VIII International Congress “Engineering, Environment and Materials in Process Industry“

THE ROLE OF IRON ADDITION ON VIVIANITE FORMATION DURING ANAEROBIC SEWAGE SLUDGE DIGESTION

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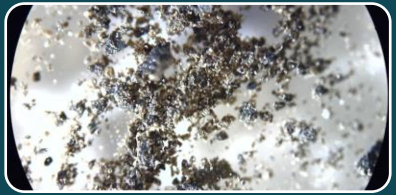
Introduction

- This study was carried out as part of the WATERMINING project, in collaboration with our partners at WETSUS University in the Netherlands.

Introduction

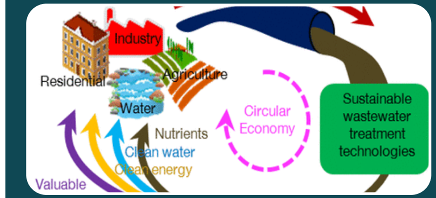
Vivianite

- a rare mineral that typically occurs as blue to greenish-blue prismatic or tabular crystals.
- a hydrated iron phosphate mineral with the chemical formula $Fe_3(PO4)_2 \cdot 8H2O$.



Vivianite is present in WWTP sludge, where phosphorus is removed by chemical precipitation (FeCl3 addition). Vivianite accounts for 2–19% of the sludge

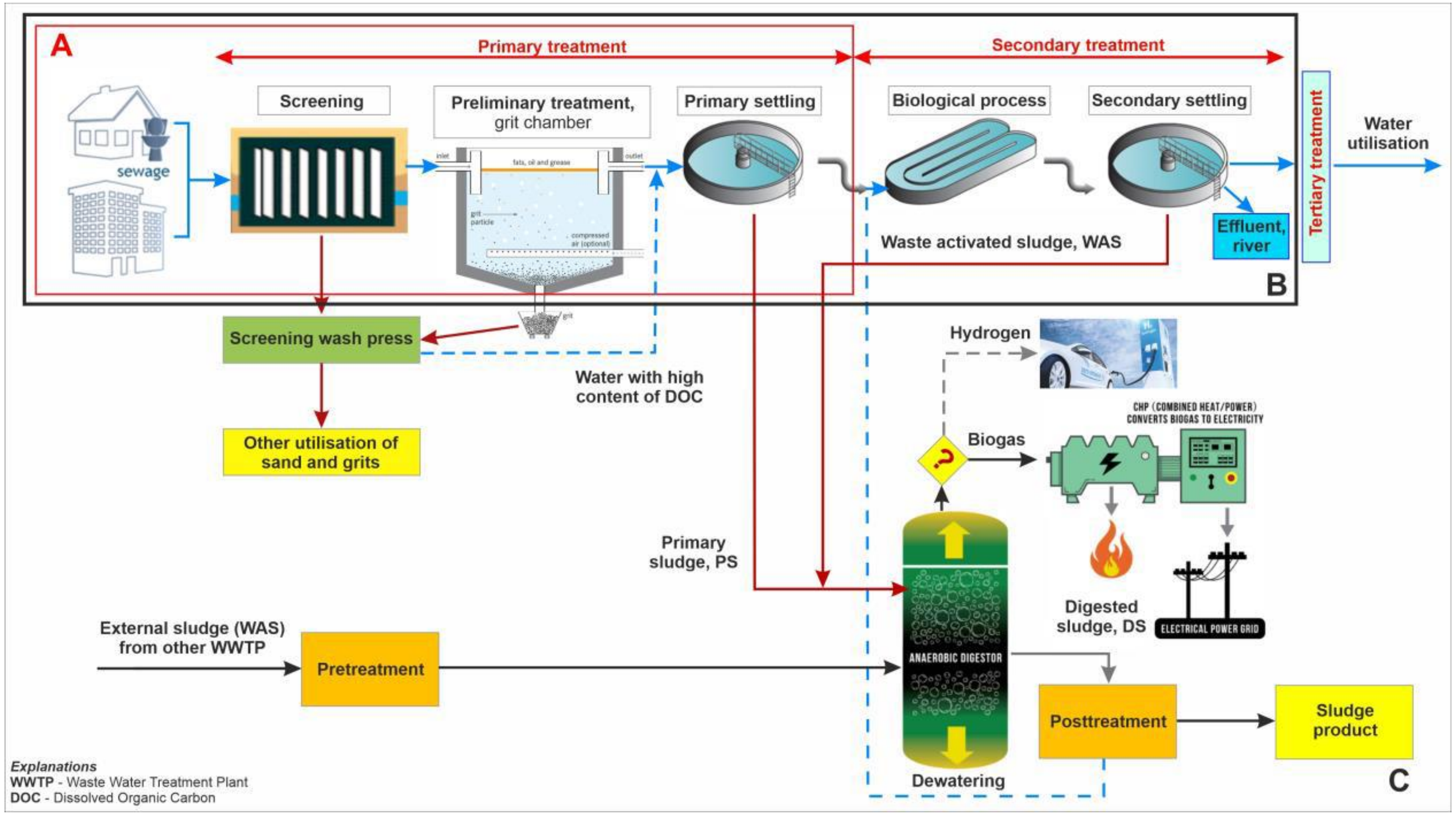
Iron can play an important role in the recovery of vivianite -phosphate from sludge.



