recirculated or used as liquid fertiliser. Velthof [17] reports an enrichment of ammonia and potassium in the liquid fertiliser by 175% and 200%, respectively. The liquid fertiliser had a nutrient value equivalent of about 12 €·m^{-3} [17].

A comprehensive market launch of the total conditioning process is limited by the rather high operating costs. The total energy consumption of the process is reported to be between 20 and 30 kWh·$m^{-3}_{digestate}$ [7, 14, 18]. With 10–15 kWh·$m^{-3}_{digestate}$ or 50–70% of the total energy demand, the ultrafiltration step is the most critical process step (see Fig. 2). The energy consumptions of the other process units are: reverse osmosis 6–8 kWh·$m^{-3}_{digestate}$, decanter 3–5

Table 1 Nutrient concentration and cumulated nutrient mass from digestates in Germany [4]

Parameter	Unit	Total nitrogen N_{total}	Ammonia NH_4^+	Phosphorus P	Potassium K^+
Concentration digestate	g kg^{-1}	1.2–9.1	1.5–6.8	0.4–2.6	1.2–11.5
Cumulated nutrient mass	t	3.9×10^5	1.7×10^5–3.2×10^5	7.4×10^4	3.3×10^5

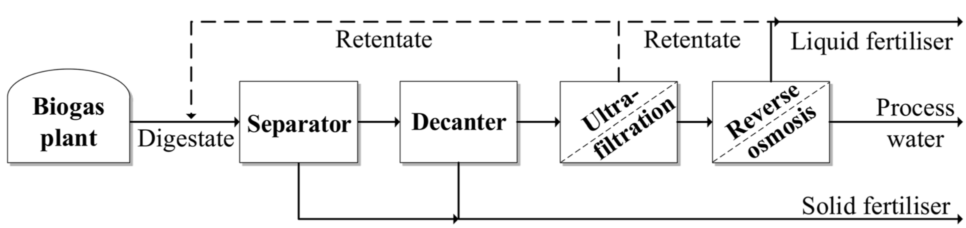

Fig. 1 Process scheme of multi-stage membrane treatment

Table 2 Dry matter (DM) and nutrient concentrations of multi-stage membrane treatment [14–16]

Parameter	Digestate	Solid fertiliser	Liquid fertiliser	Process water
DM (wt%)	7.0–7.9	15.9–22.7	2.8–3.6	≤0.13
N_{total} (g kg^{-1})	3.4–5.0	3.3–10.8	4.8–6.9	0.008–0.085
NH_4-N (g kg^{-1})	1.7–2.3	1.3–2.2	4.8–5.7	0.007–0.025
Phosphorus (g kg^{-1})	0.8–2.2	0.8–7.4	0.03–0.10	≤0.01
Potassium (g kg^{-1})	2.9–5.4	2.5–5.2	9.9–10.0	0.018–0.050

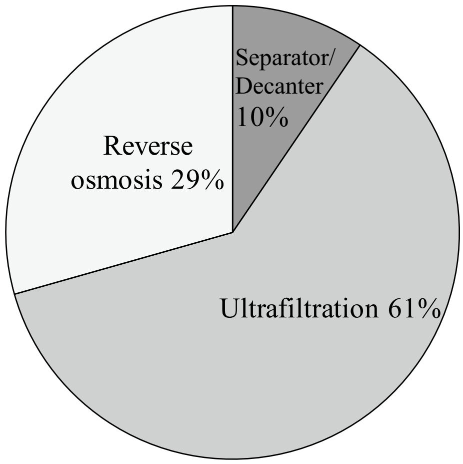

Fig. 2 Mean relative energy consumption of multi-stage membrane treatment reported by Drosg et al. [7] and Engeli et al. [18]

$kWh \cdot m^{-3}_{digestate}$, and separator 0.4–0.5 $kWh \cdot m^{-3}_{digestate}$ [7, 18].

The efficiency of the ultrafiltration step is thus responsible for the economy of the total conditioning process. Digestates and their liquid phase have a high fouling potential and require high crossflow velocities in the ultrafiltration modules, which are responsible for the exposed energy demand. Detailed knowledge of the dependence on micro- and ultrafiltration performance on biological suspensions has been reported in literature, e.g. for the filtration of activated sludge in membrane bioreactors (MBR). In particular, organic macromolecules like extracellular polymeric substances (EPS) or soluble microbial products (SMP) are known to influence membrane filtration performance [19–21]. Digestates show, like many biological sludges, a shear-thinning rheological behaviour [22], but there is only little information available in literature on sludge properties of biogas digestates.

Main objective of this paper is to identify the economic improvement potential of a membrane-based process chain for nutrient recovery from biogas digestates. Based on a systematic screening of rheological, physical and chemical parameters of digestate for a representative amount of biogas plants and the identification of relevant parameters influencing the ultrafiltration performance, the potential of enzymatic fluid modification on the energetic optimisation of the process chain is presented.

