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## ANALYSIS OF THE PRE-TREATMENT EFFICIENCY OF DIGESTATE LIQUID FRACTION FROM A MUNICIPAL WASTE BIOGAS PLANT

Due to the progressing water shortage in agriculture, digestate mass is increasingly being treated not only as an alternative fertilizer but also as a potential source of water. However, it requires the use of advanced technological processes. Due to the fact that the digestate liquid fraction contains large amounts of contaminants, it should be pre-treated before using advanced purification technologies. The conducted experiments determined the effectiveness of coagulation/chemical precipitation process with the use of CaO, FeCl<sub>3</sub> and PIX 112 during the initial purification of the digestate liquid fraction from municipal waste biogas plants. The impact of reaction time and the reagent dose on the effectiveness of reducing the organic compounds and ammonium nitrogen content was analysed. The results show that tested reagents can be applied for the digestate liquid fraction pre-treatment. The increasing of the doses of each reagent enabled an increase in the effectiveness of the process. The increase in the reaction time (slow mixing) extension did not improve the efficiency; an adverse effect due to desorption of pollutants was found. The NH<sub>4</sub><sup>+</sup>-N concentration did not depend on the dose of the reagent, but only on the reaction time (very high reduction observed after 24 hours).

### 1. INTRODUCTION

The constantly growing pollution of water, soil and air, as well as the limited availability of non-renewable resources, become the reason for the change of the environmental protection strategy towards the development of the so-called clean production. This is implemented, among others, by preventing or reducing the amount of pollution generated and producing reusable products. According to the principles of clean production, the waste generated should constitute new, wholesome products [1–3]. In 2018, the European Commission proposed introducing new regulations that aim to ensure the

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best reuse of water from treated wastewater for agricultural purposes [4]. In this area, one of the available alternative sources of water may be the liquid fraction obtained after dehydrating the residues after methane fermentation generated in biogas plants. Until now, this fraction being a waste in biogas production was mainly used as a fertilizer. In approximately 13 000 biogas plants working in Europe, nearly  $128 \times 10^9$  kg of digestate is produced annually, rich both in nutrients and a large volume of water [5]. According to recent data, there are currently 296 biogas plants in Poland, of which 96 are agricultural, 98 at landfills, 99 at WWTPs and 3 are mixed biogas plants [6]. The popularity of biogas plants is due to the tendency to use renewable energy sources and to seek techniques for waste and sludge management containing large amounts of organic carbon.

The operation of a biogas plant is associated with the formation of large amounts of digestate, roughly equivalent to the mass of substrates used in the fermentation process. The amount of digestate depends on the size of the biogas plant and can reach up to tens of thousands of tons per year [7]. Digestate, consisting of more than 90% water, also contains dissolved forms of nitrogen, phosphorus and potassium, which are easily absorbed by plants [5]. If it does not contain toxic or undesirable components, it can be directly used for irrigation of fields using sprinklers, or treated as a technological liquid in the fermentation reactor.

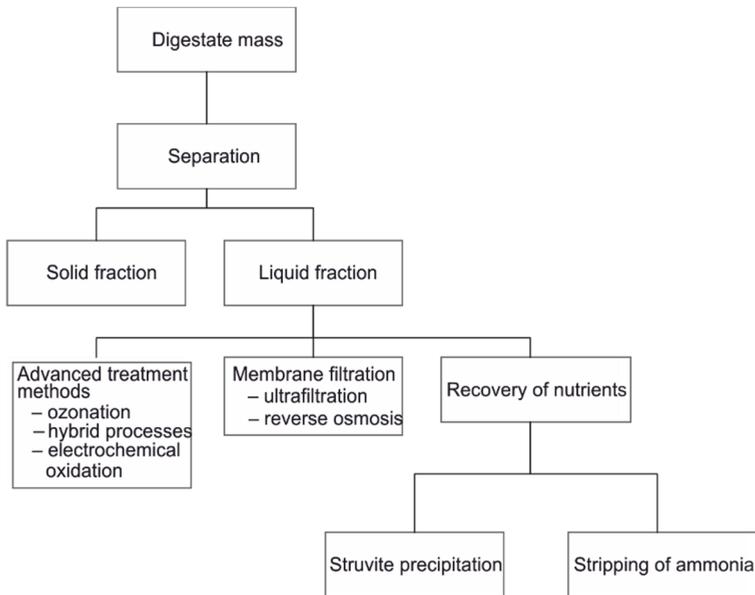


Fig. 1. The methods of the purification liquid digestate with the recovery of water and nutrients

Due to the fact that the digestate contains many usable components (organic and inorganic) and very valuable water, it is common practice to separate it into solid and liquid fractions. In the next step, each of these fractions is subjected to purification/processing in

order to recover all valuable components (including water). The most commonly used methods for recovering water and minerals from the liquid fraction are shown in Fig. 1.

