NUTRIENT RECOVERY FROM BIOGAS DIGESTATE BY OPTIMISED MEMBRANE TREATMENT

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Abstract

The large amount of biogas plants in Germany and regional gradients of number and size necessitate management, conditioning and transportation of digestates. Focus of this work is a total conditioning process for digestates based on membrane technique, i.e., centrifugation, ultrafiltration, and reverse osmosis. Products of the treatment chain are a solid N,P-fertiliser, a liquid N,K-fertiliser and water. In order to compete with other separation techniques, the energy efficiency of the process, i.e., the ultrafiltration step, needs to be improved. In this work, digestate characteristics are shown for 28 different samples of agricultural biogas plants and 6 samples of bio-waste biogas plants. The results show a large deviation of both membrane performance and rheology for different biogas plants. Energy demand of the

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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

ultrafiltration step strongly correlates with rheological properties of the digestate liquid fraction. A final focus on fluid properties and energy demand identifies energetic improvement potential of the ultrafiltration process.

Keywords

Biogas; ultrafiltration; nutrient recovery; rheology; energy demand

Highlights

- Agricultural and bio-waste digestates show large deviations in physical properties
- Nutrient fractions can be separated with a decanter centrifuge and membrane technique
- Membrane performance and pseudoplastic rheology are associated

1 Introduction

The number and electrical power of biogas plants in Germany has risen in the last years to more than 8,700 plants with a total installed capacity of about 3,900 MW_e in 2014 [1]. Biomethane, electrical and thermal energy produced in biogas plants have an important role in the ambitious targets of Germany's renewable power management. With the production of biogas, large amounts of digestates are generated. Each year, approximately 65.5 million m³ of digestate is produced by German biogas plants [2]. Depending on the input material, the quantity of digestate relative to the input material fluctuates. Biogas plants of 1 MW_{el} power class eject about 10,000 – 30,000 $t_{digestate}$ per year [3]. Digestate is a suitable fertiliser with remarkable contents of phosphorous (P_2O_5), nitrogen (org.–N and NH_4^+) and potassium (K^+). The range of nutrient concentrations of raw digestate are: phosphorous 0.4 – 2.6 $g \cdot kg_{digestate}^{-1}$, total nitrogen 1.2 – 9.1 $g \cdot kg_{digestate}^{-1}$, ammonia 1.5 – 6.8 $g \cdot kg_{digestate}^{-1}$ and potassium 1.2 – 11.5 $g \cdot kg_{digestate}^{-1}$ [2]. Based on the nutrient contents, digestate is used to fertilise local fields and cover basically P and N demand of the crops. Additionally, digestate can contribute to ordinary humus production in the soil because of its high organic load [4]. According to the German fertiliser order "*Düngeverordnung*" [5], nitrogen application (§ 4) on agricultural fields is limited to 170 $kg_N \cdot ha^{-1} \cdot a^{-1}$ and phosphorous (§ 6) to 20 $kg_{P2O5} \cdot ha^{-1} \cdot a^{-1}$ [5]. These limitations ensure a proper manuring procedure and protect drinking water quality. With the upcoming revision of the fertiliser order regulations and limitations referring phosphorus and nitrogen become more rigorous. The latest prior printed publication [6] includes the P and N output coming from biogas plants (digestate), whereas the current version [5] only regulates liquid and solid manure, dung and mineral fertiliser. Moreover, the cut-off time for manuring on agricultural fields in the winter period will be expanded from 1st November - 31st January (old) to 1st October - 31st January (new). Also a new regulation for solid fertilisers like compost or solid digestate fractions is established [6]. Some of the German federal states like Lower Saxony and North Rhine-Westphalia locally exceed the maximum amount of total nitrogen (170 $kg_N \cdot ha^{-1} \cdot a^{-1}$) for certain rural districts. In general, there is not a problem of excess for the entire federal states (e. g. Lower Saxony $N_{average} = 124\ kg_N \cdot ha^{-1} \cdot a^{-1}$) but of exposed local gradients in single rural districts. These local nutrient gradients generate a large transportation effort of about 100 - 200 km from fertiliser excess regions to fertiliser demand regions [7]. Primarily, digestate and manure have thus to be converted into transportable nutrient fractions. Different separation techniques are classified into partly conditioning and total conditioning. Partly conditioning is the procedure of separating solid components of the digestate to receive a liquid fertiliser. Decanter centrifuges, for example, realize high efficiencies of phosphorus separation of about 60 – 90 % towards the solid phase [8,9]. The liquid fraction is enriched in nitrogen as dissolved ammonia and potassium. Total conditioning further treats the liquid fertiliser phase to achieve a concentrate of ammonia and potassium, and water which can be reused as process water. The used equipment often depends on the infrastructure and availability of heat and energy. Evaporators [10], stripping units [11] and membrane processes [12,13] are applied for the conditioning procedure.

The total conditioning process by centrifugation, ultrafiltration, and reverse osmosis is based on electrical power input only (see Fig. 1). Ultrafiltration retentate is internally recirculated while permeate passes the reverse osmosis step. The permeate of the reverse osmosis is process water with low concentrations of COD (< 60 $mg \cdot L^{-1}$) and ammonia. It can be introduced in receiving water bodies [14]. According to Brüß (2014) [14] and Drosg et al. (2015) [7], the range of the total energy consumption is about 20 – 30 $kWh \cdot m^{-3}_{digestate}$. The ultrafiltration step consumes the main part of about 50 – 70 % (10 – 15 $kWh \cdot m^{-3}_{digestate}$).

