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THERMAL CONDITIONING OF CONTAMINATED DIGESTATE AT A LOCAL PIG FARM USING EXCESS HEAT FROM ANAEROBIC DIGESTION PROCESS

Eckhard Kraft* and Philipp Lorber*

*Faculty of Civil Engineering, Bauhaus-Universität Weimar (BUW), Germany

ABSTRACT

Anaerobic digestion of livestock effluents to produce bioenergy via methane is a well-established technology. Besides green electricity and thermal energy, anaerobic digestion also produces digestate which can be utilized as a plant fertilizer. This paper puts the quality of digestate in terms of xenobiotic micro-pollutants such as pathogens and veterinary pharmaceuticals at the centre of research. A demonstration unit for thermal conditioning was exclusively run with excess heat from the local combined heating and power station.

For all specific pathogens investigated, thermal conditioning had reduced the load to below 10 CFU per gram of fresh matter. This applies to coliforms, E. coli, enterobacteria, and enterococci, as well as to yeasts and moulds. The desired degradation of the digestate through the elimination of all xenobiotic loads e.g. chlortetracycline, enrofloxacin and lincomycin could not be completely achieved. The thermal treatment yet caused both increase and reduction of the corresponding concentrations. This can assumedly be attributed to biochemical metabolism which should be investigated further.

Key words*: anaerobic digestion, pig slurry, thermal conditioning, veterinary pharmaceuticals, pathogens*

INTRODUCTION

With around 9 700 biogas plants in operation in 2020 [Statista 2021] Germany can build on a wealth of experience in regard of anaerobic digestion. A large number of them are operated with focus on maximum electricity production as a result of the regulated remuneration. The thermal energy produced by the combined heating and power station (CHP) is often poorly utilised. In order to increase the profitability of existing biogas plants, the efficient utilisation of thermal energy is becoming more and more important. A decisive factor for increasing efficiency and profitability of biogas plants is the storage and distribution of heat potentials to nearby consumer structures. Between 2019 and 2021 the Bauhaus-Universität Weimar set up a pilot plant to use part of the surplus heat from the biogas process for a thermal conditioning of local contaminated digestate. The objective of the research project was to show that it is possible to not only aim for quantitative material flow and resource management, but also to provide qualitative conversion processes and conditioned end products respectively digestate that can be certified in the future.

Digestate, here, refers to fermentation residues of biogas plants. The quality of digestate has always been at the centre of various discussions in recent years. In addition to the well-known and popular macronutrients such as nitrogen (N), phosphorus (P), potassium (K) and sulphur (S), xenobiotic micro-pollutants such as pesticides and veterinary pharmaceuticals are playing an increasingly important role in fermentation residues. Moreover, so-called synthetic and environmentally alien detergents, environmental hygiene aspects such as phytopathogenicity and antibiotic resistance are progressively in the focus of research, society and politics. Research has once again shown that digestate from biogas plants is a good fertiliser and humus builder [FNR, 2018]. However, they do partly contain a variety of pollutants.

The series of trials was preceded by an extensive literature study on the degradation behaviour of pathogenic and xenobiotic agents [Kraft et al. 2021]. This paper presents the results of the field tests.

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METHODS

Location and site

In the biogas plant in Mörsdorf, Thuringia, the substrates pig manure, dry chicken manure and maize silage are fermented in two parallel treatment sections. The pig manure comes from the local pig farm, the other substrates are purchased. Usually the plant is fed with a total of about 90 m³ of pig manure, 15 m³ of chicken manure and 45 m³ of maize silage per day. The quantities can vary depending on the characteristic values like dry matter and organic dry matter and availability of the substrates. The fresh pig manure is added proportionally to both main fermenters and both secondary fermenters. A return of fermentation substrate from the secondary fermenters takes place both directly into the main fermenters and during feeding with chicken manure and maize silage in order to make these substrates pumpable. No flow meter is installed in the outlet of the covered final storage tank into the open disposal zone. However, it can be assumed that the total daily discharged volume corresponds to the input volume at about 150 m³. The analysis of characteristic values of input material, intermediates and fermentation products took place regularly throughout the entire project duration.