Materials and Methods

Sampled Biogas Plants

28 digestates from 12 different agricultural biogas plants (AGRI I–XII) and 6 digestates from 3 bio-waste biogas plants (BIO-WASTE I–III) were analysed regarding their nutrient contents as well as their fluid properties with respect to further membrane treatment. All sampled biogas plants have double stages with fermenters and post fermenters. The temperature of the first fermenter is mesophilic and often between 38–42 °C. BIO-WASTE biogas plant no. I is already equipped with a total conditioning membrane process. Average feedstock characteristics of the examined biogas plants are presented in Table 3. The agricultural biogas plants are basically fed with corn silage, liquid manure and GPS (entire crop silage). BIO-WASTE I was fed with remnants from biodiesel production and from food industry with unknown shares. BIO-WASTE plants no. II and III were fed with equivalent parts of food waste and flotation tailings. In general, input material for BIO-WASTE

Table 3 Average feedstock characteristics of examined biogas plants; others: field mangles, straw and beet pulp in small shares

Plant	Corn silage	Liquid manure	GPS	Crop	Dung	Grass silage	Others	Water
AGRI I	35.6%	27.5%	1.0%	2.2%	4.8%	13.9%	12.2%	2.7%
AGRI II	51.1%	36.5%	2.9%	3.7%	4.0%	1.7%	–	–
AGRI III	38.8%	–	10.0%	–	35.4%	9.4%	6.5%	–
AGRI IV	50.9%	22.8%	0.4%	17.8%	8.0%	–	–	–
AGRI V	41.2%	46.7%	12.1%	–	–	–	–	–
AGRI VI	59.5%	39.2%	1.2%	–	–	–	–	–
AGRI VII	96.3%	3.7%	–	–	–	–	–	–
AGRI VIII	5.1%	83.7%	–	6.8%	2.9%	–	1.6%	–
AGRI IX	57.0%	43.0%	–	–	–	–	–	–
AGRI X	23.6%	30.2%	8.7%	–	1.2%	5.8%	30.5%	–
AGRI XI	32.2%	35.0%	4.8%	–	–	3.8%	24.2%	–
AGRI XII	–	51.7%	–	–	11.7%	–	36.7%	–
BIO-WASTE I	Remnants from biodiesel production and food industry (shares unknown)							
BIO-WASTE II	50% food waste and 50% flotate							
BIO-WASTE III	50% food waste and 50% flotate							

biogas plants is subjected to stronger deviations caused by the different charges they receive from the food industry.

Sample Preparation

The samples were prepared according to VDI Norm 4630. Each sample (10–50 L) of digestate was taken from the post fermenter or digestate storage tank. Before, a certain volume of about 10 L was discharged to avoid maldistribution and pollution in the fermenter pipes. The samples were mixed until the phase was homogeneous and then directly taken for analytics. All digestate material was stored in a laboratory refrigerator at 6 °C. The centrate was produced by centrifugation at 4300 min^{-1} (3493 g) for 10 min with a laboratory centrifuge Megafuge 1.0 (HERAEUS).

Enzymatic Pre-treatment of Centrate

For optimisation purpose, a mixture of enzymes was incubated with the liquid fraction (centrate) in a heat cabinet at 50 °C for a maximum of 96 h, rotational speed was 100 min^{-1}. The enzymes were: amylase, cellulase, pectinase and protease with a concentration of 1 g L^{-1} each. As the enzymes have a defined optimum with respect to pH value, the centrate was acidified with sulphuric acid to pH 4.8 to ensure enzymatic activity of all enzymes.

Analyses of Organic Compounds and Nutrient Concentrations

Dry matter (DM in wt %) and organic dry matter (oDM in % of DM) in the digestates and their centrates were analysed according to European standard EN 12880 and EN 12879, respectively. Dry matter was determined after 24 h at 105 °C ± 5 K in a heating cabinet (Innova 4230, NEW BRUNSWICK) and organic dry matter after another 2–3 h at 550 °C ± 25 K in a muffle furnace (Thermicon P, HERAEUS). The mass was analysed with an analytic balance (Secura 224-1S, SARTORIUS) with a reproducibility of ± 0.1 mg. Centrate density ($\rho_{centrate}$) was quantified with a pycnometer (25 cm^3, BRAND) and digestate density ($\rho_{digestate}$) with a volumetric flask (500 cm^3 BRAND) because of the inhomogeneous texture. The concentration of the organic load (in g·L^{-1}) was calculated according to (Eq. 1). Measurements were carried out as repeat determination.

$$c_{org} = DM \cdot oDM \cdot \rho \qquad (1)$$

Polysaccharides and proteins were analysed according to Dubois [23] and Bradford [24], respectively. Calibration of the polysaccharide test was performed with D-Glucose-Monohydrate in a range of 0–200 mg·L^{-1} glucose. Absorption peak was determined between 480 and 490 nm, often at 488 nm. BSA (bovine serum albumin) was used for calibration of proteins from 0 to 500 mg·L^{-1} and measured at 595 nm. All measurements were carried out as double determinations and have a relative error of ≤ 5%. The EPS concentration (extracellular polymeric substances) was defined as the sum of the concentration of polysaccharides and proteins. Although EPS stands for a large number of organic components like polysaccharides, proteins, nucleic acids, lipids and humic substances, polysaccharides and proteins are the predominate fraction [25].

The investigation of dissolved organic size distribution was done by LC-OCD analysis (Liquid Chromatography—Organic Carbon Detection) at the Technical University of Berlin—Department of Water Engineering.