The energy consumption of the reverse osmosis is 6 – 8 $kWh \cdot m^{-3}_{digestate}$ and of the decanter 3 – 5 $kWh \cdot m^{-3}_{digestate}$.

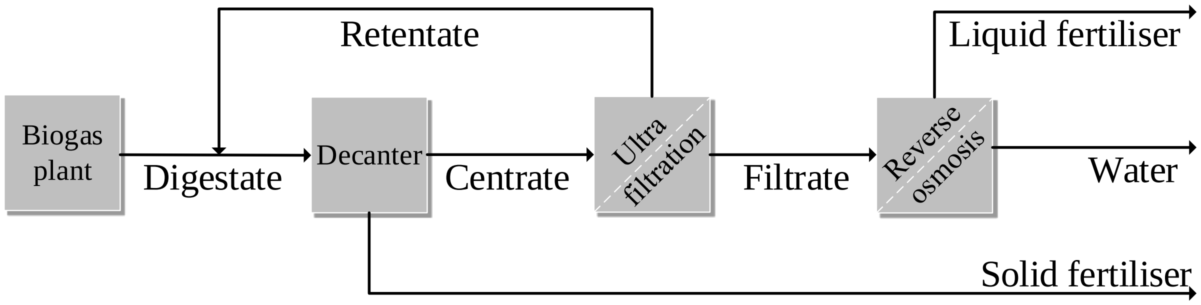

Figure 1: Process scheme of membrane treatment

The efficiency of the ultrafiltration step is thus responsible for the economy of the membrane total conditioning process. High energy consumption is based on high crossflow velocities in the ceramic modules of about 5 $m \cdot s^{-1}$, which are needed to prohibit rapid membrane fouling and to realise turbulent flow conditions. Optimisation of membrane processes requires detailed knowledge of the rheological fluid behaviour [15]. Rheological and physical parameters of the digestate have significant influences on pressure drop (pump design), heat transfer, agitators and sedimentation processes in a biogas plant [16]. Although the knowledge of rheological parameters (viscosity, yield stress, flow curve) and physical parameters (density, heat transfer coefficient) is important for plant design, information published in literature is rare. Digestates show, like many biological sludges, a shear thinning rheological behaviour [15,17]. The apparent viscosity η_{app} decreases with increasing shear rate. The objective of this paper is to investigate the rheological, physical and chemical parameters of the digestate for a representative amount of biogas plants.

2 Materials and Methods

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.

2.1 Sampled biogas plants

All sampled biogas plants have double stages with fermenters and post fermenters. The temperature of the first fermenter is mesophilic and often between 38 °C – 42 °C. BIO-WASTE biogas plant no. I is equipped with a total conditioning membrane process. Average substrate mixture of the examined biogas plants are shown in Table 1. 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 biogas plants is subjected to stronger deviations caused by the different charges they receive from the food industry.

Table 1: Average input material of examined biogas plants; others: field mangels, 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							

2.2 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 fridge at 6 °C. The centrate was produced by centrifugation at 4,300 min^{-1} (3,493 g) for 10 minutes with a laboratory centrifuge Megafuge 1.0 (HERAEUS).

2.3 Organic compounds

Dry mater (DM in wt%) and organic dry matter (oDM in % of DM) were analysed according to the European standard EN 12880 and EN 12879, respectively. The dry matter was determined after 24 h at 105 °C ± 5 K in a heating cabinet (Innova 4230, NEW BRUNSWICK) and the 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 (ρ_{centrate}) was quantified with a pycnometer (25 cm^3, BRAND) and digestate density ($\rho_{\text{digestate}}$) with a volumetric flask (500 cm^3, BRAND) because of the inhomogeneous texture. The concentration of the organic load (in $\text{g}\cdot\text{L}^{-1}$) was calculated according to *(Eq. 1)*. Measurements were carried out as repeat determination.

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

2.4 Organic compounds

Polysaccharides and proteins were analysed according to *Dubois* [18] and *Bradford* [19], respectively. The calibration of the polysaccharide test was performed with D-Glucose-Monohydrate in a range of 0 – 200 $\text{mg}\cdot\text{L}^{-1}$ glucose. Absorption peak was determined between 480 – 490 nm, often at 488 nm. BSA (bovine serum albumin) was used for calibration of proteins from 0 – 500 mg·L^{-1} and measured at 595 nm. A linear dependency of both photometric tests was determined in a given range. 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 [20] and easy to measure as a sum parameter.

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.

2.5 FOS/TAC titration

The FOS/TAC titration was done with a biogas titrator TitraLab® from HACH-LANGE. The titration occurred until pH = 5 and then until pH = 4.4 with 0.1 N sulphuric acid. The value of FOS represents the amount of volatile organic acids, the value of TAC the buffer capacity of the bicarbonate buffering system. Normally, the ratio of FOS/TAC is < 0.6 to ensure a stable biological process [21].

2.6 Nutrient concentration

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

2.7 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 – 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}) the apparent viscosity increases after constant decreasing with higher shear rates. These effects are based on *Taylor* vortices caused by turbulent flow conditions at high shear rates [15]. In this case, the critical *Taylor* number of $Ta \geq 41.2$ was exceeded and the flow behaviour changed from laminar to turbulent flow.

2.8 Flux performance

Membrane filtration tests were carried out with 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 Δp = 1 bar ± 0.1 bar, temperature ϑ = 20 °C ± 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. 2)*, the flux J_p equals to the pressure difference Δp divided by the permeate viscosity, the membrane resistance R_m and the filter cake resistance R_c.

