

Ewa WIŚNIEWSKA, Maria WŁODARCZYK-MAKUŁA

Częstochowa University of Technology, Faculty of Infrastructure and Environment
Department of Chemistry, Water and Wastewater Technology
ul. Dąbrowskiego 69, 42-200 Częstochowa
e-mail: ewisniowska@is.pcz.czyst.pl

Effect of Silicates on Methane Digestion of Sewage Sludge

Wpływ krzemianów na proces fermentacji metanowej osadów

Effect of clinoptylolite and bentonite admixture on balance of ammonium nitrogen and phosphates in reject water during methane digestion of excess sludge was evaluated. Concentration of ammonium nitrogen and phosphates in reject water separated from the sludge with silicates amendment and without it (control sludge) was analysed to compare the effectiveness of biogenic compounds removal. Simultaneously effect of silicates addition on biogas production and fractions of phosphorus was analysed. Doses of silicates at level no higher than used in wastewater treatment by activated sludge process were added to methane digestion chamber. The doses were equal to 0.5, 1.0 and 2.0 g · L⁻¹. Research work was conducted under laboratory conditions for 21 days. Admixture of silicates did not decrease concentration of ammonium nitrogen in reject water but reduced phosphates content in this medium compared to control sample. Under experimental conditions clinoptylolite was more effective in biogens removal than bentonite. Increase in biogas production was especially visible during days from 1 to 16; after that time it decreased in samples with silicates more rapidly than in control reactor. However silicates admixture increased total biogas production by maximum 17% compared to control sample. Clinoptylolite and bentonite admixture increased percent shares of phosphorus associated with carbonates in sewage sludge. Increase in II-nd fraction share was proportional to the dose of silicates. In control sample the dominant fraction of phosphorus in sewage sludge was the III-rd; in samples with silicate admixture percent shares of II-nd nad III-rd fractions were comparable. The conclusion from the research work is as follows: at doses used in wastewater treatment technology to support activated sludge process silicates do not affect the composition of reject water significantly. However addition of natural sorbents positively affected anaerobic degradation of sewage sludge.

Keywords: ammonium nitrogen, phosphates, methane digestion, silicate, reject water, sequential analysis of phosphorus

Introduction

Silicates (e.g. zeolites) are minerals with skeletal structure, which contain holes occupied by ions and water particles [1]. Because of these they are often used in water and wastewater treatment as sorbents. They have ion exchange properties [2]. Zeolite which is the most frequently used in wastewater technology is clinoptylolite (K₂, Na₂, Ca)₃Al₆Si₃₀O₇₂ · 24H₂O. Also other silicates such as bentonite

(the main component of bentonite is montmorillonite: $\text{Al}_2[(\text{OH})_2\text{Si}_4\text{O}_{10}] \cdot n\text{H}_2\text{O}$) and sepiolite ($\text{Mg}_4[\text{Si}_6\text{O}_{15}(\text{OH})_2] \cdot 6\text{H}_2\text{O}$) are used [1, 3]. Silicates can be both of natural and synthetic origin [1]. In wastewater treatment they are used for removal of biogen compounds (mainly ammonium nitrogen. They can also be used for heavy metals removal. It was stated that silicates stabilise activated sludge process because they are a good basis for growing of nitrifying bacteria. Silicates also improve sedimentation properties of activated sludge as well as increase effectiveness of organic compounds removal [4-7]. In Table 1 the effectiveness of ammonium ions removal by selected zeolites is presented.