One of the methods of digestate utilization is the separation into solid and liquid fractions using centrifuges, screw presses or various types of sieves with the digestate liquid fraction usually representing 90–95% of the total mass of digestate [8]. The liquid fraction can also be concentrated by evaporation. The product thus obtained can be directly used for fertilizing agricultural land. The percentage of components in the solid and liquid fraction compared with raw digestate is given in Table 1.

Table 1

The share of components in the solid and liquid fraction after digestate separation [%] [9, 10]

Fraction	Dry mass	Organic matter	Total nitrogen	Ammonium nitrogen	Total phosphorus	Total carbon
Solid	46–86	55–65	17–35	7–30	55–78	60–70
Liquid	14–52	35–45	65–83	70–93	22–45	30–40

The digestate liquid fraction is characterized by a large variation in the concentration of organic matter and mineral substances [11, 12]. Depending on the initial waste composition and digestate separation technology, it can contain 0.2–17.6 g O<sub>2</sub>/dm<sup>3</sup> for COD, 0.06–8.7 g N/dm<sup>3</sup> for total nitrogen, 0.03–1.5 g P/dm<sup>3</sup> for total phosphorus, 0.01–0.6 g Mg<sup>2+</sup>/dm<sup>3</sup> for magnesium, and 0.1–5.5 g K<sup>+</sup>/dm<sup>3</sup> for potassium. The content of dry matter and organic matter in digestate may vary in the ranges of 0.8–8.9% and 0.3–7.9%, respectively [13]. Therefore, before applying more advanced purification technologies, digestate is subjected to pre-treatment, e.g., by the coagulation and chemical precipitation using iron or aluminum salts as well as lime. This allows one simultaneous removal of carbonate hardness as a result of precipitation of sparingly soluble calcium and magnesium compounds, removal of mechanical and sometimes colloidal impurities, precipitation of selected toxic substances, removal of microorganisms as well as stripping of ammonia (when lime is used as a reagent) [14].

Considering the very complex composition of the liquid digestate fraction from municipal waste biogas plants, it was advisable to determine the impact of selected technological parameters of its pre-treatment by the coagulation/chemical precipitation. Therefore, the effect of reaction time and reagent dose on the effectiveness of the reduction of organic compounds and ammonium nitrogen content in the digestate liquid fraction was determined.

## 2. MATERIALS AND METHODS

Liquid digestate fraction from a biogas plant that processes organic municipal waste was the subject of this study. Its composition is given in Table 2.

Table 2

Composition of the liquid digestate fraction from the municipal waste biogas plant

Index	Value
pH	6.2
Conductivity, mS/cm	8.13
Total suspended solids, mg/dm <sup>3</sup>	254
Volatile suspended solids, mg/dm <sup>3</sup>	234
Chemical oxygen demand (COD), mg O <sub>2</sub> /dm <sup>3</sup>	8980
Biochemical oxygen demand (BOD), mg O <sub>2</sub> /dm <sup>3</sup>	9520
Dissolved organic carbon (DOC), mg C/dm <sup>3</sup>	2995
NH <sub>4</sub> <sup>+</sup> -N, mg/dm <sup>3</sup>	1250
NO <sub>2</sub> <sup>-</sup> -N, mg/dm <sup>3</sup>	0.7
NO <sub>3</sub> <sup>-</sup> -N, mg/dm <sup>3</sup>	below the limit of detection
PO <sub>4</sub> <sup>3-</sup> , mg/dm <sup>3</sup>	53
Na, mg/dm <sup>3</sup>	293.6
K, mg/dm <sup>3</sup>	688.9
Ca, mg/dm <sup>3</sup>	28.2
Mg, mg/dm <sup>3</sup>	449.7
Cl <sup>-</sup> , mg/dm <sup>3</sup>	2396
Fe, mg/dm <sup>3</sup>	2.2
Mn, mg/dm <sup>3</sup>	3.9
Cu, mg/dm <sup>3</sup>	0.096
Zn, mg/dm <sup>3</sup>	0.630
Hg, mg/dm <sup>3</sup>	0.0036
Co, mg/dm <sup>3</sup>	0.137
Ni, mg/dm <sup>3</sup>	0.270
Ba, mg/dm <sup>3</sup>	0.260
As, mg/dm <sup>3</sup>	0.0005
Cr, mg/dm <sup>3</sup>	0.240
Pb, mg/dm <sup>3</sup>	0.025
Cd, mg/dm <sup>3</sup>	0.001