Phosphate recovery

- Phosphorus is considered a critical raw material due to its essential role in global food security and its limited and finite supply
- Phosphorus is a key nutrient for plant growth and is commonly used in fertilizers to enhance agricultural productivity.
- The sustainable use and recycling of phosphorus are crucial to meet future demand while reducing the environmental impact of its extraction and production.

Technological scheme of WWTP



Possibility of using sludges from WWTP in a circular economy

Sludges can be considered a significant source of energy and raw materials which can be used in three ways:

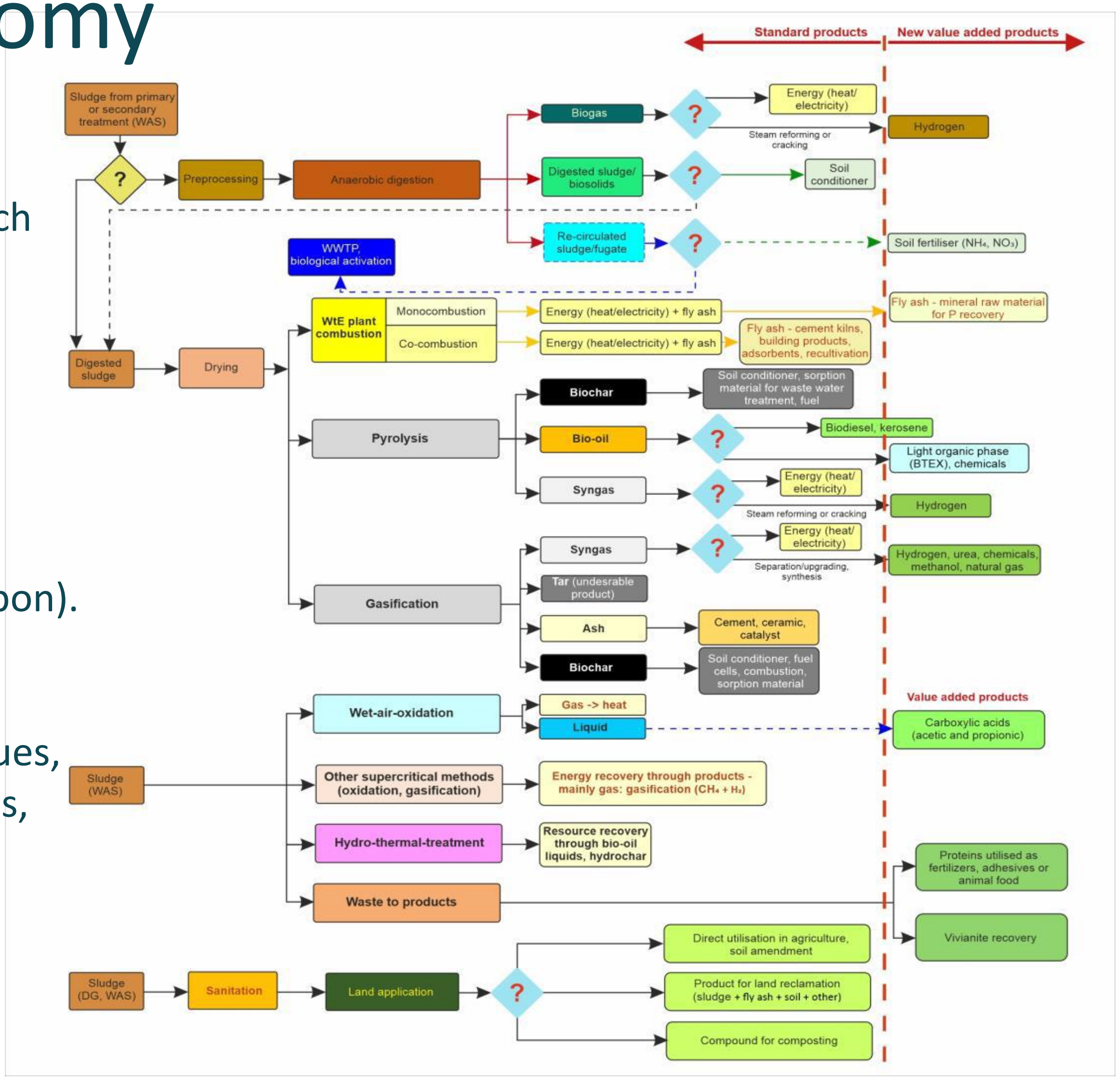
- ❑ sludge for energy recovery,
- ❑ sludge for resource and recycling,
- ❑ and in agriculture