The concentrations of the nutrient compounds total nitrogen (N_{total}), dissolved ammonia (NH_4^+), phosphorus (P_2O_5) and potassium (K^+) were measured with appropriate vial tests from HACH-LANGE. Because of the solid particles and the inhomogeneous structure of the digestate, tests were applied to the liquid phase using an UV/VIS spectrum photometer DR 5000 from HACH-LANGE.

Viscosity Measurements of Centrate

The viscosity curve of centrate was measured with a double-gap viscosity system, Anton Paar Physica MCR101, with the corresponding measuring unit DG 26.7. The viscosity curve was recorded for a shear rate between 1 and 10,000 s^{-1} in a logarithmic ramp of 75 points. Temperature was constant at 20 °C with an accuracy of ± 0.02 K during the measuring procedure. For high shear rates ($\dot{\gamma} > 5000\,s^{-1}$) *Taylor* vortices appeared, caused by turbulent flow conditions at high shear rates [21]. In this case, the critical *Taylor* number of Ta ⩾ 41.2 was exceeded and the flow behaviour changed from laminar to turbulent flow.

Ultrafiltration Flux Measurement of Centrate

Membrane filtration tests were carried out with digestate centrates in a test cell Amicon 8200 (MERCK Millipore) with an ultrafiltration membrane UP150 (MICRODYN-NADIR GMBH). The polymer membrane (polyether sulphone) UP150 has a mean pore size of 0.04 µm, which corresponds to 150 kDa. The parameters used for the membrane tests were transmembrane pressure difference $\Delta p = 1$ bar ± 0.1 bar, temperature $\vartheta = 20\,°C \pm 2$ K, rotational speed of stirrer $n = 120$ min^{-1} ± 10 min^{-1} and membrane surface $A = 0.0033$ m^2. Based on the cake layer model (Eq. 1), the flux J_p equals to the pressure difference Δp divided by permeate viscosity, membrane resistance R_m and filter cake resistance R_c.

$$J_p = \frac{\Delta p}{\eta_{permeate} \cdot \left(R_m + R_c\right)} = \frac{\dot{Q}}{A} = \frac{\Delta V}{\Delta t \cdot A} \qquad (2)$$

In pre-tests, membrane resistance was determined to $R_c = 8.49 \times 10^{10}\ m^{-1}$. The flux J_p was continuously determined as ratio of volume V and time t for the given membrane surface A with a balance Secura 2102-1S (SARTORIUS). The balance has a reproducibility of ± 0.01 g and a maximum of 2200 g. The Amicon test cell was filled with 75 g of centrate. After 10% of yield the flux remained constant. The average flux was calculated between 10 and 15% of yield. Measurements were carried out as double determinations. The ratio of cake layer resistance to membrane resistance was often 4000:1, the resistance of the membrane is thus negligible.

Results and Discussion

Description of Results and Discussion

The nutrient recovery process delivers different process streams: the original digestate is divided into a solid and a liquid fraction, which is further treated by ultrafiltration and reverse osmosis. Products of the process are an organic N,P-fertiliser (gained by centrifugation) and a liquid N,K-fertiliser (gained by ultrafiltration and reverse osmosis). The composition and physical properties of the digestate (Sect. 3.2 and 3.3) generally influence the performance of the process chain (Sect. 3.4). Modifications of the physical properties, i.e. of the digestate's liquid phase, can improve the process performance (Sect. 3.5 and 3.6).

Table 4 Averages and standard deviation σ of different physical and chemical parameters of digestate samples

Parameter	Unit	Average AGRI N = 28	σ AGRI N = 28	Average BIO-WASTE N = 6	σ BIO-WASTE N = 6
DM	wt %	7.6	2.4	3.6	0.6
oDM	wt % of DM	71.9	5.0	59.9	7.4
c_{org}	mg L^{-1}	54,256	15,858	22,411	6509
N_{total}	mg L^{-1}	$4400^{(N=8)}$	$550^{(N=8)}$	–	–
NH_4^+-N	mg L^{-1}	$2180^{(N=8)}$	$650^{(N=8)}$	–	–
P_2O_5	mg L^{-1}	$1950^{(N=8)}$	$420^{(N=8)}$	–	–
K^+	mg L^{-1}	$3980^{(N=8)}$	$240^{(N=8)}$	–	–

Composition of Digestate

The determination of the composition of digestates is based on the analytical measurements of more than 15 physical and chemical parameters. The results are divided into parameters of digestate (Table 4) and parameters of the digestate's liquid phase after centrifugation (centrate) (Table 5), as this represents the feed to the following ultrafiltration step.

Digestate compounds generally vary from digestate to digestate. Furthermore, differences between AGRI and BIO-WASTE digestate occur. Average DM of AGRI digestate is 7.6 wt%, for BIO-WASTE digestates it is 3.6 wt%. BIO-WASTE digestates have lower values of oDM, resulting in higher values for inorganic DM and therefore higher salt concentrations, which raise the conductibility. The organic concentration of AGRI digestates is about 54,000 mg L^{-1}, while BIO-WASTE digestates contain about 22,000 mg L^{-1}.

The nutrient potential of the digestate is characterised by 4.4 $kg_{Ntotal} \cdot t^{-1}$, 50% of which is ammonia nitrate, 1.95 $kg_{P_2O_5}\ t^{-1}$, and 3.98 $kg_{K^+}\ t^{-1}$. The measured concentrations are in good accordance with literature [4, 7, 14].