CaO, FeCl<sub>3</sub>·6H<sub>2</sub>O and PIX 112 coagulant were used in the research on the initial purification of the digestate liquid fraction (Table 3). The doses used in the experiments were: 1.5, 3, 4.5, 7.5, 13.5 and 19.5 g/dm<sup>3</sup> for PIX 112, 1, 2, 3, 5, 9 and 13 g/dm<sup>3</sup> (FeCl<sub>3</sub>), 2, 4, 6, 8, 10, 12, 15, 20, 25 and 30 g/dm<sup>3</sup> (CaO).

The main purpose of the pre-treatment of liquid digestate fraction was to reduce the concentration of organic compounds (measured as COD and DOC) and ammonium nitrogen contained in the leachate. The effect of reaction time and reagent dose on the efficiency of digestate pre-treatment was determined. The COD parameter and ammonium nitrogen concentration were determined using standard methods: bichromate and direct nesslerization, respectively. The DOC concentration was measured using a HACH IL550 TOC-TN analyzer.

Table 3

Coagulants used in the tests [15–17]

Parameter	CaO	FeCl <sub>3</sub> ·6H <sub>2</sub> O	PIX 112
Chemical formula	CaO	FeCl <sub>3</sub> ·6H <sub>2</sub> O	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Molecular weight, g	56.08	270.32	399.9
Physical form	solid (powder)	solid	liquid
Colour	white	yellow-brown	dark brown
Odour	odorless	chlorine	odorless
pH	12.6 (20 °C)	1.8 (1% solution)	<1
density, g/cm <sup>3</sup>	3.37	1.82	1.50–1.56

The tests were carried out in 1 dm<sup>3</sup> reactors at a stand equipped with a Velp Scientifica JLT4 mechanical stirrer. The reagent was dosed into the reactors in amounts corresponding to the given doses. Rapid mixing (150 rpm) was carried out for 2 min, then the stirrer frequency was reduced to ca. 20 rpm and slowly mixed. In studies evaluating the impact of flocculation time on the process efficiency, slow mixing was carried out for 20, 30, 40 and 60 min. Then the stirrers were turned off and digestate samples were sedimented for 30 min. In tests on the analysis of ammonium nitrogen concentration, samples after reagents dosing were mixed for 1, 6, 24 and 48 h. After a specified time, NH<sub>4</sub><sup>+</sup>-N concentration in the clarified liquid was measured. The digestate samples obtained in each case were filtered prior to analysis by medium filter paper.

### 3. RESULTS

The effectiveness of the liquid digestate fraction from municipal waste biogas plant pre-treatment depends on many factors related to both the process conditions and the properties of the used reagents. For all tested reagents, the increase of chemical dose resulted in a decrease in COD and DOC concentration (Fig. 2). For example, for 3 g/dm<sup>3</sup> of FeCl<sub>3</sub>, after 20 min of slow mixing, the COD removal efficiency was 40% and the DOC removal efficiency was 23% while at a reagent dose of 13 g/dm<sup>3</sup> – 48% and 25%, respectively. The higher the dose of reagent, the more flocks that sorb impurities in the purified digestate were found. When lime was used, these flocs mainly contained CaCO<sub>3</sub>, while for FeCl<sub>3</sub> and PIX 112, the suspension was formed as a result of Fe(OH)<sub>3</sub> precipitation.

All of the tested reagents can be effectively used for the liquid digestate fraction pre-treatment. The FeCl<sub>3</sub> and PIX 112 coagulant proven to be efficient even at relatively low doses (a few grams per dm<sup>3</sup>) while CaO required much higher doses (over 15 g/dm<sup>3</sup>) to remove organic substances to the same extent. Of the two iron-based reagents, when used at comparable doses, higher efficacy was found when PIX 112 was applied. For

all reagents used, it was also observed that the COD reduction rate was significantly higher than that found for DOC.

