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Anaerobic stabilisation of sludge produced during municipal wastewater treatment by electrocoagulation

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Abstract

Anaerobic digestion of sludge from small electrocoagulation wastewater treatment plant (SEWWTP) is described. The sludge for digestion (SEWWTP sludge) was taken from pilot-scale SEWWTP with the capacity of about 200-population equivalent (25 m^3 of municipal wastewater per day). Due to the technology of wastewater treatment, the characteristics of SEWWTP sludge was different from sludge produced in conventional mechanical–biological wastewater treatment plant. Therefore, experiments were focused on possibilities of anaerobic sludge digestion and determination of conditions and parameters (amount and quality of the sludge, biogas production, etc.).

Average COD removal efficiency in the pilot-scale SEWWTP exceeded 80%. Organic content of excess sludge (volatile suspended solids (VSS)) was in the range of 52.1–59.2% (these values are much lower compared to VSS content in raw sludge from conventional municipal wastewater treatment plant, where VSS is about 75%).

Biogas production from anaerobic digestion of SEWWTP sludge was approximately three times lower compared to standard production in conventional municipal wastewater treatment plant. Low pH (6.5–6.7), high concentration of iron (up to 1400 mg/L) and aluminium (up to 1300 mg/L) and very low (almost zero) concentration of dissolved phosphorus in sludge water were the main factors limiting the rate of anaerobic processes.

Based on these results, anaerobic digestion of SEWWTP sludge was not recommended as an appropriate stabilisation method.

Keywords: Aluminium electrodes; Anaerobic stabilisation; Electrocoagulation; Iron electrodes; Wastewater; Sludge

1. Introduction

In electrocoagulation (EC) process, the coagulant is generated in situ by electrolytic oxidation of an appropriate anode material [1]. With the direct current, colloid matters are coagulated and separated without the addition of other chemicals. Iron and aluminium electrodes are mostly used. The process of coagulation is combined also with electroflotation. Metal anode dissolution is accompanied by hydrogen gas evolution at cathode. Sludge produced in EC process is separated in clarifiers by sedimentation and flotation.

Advantages and disadvantages of EC are described in [1]. The main advantages are simple and easily operated equipment. Wastewater treated by EC gives clear, colorless, and odorless water. In addition flocs formed by EC settle easy and they are well de-waterable. Main disadvantage is dissolution of electrodes into wastewater streams as a result of oxidation. Thus electrodes need to be regularly replaced. Another disadvantage is relatively high usage of electricity during the process and high conductivity of the water suspension is required [1]. The EC process is mostly used in water treatment, however, there are also municipal or industrial wastewater treatment plants (WWTP) where EC is applied.

For example, pre-treatment of municipal wastewater with EC was described in [2]. In pilot-plant with EC tank of 0.318 m^3 wastewater with average flow of 1 m^3/h was treated. Twenty-one two-pole aluminium electrodes were used. The anodic surface was 0.15 m^2. The range of voltage at the electrodes was 0–80 V and the range of current was 0–40 A. EC was combined with pressed air flotation. Resulting COD removal efficiency was about 75%.

The use of EC for industrial wastewater treatment was described in [3–5]. Removal of surfactants as single source

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of COD was described in [3]. COD removal efficiency in the laboratory EC model ranged from 39.6 to 74.1%. Specific energy consumption was 0.3–5.3 kWh/m^3. In [4], EC separation of pollutants from restaurant wastewater was studied. Laboratory EC plant consisted of five aluminium or iron electrodes with effective surface of 56 cm^2 each and with 6 mm distance between them. Almost 100% oil and fat removal efficiency and 90% COD removal efficiency were reached. Optimum voltage ranged between 3 and 18 V and current ranged between 30 and 80 A/m^2. Consumption of aluminium electrodes was between 17.7 and 106.4 g/m^3 and the energy consumption were over 1.5 kWh/m^3. Similar results were achieved with combination of iron and aluminium electrodes. However, only iron electrodes produced yellow effluent and the electrodes corroded when disconnected. Therefore, aluminium was recommended as more appropriate material for non-continuous operation.

