Vacuum Evaporation of Liquid Fraction of Digestate

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Abstract

The aim of this work was to reduce the strain on a biogas plant by reducing the hydraulic pressure during winter using the technique of two-stage vacuum evaporation. In the first stage, the target was to concentrate as much as possible aqueous ammonium ions (NH_4^+) in condensate and neutralize it with sulfuric acid (H_2SO_4). Ammonium sulphate ($(NH_4)_2SO_4$), or AS, resulting as a product from neutralization, is an inorganic salt that can be used as a fertilizer. Since the ammonium ion content in AS is low and the volume of solution is high, transport costs are considerably high. Therefore, a second stage was needed to reduce the volume of water and concentrate the salt to an acceptable limit, determined by the mass fraction of AS, *i.e.* 35 %. The parameters of evaporation (temperature, pressure, pH values) were changed in order to find the best conditions for evaporation, and determine whether AS can be successfully used as a fertilizer. Based on experimental results, the mass balances of vacuum evaporation were calculated.

During the characterization of digestate sampled at different times, it was found that the physical and chemical characteristics fluctuate, particularly the ammonia content. This confirmed the high dependence of digestate characteristics on the conditions of anaerobic digestion. During the first stage of evaporation at 40 °C, the pH value of the digestate had not changed and remained at 7, meaning that all ammonia was in its volatile form and had converted to condensate during the process. The dependence of the evaporation rate on the concentration of the solute, *i.e.* ammonia, was established. The rate is higher at lower solute concentrations. After the neutralization of the first stage condensate, the AS content was 0.61 %. During the second stage of evaporation, the desired AS limit of 35.62 % in the concentrate was reached at 40 °C and pH 5. The AS content in the second stage condensate was 0.12 %.

On the basis of laboratory experiments, it was found that the fraction of first stage condensate based on the input of digestate was 76 % and the fraction of first stage concentrate was 24 %. After the second stage, the fraction that passed into the second stage concentrate, *i.e.* AS solution, was 8 %, while the fraction in the second stage condensate, *i.e.* clean water, was 92 %.

Keywords

Digestate, vacuum evaporation, synthetic fertilizer

1 Introduction

Digestate is a by-product of anaerobic digestion of animal and plant residue. It contains a considerable proportion of inorganic mineral elements (nitrogen, phosphorus, potassium), organic matter, and microbial biomass. Its composition and nutrient absorption kinetics are highly similar to mineral fertilizers. Therefore, digestate could be used effectively as a replacement fertilizer to improve soil fertility, plant quality, and resistance of plants to biotic and abiotic factors, considering that the pathogenic micro-organism content was low. It could also reduce the consumption of fossil fuels, which are used for the production of mineral fertilizers.[1]

Due to the high mass percentage of water in digestate, which may exceed 90 %, further processing is required. The water content increases the mass of digestate and consequently the storage and transport costs per unit of the product. Moreover, the nutrient concentration is lower compared to that of chemical fertilizers, which means that larger quantities of digestate need to be applied to land to achieve the same effect of fertilization as chemical fertilizers.[2,3] Another problem associated with digestate application is represented by the four seasons. The use of digestate is limited in late autumn and during winter due to the inactivity of nature. In order to prevent overburdening of soil due to loading of unused mineral elements, as well as the environmental pollution, digestate must be stored.[4,5] Digestate is therefore separated into a liquid fraction, rich in potassium and inorganic nitrogen, and a solid fraction, rich in organic carbon and phosphorus.[4]

Liquid fraction of digestate still contains considerable amounts of water after separation.[2] Therefore, further processing of liquid fraction is required. The aim of this work was to reduce the strain on a biogas plant by reducing the hydraulic pressure during winter, *i.e.* storage tank volume, using the technique of two-stage vacuum

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evaporation. Evaporation is a process where the solution is concentrated by evaporation of the solvent. In the case of vacuum evaporation, the process is carried out at a reduced pressure that is lower than atmospheric pressure. Consequently, the boiling temperature of the solution is lower, resulting in energy savings and the possibility of evaporation of otherwise thermally sensitive substances.[6] In the first stage, the target was to concentrate as much as possible ammonium ions (NH_4^+) in condensate from liquid slurry, and neutralize it with sulfuric acid (H_2SO_4). Ammonium sulphate ($(NH_4)_2SO_4$), or AS, resulting as a product from neutralization, is an inorganic salt that can be used as a fertilizer. Since the ammonium ion content in AS is low and the volume of solution is high, transport costs are considerably high.