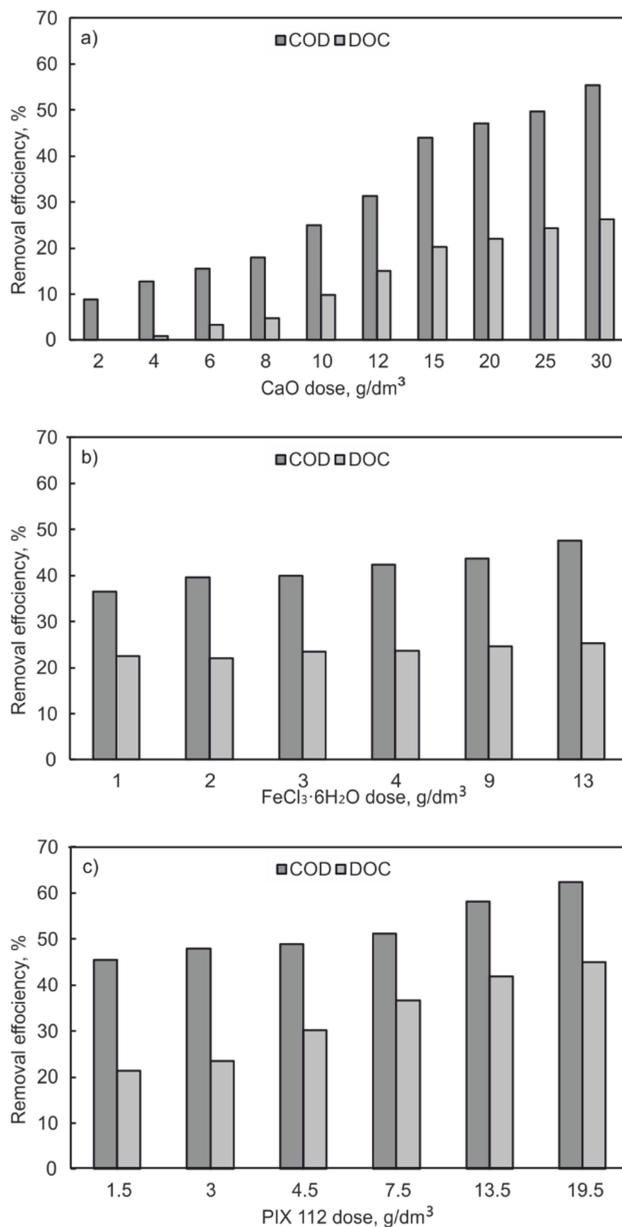


Fig. 2. COD and DOC removal efficiency for:  
a) CaO, b) FeCl<sub>3</sub>·6H<sub>2</sub>O, and, c) PIX 112 (slow mixing time 20 min)