Laboratory EC treatment of leachates from municipal waste landfills was described in [5]. Fe–Cu and Al–Cu electrodes were used. Applied voltage was 1–15 V, the surface of electrodes was 80 cm^2 (8×10 cm) with the distance of 2 cm. The reactor volume was 2 L. COD removal efficiency ranged from 30 to 50%.

Possibilities of EC treatment of wastewater from food processing, petrochemical, chemical and textile industries, as well as wastewater containing heavy metals, detergents, fluorides, and undissolved matters are specified in [1]. In all cases the characteristics of the sludge produced and separated from EC plant were specific and different compared with the sludge produced in conventional biological WWTP.

The objective of this research was to study anaerobic digestion of sludge produced in small EC wastewater treatment plant (sludge) and to determine the conditions and the main technological parameters like amount and quality of the sludge and biogas production.

2. Materials and methods

2.1. Small electrocoagulation wastewater treatment plant (SEWWTP)

SEWWTP sludge used for anaerobic digestion was separated in small EC wastewater treatment plant. Capacity of the plant was 200 PE (population equivalent) and the average volume of municipal wastewater was about 25 m^3/day. The scheme of SEWWTP is shown in Fig. 1. Municipal wastewater was flown to the buffer tank from where it was pumped alternatively to two parallel flotators. Volume of each flotator was 308 L. In 15 min long cycles, one flotator was in the status of EC connected with the electroflotation and the other one in the status of filling. At the end of a cycle, content of the flotator was mixed with pressed air. Ventilator at the top of the flotator was turned on to air. Flotated foam was directed towards the flotator's edges. The flotate was accumulated in the sludge collection tank. Water without the flotate containing settled sludge, was pumped from the flotator to the equalisation tank, from which it was flown by gravity to the lamellae settling tank (LST). The sludge that settled in LST was pumped to the same collection tank as the flotate.

The electrode system was formed from Al and Fe electrodes. Electrodes were shaped as concentric cylinders, altering each other as: $Fe^+–Al^-–Al^+–Fe^-–Al^+–Al^-–Fe^+–Al^-–Al^+–Fe^-$. Alternatively poled electrodes were fed with the direct current. The voltage at the electrodes was 40 V and the current ranged from 50 to 200 A [6].

SEWWTP was installed at municipal WWTP Kosice City (East Slovakia). After primary pre-treatment (after screens and grit chamber) wastewater was pumped to SEWWTP. Average COD removal efficiency was more than 80% (efficiency range form 66.7 to 92.4%). On one hand, high efficiency of phosphorus removal was reached arising from precipitation with Fe^{3+} and Al^{3+} ions released from the electrodes as insoluble phos-

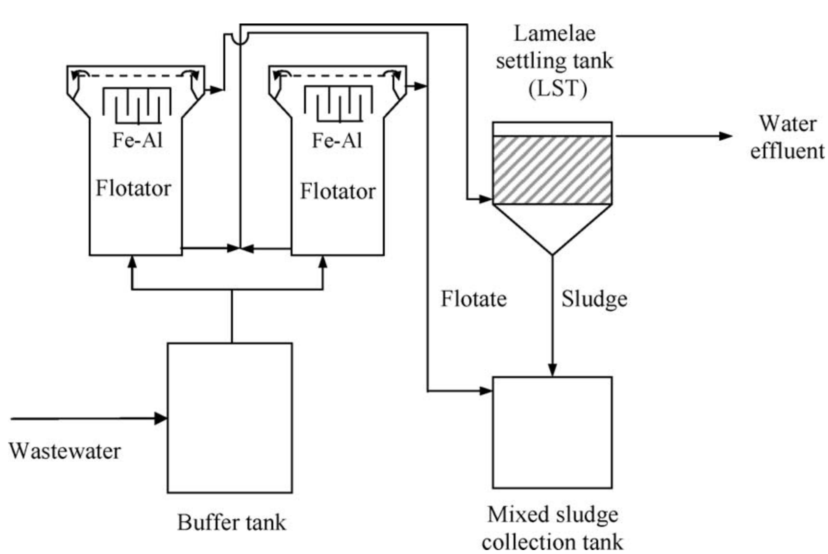

Fig. 1. The scheme of a small electrocoagulation wastewater treatment plant (SEWWTP).

phates. Output phosphorus concentration was almost zero. On the other hand, reduction of dissolved nitrogen was minimal. These results are consistent with those published in [2], where municipal wastewater was treated with EC.