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

In pre-tests, the membrane resistance was determined to $R_c = 8.49 \cdot 10^{10}$ m^{-1}. The flux J_p was continuously determined as the 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 2,200 g. The Amicon test cell was filled with 75 g of centrate. After 10 % of yield the flux remains constant. The average and constant flux was calculated between 10 % to 15 % of yield. Measurements were carried out as double determinations. The ratio of cake layer resistance to membrane resistance was often 4,000:1, the resistance of the membrane is thus negligible.

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 each 1 $\text{g}\cdot\text{L}^{-1}$. As the enzymes have a defined optimum with respect to pH value, the centrate was acidified with sulfuric acid to pH = 4.8 to ensure enzymatic activity of all enzymes.

3 Results and Discussion

3.1 Screening results of digestate and centrate

The determination of the behaviour and 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 2) and parameters of the digestate after centrifugation (centrate) (Table 3). A picture of the process streams is shown in Figure 2. The sample of digestate is rich in humic substances and organic material, which appears brown. The centrate is clearer because of lower dry mass contents. The retentate is highly concentrated because of the separation process and has thus more particles with coloured components. The filtrate after ultrafiltration is free of particles and translucent.

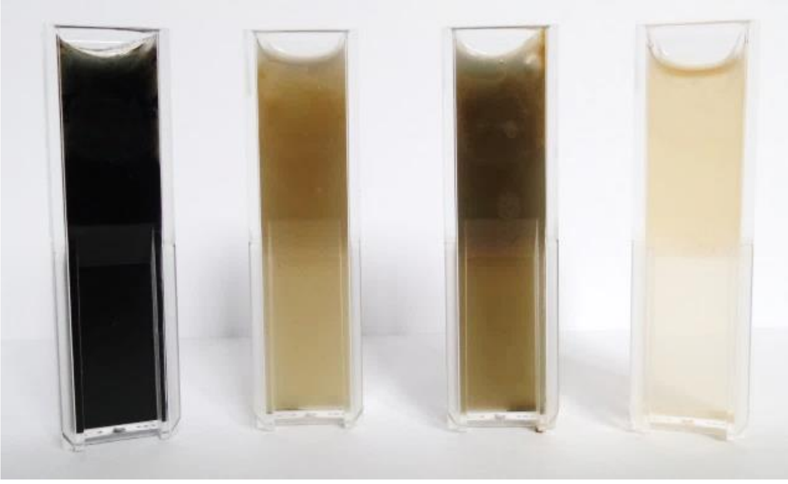

Figure 2: Picture of process streams, f.l.t.r: digestate, centrate (liquid phase after centrifugation), retentate after ultrafiltration of centrate, filtrate after ultrafiltration of centrate (BIO-WASTE III B)

The digestate compounds show big differences between AGRI and BIO-WASTE digestate. Average DM of AGRI digestate is 7.6 wt% ± 2.4 wt%, for BIO-WASTE digestates it is 3.6 wt% ± 0.6 wt%. Moreover, the oDM is lower for BIO-WASTE digestates which can also be seen in the higher value of the conductibility. The lower value of oDM gives higher values for inorganic DM and therefore higher salt concentrations, which raise the conductibility. The organic concentration of AGRI digestates is about 54000 $mg \cdot L^{-1}$, BIO-WASTE digestates have about 22000 $mg \cdot L^{-1}$.

Table 2: Averages and standard deviation σ of different physical and chemical screening parameters of digestates

Parameter	Unit	Average AGRI N = 15	σ AGRI N = 15	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
Density	$kg \cdot m^{-3}$	996.8	27.8	1015	7.6
c_{org}	$mg \cdot L^{-1}$	54256	15858	22411	6509
pH	---	7.81	0.2	8.04	0.2
FOS/TAC	mg_{HAC}/mg_{CaCO3}	0.22	0.0	0.22	0.0
Conductibility	$mS \cdot cm^{-1}$	20.7	4.9	28.2	4.8

In Table 3, the parameters are summarised analogously for the separated liquid fraction (centrate). The DM of centrate is significantly lower compared to digestate with values of 3.1 wt% and 1.4 wt% for AGRI and BIO-WASTE centrate, respectively. The reduced DM is caused by the separation process, where particles with higher density than water are separated in the centrifugal field. The oDM of both types of centrate is reduced in the decanter from 71.9 wt% to 62.6 wt% and from 59.9 wt% to 43.7 wt%. The reduction of oDM of the centrates in the decanter represents a more selective separation for organic compounds than for inorganic soluble compounds like dissolved salts. The organic concentration and the EPS concentration represent the organic matter in the centrate. The EPS concentration captures about 40 % of the organic concentration. The rest (60 %) is supposed to be nucleic acids, lipids and humic substances [20]. The EPS consists to approx. 70% of proteins. The results for both AGRI digestate and the separated liquid fraction are in good accordance with the findings from Chiumenti et al. (2013).

