

THE EFFECT OF IRON SALT ON ANAEROBIC DIGESTION AND PHOSPHATE
RELEASE TO SLUDGE LIQUORSvetlana Ofverstrom¹, Regimantas Dauknys², Ieva Sapkaitė³

Vilnius Gediminas Technical University

E-mails: ¹svetlana.ofverstrom@vgtu.lt; ²regimantas.dauknys@vgtu.lt; ³ieva.sapkaite@vgtu.lt

Abstract. Iron salts are used at wastewater treatment plants (WWTPs) for several reasons: for removing chemical phosphorus, preventing from struvite formation and reducing the content of hydrogen sulfide (H₂S) in biogas. Anaerobic digestion is a common scheme for sludge treatment due to producing biogas that could be used as biofuel. Laboratory analysis has been carried out using anaerobic digestion model W8 (Armfield Ltd, UK) to investigate any possible effect of adding FeCl₃ on the anaerobic digestion of primary sludge (PS) and waste activated sludge (WAS) mixture as well as on releasing phosphates to digested sludge liquor. The obtained results showed that FeCl₃ negatively impacted the anaerobic digestion process by reducing the volume of produced biogas. Fe-dosed sludge (max) produced 30% less biogas. Biogas production from un-dosed and Fe-dosed sludge (min) was similar to the average of 1.20 L/gVS_{fed}. Biogas composition was not measured during the conducted experiments. Phosphorus content in sludge liquor increased at an average of 38% when digesting sludge without ferric chloride dosing. On the contrary, phosphate content in sludge liquor from digested Fe-dosed sludge decreased by approx. 80%.

Keywords: anaerobic digestion, biogas, phosphate, iron salt, primary sludge, waste activated sludge.

Introduction

Anaerobic digestion is a common scheme for sludge treatment because of producing biogas the content of which includes methane (CH₄) (55–65%), CO₂ (30–35%), small amounts of other O₂, H₂S, etc. and is an environmentally friendly fuel. However, without further treatment, it can only be used at the place of production (Appels *et al.* 2008).

The anaerobic digestion of sludge leads to the formation of struvite because ammonia, phosphate and magnesium are solubilised by the digestion process (Mamais *et al.* 1994). One of the existing methods of avoiding the formation of struvite is adding FeCl₃ salts that could affect the anaerobic digestion process.

Iron salts could be used at wastewater treatment plants (WWTPs) for several reasons: for removing chemical phosphorus, preventing from struvite formation and reducing the content of hydrogen sulfide (H₂S) in biogas (Mamais *et al.* 1994).

The effect of adding iron salts on anaerobic digestion was studied by many researchers (Smith, Carliell-Marquet 2008, 2009; Novak *et al.* 2007) the majority of which reported a negative effect of dosing iron salts on a daily production of biogas comparing to un-dosed sludge (see Table 1).

The present study was undertaken to discover any possible effect of iron addition on the anaerobic digestion of the primary-waste activated sludge mixture and phosphorus release during the digestion of the sludge mixture.

Table 1. Biogas production from sludge dosed with iron salts (Partly adapted from Smith, Carliell-Marquet 2009)

Reference	Type of analysis and sludge used	Biogas production*
Dentel, Gosset (1982)	BT and SC, raw sludge dosed in lab with Fe and Al	21–32% less biogas
Mamais <i>et al.</i> (1994)	Lab-scale AD, mixture of P+WAS dosed in lab with Fe	No impact
Johnson <i>et al.</i> (2003)	Lab-scale SC, AS dosed at WWTP with Fe	32% less biogas
Smith, Carliell-Marquet (2008)	BT, AS dosed in lab with Fe	12% less biogas and 4–7% less CH ₄
Smith, Carliell-Marquet (2009)	BT, AS dosing in lab with Fe	12–20% less biogas and 10–22% less CH ₄

Key: BT – batch tests; SC – semi-continuous bench-scale; CPR – chemical phosphorus removal; WWTP – wastewater treatment plant; AS – activated sludge; AD – anaerobic digestion

* – compare to biogas production from un-dosed sludge

Materials and Methods

Primary and waste activated sludge was collected from Vilnius waste water plant (Lithuania). Primary sludge (PS) was taken from the primary sludge pumping station before thickening and waste activated sludge (WAS) was collected from the distribution chamber of the secondary sedimentation tank. Fresh sludge used to be taken from the plant every 5th day to avoid changes in sludge characterization and then stored in a refrigerator at a temperature of +4°C.