As it was explained above, there were three types of sludge during the process of wastewater treatment in the SEWTP: (a) flotate separated at the top of the flotator, (b) settled sludge (from LST) separated in the lamellae settling tank, and (c) mixed sludge formed from these. Average concentration of SS in the mixed sludge used for anaerobic stabilisation was 29.5 g/L and concentration of VSS 16.5 g/L (56%).

2.2. Methanogenic activity tests

Methanogenic activity tests at temperature of 35 °C were carried out with SEWWTP sludges. These tests provide representative information on the quality of the sludge and its anaerobic degradability. Particularly important is the maximum specific methanogenic activity (kg of methane COD per volatile suspended solids (VSS) per day). This value was calculated from the maximum methane production rate during the test. Digested sludge from conventional wastewater treatment plant (CWWTP) Bratislava-Vrakuna was used as an inoculum (its suspended solids concentration: SS was 42.95 g/L, VSS concentration was 22.07 g/L).

In the measurement of maximum methane production rate, 100 mL of SEWWTP flotate (VSS 7.2 g/L) and 100 mL of SEWWTP mixed sludge (17.4 g/L), respectively, were mixed with 500 mL of digested sludge from CWWTP. Gastight reactor was filled up to 1000 mL with potable water with removed oxygen. The volume of produced methane was measured. For endogenous production of methane by inoculating sludge blank test with 500 mL of this sludge at the same condition was realised.

Maximum methanogenic activity from initial linear methane production rate was calculated.

2.3. Laboratory models for anaerobic digestion of SEWWTP sludge

SEWWTP sludge was treated in two stirred laboratory models with volume 4 L each. The reactors were inoculated with 2 L of digested sludge from CWWTP Bratislava-Vrakuna, characteristics of which are given in the previous paragraph. Then, 2 L of potable water was added. Model No. 1 was operated under laboratory temperature that varied overtime. Temperature in Model No. 2 was kept constant at 35 °C. Hydraulic retention time (HRT) in reactors was the same as sludge retention time (SRT). Laboratory models were fed by SEWWTP sludge intermittently once a day.

The concentration of COD, NH_4–N, PO_4–P, VFA (volatile fatty acids, given as acetic acid) and pH values were measured in filtered sludge water. The concentration of undissolved solids (SS and VSS), temperature in Model No. 1 and biogas production were also measured.

All analyses were according to Standard methods [7]. VFA concentration was measured according to Kapp [8].

3. Results and discussion

3.1. Methanogenic activity tests

Maximum specific methanogenic activity of sludge with the flotate was 0.039 kg/(kg day) (kg of methane COD per kg of VSS per day). Maximum specific methanogenic activity of sludge with the mixed sludge was 0.068 kg/(kg day). Approximately 500 mL of methane was produced in 185 h with mixed sludge, but only approximately 240 mL was produced with the flotate in the same time. The endogenous methane production (blank test) was 225 mL from 500 mL of used stabilised sludge from the WWTP Bratislava-Vrakuna. The same amount of sludge was also used for methanogenic tests. It may be hypothesised from these results, that the composition of flotate inhibited production of methane. One reason may be higher content of iron or aluminium in the sludge.

3.2. Laboratory models operation

Start-up feed to the reactors was 100 mL of SEWWTP sludge. During the period of three weeks the feed was increased up to 250 mL. Under these doses HRT and SRT was 16 days. Such value is in the range recommended for anaerobic digestion of wastewater sludge. Until the 22nd day SEWWTP flotate (SS 15.66 g/L, VSS 7.17 g/L) was dosed to laboratory models, after the 23rd day the models were fed with SEWWTP mixed sludge with SS concentration of 33.35 g/L (VSS 17.36 g/L), and after the 98th day reactors were fed with SEWWTP mixed sludge with SS concentration of 25.51 g/L (VSS 13.01 g/L). The sludge was dosed daily. Results from operation are shown in Figs. 2–6.