The biogas produced is fed from the main and secondary fermenter head spaces into the final storage facilities, where it is collected and mixed. An average methane content of about 58 % was recorded. The produced gas mixture is led to the three CHPs (2x 600 kW, 1x 625 kW) and burned.

System boundary and sample taking

In order to evaluate the results of the thermal conditioning by the demonstration unit, the system boundary must be clearly defined. This is an essential factor for describing efficiency and success. The following determinations were made for this purpose:

- the system boundary for thermal conditioning of digestate starts at the inlet of the demonstration unit and ends at the outlet of the same unit,
- only pure pharmaceutical substances and their changes in concentration are considered.

Currently no consideration can be given to metabolites of xenobiotic substances due to the large number of these. At the same time, the technical-analytical detection of most metabolites in heavily polluted matrices such as fermentation substrates is to a large extent new at the time of the investigation and is not possible within the framework of the research project. Samples for different input substrates and intermediate and final products are filled into 1000 ml sample bottles and transferred cooled to internal and external laboratories for analysis.

Demonstration unit

For the thermal conditioning of the fermentation residues, a demonstration unit was built on the site of the local partners pig farm. The unit essentially consists of the following four components (figure 1):

1) boiler
2) supply panel with a) water- and b) power supply
3) Compressor for operating the pneumatic valves
4) switch cabinet as control unit

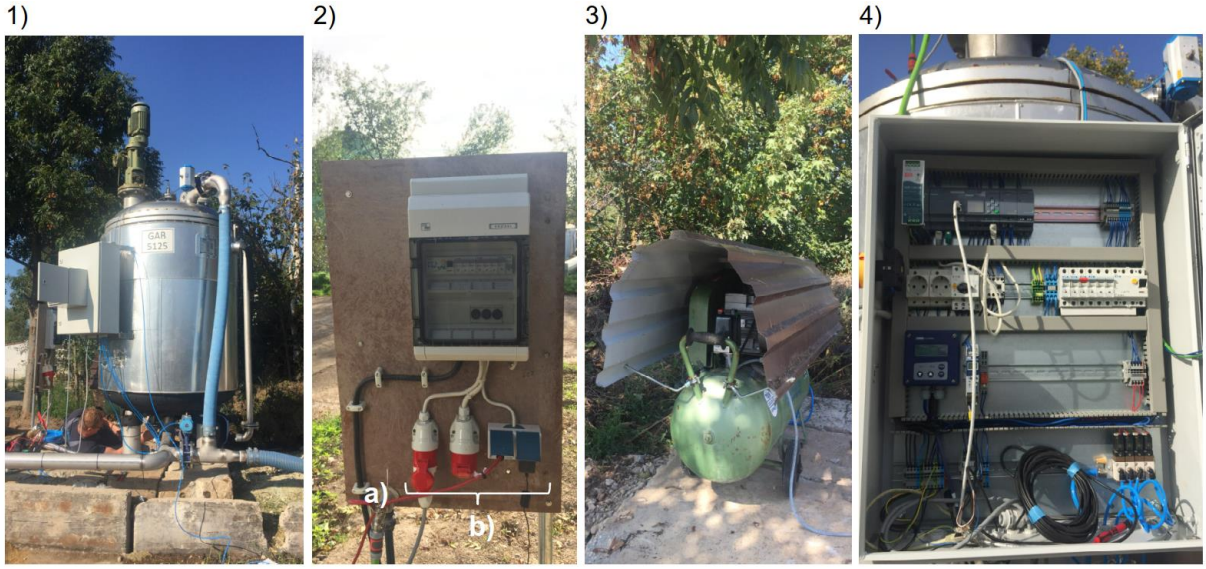
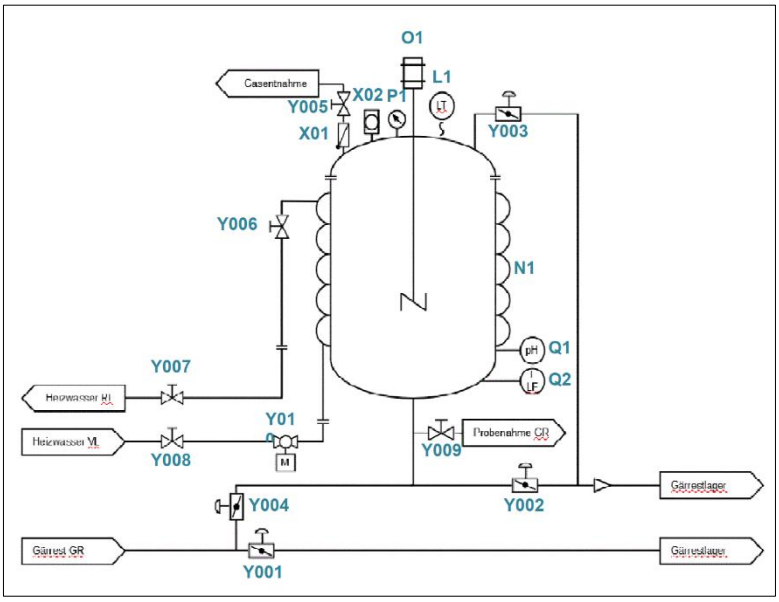