Table 3: Averages and standard deviation σ of different physical and chemical screening parameters of digestate centrates (RZB = 3493 g)

Parameter	Unit	Average AGRI N = 15	σ AGRI N = 15	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
Density	$kg\cdot m^{-3}$	1017	5.2	1015	6.9
c_{org}	$mg\cdot L^{-1}$	20667	10595	6266	2211
Proteins	$mg\cdot L^{-1}$	6422	3402	1391	795
Polysaccharides	$mg\cdot L^{-1}$	2407	1386	767	639
EPS	$mg\cdot L^{-1}$	8829	4789	2158	1434
N_{total}	$mg\cdot L^{-1}$	4558	1731	4761	1553
NH_4^+-N	$mg\cdot L^{-1}$	2320	1078	2077	831
P_2O_5	$mg\cdot L^{-1}$	484	344	272	81.9
K^+	$mg\cdot L^{-1}$	3824	1005	1839	1519

The nutrient potential of the centrates is visualised in Figure 3. The concentration of total nitrogen is the highest nutrient fraction in the centrates with approx. 4,660 $mg\cdot L^{-1}$ in average. The value for total nitrogen of BIO-WASTE centrates is slightly higher than for AGRI centrates, the standard deviation is equal. The total nitrogen consists of about 50 % ammonia (NH_4^+-N), the rest is organic nitrogen (50 %).

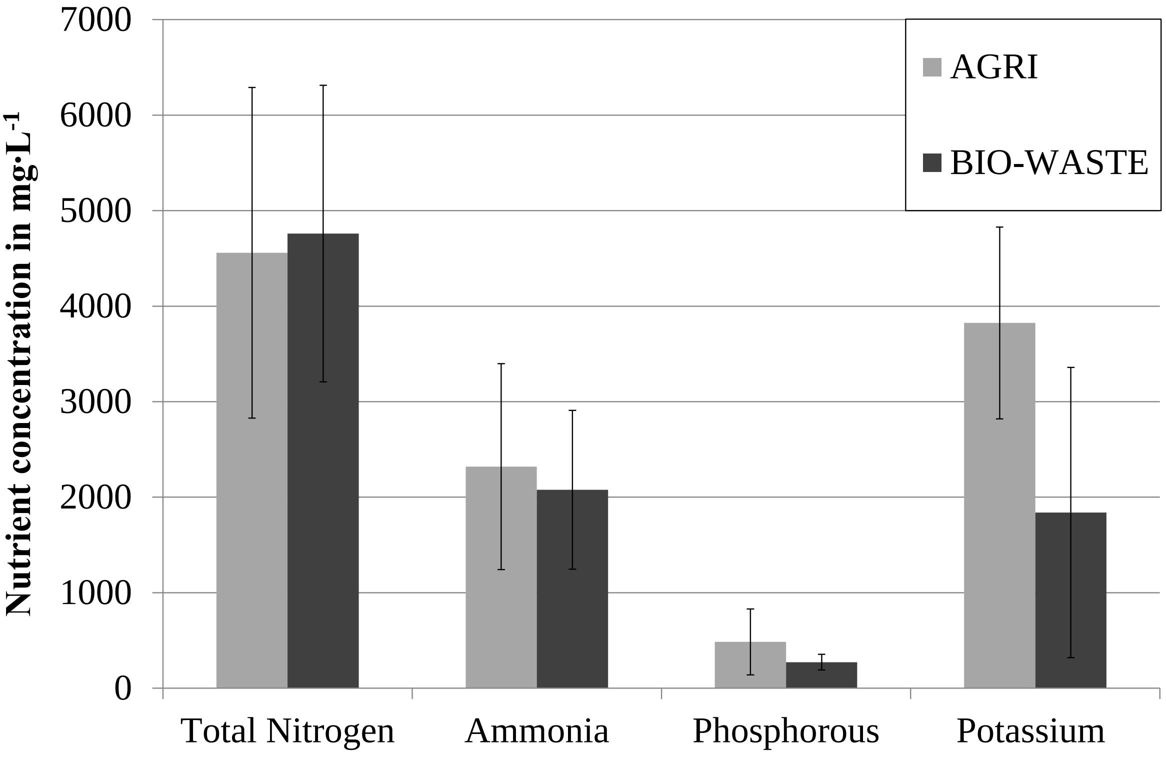

Figure 3: Nutrient concentrations of centrate (RZB = 3493 g)

Potassium is another major nutrient fraction with 3,800 mg·L^{-1} and 1,800 mg·L^{-1} for AGRI and BIO-WASTE centrates, respectively. Although the BIO-WASTE's potassium concentration is lower, the standard deviation of the samples is very high. This underlines the significant fluctuation of BIO-WASTE digestates and centrates. As the phosphorous is almost exclusively particulate, the supernatant (centrate) is lean in phosphorous. The centrate is further treated in the ultrafiltration unit and separated into filtrate and retentate (Table 4). The respective mass balancing errors are given in the last column. They are smaller than 5 %. The particulate components measured as DM and oDM are retained by the ultrafiltration membrane. The organic concentration decreases from 22.4 mg·L^{-1} in the centrate to 5.0 mg·L^{-1} in the filtrate. Only soluble organic and inorganic compounds < 150 kDa such as (oligo-) saccharides, proteins and salts pass the membrane. The viscosity of the filtrate is equal to water, the viscosity of the retentate accordingly increases. Moreover, the ultrafiltration membrane is selective for phosphorous and decreases the concentration to 25 % (1,356 mg·L^{-1}

to 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 passes the membrane.