Therefore, a second stage was required to reduce the volume of water and concentrate the salt to an acceptable limit, determined by the mass fraction of AS, *i.e.* 35 %. By changing the parameters of evaporation (temperature, pressure, pH values), we tried to find the best conditions for evaporation and, in accordance with the law, determined whether AS could be successfully used as a fertilizer. Based on experimental results, we also calculated the mass balances of vacuum evaporation.

2 Experimental design

The following methods were used to characterize the digestate:

- spectrophotometric determination of PO_4^{3-} and NH_4^+ ions,
- determination of dry matter content,
- measurement of opacity and spectrophotometric determination of colour,
- measurement of conductivity and pH value, and
- AES determination of K^+ and Na^+ ions.

For sample analysis before, during, and after evaporation, the following methods were used:

- spectrophotometric determination of NH_4^+ ions,
- measurement of conductivity and pH value, and
- determination of SO_4^{2-} ions with ion exchange chromatography (IEX).

2.1 Turbidity and colour

The turbidity of digestate was determined with a laboratory turbidimeter 2100P (Hach). The colour of digestate was determined spectrophotometrically with a UV/VIS spectrophotometer. Absorbance (A) was measured at 254 nm and 436 nm. Samples were diluted appropriately.

2.2 pH and conductivity

The pH value was measured with pH meter Multi 3410 (WTW) and electrical conductivity (κ) was measured using a conductometer LF 537 (WTW) in samples of digestate, condensate, and concentrate from the first and second stages of evaporation.

2.3 Dry matter

Dry matter content (TS) was determined in samples of digestate. The sample was placed in a dryer for about 2 h at 105 °C. After drying, the sample was left in a desiccator until it reached ambient temperature (approximately 30 min). Percentage of TS was calculated using Eq. 1.

$$TS = \frac{m_{\text{sample after drying}} - m_{\text{crucible}}}{m_{\text{sample before drying}} - m_{\text{crucible}}} \cdot 100 \qquad (1)$$

2.4 Acid digestion

Digestate was treated with acid digestion using HNO_3 to prepare it for further analysis. The method is in accordance with ISO15587-2:2002. Samples were diluted due to foaming.

2.5 Spectrophotometric determination of phosphate and ammonium ions

For the spectrophotometric determination of phosphate ions (PO_4^{3-}) in digestate after sample preparation with acid digestion, the method according to ISO6878:2004 was used. Phosphate ions were determined with ammonium molybdate in an acidic medium at 865 nm using an UV/VIS spectrophotometer. The calibration curve (Fig. 1) was prepared using potassium dihydrogen phosphate as standard solution. For the spectrophotometric determination of ammonium ions (NH_4^+) in samples of digestate, condensate, and concentrate after evaporation, we used the method according to ISO7150-1:1984. The method is based on the reaction of ammonium ions with salicylate and hypochlorite in the presence of sodium nitroprusside. Samples were appropriately diluted and filtered to remove any solids. Absorbance was measured at 655 nm using an UV/VIS spectrophotometer. The calibration curve (Fig. 2) was prepared using ammonium chloride as standard solution.