Figure 1: Components of the demonstration unit for thermal conditioning of digestate

The boiler consists of a converted stainless-steel tank with double jacket, insulation and a stirring device. Connections for measurement technology and control cabinet are integrated subsequently. The boiler has a volume of about 2 m^3. Pneumatic valves are used to fill and empty the boiler with fermentation residue. In the control cabinet attached to the boiler, measurement data on temperature, pH value, conductivity and filling level are recorded and visualised. The level measurement is radar-based. A schematic of the demonstration unit is shown in figure 2. Heat is supplied via a heating water circuit which is connected to the heat surplus of the CHP units via a heat exchanger.

Due to the experimental setup, the maximum heating of the boiler is limited by the heat supply of the heating circuit. The conditioning is tested at three different temperatures (60°C, 70°C and 80°C) where 80°C is the technical maximum. These three heating scenarios are applied to the different durations of 60, 120 and 300 min. This results in a matrix of nine different experimental configurations that are realised and carried out at the site.



With:

L1 fill level indicator (radar-based)
N1 heating jacket
O1 electrical stirring device
P1 pressure sensor
Q1 pH value sensor
Q2 conductivity and temperature sensor

X01 check valve
X02 inspection glass

Y001-004 pneumatic valves
Y005-009 manual valves
Y01 magnetic valve

Figure 2: Schematic of the demonstration unit

The success of the thermal treatment is to be determined by measuring the residual concentrations in the feed of the conditioning unit and the corresponding effluent. In this way, a direct comparison is made between the potential harmful effects that can still be contained in the fermentation product according to the current state of the art and the reduced contents that can still exist after thermal conditioning.

Detection of xenobiotic substances in digestate

To investigate the degradation and conversion behaviour of xenobiotics like antibiotics in pig slurry and digestate, a screening method is used that allows both qualitative and quantitative conclusions to be drawn about the content of the sample. Covering a broad spectrum of active substances of the wide range of antibiotics, the relevance for use in industrial livestock farming and the compensation of complex matrix effects form the basis for the analytical measurement method used. The focus is on characteristic representatives from the active substance classes of antibiotic anti-infectives; in particular tetracyclines, sulfonamides, ß-lactams, quinolones, macrolides as well as selected pleuromutils, aminoglycosides and amphenicols. An overview of all substances investigated is given in table 1.