Table 4: 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	Filtrate	Retentate	rel. Error
DM	WT%	3.8	1.6	5.0	4%
oDM	WT% of DM	58.7	32.2	63.1	---
Polysaccharides	mg·L^{-1}	3266	373	4900	4%
Proteins	mg·L^{-1}	5520	359	8145	1%
Flux	L·m^{-2}·h^{-1}	1.33	---	1.25	---
Viscosity $_{1000\ 1/s}$	Pa·s	0.006	0.001	0.012	---
Nitrogen	mg·L^{-1}	5227	3817	5877	-1%
Ammonia	mg·L^{-1}	4273	3881	4484	0%
Phosphorus	mg·L^{-1}	1356	355	1933	4%
Org. concentration	mg·L^{-1}	22.4	5.0	32.2	4%

3.2 Centrate viscosity

Figure 4 shows the average apparent viscosity of the centrate for 12 AGRI plants and 3 different BIO-WASTE plants. As the viscosity is a function of the shear rate (shear thinning behaviour), two representative shear rates $\dot{\gamma}$ = 100 s^{-1} and $\dot{\gamma}$ = 1000 s^{-1} were chosen to compare viscosity results. Due to the higher organic concentrations, the average viscosity of both centrates is noticeable higher with a factor of 10 – 130 compared to water viscosity ($\eta_{water,20\ °C}$ = 0.001 Pa·s). BIO-WASTE centrates have smaller viscosities for both shear rates compared to AGRI centrates.

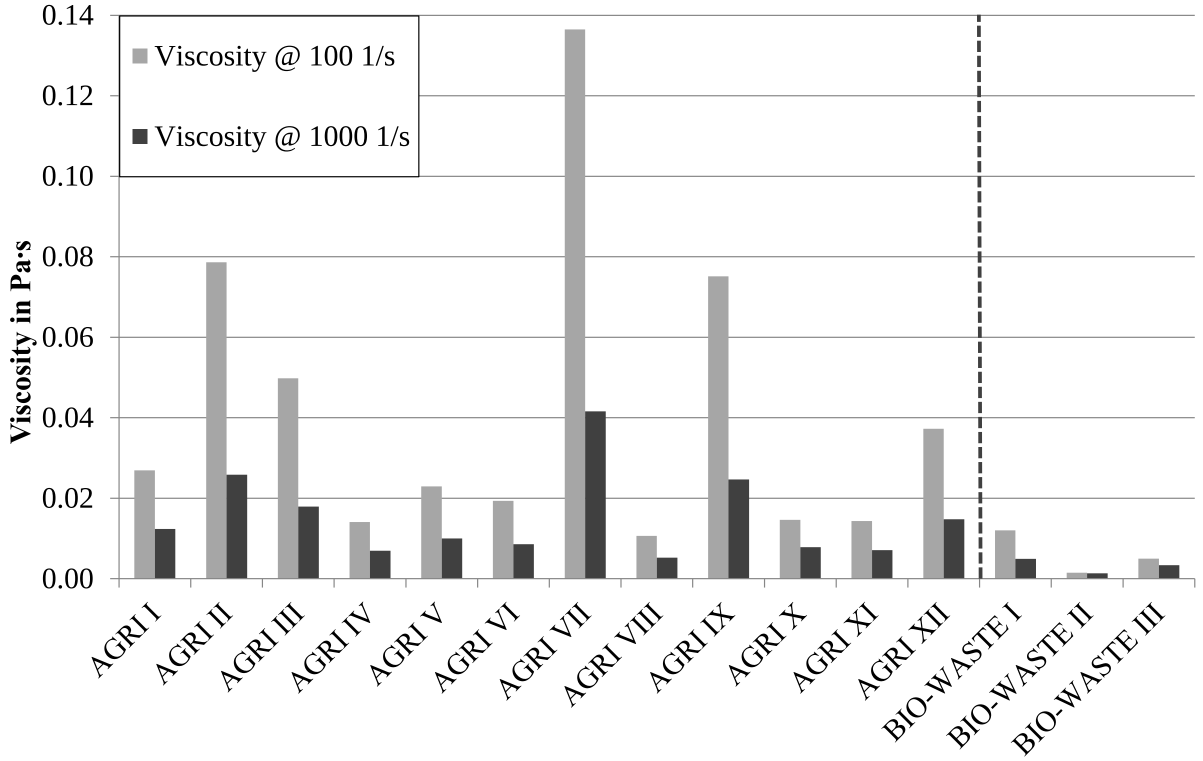

Figure 4: Viscosity at 20 °C of centrate from 12 AGRI and 3 BIO-WASTE biogas plants for different shear rates (RZB = 3493 g)

Values for the measurements of 100 s^{-1} are in every case higher than those for 1,000 s^{-1}, which underlines the shear thinning behaviour for all centrates. Between the low and high shear rate, the viscosity of AGRI and BIO-WASTE centrates decreases to 37.8 % and 52.2 % in average, respectively (Table 5). The large deviation of the values is evaluated by the standard deviation σ. For AGRI and BIO-WASTE centrates the standard deviations are in the order of magnitude of the value itself. The high deviation is caused by the alternating input material of the plants, the hydraulic retention time, the reaction temperature and many more characteristic parameters of the biogas plant.

Table 5: Averages and standard deviation σ of viscosity measured at 100 s^{-1} and 1000 s^{-1} for the different types of digestates (RZB = 3493 g)

Parameter	Unit	Average AGRI N = 15	σ AGRI N = 15	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

3.3 Filtration performance

The flux of the analysed centrates is given in Figure 5. BIO-WASTE centrates (black bars) are detected to have the highest flux values between 2.5 – 7.5 $L \cdot m^{-2} \cdot h^{-1}$. For AGRI centrates (grey) values are lower between 0.5 – 2 $L \cdot m^{-2} \cdot h^{-1}$. 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 are detected. Based on 2 – 6 different charges for one biogas plant, the centrates fluctuate in membrane performance up to 33.7 % (AGRI VII). This seasonal deviation is based on variations and through-put of input material. E.g., the flux of AGRI VII changed within a few months from 2.07 to 0.47 $L \cdot m^{-2} \cdot h^{-1}$, while increasing the share of maize from 62 % to 98 %, respectively. Mono fermentation of maize is thus suspected to lead to lower membrane performance caused by poorly degradable lignocellulose residues.