Table 1. **The effectiveness of ammonium ions removal by various zeolites [8]**

| Kind of zeolite | Effectiveness of ammonium ions removal, mg N-NH ₄ ⁺ /g d.m. |
|------------------------------------|---|
| Clinoptylolite (China) | 2.7÷3.2 |
| Clinoptylolite (Turkey) | 5.2÷8.1 |
| Clinoptylolite (Ukraine) | 6.6÷21.5 |
| Clinoptylolite (New Zealand) | 7.1÷8.1 |
| NaOH-clinoptylolite | 7.3÷8.4 |
| Clinoptylolite (Croatia) | 7.7÷17.6 |
| NaHCO ₃ -clinoptylolite | 8.1÷9.3 |
| Clinoptylolite (New Zealand) | 8.5 |
| Clinoptylolite (China) | 11.2 |
| Natural zeolite (Chile) | 11.4÷14.8 |
| Clinoptylolite (China) | 12.3÷13.9 |
| HCl-clinoptylolite | 13.4÷16.8 |
| Clinoptylolite (Turkey) | 14.5÷15.4 |
| Clinoptylolite (Iran) | 17.8 |
| Clinoptylolite (Canada) | 18.4÷22.9 |
| Clinoptylolite (China) | 18.5 |
| Clinoptylolite (USA) | 18.5 |
| Ca-clinoptylolite (China) | 20.2÷26.3 |
| Na-clinoptylolite (China) | 22.6 |

Doses of silicates applied in wastewater treatment are in the range of several dozen to 1000 mg · L⁻¹ [6, 7]. In wastewater treatment systems silicates are mainly introduced into activated sludge chambers or into recirculated sludge [4-7].

In contrast to aerobic treatment processes effect of silicates on anaerobic processes (e.g. methane digestion) was less often investigated. According to Montalavo et al. [9] during anaerobic wastewater treatment processes zeolites are mainly used as basis for anaerobic microorganisms growth. Weiss et al. [10] showed that under anaerobic conditions colonisation of zeolite surface by anaerobic microorganisms

has taken place 5-84 days after they had introduced this material into bioreactor. When liquid waste was treated zeolite addition allowed for minimizing toxic effect of ammonia [9]. Similar effect was observed during digestion of cattle manure [11] and swine manure [12]. According to Zheng et al. [12] in anaerobic bed filled with zeolite also higher volumes of biogas were generated compared to control reactor. Higher production of biogas was obtained even at ammonium nitrogen concentration in manure equal to $7500 \text{ mg N-NH}_4^+/\text{dm}^3$, while strongly toxic effect of this compound on anaerobic processes is usually observed at concentration in the range $1500\div 3000 \text{ mg N-NH}_4^+\cdot\text{L}^{-1}$ [13]. The results obtained by Zheng et al. [12] can be explained by synergic effect of ammonium nitrogen sorption on zeolite and high biomass of methanogens, which was cultivated on the surface of the silicates. Similarly during methane digestion of manure and straw statistically important increase of biogas production was observed when zeolites were introduced into the bioreactor [14]. The optimal dose of zeolite was equal to $1.4 \text{ g}\cdot\text{L}^{-1}$ of waste material. Similar effects were obtained by Tada et al. in the case of sewage sludge [15]. The authors stated that the most effective removal of ammonium nitrogen was obtained when mordenite was introduced into the reactor in the dose of $5\div 10\%$. Ca^{2+} ions were released from mordenite into the reaction environment. Ca^{2+} ions were replaced by N-NH_4^+ ; this resulted in decrease of ammonium nitrogen concentration in liquid phase. Biogas production was about 1.7 times higher compared to control reactor.

Taking into consideration results obtained by other authors it can be stated that zeolite amendment under anaerobic conditions increased biogas production and decreased toxic effects of ammonium ions on methane digestion. It is extremely important in the case of treatment of waste and wastewaters containing high concentrations of this compound. Obtained effects were affected by kind and origin of zeolite used during the studies. There are, however, no detailed research works on the effect of silicate presence in activated sludge (excess sludge) on the process of methane digestion, especially on the changes of biogens concentration in supernatant. The aim of the present investigation was to evaluate the effect of silicates addition on nitrogen and phosphorus balance in reject water. Excess sewage sludge was used during the study. Forms of phosphorus were evaluated in the sludge after methane digestion process.