As can be seen in Figs. 2–6 no significant differences were measured between Models 1 and 2 as similar concentrations of COD – Fig. 2, NH_4–N – Fig. 3, PO_4–P, pH and suspended solids were found in both models. Because of higher temper-

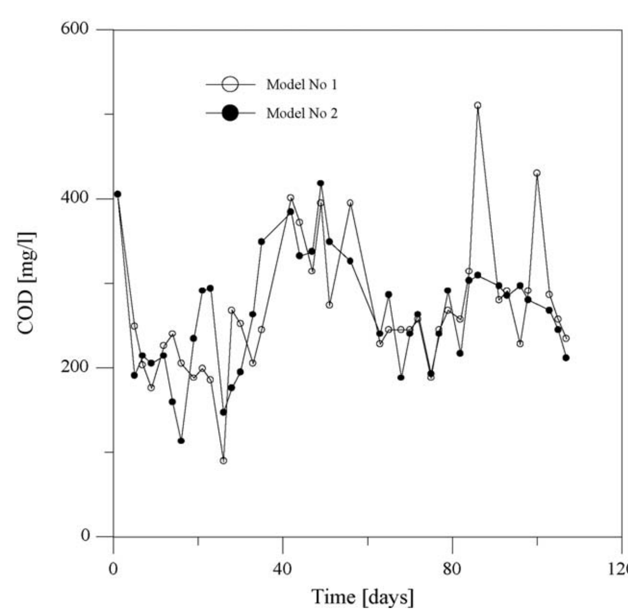

Fig. 2. COD concentrations in sludge water from laboratory models.

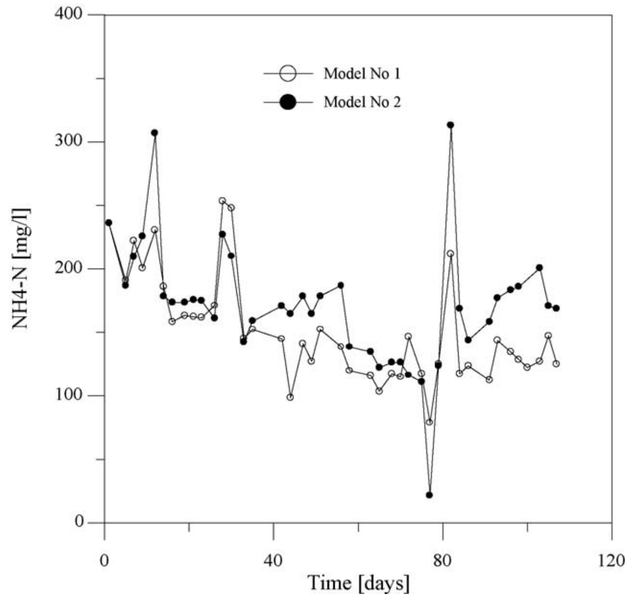

Fig. 3. NH_4–N concentration in the sludge water from laboratory models.

atures in laboratory (summer time, see temperatures in Model No. 1: Fig. 4), till the 40th day of operation biogas productions differed just slightly (Fig. 5). After the temperatures started to drop biogas production in Model No. 1 was significantly lower than in Model No. 2.

3.2.1. Biogas production in the laboratory models

Fig. 5 shows cumulative production of biogas in laboratory models. The most important finding is relatively low average specific biogas productions. Detailed results are shown in Table 1. As can be seen in Table 1, average biogas production was significantly lower than the values typical for anaerobic digestion of sludge from municipal CWWTP since the beginning of laboratory models operation. Biogas production at CWWTP