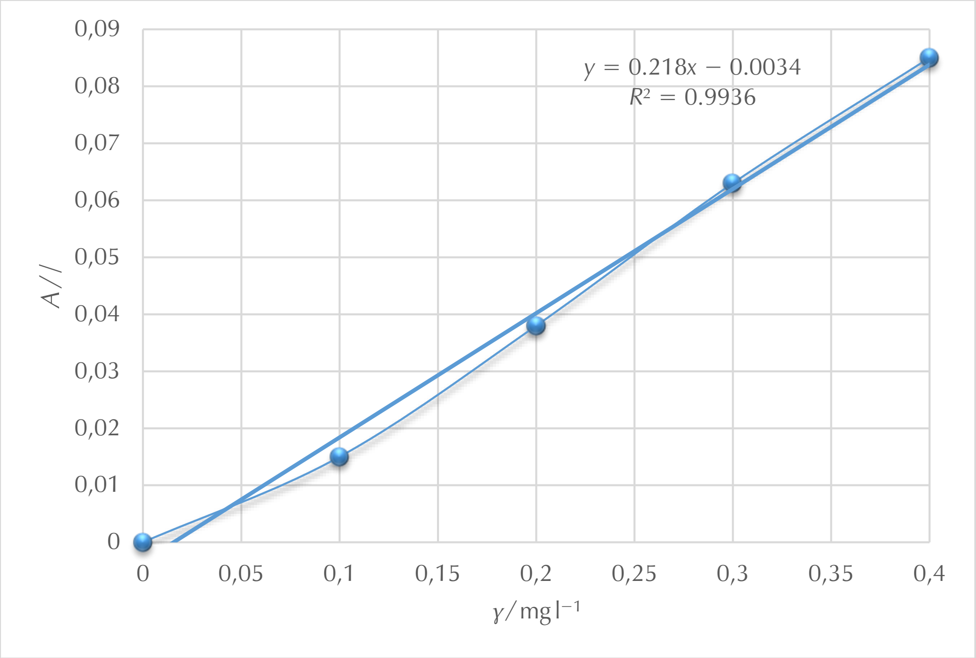

Fig. 1 – Calibration curve for determination of phosphate ions
Slika 1 – Baždarna krivulja za određivanje fosfatnih iona

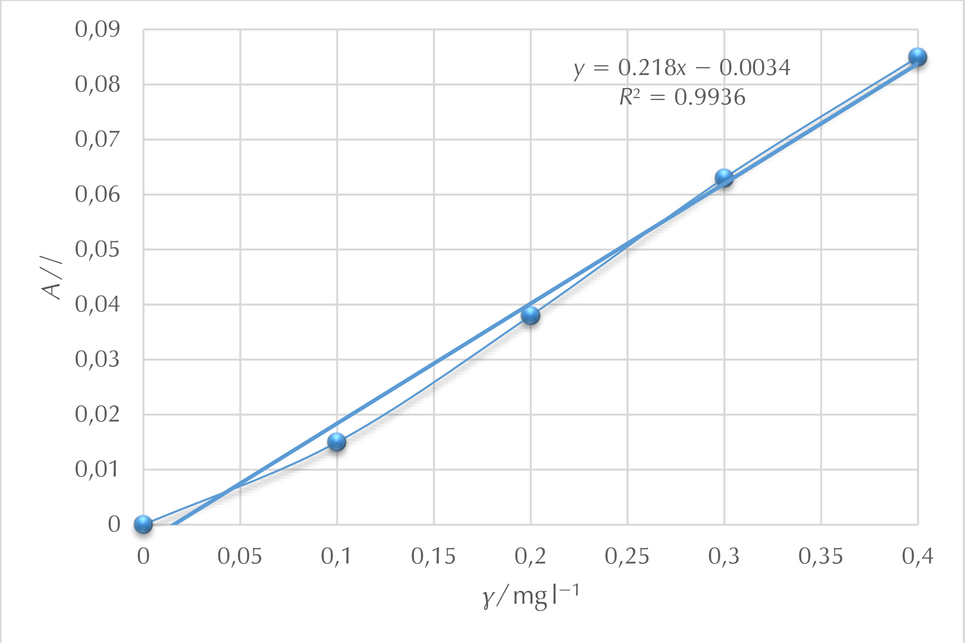

Fig. 2 – Calibration curve for determination of ammonium ions
Slika 2 – Baždarna krivulja za određivanje amonijevih iona

2.6 Determination of potassium ions using atomic emission spectroscopy

The concentration of potassium ions (K^+) in digestate after acid digestion was determined spectroscopically with atomic emission spectroscopy (AES) in accordance with DIN 38406-E13:1992. The calibration curve (Fig. 3) was prepared using potassium chloride as standard solution.