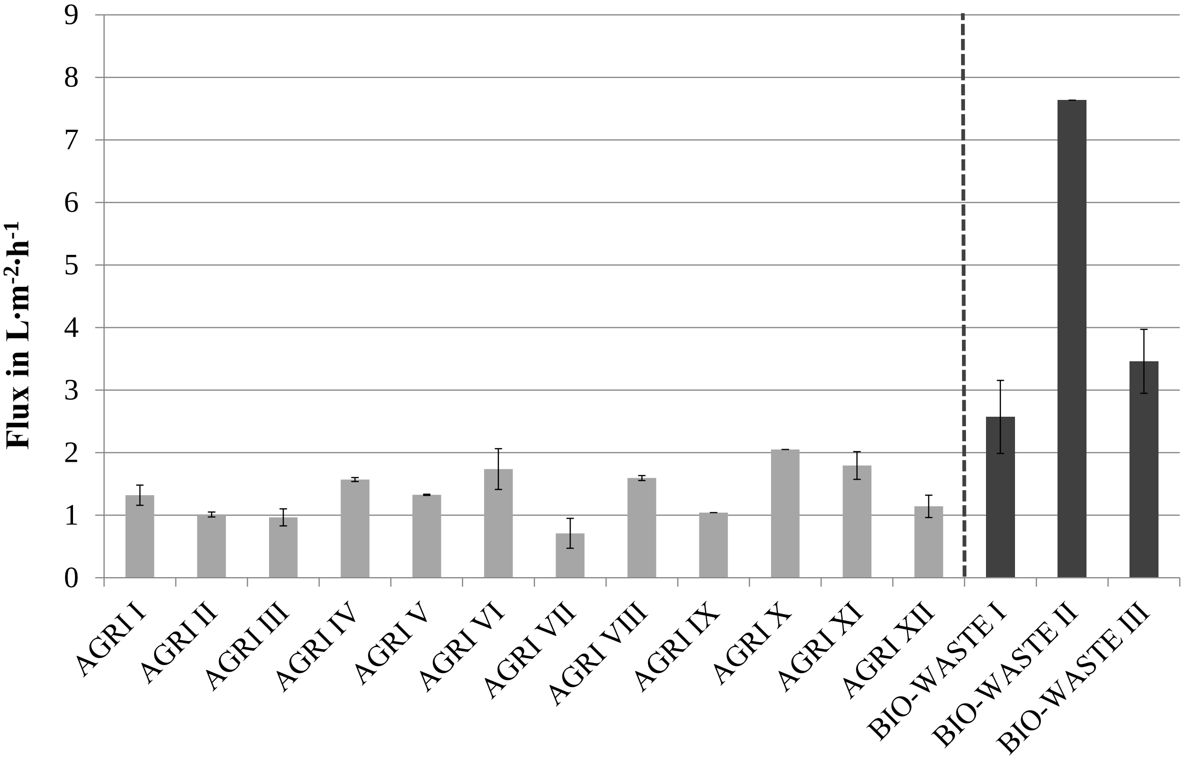

Figure 5: Flux of different centrates (RZB = 3493 g), UF 0.04 µm, 1 bar, 20 °C, rotational speed: 120 min^{-1}

The average flux of AGRI centrates and BIO-WASTE centrates are 1.38 $L \cdot m^{-2} \cdot h^{-1}$ and 3.86 $L \cdot m^{-2} \cdot h^{-1}$, respectively. Thus, the flux of BIO-WASTE centrates is factor 2.8 higher than compared to AGRI centrates. Moreover, the standard deviation is significantly higher for BIO-WASTE centrates with $\sigma = 1.8$ $L \cdot m^{-2} \cdot h^{-1}$ (AGRI: $\sigma = 0.39$ $L \cdot m^{-2} \cdot h^{-1}$).

3.4 Optimisation of membrane performance by pre-treatment

Main target of the optimisation was to decrease the shear-thinning centrate viscosity and accordingly increase the membrane performance in the ultrafiltration step of a total conditioning process. The outcome of biological pre-treatment by a mixture of different enzymes, i.e., amylase, cellulase, pectinase and protease (each 1 $g \cdot L^{-1}$), is demonstrated in Figure 6.With increasing incubation time, the centrate viscosity constantly decreases and the slope of the curve becomes more horizontally (more Newtonian). For very high shear rates (>

3000 – 5000 s^{-1}) Taylor vortices are noticeable.