Table 1: List of all substances initially analysed with its correspondent CAS Registry Number

Substance	***CAS RN***	***Substance***	***CAS RN***	***Substance***	***CAS RN***
Amoxicillin	26787-78-0	Dicloxacillin	3116-76-5	Penicillin G	61-33-6
Ampicillin	69-53-4	Doxycycline	564-25-0	Penicillin V	87-08-1
Cefalonium	5575-21-3	Enrofloxacin	93106-60-6	Spectinomycin	1695-77-8
Cefapirin	21593-23-7	Florfenicol	73231-34-2	Streptomycin	57-92-1
Cefoperazone	62893-19-0	Roxithromycin	80214-83-1	Sulfadiazine	68-35-9
Cefquinome	84957-30-2	Sulfadimethoxine	122-11-2	Sulfaguanidine	57-67-0
Ceftiofur	80370-57-6	Lincomycin	154-21-2	Sulfamethazine	57-68-1
Cefalexin	15686-71-2	Marbofloxacin	115550-35-1	Sulfamethoxazole	723-46-6
Chlortetracyclin	57-62-5	Minocycline	13614-98-7	Sulfaquinoxaline	59-40-5
Ciprofloxacin	85721-33-1	Nafcillin	985-16-0	Tetracycline	60-54-8
Clarithromycin	81103-11-9	Neomycin	1404-04-2	Tiamulin	55297-95-5
Clindamycin	18323-44-9	Norfloxacin	70458-96-7	Trimethoprim	738-70-5
Cloxacillin	61-72-3	Ofloxacin	82419-36-1	Tylosin	1401-69-0
Danofloxacin	112398-08-0	Oxacillin	66-79-5		
Demeclocycline	127-33-3	Oxytetracycline	79-57-2		

The substrates to be analysed are first freeze-dried, ground and weighed in 1 g dry matter each in double determination. Defined amounts of internal standards are added for quantification as well as for process monitoring. The substrate samples are then extracted several times, purified and concentrated and thus prepared for measurement by liquid chromatography-mass spectrometry (LC-MS).

The results of the measurements are evaluated by means of a calibration carried out in advance with reference standards in each case in the low and high concentration range to be expected. With the help of the internal standard, the detected signals (peak areas) are set in relation to the calibration, which makes quantification possible, figure 3. Subsequently, the measured concentration is converted considering the dry mass determined at the beginning.

The degree of degradation of xenobiotic residues is defined as the percentage change of concentration in the influent and effluent of the balance frame respectively system boundary. The significance of the degradation rates must be discussed in terms of the proportion of metabolised medicinal products that are no longer measurable due to the analytics.

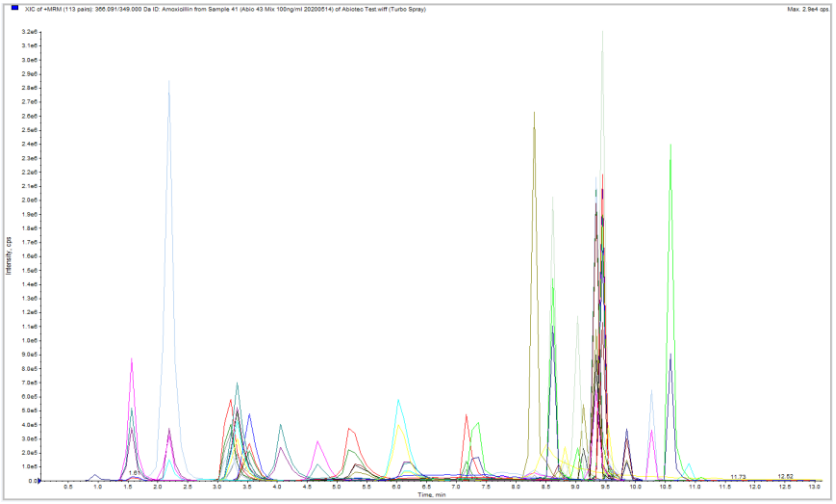


Figure 3: Example of a chromatogram of a solution of reference standards

Detection of pathogens in digestate

The analysis of input substrates, intermediates and digestate for bacteria and moulds is carried out by an external microbiological laboratory. The microorganisms and pathogens analysed and the corresponding culture media used for cultivation are shown in table 2.