The proportion of (volume basis) primary and waste activated sludge was 1:2. The average characteristics of the feed of the primary-waste activated sludge mixture are shown in Table 2.

Table 2. The average characteristics of sludge fed

Parameter	Total solids (TS), g/L	Volatile solids (VS), g/L	pH	VS loading, gVS/L/d
Sludge mixture	15.8–23.8	11.6–17.4	6.03–6.34	0.67–0.88

The characterization of PS could vary depending on the presence of solids in wastewater, the types of units, etc. (Smith, Carliell-Marquet 2008, 2009).

The feed was screened with a sieve to avoid large particles and was not thickened due to the narrow tubes (4 mm) of peristaltic pumps. The total solids (TS) concentration in the sludge mixture was 1.6–2.4%. Regular analysis was performed to determine the characteristics and consistency of the feed material.

Experiments were carried out at Vilnius Gediminas Technical University (Lithuania) using anaerobic digestion model W8 (Armfield Ltd, UK) (see Fig. 1).

This model consists of two separate high-rate digesters – 4.8 L each. Reactors were continually mixed using internal mechanical stirrer. Flow rates to the vessels are set and controlled by calibrated peristaltic pumps. The temperature of each reactor was controlled by an electric heating mat wrapped around the external wall. Gas off-take from each reactor was taken into a volumetrically calibrated collector vessel (3300 ml) operating by water displacement. Each reactor was inoculated with anaerobic inoculum obtained from the previous experiment with the anaerobic digestion of the primary-waste activated sludge mixture (Ofverstrom *et al.* 2010).

The sludge mixture was pumped daily during 6 hours through the system using peristaltic pumps. The amount of feed sludge was 0.24 L/d with volatile solids loading (VS_{load}) from 0.67 to 0.88 gVS/l/d with an average of 0.76gVS/d. Sludge was not thickened due to a small di-

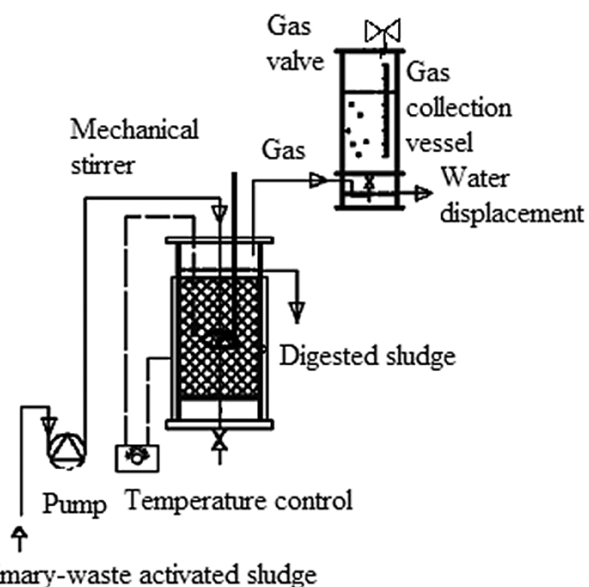


Fig. 1. A scheme of anaerobic digestion model W8 (Armfield Ltd, UK)

ameter of flexible connection pipes. Anaerobic digestion was made under mesophilic conditions at a temperature of 35°C with a solid retention time (SRT) of 20 days.

Laboratory analyses were made in April-June 2010. The total amount of experiments were three – the anaerobic digestion of un-dosed and Fe-dosed sludge mixtures. The doses of Fe were selected according to the Gothenborg (Sweden) WWTP average amounts of Fe in sludge in 2008. It was obtained that the amount of Fe was 52–81 mgFe/gTS. Minimum and maximum doses selected were 50 and 100 mgFe/gTS respectively.

The average concentration of TS in the sludge mixture was 16.8gTS/L. Fe salts selected for the conducted experiment were $FeCl_3 \cdot 6H_2O$ and were dosed daily into the feed sludge mixture (See Table 3).

Table 3. Selected experimental doses of Fe salt

Reactor	Fe (III), mg/gTS	Fe (III), g/L	$FeCl_3 \cdot 6H_2O$, g/L
I	50	0.84	4.17
II	100	1.68	8.34

The final concentration of Fe in the anaerobic digester was 0.84gFe/L for min and 1.68gFe/L for max doses respectively.