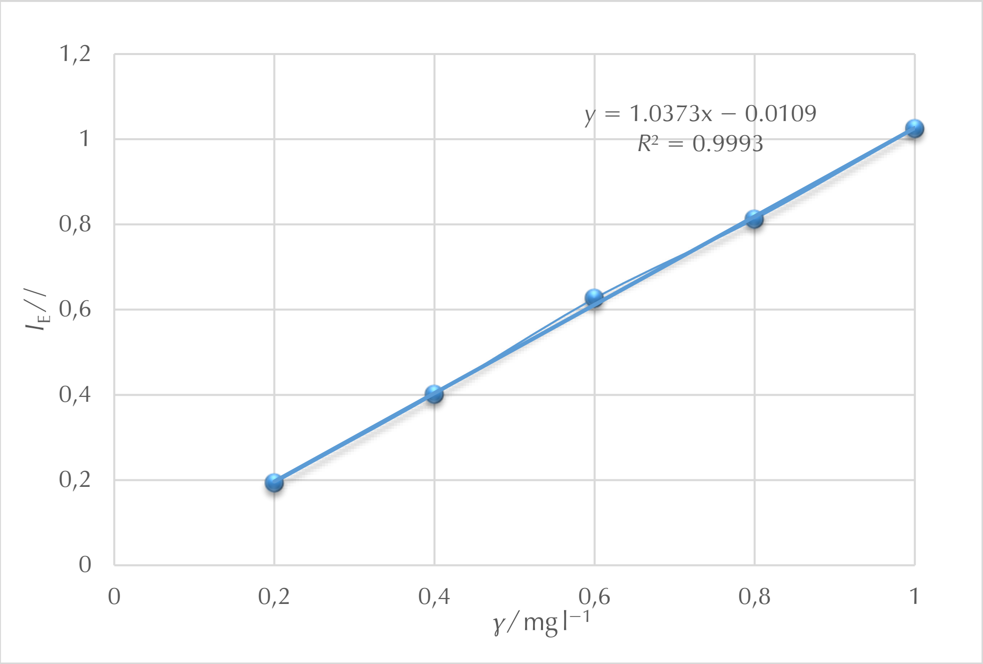

Fig. 3 – Calibration curve for determination of potassium ions

Slika 3 – Baždarna krivulja za određivanje kalijevih iona

2.7 Determination of sulphate ions

Sulphate ions (SO_4^{2-}) were determined in samples of condensate and concentrate after evaporation using ion exchange chromatography (IEX). The concentration of ions was calculated according to the obtained results from standard measurement. The method is in accordance with ISO10304-1:2007.

2.8 Vacuum evaporation

Experiments were carried out using a laboratory rotary evaporator. In the first step of evaporation, 200 ml of liquid digestate was added in a round bottomed flask. The experiments were carried out under vacuum at 40 °C and 72 mbar. The pH value of digestate was not adjusted, since it was high enough (approximately 8.1) for ammonia to be in its volatile form, enabling it to evaporate with water into first stage condensate. First stage of evaporation lasted until the last droplet of water was condensed, that is, 210 min.

The first stage condensate was then neutralized using sulphuric acid (H_2SO_4), thereby obtaining ammonium sulphate (AS), which was later introduced to a second evaporation stage. The second stage of evaporation was carried out at various temperatures and corresponding pressures (40 °C and 7 mbar, 60 °C and 200 mbar) and pH values (2, 4, and 5). Optimal conditions were searched for concentrating AS. Change in mass, volume, pH value, conductivity, ammonium ion concentration, and sulphate ion concentration were observed at 15-min intervals. Evaporation of second stage lasted 60 min.

3 Results and discussion

3.1 Characterization of liquid fraction of digestate

Table 1 shows the results of the characterization of the liquid fraction of digestate. During the experimental work, different digestates were sampled and analysed, all produced under the same conditions. In this and subsequent tables, the temperatures in the brackets signify the temperatures at which the corresponding, temperature dependant parameters were measured. In digestate 3, the ammonia content was the lowest. During sampling of digestate 3, the fermenter was emptied and cleaned. Therefore, we concluded that operating conditions had not achieved steady state equilibria for optimal functioning of microorganisms, which resulted in a lower rate of anaerobic digestion and consequently lower ammonia content.

This is implied by higher content of TS and a higher absorbance at 254 nm (where we determined the colour rate of organic substances). The fluctuation of ammonia levels could also be a consequence of the variation of the composition of substrate. Chicken manure contains high concentrations of nitrogen; therefore, it should be mixed with silage to lower its content.

The phosphate levels are dependent only on the composition of substrates and independent of anaerobic digestion. The phosphate levels in digestate 3 were very high, therefore we concluded that the low content of ammonia may also be influenced by substrate composition.

3.2 First stage vacuum evaporation results

Table 2 shows the results of the characterisation of condensate after first stage evaporation. The head of the table marks the conditions at which the samples were used in second stage evaporation, as well as which digestate was used. The results show that the maximum amount of aqueous ammonia solution had evaporated in samples of digestate 3, which were later used in second stage evaporation at 40 °C and pH 4 and 5, and also at 60 °C at pH value of 4. In these samples, the lowest amount of ammonia was determined.