Table 2: List of all pathogens and correspondent nutrient media

Pathogenic germs	***Nutrient media***
Total bacteria count	CASO agar
Coliform bacteria	Chromocult® agar
E. coli	Chromocult® agar
Enterobacteriaceae	VRBD agar
Enterococci	VRBD agar
Salmonella	XLD agar
Sulfite-reducing clostridia	TSC agar
Yeasts and moulds	YGC agar

The analysis procedure initially involves the preparation of dilution series. Defined sample volumes are plated out onto the named culture media from the dilution levels that indicate a countable number of colony-forming units. The infected nutrient media listed in table 2 are then incubated aerobically at 37°C for 24 - 48 h. The samples for the detection of clostridial colonies are then tested. The cultivation of the plates for the detection of fungi was carried out aerobically at 25°C. The evaluation takes place after 4 days of incubation.

RESULTS

Impact of thermal conditioning of digestate on pathogens

The conditioning tests with regard to the pathogenic load yielded the following results. Table 3 shows average values for pathogens recorded in the fermentation residuesas in the main and secondary fermenters and in the covered storage tanks. The values overall indicate a decrease of pathogenic agents within the anaerobic biogas process for most of the analysed pathogens. The values recorded for the substrate in the storage tanks represents the input load of pathogens in the demonstration unit since the substrate comes directly from there.

Table 3: Extract from the results of the analysis on pathogenic agents

Substance	***Main fermenter***	***Secondary fermenter***	***Storage tanks***
	CFU/g_{FM}	CFU/g_{FM}	CFU/g_{FM}
Total bacteria count	7,34E+06	4,34E+06	3,88E+06
Coliforms*	1,42E+03	1,01E+03	1,83E+02
E. coli	4,93E+03	4,55E+02	5,28E+02
Enterobacteriaceae	3,70E+04	6,06E+04	1,09E+04
Salmonella	<100	<100	<10
Sulfite-red clostridia	6,13E+04	4,53E+04	4,04E+04
yeasts	5,80E+02	6,80E+02	2,80E+01
moulds	1,31E+03	1,32E+03	1,72E+02
Enterococci	5,76E+04	1,08E+04	2,92E+03

*) Coliforms without E. coli

Figure 4 shows the total bacterial count in the input substrate of the conditioning unit, as well as after 60, 180 and 300 min (1 h, 3 h, 5 h) test duration at the specified temperature. In the case of thermal conditioning at 80°C, the total bacterial count decreases over all test durations. At 60°C, a decrease in the load can also be seen after 60 and 180 min. After 300 min (5 h) the value is 0.3x10^6 CFU/g higher than after 180 min. It is assumed that this is due to measurement inaccuracies and that the deviation could be avoided by additional investigations. At 70°C, the course is relatively constant at a low level over the different durations. After 5 h at 70°C, the reduction of the total bacterial count is about 27 %.

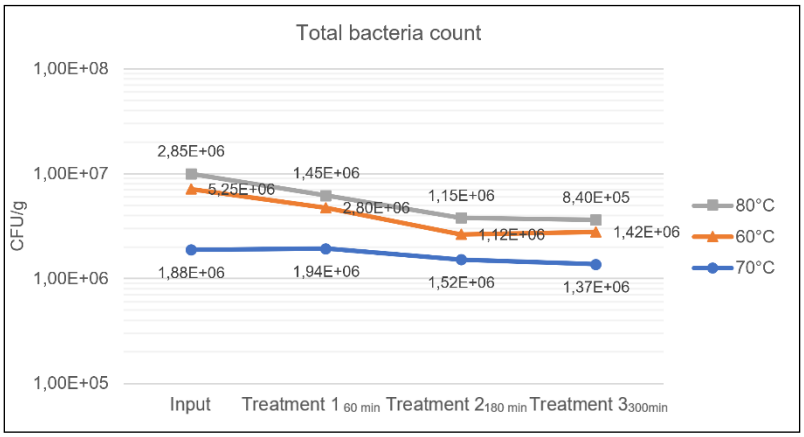


Figure 4: Total bacteria count for input material and conditioned digestate

The results for sulfite-reducing clostridia are shown in figure 5. The load clearly decreases with thermal conditioning. Only in the test series at 80°C is the number of colony-forming units higher after a duration of 5 h than after one or three hours. This can probably also be attributed to measurement inaccuracies. For all other pathogens examined, the thermal conditioning reduced the load to below 10 CFU/g_{FM}. This applies to coliforms, E. coli, enterobacteria and enterococci, as well as yeasts and moulds. The salmonella load was already <10 CFU/g_{FM} at the start of the trial.