Process performance was routinely monitored by measuring pH, influent and effluent TS and VS, alkalinity (ALK), volatile fatty acids (VFA), biogas production and phosphate concentration in sludge liquor. The composition of biogas produced was not measured during the experiment. All analyses were performed according to Standard Methods (APHA 2000).

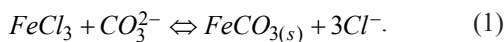
Results and Discussion

The examination of data on digested sludge mixture ALK, VFA and pH showed a reduction in alkalinity in digesters receiving sludge with a max dose of Fe (see Table 4).

Table 4. Experiment results

Parameter		Control digester	Fe-dosed sludge (min)	Fe-dosed sludge (max)
Biogas, L/gVS _{fed}	Min	844	853	500
	Max	1750	1559	1029
	average	1204±339	1212±276	832±211
ALK, mg/L	Min	1600	900	250
	Max	1850	1000	450
	average	1714±85	963±48	367±104
VFA, mg/L	Min	60	60	120
	Max	360	300	180
	average	213±116	135±114	140±35
pH	Min	6.80	6.48	6.31
	Max	7.00	6.72	6.37
	average	6.90±0.06	6.58±0.10	6.34±0.03

During digestion, Fe-dosed sludge with max dose pH was only 6.32–6.37, which is possibly due to lower alkalinity (only 250–450 mg/L) and probably because of FeCO_{3(s)} precipitation during the first days of the experiment (Mamais *et al.* 1994):



Within the first days of adding Fe salt to feed the sludge mixture, biogas production decreased by about 20–25% and 50% for Fe-dosed sludge with minimum and maximum doses (data is not showed). Biogas production was evaluated from the 10th day of the experiment (after process stabilization). The average biogas production from the un-dosed primary-waste activated sludge mixture was 1204 mL/gVS_{fed}, depending on the VS load of the fed sludge mixture which was similar to average biogas production from Fe-dosed sludge (min dose) – 1212 mL/gVS_{fed}. Biogas production from Fe-dosed sludge (max) was only from 500 to 1029 mL/gVS_{fed} with an average of 832 mL/gVS_{fed} which were ~30% lower than from both un-dosed and Fe-dosed (min) sludge (See Table 4).

Daily biogas production (mL/gVS_{fed}) from the un-dosed and Fe-dosed sludge mixture as 2-days running averages is shown in Fig. 2.

Biogas production from un-dosed and Fe-dosed sludge with a minimum dose was decreasing during the 10th–16th days of the experiment probably due to feeding the stored sludge mixture.

A fresh sludge mixture was dosed from the 16th day of the experiment which affected biogas production: Fe-dosed

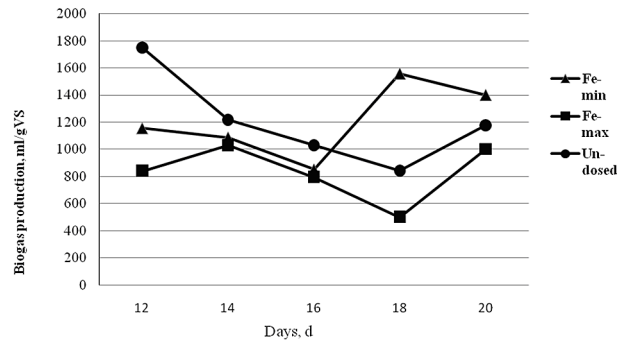


Fig. 2. Biogas production ml/gVS from un-dosed and Fe-dosed sludge digestion

with a minimum dose became higher directly after feeding of fresh sludge. Biogas production from un-dosed and Fe-dosed sludge with a maximum dose was changing from the 18th day and was slower than that for Fe-dosed sludge with a minimum dose. Iron is a necessary element for the growth of microorganisms as it forms an important component of a number of enzymes involved in the metabolic processes of bacteria. Iron was as a trace metal for Fe-dosed sludge with a minimum dos, was overdosed for Fe-dosed sludge with a maximum dose and was toxic for methanogens.

The average phosphate concentration in fed sludge mixture liquor was 42.7 mg/L. The average phosphate content in digested sludge liquor from un-dosed sludge increased by 38% due to the solubilization of phosphate during anaerobic digestion and varied from 42.8 to 68.4 with an average of 56.0 mg/L. The pH of un-dosed digested sludge was from 6.80 to 7.0 that was low for the precipitation of struvite (NH₄MgPO₄). Struvite precipitates at pH 8.5 at higher (Mamais *et al.* 1994).