Roughly half of the solid fraction of the digestate is separable by centrifugation (Table 5), giving average DM values of 3.1 and 1.4 wt% for AGRI and BIO-WASTE centrate, respectively. The separated solid fraction contains organic material, phosphorus, and nitrogen, thus representing a valuable organic fertiliser. The oDM of both types of centrate is reduced in the decanter from 71.9 to 62.6 wt%

Table 5 Averages and standard deviation σ of different physical and chemical parameters of digestate centrate samples after centrifugation with 3493 g

Parameter	Unit	Average AGRI N = 28	σ AGRI N = 28	Average BIO-WASTE N = 6	σ BIO-WASTE N = 6
DM	wt %	3.1	1.2	1.4	0.2
oDM	wt % of DM	62.6	7.4	43.7	13.5
c_{org}	mg L^{-1}	20,667	10,595	6266	2211
Proteins	mg L^{-1}	6422	3402	1391	795
Polysaccharides	mg L^{-1}	2407	1386	767	639
EPS	mg L^{-1}	8829	4789	2158	1434
N_{total}	mg L^{-1}	4558	1731	4761	1553
NH_4^+–N	mg L^{-1}	2320	1078	2077	831
P_2O_5	mg L^{-1}	484	344	272	81.9
K^+	mg L^{-1}	3824	1005	1839	1519

and from 59.9 to 43.7 wt%. The reduction of oDM of the centrates in the decanter represents a selective separation of (particulate) organic compounds compared to inorganic soluble compounds like dissolved salts. Further analysis of the organic fraction in the liquid phase delivers that about 40% are accounted for by polysaccharides and proteins, often summed as extracellular polymeric substances. Other organic substances are expected to be nucleic acids, lipids, and humic substances [25]. The inorganic fraction consists of salts and the valuable nutrients ammonia and potassium. The concentration of phosphorus was reduced by 77% on average due to centrifugal treatment. These findings are in good accordance with literature [8, 9]. Lukehurst et al. showed that phosphorus-related separation efficiency can be further improved from 64–79% to 82–93% when using polymeric flocculants before centrifugation [9].

Figure 3 visualises the remaining nutrient concentrations in the centrate. With approx. 4660 mg L^{-1}, total nitrogen provides the highest nutrient fraction. The value for BIO-WASTE centrates is slightly higher than the value for AGRI centrates. Total nitrogen consists of 50% ammonia (NH_4^+-N) and organic nitrogen each. Potassium is another major nutrient fraction with 3800 and 1800 mg L^{-1} for AGRI and BIO-WASTE centrates, respectively. As phosphorus is almost exclusively particulate, centrate is lean in phosphorus.

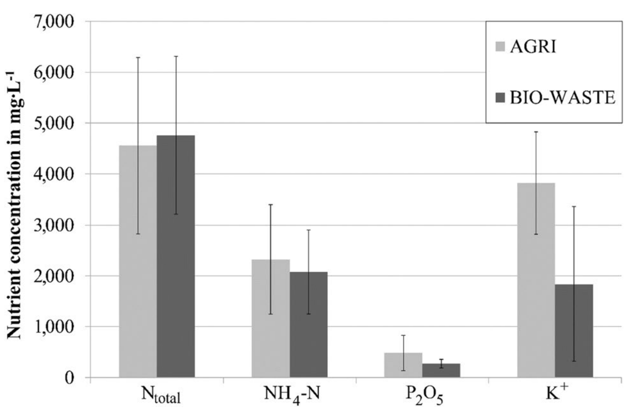

Fig. 3 Nutrient concentrations of digestate centrate (RZB = 3493 g)

Organic nitrogen and phosphorus in the centrate are particulate while ammonia and potassium are dissolved ions. Ultrafiltration membranes are applied for further separation of the remaining particulate fractions (Table 6). The organic concentration decreases from 22,382 mg•L^{-1} in the centrate to 4982 mg•L^{-1} in the ultrafiltration permeate. Soluble organic and inorganic compounds < 150 kDa such as (oligo-) saccharides, proteins and salts pass the membrane. The ultrafiltration membrane is selective for phosphorus and decreases the concentration to 25% (1356–355 mg•L^{-1}). In terms of nitrogen, the membrane is slightly selective for organic nitrogen but only little selective for ammonia. Approximately 90% of ammonia pass the membrane. Due to its high nutrient value, it can be transferred into a mineral fertiliser product by membrane filtration.

Physical Properties of Digestate and Its Centrate

Four different process fractions are shown in Fig. 4. The sample of digestate is brown and of high turbidity due to humic substances and organic material. The measured density is 997–1015 kg·m^{-3} and pH value is slightly above water (pH 7.8–8). The centrate is clearer because of lower dry mass contents. The UF permeate is free of particles and translucent, but still slightly coloured. The RO retentate is particle-free and of brown colour, the RO permeate is particle-free and clear (both not shown).