1. Materials and methods

1.1. Sewage sludge

Excess sewage sludge used in the study was taken from municipal wastewater treatment plant (MWWTP). The sludge was homogenised before use by sieving through a thick sieve (diameter of mesh sieve equal to 2 mm). Biological nutrient removal processes such as phosphorus luxury uptake, denitrification and nitrification take place in the MWWTP. Excess and digested sludge were mixed at ratio 7:1.

1.2. Methane digestion of the sludge

Methane digestion was performed in 1 L glass reactors under mesophilic conditions ($37 \pm 1^\circ\text{C}$) for 21 days. Bioreactors were placed in laboratory incubator. Samples were mixed manually once a day. Clinoptylolite and bentonite at doses equal to 0.5, 1.0 and $2.0 \text{ g}\cdot\text{L}^{-1}$ were added to the sludge at the beginning of experiment. Control reactors without silicates amendment were run simultaneously. Each experiment was set at three repetitions.

1.3. Analyses of chemical properties

The following chemical properties of reject waters were analysed:

- a) ammonium nitrogen - by Nessler method,
- b) phosphates - by molybdenate method,
- c) pH - potentiometrically.

Analyses were performed according to standard methods [16] at day 0 and after 7, 14 and 21 days of digestion.

Sequential analysis of phosphorus in sewage sludge was done according to Golterman method adapted by Bezak-Mazur and Mazur [17]. Four phosphorus fractions were distinguished:

- I - phosphorus associated with oxides and hydroxyoxides of iron, aluminium and manganese (extraction with 0.05M Ca-EDTA for 2 hours),
- II - phosphorus associated with carbonates (extraction with 0.1 M EDTA for 18 hours),
- III - phosphorus present in soluble combinations with organic matter (2 hours, $0.5 \text{ M H}_2\text{SO}_4$),
- IV - the remaining phosphorus, including the one bonded with aluminosilicates and present in organic matter in the form of complexes unaffected by sulphuric acid in fraction III (extraction 2.0 M NaOH , 2 hours).

In 24-hours intervals volume of generated biogas was measured. Pressure of biogas in the reactors was measured by manometer. Volume of generated biogas was calculated based on Boyle- Mariott equation:

$$V_0 = \frac{p_1 \cdot V_1}{p_0}$$

where:

- V_0 - volume of generated biogas, L,
- p_1 - pressure of biogas in the bioreaktor, hPa,
- V_1 - free space in the bioreaktor, L,
- p_0 - atmospheric pressure, hPa.

2. Results

Ammonium nitrogen concentrations in reject water compared to content in the control reactor are given in Figure 1.

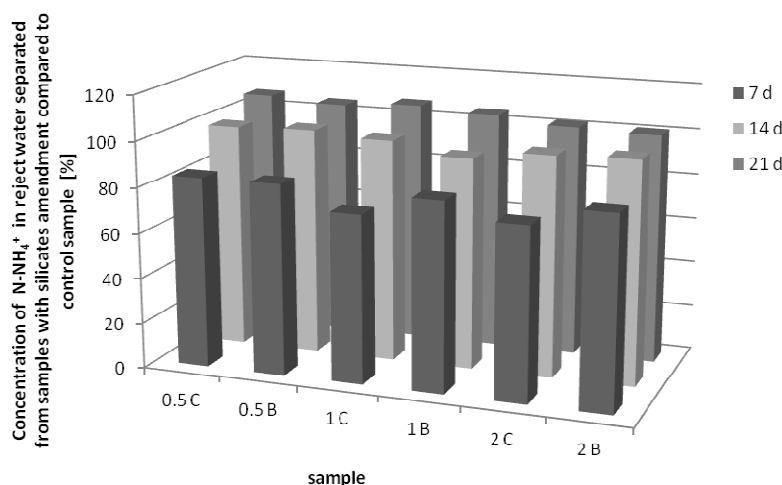


Fig. 1. Concentration of ammonium nitrogen in reject water compared to content in control reactor: 0.5 C - 0.5 g of clinoptylolite · L⁻¹, 1 C - 1 g of clinoptylolite · L⁻¹, 2 C - 2 g of clinoptylolite · L⁻¹, 0.5 B - 0.5 g of bentonite · L⁻¹, 1 B - 1 g of bentonite · L⁻¹, 2 B - 2 g of bentonite · L⁻¹ (concentration in control sample = 100%)