Table 1 – Characterization of liquid fraction of digestate
Tablica 1 – Karakterizacija tekuće frakcije digestata

Digestate Digestat	pH	κ / mS cm^{-1}	TS /%	Turbidity Turbiditet /NTU	Colour Boja		$\gamma(NH_4^+)$ / mg l^{-1}	$\gamma(PO_4^{3-})$ / mg l^{-1}	$\gamma(K^+)$ / mg l^{-1}	$\gamma(Na^+)$ / mg l^{-1}
					254 nm	436 nm				
1	8,17 (24.3 °C)	30 (24.9 °C)	6.56	26300	234	243	2662	5858	3027	440
2	8,12 (18.5 °C)	29 (19.7 °C)	6.25	28600	240	225	2624	5080	3595	500
3	8,07 (9.8 °C)	29 (12.8 °C)	6.77	24300	370	180	1085	7151	3552	460

Table 2 – Results of the characterisation of condensate after first stage evaporation
Tablica 2 – Rezultati karakterizacije kondenzata poslije prve faze uparavanja

	40 °C			60 °C		
	pH=5	pH=4	pH=2	pH=5	pH=4	pH=2
Digestate sample number *Broj uzorka digestata*	3	3	2	1	3	2
pH	9.88 (15.1 °C)	9.74 (20.6 °C)	9.18 (21.9 °C)	9.60 (22,0 °C)	9.69 (21.2 °C)	9.64 (21.8 °C)
κ/mS cm^{-1}	2.19 (14.9 °C)	2,20 (20,8 °C)	8.15 (22.1 °C)	7.38 (22.6 °C)	3.10 (21.5 °C)	6.68 (24.4 °C)
m/g	155.3	176,4	133.7	152.4	172.8	145.3
V/ml	155	174	128	152	175	144
$\gamma(NH_4^+)$/mg l^{-1}	1724	1722	5329	3409	2600	3929

3.3 Second stage vacuum evaporation results

During second stage of vacuum evaporation, the mass and volume of condensate and concentrate showed linear behaviour, while the content of ammonia and percentage of AS showed exponential behaviour. After neutralization with H_2SO_4, conductivity increased since the conductivity of sulphate ions is higher than that of ammonia ions. Conductivity in concentrate samples increased with time, since the AS content was being concentrated. The pH value also increased with time in concentrate. The condensates contained very low ammonia concentrations, maximum 16 mg l^{-1}. Conductivity (maximum 85 µS cm^{-1}) was also low. Therefore, we concluded that the condensate was clean water, which could be used as technical water in other process units. The desired AS content was reached at 40 °C and pH 5 after 60 min of evaporation. However, due to the low volume, a measurement and calculation error is possible. Since the volume of concentrate at these conditions was very low, pH and conductivity measurement were not possible. Table 3 and Table 4 show the results after vacuum evaporation in concentrate and condensate at 40 °C and pH 5. Fig. 4 shows AS content with time at 40 °C, and Fig. 5 at 60 °C in concentrate samples.

Table 3 – Characteristics of concentrate during second stage evaporation at 40 °C and pH=5
Tablica 3 – Karakteristike koncentrata za vrijeme druge faze uparavanja pri 40 °C i pH 5

t/min	pH	κ / µS cm^{-1}	m/g	V/ml	$\gamma(NH_4^+)$ / mg l^{-1}	$\omega((NH_4)_2SO_4)$/%	$\gamma(SO_4^{2-})$ / mg l^{-1}
0	4.81 (19.6 °C)	6490 (20.2 °C)	154.3	158	1623	0.61	–
15	5.38 (36.7 °C)	9680 (36.8 °C)	105.8	105	2061	0.75	–
30	4.75 (34.5 °C)	13140 (34.4 °C)	64.1	63	3275	1.18	–
45	4.31 (30.8 °C)	31300 (28.2 °C)	22.5	21	7403	2.53	33631
60	–	–	1.1	1	106864	35.62	569343

Table 4 – Characteristics of condensate during second stage evaporation at 40 °C and pH=5
Tablica 4 – Karakteristike kondenzata za vrijeme druge faze uparavanja pri 40 °C i pH 5

t/min	pH	κ/ µS cm^{-1}	m/g	V/ml	$\gamma(NH_4^+)$/mg l^{-1}	$\omega((NH_4)_2SO_4)$/%
15	8.90 (29.1 °C)	27 (28.5 °C)	42.7	42	14	0.12
30	8.96 (27.7 °C)	24 (27.5 °C)	78.4	78	12	0.05
45	7.78 (26.2 °C)	27 (26.5 °C)	114.8	104	10	0.03
60	7.56 (25.3 °C)	27 (24.9 °C)	130.5	132	10	0.03

Since the desired AS limit was reached only at 40 °C and pH 5, other data was extrapolated. The extrapolation was exponential. Equations 2–6 show the calculation of the evaporation time required to reach 35 % of AS. The equations are based on the extrapolation of experimental curves depicted in Figs. 4 and 5. The calculated times are purely theoretical. In practice, at laboratory levels due to low volumes of concentrate, it is not attainable. We concluded that the initial concentration of ammonia in liquid slurry was not high enough to reach the desired AS concentration.