The benefit of recycling is:

- ❑ the use of nutrients (N, P, K, and carbon).

The damage of sludge recycling:

- ❑ Organic micropollutants - drug residues, microplastics, drugs, biocides, hormones, and endocrine-disrupting compounds



EU Strategies to promote sustainable phosphorus management

The EU Green Deal and the Circular Economy Action Plan include measures to promote phosphate recovery from waste streams, such as sewage sludge, animal manure, and food waste. Phosphate recovery can help reduce the EU's dependence on imports and promote a circular economy.

The EU has established a regulation on fertilizers, which allows for the use of recovered phosphorus as a component of fertilizers. The regulation sets out requirements for the production and placing of fertilizers on the market, including the use of recovered phosphorus.

The EU has also funded research and innovation projects aimed at developing new technologies and business models for phosphate recovery. These projects aim to develop cost-effective and environmentally sustainable solutions for recovering phosphorus from waste streams.

Objectives

- To demonstrate the possibility of phosphorus recovery in the form of crystalline vivianite and energy recovery from anaerobically digested municipal sewage sludge
- To examine the effects of different iron sources added:
  - Ferrous (Fe2+)
  - Ferric (Fe3+)
  - Metallic Iron (Fe0)
  - Recycled ferric iron
- To explore the possible symbiotic link between a wastewater treatment plant and a water treatment plant

Materials & Methods

- The Biochemical Methane Potential (BMP) test is used to determine the biodegradability of an activated sludge substrate under anaerobic conditions
- Activated sludge samples - from Larnaca WWTP, Cyprus
  Inoculum, an anaerobic sludge - from the Metamorphosis Wastewater Treatment Centre (KELM)
- BMP tests were performed in an automated BMP system for approximately 20 days. The tests are carried out at 37 °C in triplicates with an inoculum to substrate ratio (I/S ratio) =1
- The tests are carried out using batch reactors with a working volume of 1l.
- Blank samples are included in the test to measure the indigenous methane production from the inoculums and the positive controls (glucose) are used to test the activity of the inoculum
- Activated sludge and activated sludge with an excess of 4 different iron sources were tested in this study.
- Amount of iron added: based on the stoichiometrically molar ratio of Fe:P= 1.5