As can be seen from the data presented in Figure 1 after 7 days of methane digestion concentration of ammonium nitrogen in samples which contained silicates admixture consisted of 74 to 84% of N-NH₄⁺ content in control reactor. Concentration of ammonium nitrogen in reject water separated from sludge amended with silicates increased over time. After 14 days of digestion concentrations of N-NH₄⁺ made up 93 to 99% of the control sample concentration. After 21 days of digestion no significant differences in ammonium nitrogen concentration was stated between samples which contained silicates and control sample. The results indicate also that clinoptylolite was more effective in ammonium nitrogen removal compared to bentonite.

Concentrations of phosphates are presented in Figure 2. In contrast to nitrogen ammonium, concentration of phosphates in reject water separated from samples which contained silicates was during the entire experiment lower than in control reactor. This phenomenon was observed during the whole process. No clear correlation was stated between the time of methane digestion and concentration of phosphates in supernatant. Clinoptylolite was however stated better phosphates adsorbent than bentonite. Changes in pH during methane digestion are presented in Figure 3.

pH of reject waters separated from samples with silicates amendment was higher than in control reactor. The differences were more visible after 7 days of methane digestion. As time of digestion was longer the differences were lower.

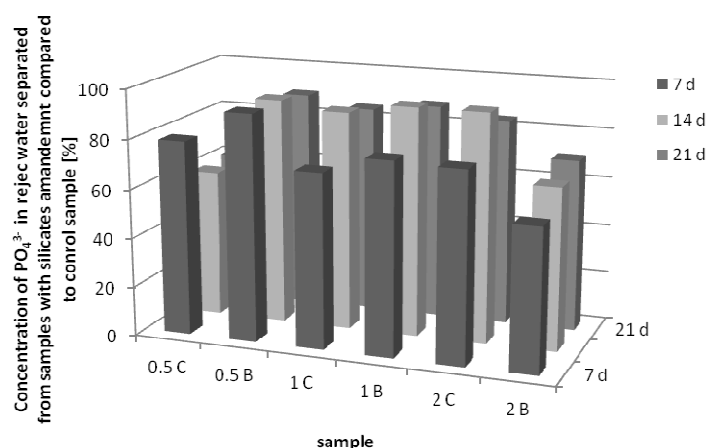


Fig. 2. Concentration of phosphates in reject water compared to content in control reactor: 0.5 C - 0.5 g of clinoptylolite $\cdot \text{L}^{-1}$, 1 C - 1 g of clinoptylolite $\cdot \text{L}^{-1}$, 2 C - 2 g of clinoptylolite $\cdot \text{L}^{-1}$, 0.5 B - 0.5 g of bentonite $\cdot \text{L}^{-1}$, 1 B - 1 g of bentonite $\cdot \text{L}^{-1}$, 2 B - 2 g of bentonite $\cdot \text{L}^{-1}$ (concentration in control sample = 100%)

