Effect of different iron sources on vivianite formation and anaerobic sewage sludge digestion

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Introduction

Phosphorus is an essential nutrient for all living organisms and is a key element for global food production as it is widely used as fertilizer. The mineral fertilizer use increased due to the global population growing in numbers as well as due to the changes in food consumption habits over the years. So, it is of paramount importance to exploit secondary sources of phosphorus like sewage sludge. Phosphorus is present in wastewater mainly due to household cleaners and human excrements and is also identified as one of the main causes of eutrophication in water resources. While phosphorus removal technologies are well-established and widely applied, phosphorus recovery remains a challenge. Formation of Vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), a hydrated insoluble iron phosphate mineral, could increase the share of magnetically recoverable P in sludge by higher Fe dosing. The present study concentrates on the effects of different iron sources like Ferrous (Fe^{2+}), Ferric (Fe^{3+}), Metallic Iron (Fe^0) and recycled ferric iron on vivianite formation and biomethane production during anaerobic sludge digestion.

Aim

The main purpose of this research is to study the recovery of phosphorus from municipal waste in the form of crystalline vivianite from the sludge produced during aerobic sludge digestion. Also, to identify the parameters that affect the production of biogas and vivianite and on the other hand to identify possible symbiotic link between a wastewater treatment plant and a water treatment plant, where the one will be the producer of mineral vivianite sustainably and the other will be the iron source provider (recycled ferric iron) so that the whole process will be in line with the circular economy model and sustainable development

Materials & Methods

- Activated sludge samples were obtained from excess sludge (Larnaca WWTP) before mechanical thickening by a screw thickener. As Inoculum an anaerobic sludge from the Metamorphosis Wastewater Treatment Center (KELM) is used
- For vivianite formation sludge needs to be anaerobically digested, and iron must be added to the sludge.
- The experiments are performed in triplicates batch-wise [1]
- Different iron sources are tested for vivianite formation during anaerobic sludge digestion and compared to a control sample without iron addition.
- VS Inoculum to substrate Ratio is set to 1 and the digestion period was approximately 20 days.
- The amount of iron that is added is calculated based on the stoichiometrically molar ratio of Fe:P= 1.5 that is required for vivianite formation.

Figure 1: Experimental set up for Anaerobic Digestion and Biomethane Potential Tests

Analysis performed for sample characterization before and after anaerobic digestion:

- Determination Of Total Solids (TS)
- Determination Of Volatile Solids (VS)
- Determination Of Total Suspended Solids (TSS)
- Determination Of Volatile Suspended Solids (VSS)
- Determination Of Total Dissolved Solids (TDS)
- Determination Of Metals Cd, Cr, Cu, Mn, Ni, Pb, Zn With Atomic Absorption
- Determination Of Total Organic Carbon (TOC)
- Determination Of Total Nitrogen (TN)
- XRD ANALYSIS
- Optical Microscope Analysis (OM)

Results

Sludge Characteristics												
Parameter	pH	ORP	Conductivity	TS	VS	TSS	VSS	TDS	Total P	Total COD		
Unit	-	mV	mS	g/l	g/l	g/l	g/l	g/l	g/l	g/l		
Inoculum	8,24	-6,9	8,11	37,99	24,47	29,66	19,80	1,20	0,140	47,70		
Substrate	6,77	21,5	3,12	14,86	9,70	13,48	10,18	1,96	0,460	14,58		
Liquid Phase												
Parameter	K	Na	Ca	Mg	Fe	Dissolved TOC	Dissolved TN	Dissolved P	Dissolved Sulfate			
Unit	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l			
Inoculum	193,6	251,1	104,3	14,7	n.d.	147,8	914,7	41,6	210,0			
Substrate	312,2	402,2	166,8	22,4	n.d.	414,1	378,1	121,0	21,0			
Solid Phase												
Parameter	Cr	Cu	Mn	Ni	Cd	Pb	Zn	K	Na	Ca	Mg	Fe
Unit	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg
Inoculum	1,17	1,15	0,49	0,16	0,00	0,00	3,33	7,39	21,73	59,35	10,13	32,62
Substrate	0,05	0,18	0,24	0,04	0,00	0,00	0,89	15,31	13,28	203,12	20,26	20,48