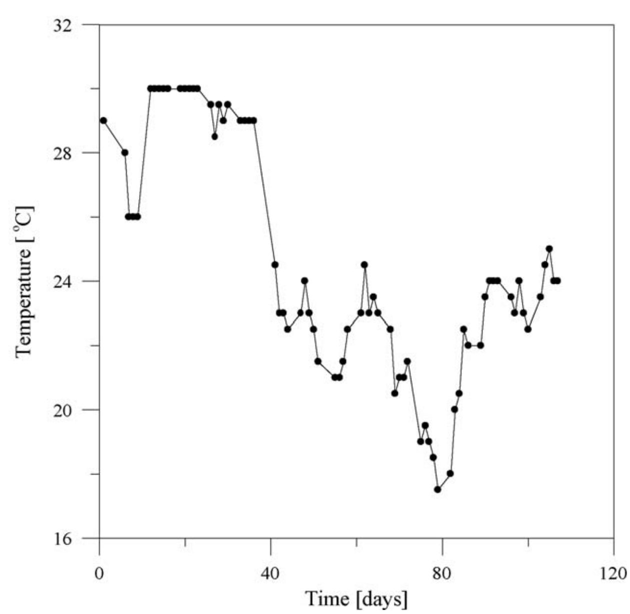

Fig. 4. Temperatures measured in Model No. 1.

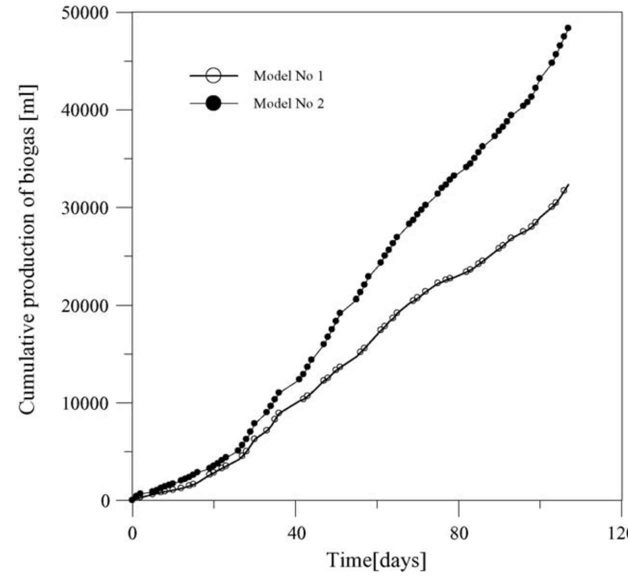

Fig. 5. Cumulative production of biogas in laboratory models.

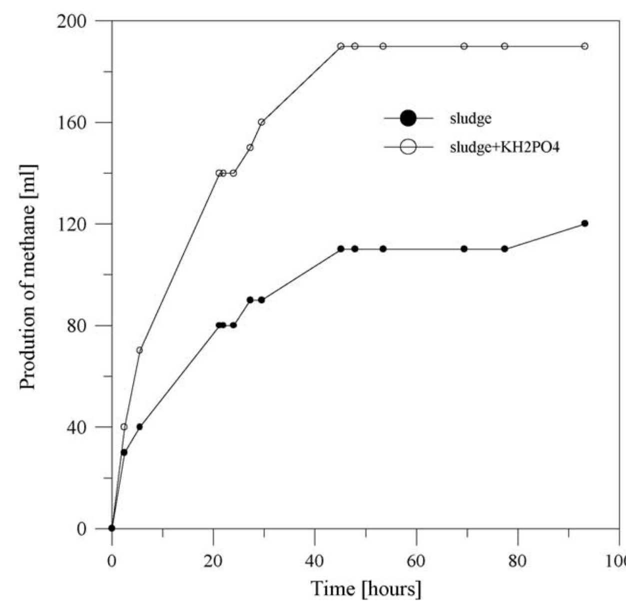

Fig. 6. Methanogenic activity test without and with added phosphorus (sludge from the Model No. 2).

is approximately 500–750 L per kg of sludge VSS loading [9,10].

Total amount of SS treated in both models was 603.8 g of SS (259.13 g VSS). Total production of biogas was 32.34 L in Model No. 1 and 48.35 L in Model No. 2, respectively. Average

Table 1
Average specific biogas production in laboratory models (m^3 per kg VSS)

Day of operation	Specific biogas production	
	Model No. 1	Model No. 2
0–22	0.181	0.226
23–97	0.113	0.170
98–106	0.191	0.309

specific production of biogas was 0.125 m^3/kg VSS in Model No. 1 and 0.187 m^3/kg VSS in Model No. 2. These values were approximately 70% lower compared to specific biogas production presented in literature [9,10] for sludge produced at municipal CWWTP under comparable loading of digesters (average load of laboratory reactors was around 1 kg/(m^3 day) VSS).