$$t_{\mathrm{pH=4}} = \frac{\ln(\frac{35}{0.0744})}{0.0852} = 72\ \mathrm{min} \qquad (2)$$

$$t_{\mathrm{pH=2}} = \frac{\ln(\frac{35}{1.3254})}{0.0148} = 221\ \mathrm{min} \qquad (3)$$

$$t_{\mathrm{pH=5}} = \frac{\ln(\frac{35}{0.8433})}{0.0212} = 176\ \mathrm{min} \qquad (4)$$

$$t_{\mathrm{pH=4}} = \frac{\ln(\frac{35}{0.705})}{0.0112} = 349\ \mathrm{min} \qquad (5)$$

$$t_{\mathrm{pH=2}} = \frac{\ln(\frac{35}{1.1323})}{0.0134} = 256\ \mathrm{min} \qquad (6)$$

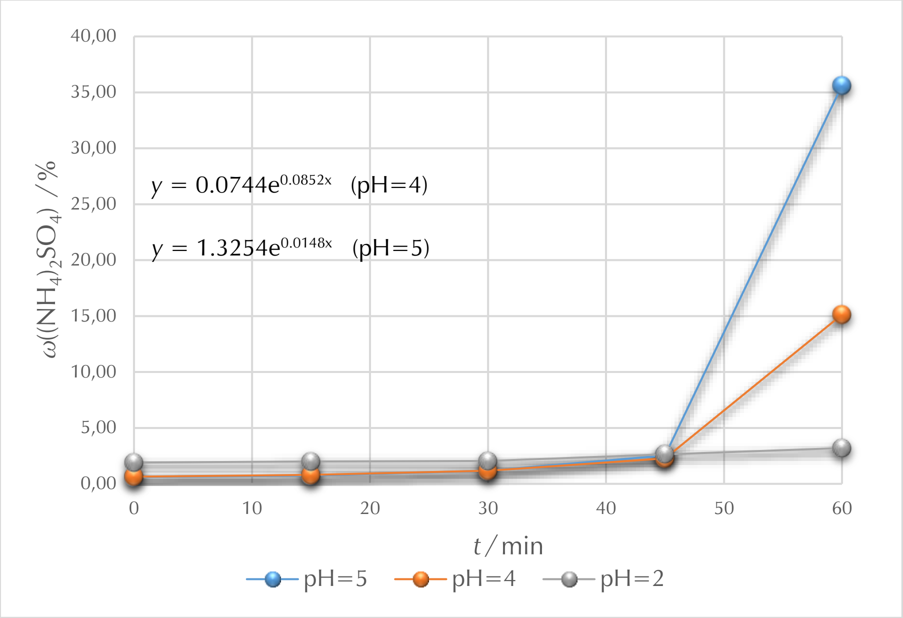

Fig. 4 – AS content in concentrate at 40 °C

Slika 4 – Udjel AS u koncentratu pri 40 °C

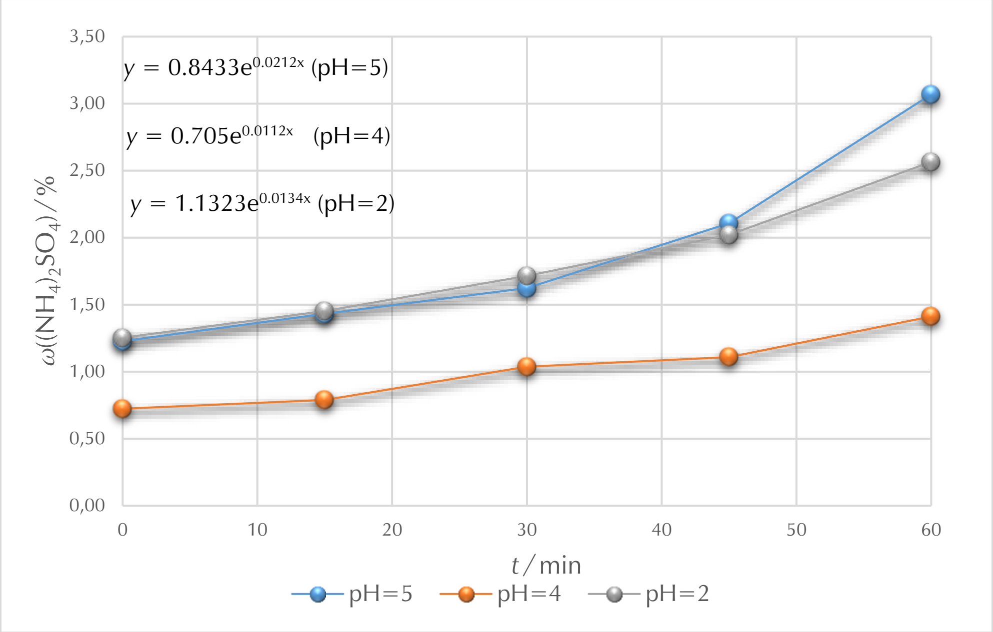

Fig. 5 – AS content in concentrate at 60 °C

Slika 5 – Udjel AS u koncentratu pri 60 °C

3.4 Mass balances

The mass balances of evaporation were calculated based on the optimal experimental conditions, *i.e.*, at 40 °C and pH 5. The process diagram of two-stage vacuum evaporation with mass balances is shown in Fig. 6. Based on laboratory experiments, we found that the fraction of first stage condensate based on the input of digestate was 76 % and the fraction of first stage concentrate was 24 %. After the second stage, the fraction that passed into the second stage concentrate, *i.e.* AS solution, was 8 %, while the fraction in the second stage condensate, *i.e.* clean water, was 92 %.

If we transfer our findings to a practical case, the data is as follows: The biogas plant produces annually approximately 20000 t a^{-1} of liquid digestate.