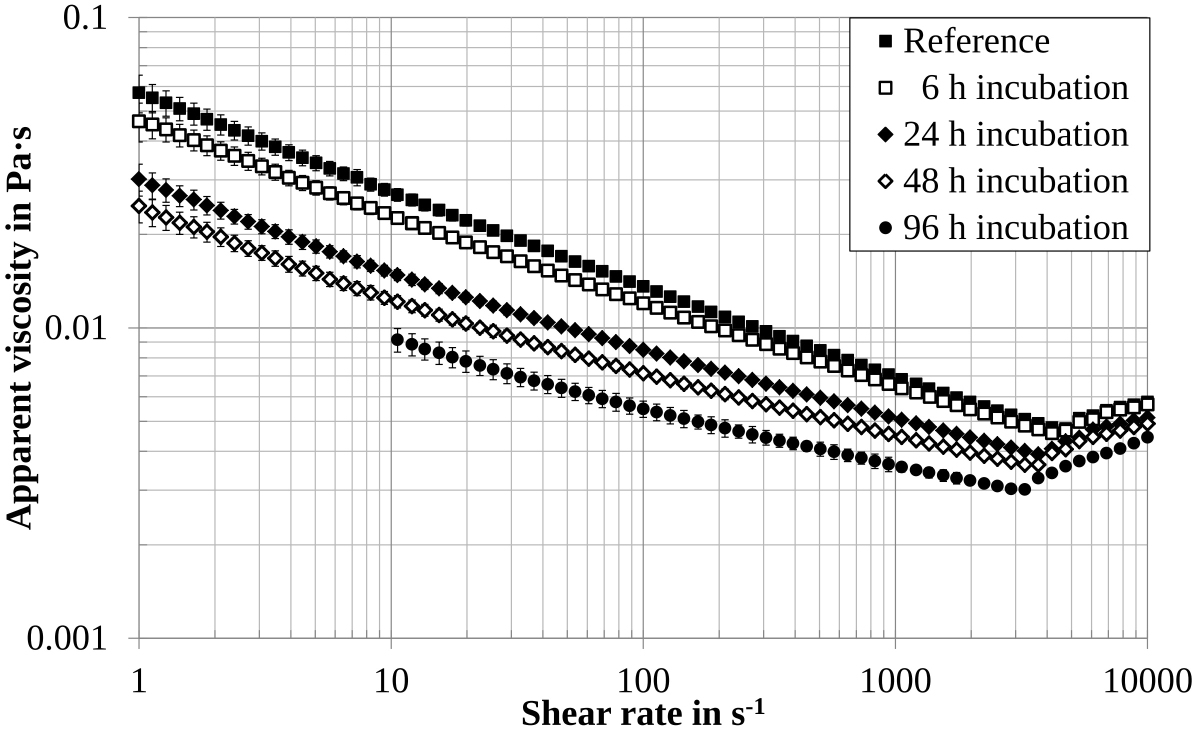

Figure 6: Apparent viscosity (20 °C) of AGRI III A with amylase, cellulase, pectinase and protease (each 1 $g \cdot L^{-1}$), pH = 4.8, incubation temperature 50 °C, rotational speed: 100 min^{-1}

The different centrates treated with enzymes were analysed with a LC-OCD (Figure 7). After short retention times in the column, a bypass signal of the organic load was detected. The enzymatic treated material has a higher bypass signal because of the organic based enzymes. After about 40 minutes biopolymers were detected. The comparison of the reference and the treated material shows differences in the fractions of biopolymers, low molecular weight acids and low molecular weight neutrals. For the reference, higher peaks und thus higher concentrations of biopolymers were found. The treated material has lower concentrations of biopolymers but significantly higher concentrations in the smaller fractions of low molecular weight acids and neutrals. Due to enzymatic treatment a shift from large to smaller particles was detected. Obviously, the smaller fractions appear to have lower viscosities than large and steric biopolymers.

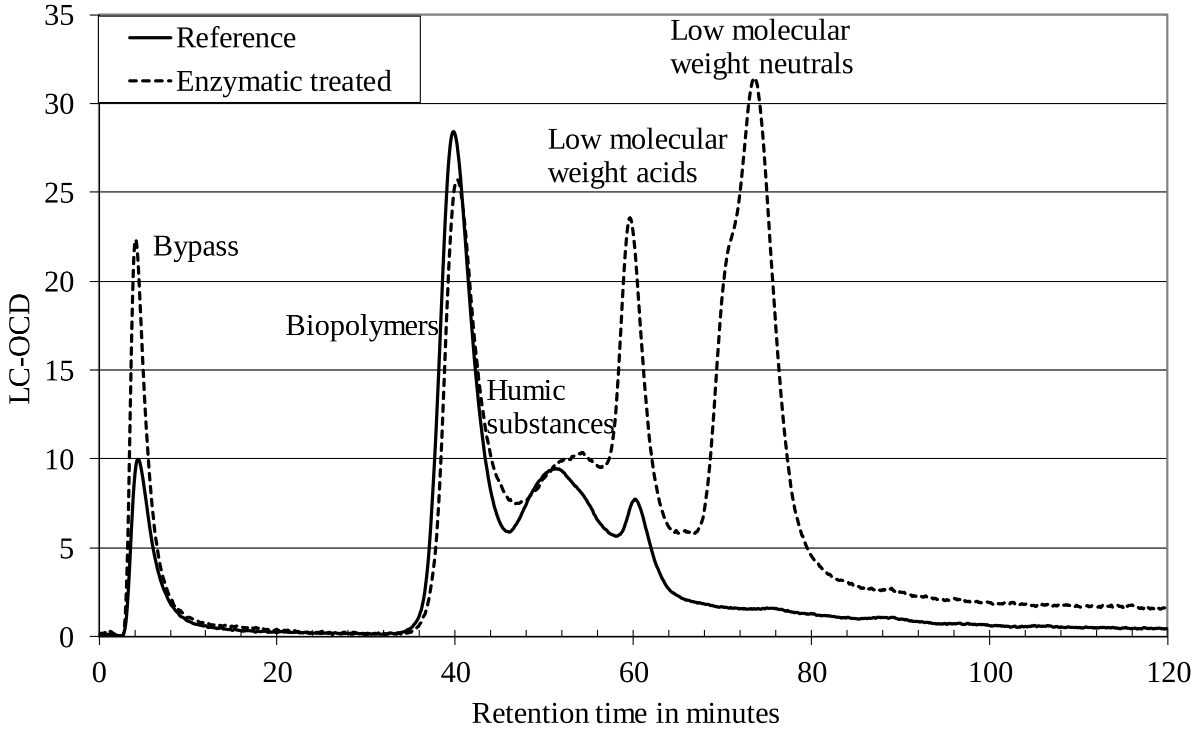

Figure 7: LC-OCD analysis for enzymatic treatment, pH = 4.9, incubation temperature 50 °C, incubation time 43 h, rotational speed: 100 min^{-1}