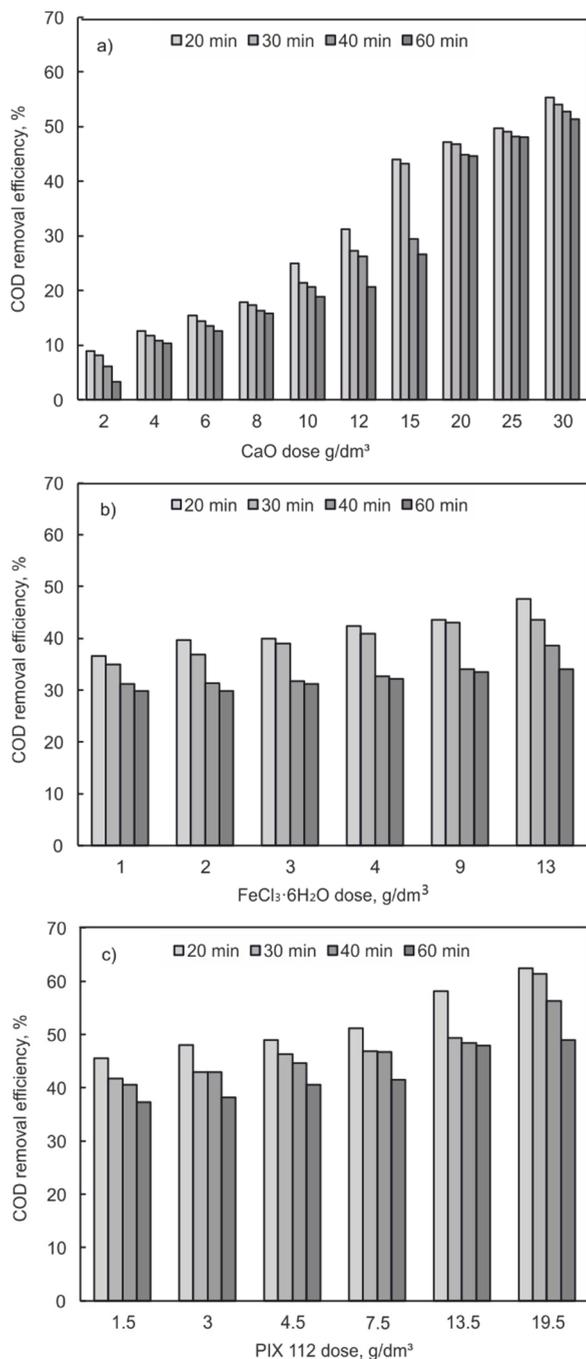


Fig. 3. Dependences of the COD removal efficiency on the slow mixing time for: a) CaO, b) FeCl<sub>3</sub>·6H<sub>2</sub>O, and, c) PIX 112

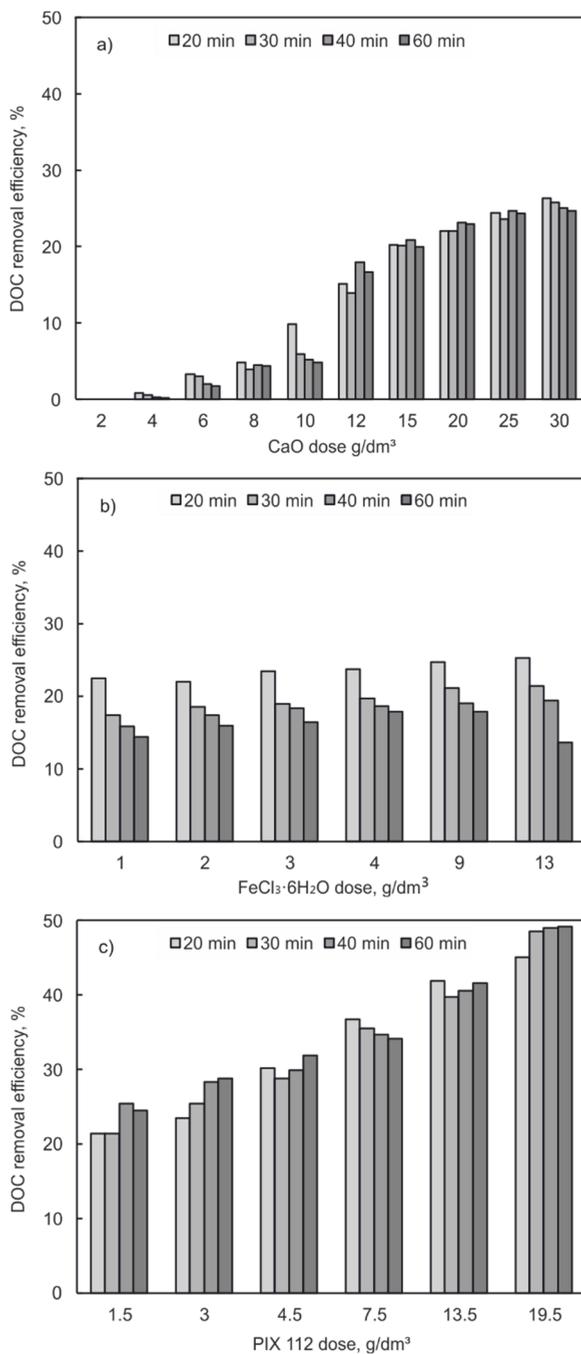


Fig. 4. Dependences of the DOC removal efficiency on the slow mixing time for: a) CaO, b) FeCl<sub>3</sub>·6H<sub>2</sub>O, and, c) PIX 112

Due to the fact that in many physicochemical processes, the reaction time, in this case mixing time, can have a significant impact on the effectiveness of impurities elimination, in the next stage of the experiments, the values of COD and DOC were assessed depending on the flocculation time. It was found that regardless of the type of reagent tested, extending the reaction time above 20 minutes did not improve the efficiency of the process (Figs. 3 and 4). Only when PIX 112 was used it was observed that the extension of slow mixing time resulted in increased efficiency of organic compounds removal (DOC). As the mixing time increased, a slight increase in the content of organic compounds could be observed in all cases. The explanation for this phenomenon is probably the desorption of contaminants from the surface of previously formed flocs. Mixing for too long caused partial disintegration of flocs and desorption of compounds previously adsorbed in the coagulation process. Considering the observations described above, it can be concluded that the optimal (from the point of view COD and DOC concentration decrease) slow mixing time is 20 min.