Table 1: Characteristics of the Inoculum and activated sludge used in the batch experiments

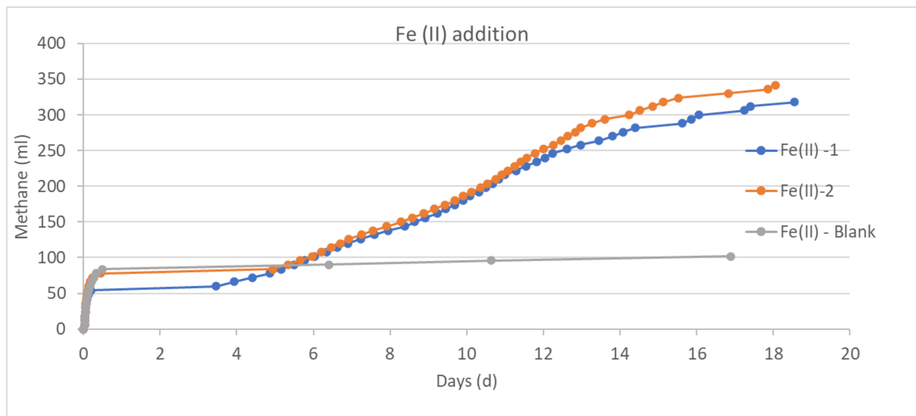

Figure 2: Methane production during anaerobic digestion of samples with excess of Fe (II) source

Figure 2 presents typical methane production during anaerobic digestion of samples with excess of FeCl2 as Fe(II) source. After the 4th day, the methanogenic microorganisms start methane production. There is almost a linear increase in the methane production until about the 10th day when a decline in the production rate is observed up to the 18th day when methane production nearly stops. The initial linear methane production increase may be due to consumption of readily biodegradable organic material by microorganisms firstly, and then the remaining biodegradable organic fractions.

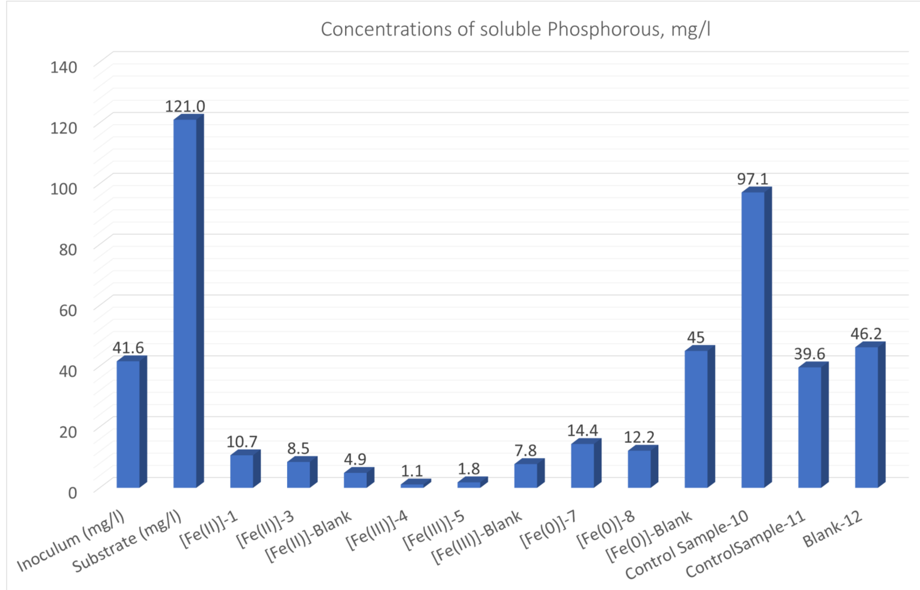

Figure 3: Concentration of soluble phosphorous before and after anaerobic digestion

After anaerobic digestion, soluble phosphorus (Fig. 2) in all samples occurs in lower concentrations than initially, which indicates the formation and presence of vivianite in the sludge