Digestates have a high apparent viscosity (500–7000 mPa·s) and shear-thinning rheological behaviour. The centrate's viscosity is lower but still considerably higher than water viscosity. Figure 5 shows the average apparent viscosity of the centrate for 12 AGRI and 3 different BIO-WASTE plants. As centrate is a shear-thinning fluid, two representative shear rates $\dot{\gamma} = 100$ and 1000 s^{-1} were chosen to compare viscosity results. All values are 10–130 times higher than water viscosity. Compared to AGRI centrates,

Table 6 Example of separation with an ultrafiltration unit (50 nm) for AGRI XII A, yield = 33%, centrate after sieve centrifuge (120 µm, RZB = 2200 g)

Parameter	Unit	Centrate	UF permeate	UF retentate	Rel. error
DM	wt%	3.8	1.6	5.0	4%
oDM	wt% of DM	58.7	32.2	63.1	–
c_{org}	mg L^{-1}	22,382	4982	32,225	4%
Polysaccharides	mg L^{-1}	3266	373	4900	4%
Proteins	mg L^{-1}	5520	359	8145	1%
EPS	mg L^{-1}	8786	732	13,045	–
N_{total}	mg L^{-1}	5227	3817	5877	−1%
NH_4^+–N	mg L^{-1}	4273	3881	4484	0%
P_2O_5	mg L^{-1}	1356	355	1933	4%

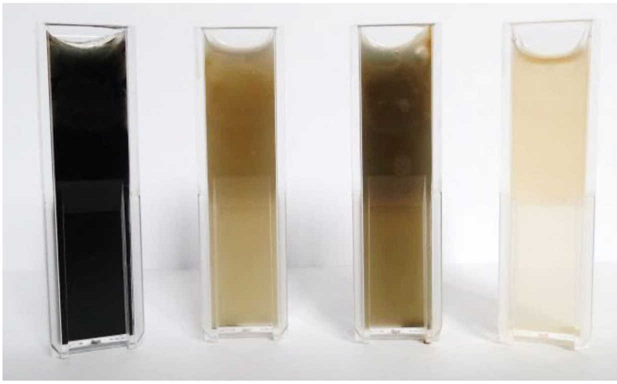

Fig. 4 Picture of some process samples, f.l.t.r: digestate, centrate (liquid phase after centrifugation), retentate after ultrafiltration of centrate, permeate after ultrafiltration of centrate (BIO-WASTE III B)

BIO-WASTE centrates show lower viscosities for both shear rates.

Between low and high shear rate, viscosity of AGRI and BIO-WASTE centrates decreases to 37.8 and 52.2% on average, respectively (Table 7). The rheological parameters of the power-law equation given in Table 7 were gained by modelling the viscosity curves. For AGRI and BIO-WASTE centrates, standard deviations σ of the average viscosities are in the order of magnitude of the value itself. The high deviation can be explained by fluctuating operation parameters of the biogas plants like e.g. alternating feedstock management, hydraulic retention time, and process temperature. Both centrates were characterised by shear-thinning behaviour with a power-law index of 0.644 (AGRI) and 0.844 (BIO-WASTE). The consistency factor of AGRI centrates was 0.261 Pa $s^{0.644}$, thus significantly higher than for BIO-WASTE centrates (0.020 Pa $s^{0.844}$). Linking these results with those published in literature, the shear-thinning rheological behaviour of the centrate is comparable to diluted algae biomass [26] and waste activated sludges [27].

Ultrafiltration Performance

Figure 6 shows the permeate flux in a standard ultrafiltration cell of the analysed centrates. Flux values obtained in the test cell are considerably lower than in full-scale ultrafiltration modules due to lower shear velocities, but it is an adequate tool to compare filtration performance of different digestates. BIO-WASTE centrates (black bars) are detected to

Fig. 5 Viscosity at 20 °C of centrate from 12 AGRI and 3 BIO-WASTE biogas plants for different shear rates

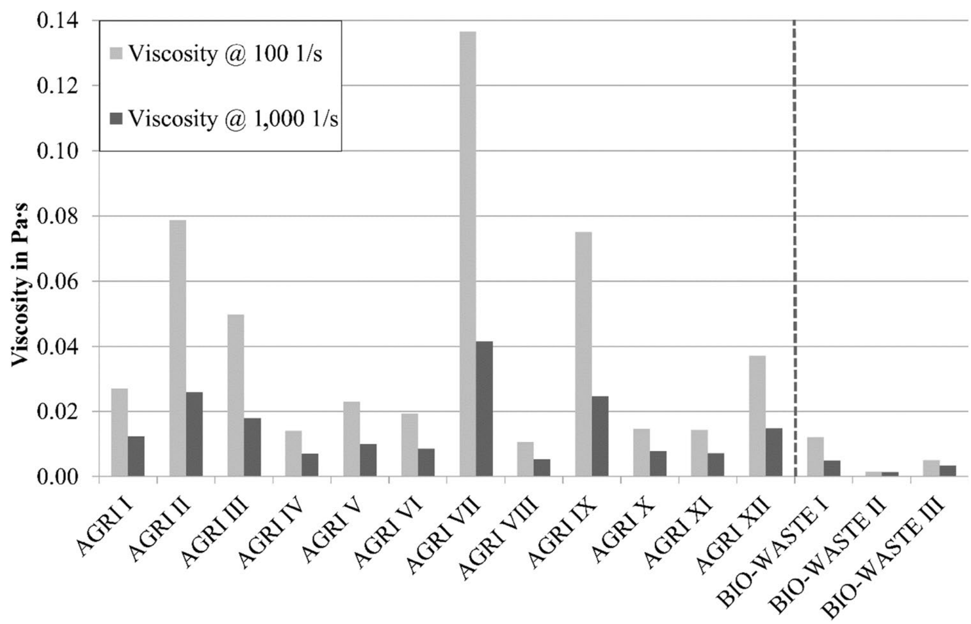

Table 7 Averages and standard deviation σ of viscosity measured at 100 and 1000 s^{-1} for the different types of digestate centrates