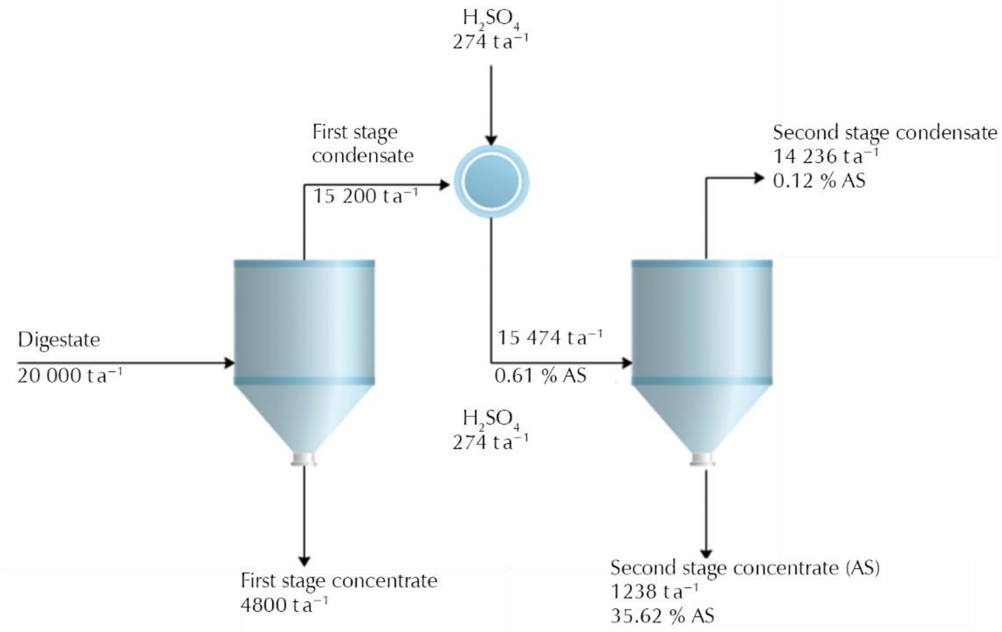

Fig. 6 – Process flow diagram of a two-stage evaporation system with mass balances
Slika 6 – Dijagram toka procesa dvostupanjskog uparavanja s pripadajućom bilancom tvari

At the first stage of evaporation, the amount of condensate is 15200 t a^{-1} and the amount of concentrate 4800 t a^{-1}. After the second evaporation step, the amount of condensate is 14236 t a^{-1} and the amount of concentrate 1238 t a^{-1}.

4 Conclusion

During the characterization of digestate sampled at different times, was found that the physical and chemical characteristics fluctuate, particularly the ammonia content. This confirmed the high dependence of digestate characteristics on the conditions of anaerobic digestion. During the first stage of evaporation at 40 °C, the pH value of the digestate had not changed (pH = 7), meaning that all ammonia was in its volatile form and had converted to condensate during the process. We established the dependence of the evaporation rate on the concentration of the solute, *i.e.* ammonia. The rate is higher at lower solute concentrations. After the neutralization of the first stage condensate, the AS content was 0.61 %. During the second stage of evaporation, the desired AS limit of 35.62 % in the concentrate was reached at 40 °C and pH 5. The AS content in the second stage condensate was 0.12 %.