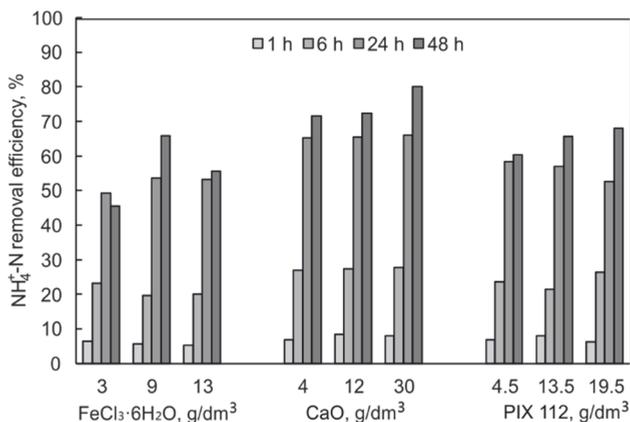


Fig. 5. Impact of reaction time on the  $\text{NH}_4^+\text{-N}$  removal efficiency using CaO,  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ , and, PIX 112

Because ammonium nitrogen is present in the liquid fraction of digestate in very high concentrations, and its presence in the recovered water is not desirable, in subsequent series of tests the effect of mixing time of the solution (after reagents dosing) on changes in ammonium nitrogen concentration was determined (Fig. 5). Based on the obtained test results, it was found that for all used chemicals, in contrast to COD and DOC, the concentration of  $\text{NH}_4^+\text{-N}$  in the treated liquid did not depend on the reagent dose, but only on reaction time. Extending the process duration from 1 h to 48 h increased  $\text{NH}_4^+\text{-N}$  removal efficiency from 7 to 72%, from 6 to 45% and from 7 to 60% for lowest examined dose of CaO,  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ , and PIX 112, respectively. In each case, in the initial phase of the process, the  $\text{NH}_4^+\text{-N}$  removal efficiency was low and after 1 hour ranged from 5 to 8%, then after 6 hours increased to 20–28%. As the reaction

progressed, the reduction in ammonium nitrogen content increased. After 24 hours of the test, it was in the range of 49–66%. Further extending the duration of liquid mixing for another 24 h only slightly increased, up to 80%, the  $\text{NH}_4^+$ -N removal. Therefore, mixing time of 24 h was chosen as the most favorable from the point of view of eliminating ammonia from the liquid fraction of digestate. In addition, it was found that the type of reagent used was not without significance when determining the efficiency of  $\text{NH}_4^+$ -N removal from the digestate liquid fraction. As expected, the best results were achieved when CaO was used as a reagent. At the examined CaO doses (4, 12 and 30  $\text{g}/\text{dm}^3$ ), pH was 12 and higher. Under these conditions,  $\text{NH}_4^+$ -N is present in the form of gaseous ammonia, which can be released into the atmosphere. It was surprising to find that application as a reagent iron-based chemicals ( $\text{FeCl}_3$  or PIX 112) also resulted in the significant decrease of ammonium nitrogen concentration in the treated liquid. Both of these reagents caused a decrease in pH of the solutions (at the maximum dose of  $\text{FeCl}_3$  to 7.5, and for PIX 112 to 6.26) which definitely prevented the occurrence of ammonia desorption. Explanation of the results of  $\text{NH}_4^+$ -N elimination using iron-based chemicals will require further detailed analysis.

#### 4. SUMMARY

- All tested reagents can be effectively used for preliminary digestate liquid fraction treatment.
- The reagent dose and slow mixing time determine the effectiveness of organic compounds removal.
- An increase in the reagent dose improved the quality of digestate.
- The increase in reaction time (above 20 min) did not improve the efficiency of the process; an adverse effect was observed: the content of organic compounds increased as a result of their desorption,
- The use of CaO or iron-based reagents for the pretreatment of the digestate liquid phase significantly reduced the  $\text{NH}_4^+$ -N concentration in solution. For all the reagents used, the increase in efficiency was observed along with the extension of the reaction time.

#### ACKNOWLEDGMENTS

The research was conducted as part of the interdisciplinary project *Sustainable technology for the staged recovery of an agricultural water from high moisture fermentation products RECOATDIG* carried out under the Water Joint Programming Initiative co-financed by 20 Funding Partner Organisations from 18 countries and with the support of the European Commission (full list: [http://www.waterjpi.eu/images/documents/JC2018/water\\_jpi\\_2018\\_joint\\_call\\_participating\\_countries.pdf](http://www.waterjpi.eu/images/documents/JC2018/water_jpi_2018_joint_call_participating_countries.pdf)).

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