Lower biogas production may be related to:

- low pH values in reactors;
- inhibition caused by high concentration of iron and aluminium;
- lack of phosphorus. Anaerobic digestion is a biological process and the presence of macronutrients (nitrogen and phosphorus) is vital. As almost all phosphorus in the reactors was precipitated with iron and aluminium it was inaccessible for anaerobic microorganisms.

3.2.2. pH in laboratory models

In both laboratory models, pH was measured. These values gradually decreased from 7 to 6.5–6.8 over reactors operation. Average pH value in Model No. 2 was just slightly higher compared with Model No. 1. Lower pH in SEWWTP sludge mixture may be caused by:

- high concentration of Fe^{3+} and Al^{3+}. H^+ is produced in hydrolysis reaction of these cations simplified reaction;

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

- lower concentration of ammonia nitrogen NH_4–N compared to sludge water in conventional anaerobic digesters at municipal CWWTP. In conventional anaerobic digesters NH_4–N concentrations in sludge water normally exceed 500 mg/L. As is shown in Fig. 3, average concentration of NH_4–N in Model No. 1 was 151 mg/L and in Model No. 2 172 mg/L. Ammonia is the most important buffering agent in anaerobic digestors and its lack is the reason of slightly acidic pH.

Relatively low concentration of NH_4–N in laboratory models results from different composition of the sludge. At CWWTP primary sludge is digested together with excess (biological) sludge, which contains much higher amount of nitrogen. This nitrogen is released in sludge water mainly as NH_4–N. At SEWWTP only primary sludge containing lower amount of nitrogen is separated and digested. Removal of dissolved NH_4–N in EC process and its accumulation in SEWWTP sludge is negligible.

3.2.3. Concentration of SS in laboratory models

The concentrations of suspended solids in both laboratory models were similar and sludge concentration in reactors stabilised at the value around 27 g/L. Average percentage of VSS was 47.7% in the Model No. 1 and 45.3% in the Model No. 2. Sludge in the Model No. 2 was slightly better stabilised because of higher temperature.

3.2.4. Concentrations of iron and aluminium in SEWWTP sludge and laboratory models

Concentrations of iron and aluminium were measured in SEWWTP sludge samples in both laboratory models at the end of their operation (107th day). Summary of results is given in the Table 2.

Specific concentrations of iron (40–70 g per kg of dry sludge), aluminium (30–50 g per kg of dry sludge) and concentrations of iron and aluminium in both models (almost 1500 g/L) are extremely high. Under such conditions significant inhibition of anaerobic processes can be expected. Authors in work [11] studied the impact of iron used for phosphorus precipitation on anaerobic sludge digestion at CWWTP. Iron was gradually accumulated in anaerobic digester up to 1000 mg/L and higher. The following effects were observed, comparing digestion of sludge with and without iron [11]:

- efficiency of digestion and methane production was lower in reactor with iron (measured under load of 1.9 kg/m^3 day – kg of raw sludge SS);
- inhibition of methanogenesis depended on the feeding mode (number of raw sludge doses per day). At one dose per day almost 50% inhibition was achieved. After the feeding was split to three doses, inhibition dropped to 15–20%.

Negative impact of iron on activated sludge digestion was also presented in work [12]. Iron was added to activate sludge process to remove phosphorus. Anaerobic digestion of this sludge resulted in 32% decrease in biogas production.

Table 2
Concentrations of iron and aluminium measured in the samples

Sample	SEWWTP mixed sludge	SEWWTP flotate	SEWWTP sludge from LST	Model No. 1	Model No. 2
Concentration of iron					
Homogenised (mg/L)	1183.6	59.5	298.0	1477.8	1446.9
Filtrate (mg/L)	22.3	13.2	54.9	34.7	24.1
Specific concentration (g/kg)	46.6	41.0	67.4	53.6	53.6
Concentration of aluminium					
Homogenised (mg/L)	1108.4	36.12	117.7	1405.8	1334.7
Filtrate (mg/L)	0.2	0	0.23	0.13	0
Specific concentration (g/kg)	43.98	31.96	32.55	52.2	50.3

In work [13] impact of aluminium on anaerobic sludge digestion was discussed. Laboratory measurements in a long-term operated batch model shown that aluminium concentration of about 1000 mg/L (as $Al(OH)_3$) caused 50–70% decrease of specific methanogenic activity. Slight biomass adaptation on aluminium was observed after 55 days, which resulted in 44% decrease of methanogenic activity. Nevertheless, the negative impact of aluminium in such concentration on anaerobic processes was clearly proved.