Based on laboratory experiments, we found that the fraction of first stage condensate based on the input of digestate was 76 %, and the fraction of first stage concentrate was 24 %. After the second stage, the fraction that passed into the second stage concentrate, *i.e.* AS solution, was 8 %, while the fraction in the second stage condensate, *i.e.* clean water, was 92 %.

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List of abbreviations and symbols
Popis kratica i simbola

A – absorbance, /
– apsorbancija, /
I_E – intensity of energy, /
– intenzitet energije, /
m – mass, g
– masa, g
pH – pH value, /
– pH vrijednost, /
V – volume, ml
– volumen, ml
γ – mass concentration, mg l^{-1}
– masena koncentracija, mg l^{-1}
λ – wavelength of light, nm
– valna duljina svjetla, nm
κ – conductivity, mS cm^{-1}
– vodljivost, mS cm^{-1}
ω – mass fraction, %
– maseni udjel, %

AS – ammonium sulphate
– amonijev sulfat
AES – atomic emission spectroscopy
– atomska emisijska spektroskopija
IEX – ion exchange chromatographyionsko-izmjenjivačka kromatografija
NTU – nephelometric turbidity unit jedinica nefelometrijskog turbiditeta
TS – total solids
– ukupne čvrste tvari
UV – ultraviolet spectrum
– ultraljubičasti spektar
VIS – visible spectrum
– vidljivi spektar

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SAŽETAK

Vakuumsko uparavanje kapljevite frakcije digestata

*Tajda Simonič** i *Marjana Simonič*

Cilj ovog rada bio je rasterećenje postrojenja za proizvodnju bioplina smanjenjem hidrauličkog tlaka tijekom zime primjenom dvostupanjskog vakuumskog uparavanja. U prvom stupnju cilj je što više povećati koncentraciju amonijevih iona u vodenoj otopini (NH_4^+) i neutralizirati ih sumpornom kiselinom (H_2SO_4). Amonijev sulfat ($(NH_4)_2SO_4$), skraćeno AS, koji nastaje kao proizvod neutralizacije, anorganska je sol koja se može upotrijebiti kao gnojivo. S obzirom na to da je koncentracija amonijevih iona u AS-u mala, a volumen otopine velik, troškovi transporta su znatni.

Radi toga je potrebno uvesti drugi stupanj uparavanja kako bi se smanjio volumen vode, a udjel AS-a povećao do prihvatljive vrijednosti 35 mas. %. Parametri procesa uparavanja (temperatura, tlak i pH) podešavani su kako bi se pronašli najbolji uvjeti i utvrdilo može li se AS uspješno upotrijebiti kao gnojivo. Na temelju eksperimentalnih rezultata izvedene su bilance tvari procesa.

Tijekom karakterizacije uzoraka digestata prikupljenih tijekom vremena provođenja eksperimenta utvrđeno je da se njegova fizikalna i kemijske svojstva kolebaju, a posebno udjel amonijaka. Time je potvrđen velik utjecaj svojstava digestata na uvjete anaerobne digestije. Tijekom prvog stupnja uparavanja pri 40 °C, pH vrijednost digestata iznosila je 7 i nije se mijenjala, što znači da je sav amonijak prisutan u hlapljivom obliku i tijekom procesa prelazi u kondenzat. Utvrđena je ovisnost brzine isparavanja o koncentraciji otopljene tvari, odnosno amonijaka. Brzina isparavanja je viša pri nižim koncentracijama. Poslije neutralizacije u prvom stupnju udjel AS-a bio je 0,61 %. Tijekom drugog stupnja, ciljani udjel AS-a postignut je pri 40 °C i pH = 5, a iznosio je 35,62 %. Udjel AS-a u kondenzatu drugog stupnja bio je 0,12 %.

Na temelju eksperimenta utvrđeno je da je udjel kondenzata temeljen na ulaznoj količini digestata 76 %, a koncentrata 26 %. Nakon drugog stupnja udjel koncentrata (otopina AS) temeljen na količini koncentrata prvog stupnja koji u njega ulazi iznosi 8 %, a udjel kondenzata (čista voda) 92 %.

Ključne riječi

Digestat, vakuumsko uparavanje, sintetičko gnojivo

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Faculty of Chemistry and Chemical Engineering
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