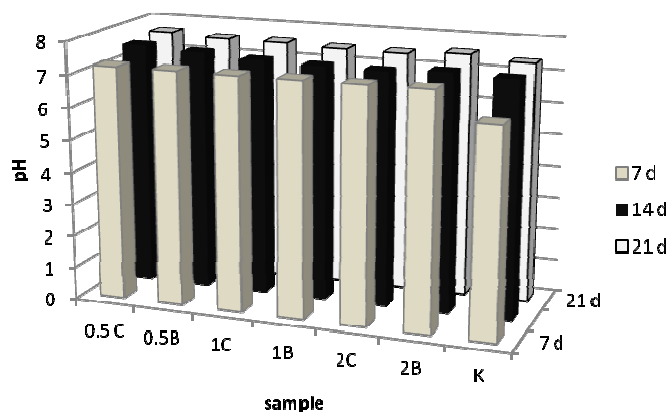


Fig. 3. pH of reject water during methane digestion of sewage sludge: 0.5 C - 0.5 g of clinoptylolite $\cdot \text{L}^{-1}$, 1 C - 1 g of clinoptylolite $\cdot \text{L}^{-1}$, 2 C - 2 g of clinoptylolite $\cdot \text{L}^{-1}$, 0.5 B - 0.5 g of bentonite $\cdot \text{L}^{-1}$, 1 B - 1 g of bentonite $\cdot \text{L}^{-1}$, 2 B - 2 g of bentonite $\cdot \text{L}^{-1}$, K - control reactor

Daily biogas production in samples is presented in Figure 4. Based on the obtained results it can be stated that in samples with silicate amendment conditions for methanogens development were more favourable than in control reactors.

As can be seen from Figure 4 in most of samples with silicate amendment daily biogas production was higher than in control sample (volume of biogas in control sample = 100%). It was especially visible during the first 16 days of digestion. After that time in half of the samples with silicate amendment biogas production decreased.

Cumulative production of biogas in samples with silicate amendment compared to control sample is presented in Figure 5. Cumulative production of biogas in samples with silicate amendment was about 17% higher than in control sample. Compared

to research work done by other authors [15] increase of biogas production obtained during the study was lower. It was probably connected with dose and kind of zeolite. Tada et al. introduced into methane digestion chamber zeolites at dose 5÷10%. The best results they obtained for mordenite $((Ca, K_2, Na_2)[Al_2Si_{10}O_{24}] \cdot 7H_2O)$. The dose used in this study was 0.1÷0.2%. Obtained results confirm however that silicates and zeolites can effectively increase biogas production.

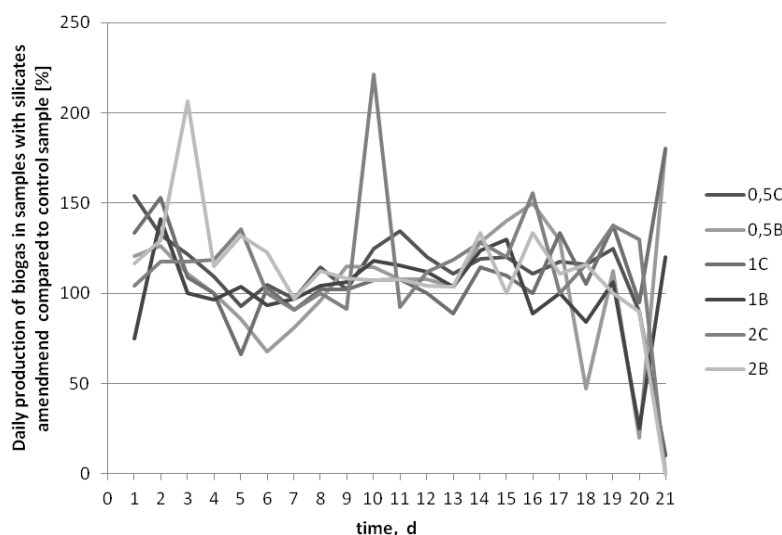


Fig. 4. Biogas production in samples containing silicates compared to content in control reactor: 0,5 C - 0,5 g of clinoptylolite $\cdot L^{-1}$, 1 C - 1 g of clinoptylolite $\cdot L^{-1}$, 2 C - 2 g of clinoptylolite $\cdot L^{-1}$, 0,5 B - 0,5 g of bentonite $\cdot L^{-1}$, 1 B - 1 g of bentonite $\cdot L^{-1}$, 2 B - 2 g of bentonite $\cdot L^{-1}$ (biogas production in control reactor is equal to 100%)