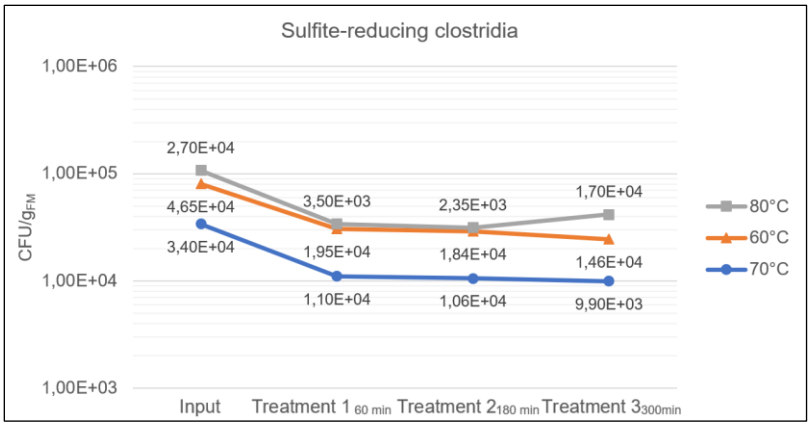


Figure 5: Sulfite-reducing clostridia in input material and conditioned digestate

Impact of thermal conditioning of digestate on xenobiotic contamination

The conversion of xenobiotics during the conditioning process is not as easy to display. After preliminary investigations substances prioritised for the final trials were chlortetracycline, enrofloxacin, lincomycin, sulfadiazine, sulfaguanidine, tetracycline and trimethoprim. The concentration of these substances in the digestate was analysed by liquid chromatography–mass spectrometry (LC–MS) before and after treatment in the demonstration unit. It occurred that concentrations of some substances were higher after treatment whereas other concentrations decreased. The increase of concentration can be ascribed by accumulation caused by adsorption to the organic matrix. The decrease of concentration can partly be ascribed by enzyme activity and hydroxylation. Both de- and increase of concentrations can be attributed to metabolism which means a minor biochemical transformation of the substance. This makes it difficult and a complex task to observe and follow the conversion of xenobiotic agents in the digestate caused by thermal conditioning.

For a better visualisation of the results, the conversion rates in table 4 were coloured differently. Values highlighted in green indicate negative conversion rates, i.e. a reduction in the concentration in the digestate was detected after conditioning. Values highlighted in red represent positive conversion rates. Here, higher concentrations of respective substances were detected in the treated material. All values are mean values and refer to a relatively small data basis.

Table 3: Calculated conversion rates for xenobiotic substances as a result of thermal conditioning (green: reduction, red: cumulation)

Conversion rate		Chlor-tetracycline	Enrofloxacin	Lincomycin	Sulfa-diazine	Sulfa-guanidine	Tetracy-cline	Trimetho-prim
60°C	1 h	0%	30%	7%	0%	6%	0%	-13%
	3 h	-1%	20%	3%	-8%	9%	-1%	-15%
	5 h	3%	52%	5%	-4%	4%	-3%	-9%
70°C	1 h	-7%	1%	4%	-13%	3%	2%	-5%
	3 h	-15%	-14%	-2%	-13%	-2%	-1%	-6%
	5 h	-17%	-15%	-3%	-14%	-4%	-6%	-12%
80°C	1 h	-17%	-30%	-4%	13%	-1%	14%	30%
	3 h	-8%	-55%	-13%	-52%	-25%	36%	-13%
	5 h	-16%	-53%	-33%	-67%	-34%	41%	-26%

The content of e.g. enrofloxacin rose during the treatment at 60°C and decreased to a similar extent at a treatment at 80°C. The concentration of enrofloxacin was cut by approx. 50 % during the treatment for 3 hours at 80°C.

Lincomycin showed a clear progression from initially low positive conversion rates to negative conversion rates with increasing temperature and duration. Little is known about the biotransformation of lincomycin, although biotic processes probably play a minor role at these temperature ranges.