3.2.5. Phosphorus concentration in sludge water in laboratory models

PO_4–P concentration in sludge water was completely different compared to sludge water from conventional anaerobic sludge digesters. Higher concentrations of PO_4–P were measured only during the first days of operation (phosphorus added with digested sludge from CWWTP dosed at the beginning of operation as inoculum). PO_4–P concentration dropped below 0.5 mg/L within a week. It is evident that all phosphorus was just in an insoluble form arising from the presence of iron and aluminium.

Kinetic test of methanogenic activity after excess phosphorus dose was realised to confirm the hypothesis that the lack of soluble phosphorus limited the methanogenesis. One liter of sludge was taken from the Model No. 2 and divided into two reactors. Potable water was added so that the overall volume of sludge mixtures in reactors was 1 L. To ensure sufficient PO_4–P concentration, 4 g/L of KH_2PO_4 was dosed to one of the reactors. Soluble PO_4–P concentration in the sludge water in this reactor ranged between 122.6 mg/L (at the beginning of the test) to 43.4 mg/L at the end of the test. After 96 h, phosphorus was gradually precipitated with iron and aluminium. No KH_2PO_4 was dosed into other reactor. Temperature in both reactors was identical to that in the Model No. 2 (35 °C). In both reactors pH was maintained at the value of 7.

Fig. 6 clearly shows that the addition of phosphorus results in significantly increased methane production rate. Maximum specific methanogenic activity within the first 24 h was calculated as 0.032 kg/(kg day) for the test without phosphorus and 0.058 kg/(kg day) for the test with added phosphorus (kg of methane COD per kg of VSS per day). Methane production rate after phosphorus addition was almost doubled of that without phosphorus addition. It is evident that phosphorus limitation was one of the main reasons for lower biogas production in anaerobic digestion of SEWWTP sludge. Next effect beyond that of lack of phosphorus include also precipitation of dissolved iron. Table 2 shows that concentration of dissolved iron in laboratory models was about 25–35 mg/L and concentration of dissolved aluminium about 0–0.13 mg/L.

4. Conclusions

The main results from operation of SEWWTP and from anaerobic digestion of SEWWTP sludge can be summarized as:

- COD removal efficiency in pilot-scale SEWWTP was in the range 67–91%. Average efficiency was higher as 80%;
- quality of SEWWTP sludge differed to that produced in conventional municipal WWTP. VSS content was 52.1–59.2%, iron concentration 40–70 g/g SS, aluminium concentration 30–50 g/g SS;
- biogas production from anaerobic digestion of SEWWTP sludge was significantly lower compared to anaerobic digestion of the sludge from municipal CWWTP. Lower biogas production was caused mainly by almost zero concentration of dissolved phosphorus, high concentrations of iron and aluminium in sludge and slightly acidic pH;
- lower pH in anaerobic digestor (6.5–6.7) was influenced by high concentrations of iron and aluminium in sludge mixture and low concentration of ammonia in sludge water;
- the difference between portion of VSS in the sludge stabilised at laboratory temperature and temperature of 35 °C was not significant.

Based on these results anaerobic digestion of SEWWTP sludge is much more complicated and less effective compared to anaerobic digestion of the sludge from municipal CWWTP. More appropriate method could be, for example, use of SEWWTP sludge in composting process with other materials or its transport to large municipal WWTP. However addition of smaller, but controlled amount of SEWWTP sludge to not overloaded anaerobic digester at municipal CWWTP can improve quality of sludge water (lower amount of phosphorus will be recirculated from thickening and dewatering to activation).

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