Parameter	Unit	Average AGRI N = 28	σ AGRI N = 28	Average BIO-WASTE N = 6	σ BIO-WASTE N = 6
Viscosity ($\dot{\gamma} = 100\ s^{-1}$)	Pa s	0.0373	0.0355	0.0067	0.0064
Viscosity ($\dot{\gamma} = 1000\ s^{-1}$)	Pa s	0.0141	0.0099	0.0035	0.0019
Consistency factor k	Pa s^n	0.261	0.371	0.020	0.026
Power-law index n	–	0.644	0.069	0.844	0.078

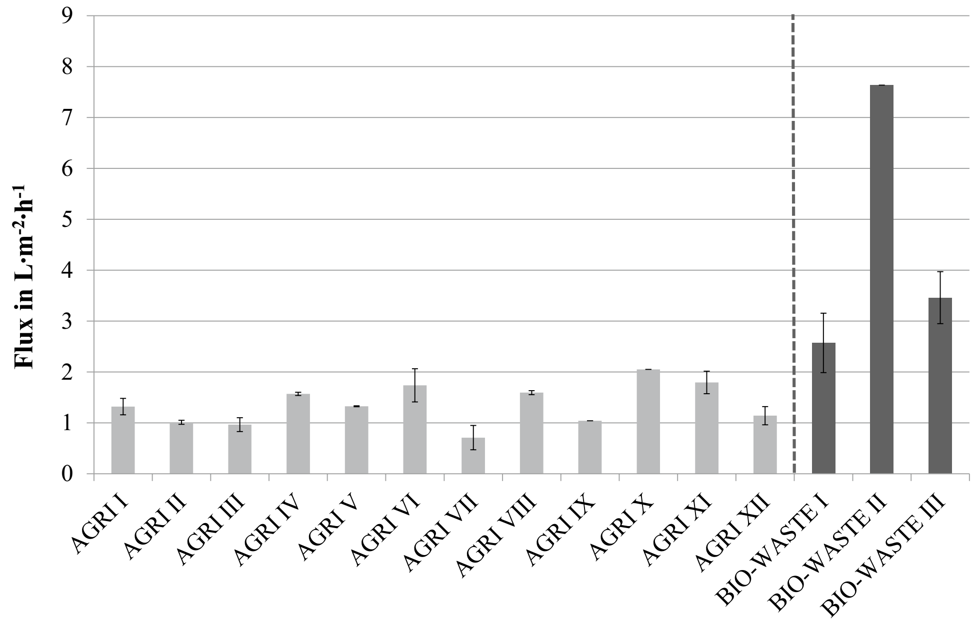

Fig. 6 Ultrafiltration flux of different centrates measured in the Amicon test cell (UF: 0.04 µm, TMP: 1 bar, T: 20 °C, rotational speed: 120 min^{-1})

have the highest flux values between 2.5 and 7.5 $L·m^{-2}·h^{-1}$. For AGRI centrates (grey), values are lower between 0.5 and 2 $L·m^{-2}·h^{-1}$. The corresponding error bars are calculated by standard deviations of the different charges for one biogas plant based on multiple charges per biogas plant. For some of the biogas plants like AGRI VI, VII, XI, XII and BIO-WASTE I and III, huge deviations were analysed. Based on 2–6 different charges for one biogas plant, membrane performance fluctuates up to 33.7% (AGRI VII). This seasonal deviation is based on variations and throughput of feedstock to the biogas plants. e.g., the flux of AGRI VII changed within a few months from 2.07 to 0.47 $L·m^{-2}·h^{-1}$, while increasing the share of maize in the biogas plant from 62 to 98%. Mono fermentation of maize is thus suspected to lead to lower membrane performance caused by poorly degradable lignocellulose residues.

Average flux of AGRI centrates and BIO-WASTE centrates is 1.38 and 3.86 L m^{-2} h^{-1}, respectively. Thus, the flux of BIO-WASTE centrates is factor 2.8 higher than AGRI centrate fluxes. Moreover, the standard deviation is significantly higher for BIO-WASTE centrates with $\sigma = 1.8$ L m^{-2} h^{-1} (AGRI: $\sigma = 0.39$ L m^{-2} h^{-1}). The great differences in membrane flux, induced by different feeding strategies of the biogas plants, correlate on one hand with dry matter concentration of the centrate and on the other hand with its apparent viscosity. Dry matter concentration of AGRI centrates was factor 2.2 higher than in BIO-WASTE centrates (compare Table 5). Again, similarities to other membrane applications in biological solutions, e.g. membrane bioreactors (MBR), were found. There is clear evidence that the (organic) dry matter is closely linked to the apparent viscosity and membrane flux for sludges [20]. With increasing (organic) dry matter content, increasing viscosity and decreasing membrane flux can be observed. Obviously, known relations for activated sludges are transferable for separated anaerobic digested sludges.