The effect of the pH of the digested sludge mixture on the concentration of phosphates in sludge liquor is showed in Fig. 3. Strong power correlation ($R^2 = 0.869$) was found between pH and phosphate concentration. During the digestion of Fe-dosed sludge, pH was lower than 6.7 and an aver-

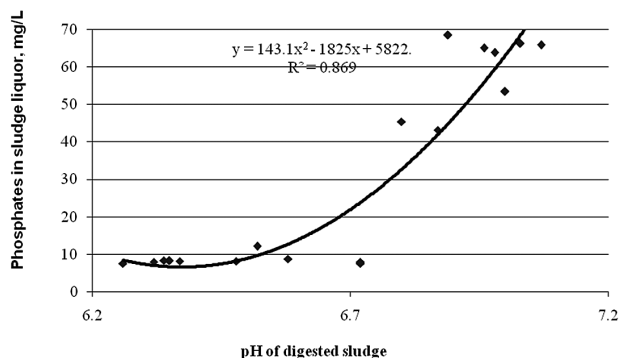


Fig. 3. The effect of pH on phosphate concentration in digested sludge

age concentration of phosphates in digested sludge liquor was 9.2 for Fe-dosed sludge with a maximum dose and 8.6 for Fe-dosed sludge with a minimum dose. Mamais *et al.* 1994 suggested that when iron dose is increased, soluble PO_4^{3-} decreases if $\text{Fe}_3(\text{PO}_4)_2(\text{s})$ precipitates.

During the experiment, phosphate content in digested Fe-dosed sludge liquor decreased by 80% for both sludges compared to the content of phosphates in fed sludge liquor.

Conclusions

The effects of adding iron salt on the digested primary-waste activated sludge mixture were investigated through experimental studies making the following conclusions:

1. The obtained results showed that the anaerobic digestion of Fe-dosed sludge (min) with the Fe concentration of 0.84 gFe/L resulted similar biogas production as from un-dosed sludge mixture. The average biogas production was 1.20 L/gVS_{fed}.
2. Fe-dosed sludge (max) produced 30% less biogas in comparison with biogas production from un-dosed sludge.
3. The average phosphate content in digested sludge liquor from un-dosed sludge increased by 38% due to the solubilization of phosphate during anaerobic digestion.
4. Phosphate content in digested Fe-dosed sludge liquor decreased by 80% for both Fe-dosed sludges compared to phosphorus content in fed sludge liquor.
5. It is necessary not to overdose Fe salt during sludge digestion. Higher Fe salt doses could negatively affect biogas production.
6. For a better understanding of Fe effect on the anaerobic digestion process of the primary-waste activated sludge mixture, biogas composition analysis is required.

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GELEŽIES DRUSKOS ĮTAKA ANAEROBINIO DUMBLO PŪDYMO PROCESUI IR FOSFATŲ IŠSISKYRIMUI Į DUMBLO VANDENĮ

S. Ofverstrom, R. Dauknys, I. Sapkaitė

Santrauka

Nuotekų valymo įrenginiuose geležies druskos naudojamos cheminiam fosforui šalinti, sieros vandeniliui biodujose mažinti ir struvito nuogulų formavimosi prevencijai. Tyrimai atlikti laboratorinėmis sąlygomis naudojant anaerobinio pūdymo modelį W8 (Armfield Ltd., Didžioji Britanija) ir pūdamą pirminio perteklinio dumblo mišinį, į kurį buvo dedama geležies druskos, siekiant nustatyti geležies druskos naudojimo efektą anaerobinio pūdymo procesui ir fosfatų išsiskyrimui į dumblo vandenį. Rezultatai parodė, kad pūdamą dumblą be geležies druskos ir dedant geležies druskos minimalią dozę, susidarė vidutiniškai vienodi kiekiai biodujų (mL/gBSM_{teikiam.}), bet į pūdomą dumblą dedant maksimalią geležies dozę, biodujų išeiga vidutiniškai sumažėjo 30 %. Į pūdomą dumblą nededant geležies chlorido, fosfatų koncentracija dumblo vandenyje vidutiniškai padidėjo 38 %. Ir priešingai, geležies chlorido dozės fosfatų koncentraciją pūdyto dumblo vandenyje sumažino 80 %.

Reikšminiai žodžiai: anaerobinis pūdymas, dumblo mišinys, fosfatai, geležies druska.