BMP TEST –CJC labs

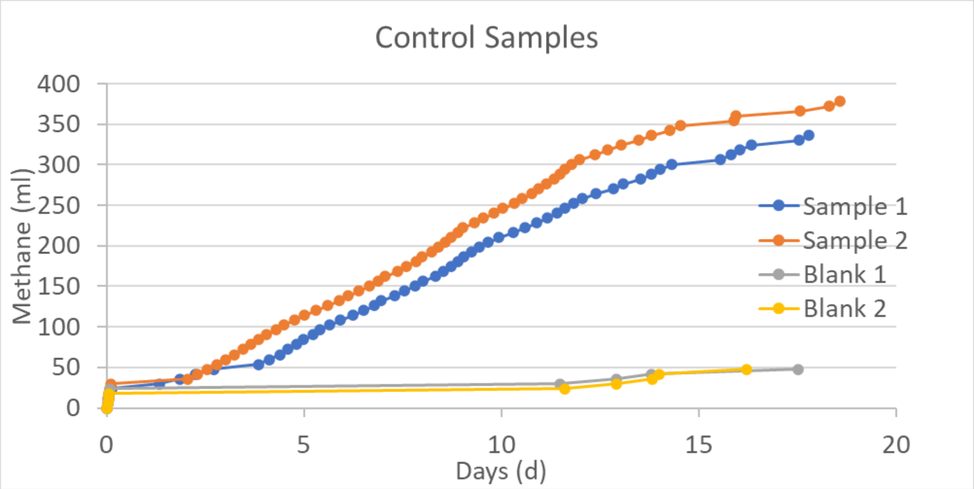
Results – Sludge composition

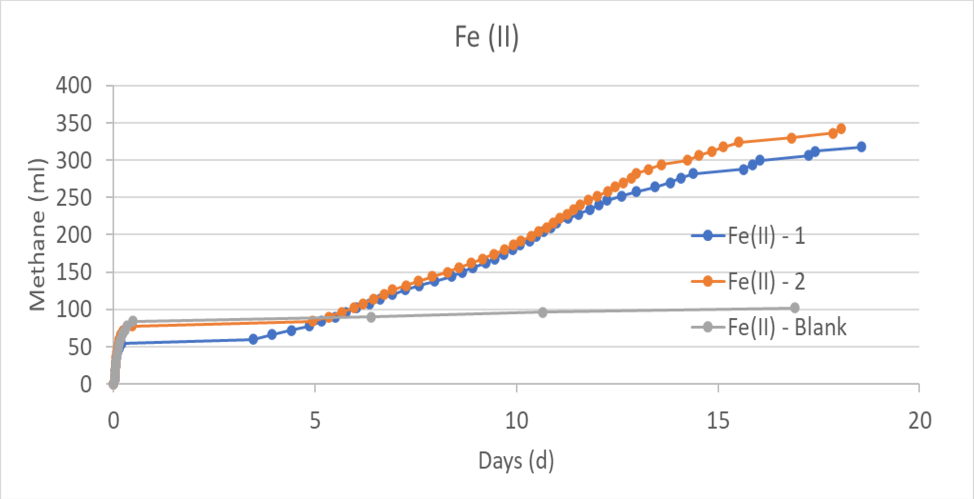
Parameter	Unit	Inoculum	Substrate
pH	-	8,24	6,77
ORP	mV	-6,9	21,5
Conductivity	mS	8,11	3,12
TS	g/l	37,99	14,86
VS	g/l	24,47	9,70
TSS	g/l	29,66	13,48
VSS	g/l	19,80	10,18
TDS	g/l	1,20	1,96
Total P	g/l	0,140	0,460
Total COD	g/l	47,70	14,58
ACID EXTRACTED			
Total Fe	g/l	0,036	0,090
Fe(II)	g/l	0,026	0,012
Fe(III)	g/l	0,010	0,078
LIQUID PHASE			
K	mg/l	193,6	312,2
Na	mg/l	251,1	402,2
Ca	mg/l	104,3	166,8
Mg	mg/l	14,7	22,4
Fe	mg/l	n.d.	n.d.
Dissolved TOC	mg/l	147,8	414,1
Dissolved TN	mg/l	914,7	378,1
Dissolved P	mg/l	41,6	121,0
Dissolved sulfate	mg/l	210,0	21,0

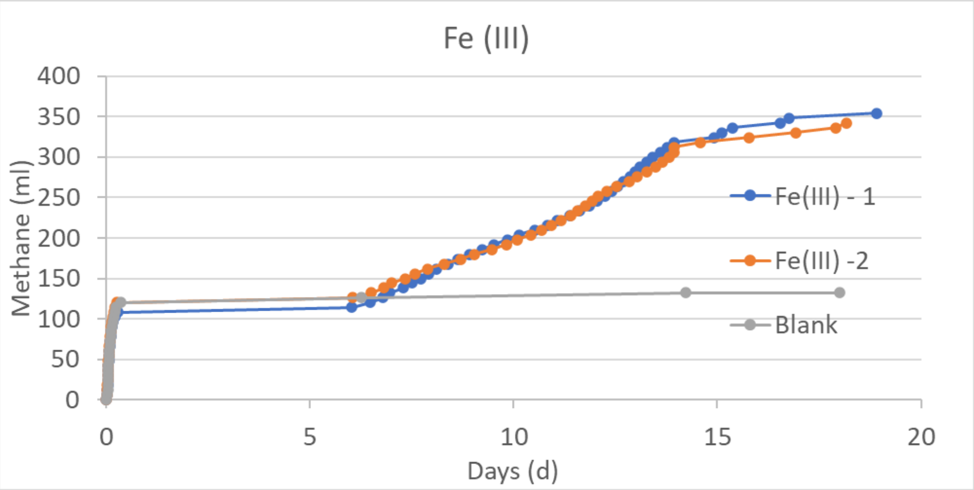
Parameter	Unit	Inoculum	Substrate
SOLID PHASE			
Cr	mg/kg	1,17	50
Cu	mg/kg	1,15	180
Mn	mg/kg	0,49	240
Ni	mg/kg	0,16	40
Cd	mg/kg	0,00	n.d.
Pb	mg/kg	0,00	n.d.
Zn	mg/kg	3,33	830
K	g/kg	7,39	15,31
Na	g/kg	21,73	13,28
Ca	g/kg	59,35	203,12
Mg	g/kg	10,13	20,26
Fe	g/kg	32,62	20,48
TOC (TC-IC)	%	43,30	41,31
TN	g/kg	41,26	40,43