Optimisation of Membrane Performance by Pre-treatment

Main target of the presented study is the economic improvement of the ultrafiltration step. Based on the screening results, aim of further investigations was set on the reduction of the centrate's viscosity. Changing the feedstock composition of biogas plants is not a (general) option. Therefore, the potential of enzymes on modifying the fluid viscosity was investigated. The outcome of pre-treatment by a mixture of different enzymes, i.e., amylase, cellulase, pectinase and protease (each 1 g L^{-1}), is demonstrated in Fig. 7. With increasing incubation time, centrate viscosity constantly decreases and the rheological behaviour becomes more Newtonian. For very high shear rates (> 3000–5000 s^{-1}), Taylor vortices are noticeable.

The reference sample and the treated centrate with 48 h incubation time were further analysed with the Amicon test cell. The flux of the reference was 1.1 $L·m^{-2}·h^{-1}$, the flux of the treated material after 48 h incubation time was 3.1 $L·m^{-2}·h^{-1}$. By using enzymes it was thus possible to improve both viscosity and membrane performance by factor 2.8. Similar results were found for sludge samples of other biogas plants.

Original and modified centrates were compared by LC-OCD analysis (Fig. 8), which provides a good estimation of the type of colloidal and soluble substances in the centrates.

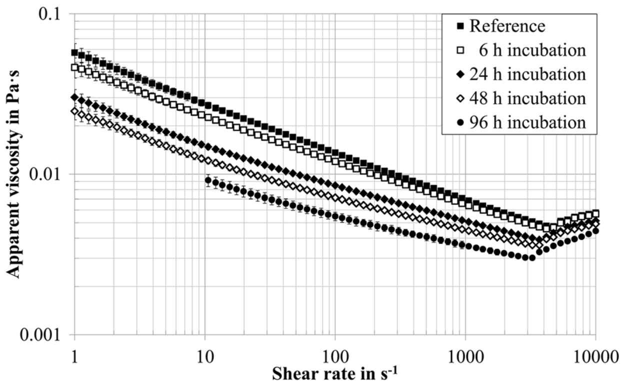

Fig. 7 Apparent viscosity (20 °C) of AGRI III A with amylase, cellulase, pectinase and protease (each 1 g L^{-1}), pH 4.8, incubation temperature 50 °C

The enzymatic treated material has a higher bypass signal because of the organic based enzymes. Comparison of the reference and the treated material shows differences in the fractions of biopolymers, low molecular weight acids and low molecular weight neutrals. The reference exhibits the highest peak and thus highest concentrations for biopolymers with low peaks for humic substances and low molecular weight acids. The modified material shows significantly higher peaks in the smaller fractions of low molecular weight acids and neutrals which are in the same order of magnitude as the biopolymer peak. Due to enzymatic treatment, a shift from large to smaller molecules was thus detected. Thus, the fraction of biopolymers in the digestate of a biogas plant has a major impact on the rheological behaviour of its liquid phase and consequently on the membrane performance of the nutrient recovery process.

Energetic Potential of Process Optimisation by Biological Pre-treatment Prior to Ultrafiltration

Pumping energy is the predominant energy demand of the ultrafiltration process and the main part of the total membrane treatment, due to the high velocity needed to ensure high shear strain to control the fouling layer. Often, crossflow velocities of $\bar{v} = 3\text{–}5\ \text{m}\cdot\text{s}^{-1}$ are needed. The pumping energy P_{el}correlates linearly with the pressure drop Δp, the volume flow $\dot{Q}$and reciprocally with the efficiency of the pump η_{pump} according to Eq. 3.

$$P_{el} = \frac{\Delta p \cdot \dot{Q}}{\eta_{pump}} \tag{3}$$

Turbulent flow conditions in tubular ultrafiltration modules require Reynolds numbers $Re > 2300$. The definition of the Reynolds number for non-Newtonian fluids Re_{n-N} is given in Eq. 4, while the shear dependent viscosity of digestate and centrate is described by the power-law equation from Ostwald/de Waele $\eta(\dot{\gamma}) = k \cdot \dot{\gamma}^{n-1}$.

$$Re_{n-N} = \frac{\bar{v}^{(2-n)} \cdot d^n \cdot \rho}{k \cdot \left(\frac{1+3\cdot n}{4\cdot n}\right)^n \cdot 8^{n-1}} \tag{4}$$

The correlation between average flow velocity, power, and fluid rheology can be shown for laminar flow in Eqs. 5–7.

$$\Delta p = \xi \cdot \frac{\rho}{2} \cdot \bar{v}^2 \cdot \frac{L}{d} \quad \rightarrow \quad \Delta p \sim \bar{v}^2 \tag{5}$$

$$\xi = \frac{64}{Re_{n-N}} \quad \rightarrow \quad \xi \sim \frac{1}{\bar{v}^{2-n}} \tag{6}$$