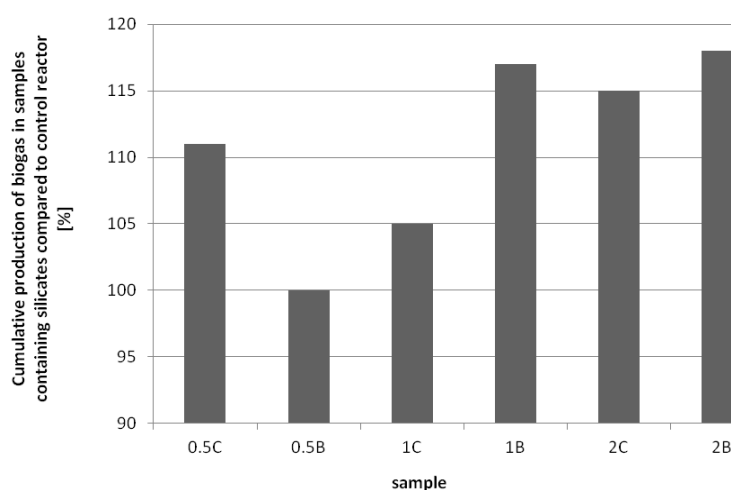


Fig. 5. Cumulative biogas production in samples with silicate amendment compared to control reactor: 0,5 C - 0,5 g of clinoptylolite $\cdot L^{-1}$, 1 C - 1 g of clinoptylolite $\cdot L^{-1}$, 2 C - 2 g of clinoptylolite $\cdot L^{-1}$, 0,5 B - 0,5 g of bentonite $\cdot L^{-1}$, 1 B - 1 g of bentonite $\cdot L^{-1}$, 2 B - 2 g of bentonite $\cdot L^{-1}$ (biogas production in control reactor = 100%)

Amendment of silicates affected also fractions of phosphorus in sewage sludge. In control sample the dominant fraction was III (phosphorus present in soluble combinations with organic matter) - Figure 6. In samples with silicate amendment increase in II-nd fraction (phosphorus associated with carbonates) was observed. Concentration of II-nd fraction in samples with silicate amendment increased as clinoptylolite and bentonite concentration increased. Compared to the results obtained by Bezak-Mazur and Stoińska [18] percent share of mobile fraction was relatively low. It is probably connected with differences between composition of sludge from various wastewater treatment plants, which was proved by Kuziemska [19].

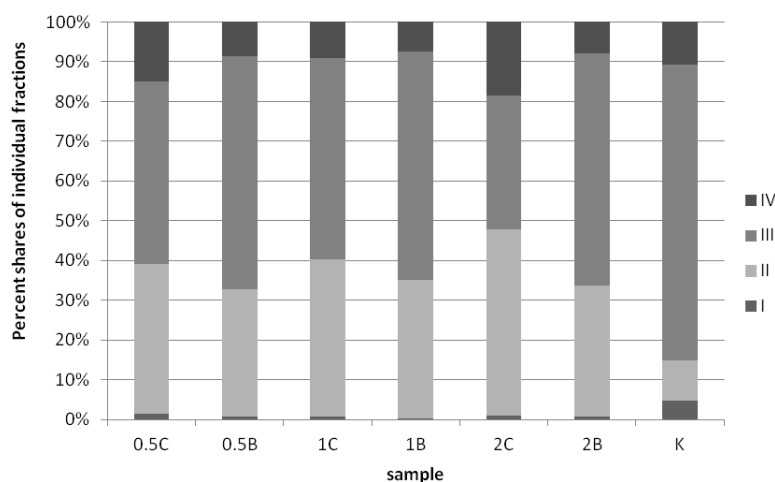


Fig. 6. Percent shares of phosphorus fractions in samples with silicate amendment compared to control sample: 0.5 C - 0.5 g of clinoptylolite · L⁻¹, 1 C - 1 g of clinoptylolite · L⁻¹, 2 C - 2 g of clinoptylolite · L⁻¹, 0.5 B - 0.5 g of bentonite · L⁻¹, 1 B - 1 g of bentonite · L⁻¹, 2 B - 2 g of bentonite · L⁻¹, K - control reactor