Furthermore, the flux of the reference and the treated centrate (after 48 h) were analysed with the Amicon test cell. The flux of the reference was 1.1 $L \cdot m^{-2} \cdot h^{-1}$, the flux of the treated material after 48 h incubation time was 3.1 $L \cdot m^{-2} \cdot h^{-1}$. By using enzymes it was thus possible to improve both viscosity and membrane performance by a factor of 2.8.

3.5 Energetic potential of the 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. Main problem is the high velocity needed to ensure high shear strain to control the filter cake. Often, module velocities of about $\bar{v}$ = 3 – 5 m·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 Equation *3*.

$$P_{el} = \frac{\Delta p \cdot \dot{Q}}{\eta_{pump}} \qquad (Eq.\ 3)$$

Turbulent flow conditions in tubular ultrafiltration modules require Reynolds numbers Re > 2,300. The definition of the Reynolds number for non-Newtonian fluids Re_{n-N} is given in Equation *4*, while the shear dependent viscosity of digestate and centrate is described by the power-law equation from Ostwald/ de Waele $\eta(\dot{\gamma}) = k \cdot \dot{\gamma}^{n-1}$.

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

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

$$\Delta p = \xi \cdot \frac{\rho}{2} \cdot \bar{v}^{2} \cdot \frac{L}{d} \qquad \rightarrow \Delta p \sim \bar{v}^{2} \qquad (Eq.\ 5)$$

$$\xi = \frac{64}{Re_{n-N}} \qquad \rightarrow \xi \sim \frac{1}{\bar{v}^{2-n}} \qquad (Eq.\ 6)$$

$$\dot{Q} = \bar{v} \cdot A \qquad \rightarrow \dot{Q} \sim \bar{v} \qquad (Eq.\ 7)$$

$$\rightarrow P_{el} \sim \bar{v}^{1+n} \qquad (Eq.\ 8)$$

The combination of all single terms (Eq. *8*) give a relation of the electrical power input of $P_{el} = v^{1+n}$. The power-law index *n*, according to the viscosity model of Ostwald/ de Waele, has values between 0 < n < 1 for shear-thinning fluids. For digestate centrates, the power-law index is 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 zeta decreases and accordingly the influence of velocity on the pump's power demand even increases. Turbulent flow with Reynolds numbers > 2,300 is a necessary precondition for successful membrane filtration.

Based on the reduction of the viscosity with enzymes (Figure 6), the relative electrical power input for a Reynolds number of 2,300 can be calculated. For the reference (untreated centrate) the power-law index is n = 0.71 and the consistency factor is k = 0.0525 $Pa \cdot s^{0.709}$. The enzymatically treated sample after 96 h has values of n = 0.828 and k = 0.0118 $Pa \cdot s^{0.828}$, heading to Newtonian behaviour (n = 1). To achieve a Reynolds number of 2,300, the velocity calculates to 2.92 $m \cdot s^{-1}$ and 1.97 $m \cdot s^{-1}$ for the untreated and treated material, respectively. The relative power input is calculated in *Eq. 9.*

$$\theta_{el} = \frac{P_{el}, after}{P_{el}, before} = \frac{1.97^{1+0.83}}{2.92^{1+0.71}} = 0.553 = 55.3\ \% \qquad (Eq.\ 9)$$

By modifying the rheological behaviour it is possible to save about 45 % of the needed pumping energy for the same flow conditions.

4 Conclusion

New regulations of the fertiliser law in Germany require an adequate separation technique for digestates to separate the main nutrient fractions. The total conditioning process by decantation, ultrafiltration, and reverse osmosis is a preferred option in terms of throughput and water quality. For fertiliser production, membrane technique is useful because of its solid phosphorous fertiliser and liquid nitrogen/ potassium fertiliser. Often, agricultural fields have different demands in phosphorous or nitrogen. With about 50 – 70 % of the total process energy, most of the process energy consumption results from pumping energy within the ultrafiltration step. The viscosity of the centrate has a strong influence on the flux of the ultrafiltration membrane and accordingly on the total energy demand. Process optimisation, e.g., the demonstrated enzymatic pre-treatment of the centrate, can reduce the overall viscosity as well as the shear thinning properties of the centrate. The exemplarily shown pre-treatment results in energy savings of 45 % of the required pumping energy for turbulent flow conditions within the ultrafiltration modules. Optimisation of the fluid characteristics and control of fluid dynamics were shown to offer great potential for energy savings.

Acknowledgements

This research project is supported and financed by German Federal Environmental Foundation (Deutsche Bundesstiftung Umwelt). The scientific research was organised at Osnabrück, University of Applied Science in cooperation with the company A3 Water Solution GmbH. Furthermore, the authors thank for the cooperation for LC-OCD analysis done at the Technical University of Berlin- Department of Water Engineering.

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