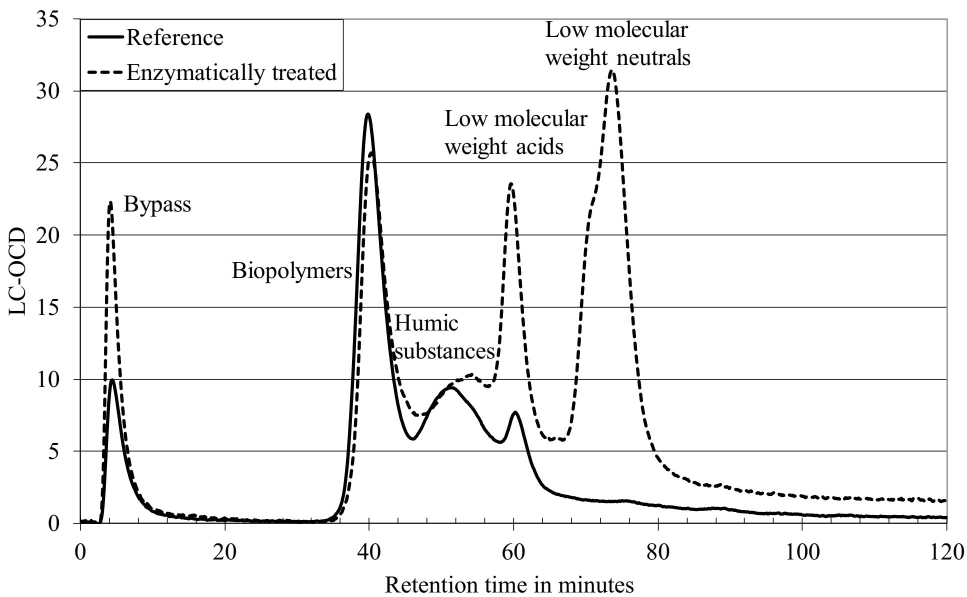

Fig. 8 LC-OCD analysis of centrate of digestate AGRI I, with and without enzymatic treatment (pH 4.9, incubation temperature 50 °C, incubation time 43 h)

$$\dot{Q} = \bar{v} \cdot A \;\rightarrow\; \dot{Q} \sim \bar{v} \tag{7}$$

$$\dot{Q} = \bar{v} \cdot A \;\rightarrow\; P_{el} \sim \bar{v}^{1+n} \tag{8}$$

The combination of all single terms (Eq. 8) provides a relation of electrical power input of $P_{el} \sim v^{1+n}$. The power-law index n, according to the viscosity model of Ostwald/de Waele, is $0 < n < 1$ for shear-thinning fluids. For digestate centrates, the power-law index was determined to be $0.5 < n < 0.8$. The electrical power input of the pump can be significantly decreased with decreasing flow velocity.

For turbulent flow conditions, the influence of Re on ξ decreases and accordingly the influence of velocity on the pump's power demand further increases. Turbulent flow with Reynolds numbers > 2300 is a necessary precondition for successful membrane filtration.

Based on the reduction of viscosity with enzymes (Fig. 7), the relative electrical power input for a Reynolds number of 2300 can be calculated. For the reference (untreated centrate) the power-law index is $n = 0.71$ and the consistency factor was measured to $k = 0.0525$ Pa•s$^{0.709}$. Power-law parameters of the enzymatically treated sample after 96 h are $n = 0.828$ and $k = 0.0118$ Pa•s$^{0.828}$, heading towards Newtonian behaviour ($n = 1$). Critical Reynolds numbers of 2300 are achieved by velocities of 2.92 and 1.97 m s^{-1} for the untreated and treated material, respectively. The relative power input is calculated in Eq. 9.

$$\theta_{el} = \frac{P_{el}, after}{P_{el}, before} = \frac{1.97^{1+0.83}}{2.92^{1+0.71}} = 0.553 = 55.3\ \% \tag{9}$$

By modifying the rheological behaviour, it is thus possible to save about 45% of the pumping energy for the same flow conditions. Both rheology and cross-flow velocities have high influences on energy demand and membrane performance of the ultrafiltration unit.

Conclusion

The total conditioning process by decantation, ultrafiltration, and reverse osmosis is a suitable technology chain for the production of well-defined concentrated fertiliser products from digestate. Besides clean water, it produces a solid organic nitrogen/phosphorus fertiliser (8.2–12.0 kg t^{-1} N_{total} and 5.6–10.4 kg t^{-1} P_2O_5) and a liquid nitrogen/potassium fertiliser (2.9–5.6 kg t^{-1} NH_4^+–N and 6.2–9.2 kg t^{-1} K^+), which can be further concentrated by factor 2–3 by optimising the reverse osmosis step, as needed.

Market launch of the technology is limited by its high operating costs of the technology. With about 50–70%, most of the process energy consumption results from pumping energy within the ultrafiltration step. A systematic screening of digestates and centrates from 15 different biogas plants revealed that both composition and ultrafiltration performance of different samples—even from identical biogas plants taken at different times—vary considerably. The concentration of biopolymers in the liquid phase of the digestate and accordingly its viscosity were identified as influencing ultrafiltration flux performance the most.

Based on the screening results, enzymatic pre-treatment of the centrate was chosen to modify the structure of the fluid by destroying colloidal biopolymers into low molecular weight components. Modification of the fluid reduced apparent viscosity as well as the shear-thinning properties of the centrate.

The exemplarily shown pre-treatment can induce energy savings of approx. 45% of the required pumping energy for constant flow conditions within ultrafiltration modules. Thus, it offers great potential for further rollout of the membrane-based digestate treatment.

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