Apart from a few outliers, sulfadiazine showed relatively good degradation rates, which seemed to increase with temperature and duration. This can be justified with findings from the literature, according to which sulfadiazine is transformed by hydroxylation in the anaerobic environment [Reis et al. 2020].

The degradation of sulfaguanidine during the thermal conditioning experiments was similar to that of lincomycin. At temperatures of 60°C and 70°C hardly any changes were measurable, while at 80°C a degradation of more than -30% is recorded. Here, an abiotic transformation under the influence of temperature and time is suspected.

The concentration of tetracycline hardly seemed to change at temperatures of 60°C and 70°C, whereas at 80°C a clear accumulation was recognisable. The concentration in the dry matter of the digestate increased by up to 40%. The same reasoning is used here as for chlortetracycline, namely that the transformation occurs mainly abiotically by adsorption to the organic matrices.

The degradation of trimethoprim was predominantly negative during the trials. Degradation rates between -5 and -15% on average were detected. This can be explained by the fact that trimethoprim tends to adsorb only slightly. At the same time, trimethoprim is typically persistent to biotic transformation, at least in the aerobic environment. Therefore, it is assumed that the degradation is due to abiotic processes. The values for the test scenario 80°C/1h are assessed as outliers or measurement errors.

CONCLUSION

The main task for this research project was to set up a demonstration unit to use part of the surplus heat from the local biogas plant for thermal conditioning of digestate. It should demonstrate a future-oriented form of biomass conversion. Special focus was placed on the elimination of pathogens in the digestate, as well as the reduction of concentrations of xenobiotics such as antibiotic drug residues.

As first steps preliminary investigations on the input substrates and intermediates of the biogas plant provided an initial picture of how the content of pathogens and xenobiotics changes during biomass conversion. Though the focus of this paper was the effect of thermal conditioning of just the digestate, the end product of the fermentation process. The investigation programme envisaged conditioning the digestate at different temperatures and durations. A temperature range of 60°C - 80°C was selected. The conditioning tests took place at one, three and five hours. The results regarding the reduction of pathogenic germs can be rated as good and little surprising. Thermal conditioning is a legitimate and well-tested procedure in the field of hygenisation of digestate.

The desired degradation of the digestate through the elimination of all xenobiotic loads could not be completely achieved. The effects achieved by thermal conditioning on different antibiotic substances must be viewed in a differentiated manner. Degradation rates of over 30% at 80°C were determined for the substances enrofloxacin, sulfadiazine and occasionally for lincomycin and sulfaguanidine. At the same time, tetracycline seemed to have a greater tendency to adsorb or accumulate in the solid matrix at the same temperatures, as the measured concentrations were higher than in the input of the respective trials. In the conditioning experiments at 60°C and 70°C, the measured concentration changes and degradation rates are relatively low. A reliable statement is not yet possible at the present time and on the basis of the test results.

Still the results are evaluated as a necessary and successful contribution in the research field of reducing antibiotic residues in biogas plants. Likewise, the successful implementation of the demonstration unit in the operation of the biogas plant can be seen as a positive step in the development and propagation of new utilisation concepts of heat surpluses on biogas plants.

There is great potential for the continuation or deepening of the research work started here, e.g. in the specialisation and concrete examination of individual antibiotic substances with regard to biogenic conversion. The claim of the present project to identify and render harmless all xenobiotics in the digestate could only be partially fulfilled during the implementation.

The abundance of different active substances and their specific properties with regard to biotic and abiotic transformation requires even more targeted investigations into their behaviour in the digestate matrix and during thermal conditioning. However, the informative value of the degradation rates must be further discussed considering the proportion of metabolites, which were not measurable due to analytics. This necessary specialised consideration is contrasted by the need to broaden the horizon of observation. This means the fate and the biotic and abiotic transformation of the pesticides introduced into the biogas process through e.g. the fermentation of renewable raw materials. These substances could not be taken into account in this work, as the focus was deliberately on the residual contents of veterinary pharmaceuticals.

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