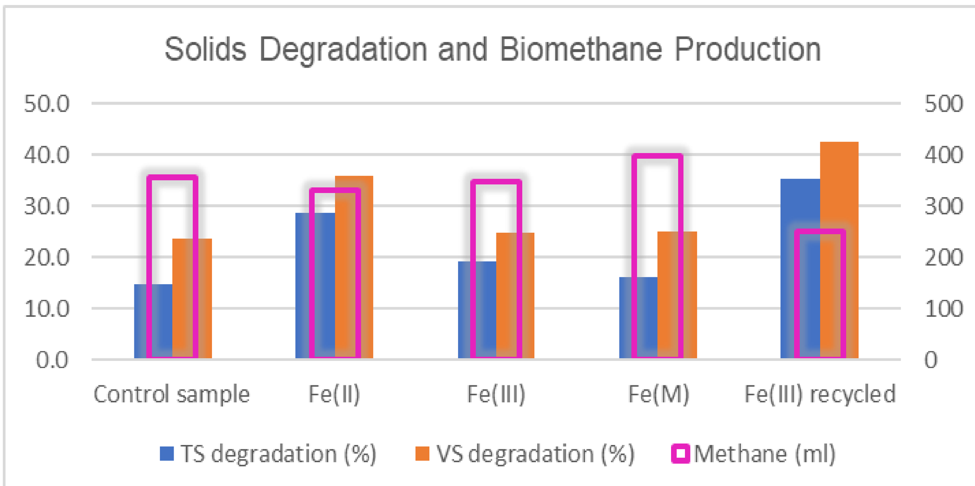

Figure 4: Solids degradation and Biomethane production per category iron source added

The highest methane production per g TS and VS occurs in samples with metallic iron. It seems that the presence of ferric and ferrous iron slightly suppresses the production of biomethane. The highest solids degradations (Fig.4) were observed in the samples with these iron sources which may indicate that the production of CO2 is favored over biomethane.

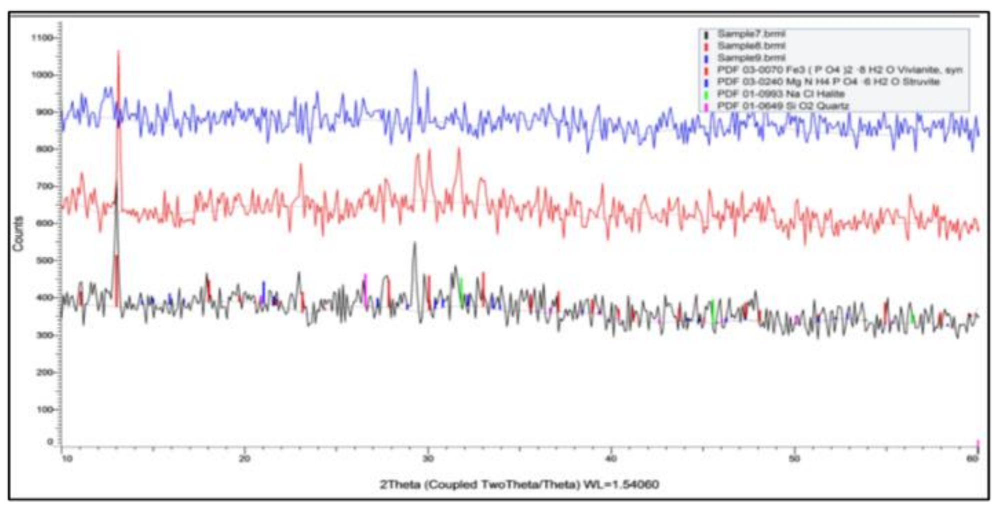

Figure 4: XRD analysis of samples with additional metallic iron

Vivianite formation with the characteristic peak at 2θ ≅ 13° can be observed in all samples with excess iron. Apart from, vivianite the crystallin structure of struvite, halite, calcite, and quartz can also be noticed. No formation of vivianite is detected in control samples (Fig.4).

Conclusions

This study shows that the use of extra iron during anaerobic digestion of the sludge can affect to some extent biomethane production i.e. 60-70 mlCH4/gVS were produced when an excess of ferrous or ferric iron is added, while 90-100 mlCH4/gVS were produced by control samples (without excess iron) and samples with metallic iron source. Vivianite formation is demonstrated in digested sewage sludge for each iron source tested. Almost all phosphate in sewage sludge can be bound in vivianite. XRD analysis proves presence of vivianite and Optical Microscope analysis indicates its presence as free particles. This fact could potentially allow vivianite separation from the sludge and high phosphate recovery.

References

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