When we compare phosphorus fractions in samples before and after methane digestion we can state that silicate amendment affected removal of a part of phosphates by carbonate precipitation. As a result permanent removal of these compounds took place. Based on this can be stated that decrease of phosphates in reject water was permanent. In the case of ammonium nitrogen probably sorption on silicates occurred. The doses of silicates used during the study were relatively low compared to the ones used by other authors [15]. When sorption capacity of silicates was exhausted ammonium nitrogen generated during decomposition of proteins was not adsorbed. That was the reason for ammonium nitrogen concentration increase in reject water. Because simultaneously volume of generated biogas increased compared to control reactor, it can be stated that silicates supports methane digestion processes.

Conclusions

Based on the results obtained during the study the conclusions are as follows:

1. Both clinoptylolite and bentonite at concentrations used during the study caused decrease in phosphates concentration in reject water compared to control sample. Concentration of ammonium nitrogen was at similar level in all samples.
2. At concentrations used in the study silicate amendment increased biogas production by about 17% compared to control reactor.
3. Amendment of silicates increased percent share of phosphorus associated with carbonates.

Acknowledgements

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Streszczenie

W badaniach analizowano wpływ dodatku dwóch rodzajów krzemianów - klinoptylolitu i bentonitu na stężenie azotu amonowego oraz fosforanów w cieczach osadowych podczas fermentacji metanowej nadmiernych osadów ściekowych pobranych z oczyszczalni z biologicznym usuwaniem związków biogenych. Wyniki porównywano z uzyskiwanymi w próbkach bez domieszki krzemianów. Analizowano także wpływ dodatku krzemianów na produkcję biogazu oraz frakcje fosforu w osadach. Stosowane dawki krzemianów były porównywalne do wykorzystywanych w procesach tlenowego rozkładu zanieczyszczeń w technologii osadu czynnego. Stosowane dawki wyniosły 0,5, 1 i 2 g krzemianu/dm³. Fermentację osadów prowadzono w warunkach laboratoryjnych przez 21 dób. Właściwości fizyczno-chemiczne oznaczano w dniu 0 oraz po 7, 14 i 21 dobach. Po wprowadzeniu krzemianów nie uzyskano zmniejszenia stężenia azotu amonowego w cieczach osadowych, jednakże zaobserwowano obniżenie stężenia fosforanów w porównaniu z próbką kontrolną. W warunkach eksperymentu klinoptylolit był bardziej efektywny w usuwaniu związków biogenych niż bentonit. Obecność krzemianów miała wpływ na wzrost produkcji biogazu o ok. 17% w porównaniu z próbką kontrolną. Było to szczególnie widoczne w pierwszych 16 dniach prowadzenia procesu. Po tym czasie w reaktorach zawierających krzemiany nastąpiło szybsze załamanie się produkcji biogazu niż w próbce kontrolnej. Ponadto w obecności krzemianów zwiększył się udział w osadzie frakcji fosforu zasocjowanej z węglanami (frakcja II). Wzrost udziału frakcji II był proporcjonalny do wzrostu dawki krzemianów. W próbce kontrolnej dominującą frakcją była frakcja III. Na podstawie przeprowadzonych badań można stwierdzić, że w dawkach stosowanych w technologii ścieków do wspomaganie procesów biologicznych krzemiany nie powodowały istotnych statystycznie zmian stężenia biogenów w cieczach osadowych w porównaniu z próbką kontrolną. Dodatek krzemianów pozytywnie wpływał na przebieg fermentacji metanowej osadów, m.in. umożliwiając zwiększenie ilości wytwarzanego biogazu.

Słowa kluczowe: azot amonowy, fosforany, fermentacja metanowa, krzemiany, ciecz osadowa, analiza sekwencyjna fosforu