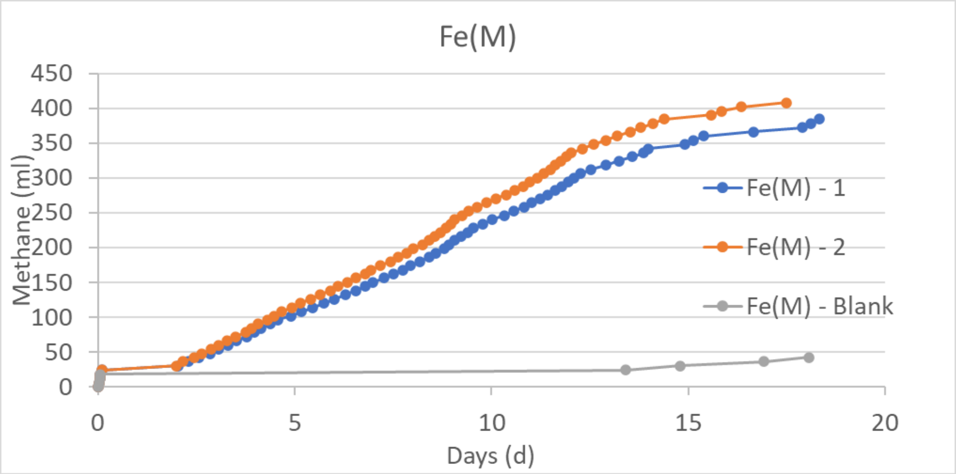
Characteristics of the Inoculum and activated sludge used in the batch experiments

Biomethane potential tests

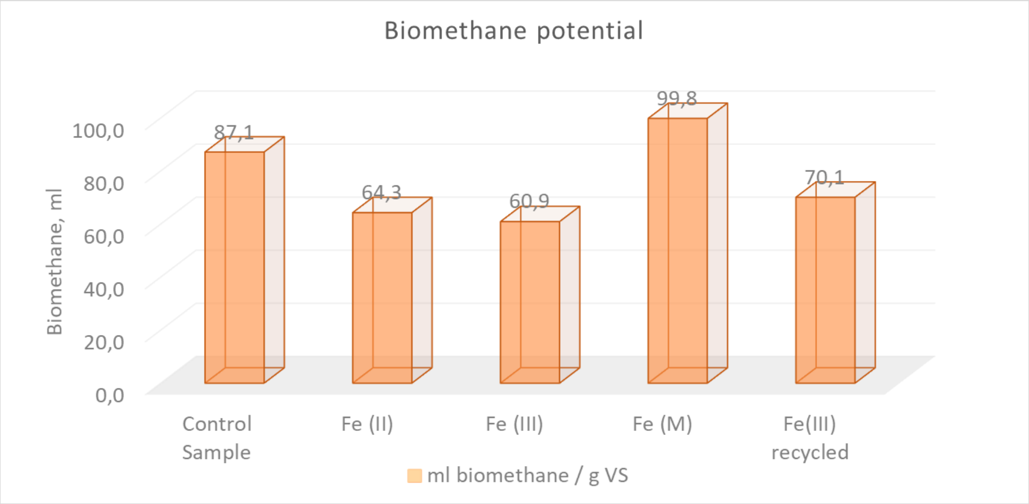


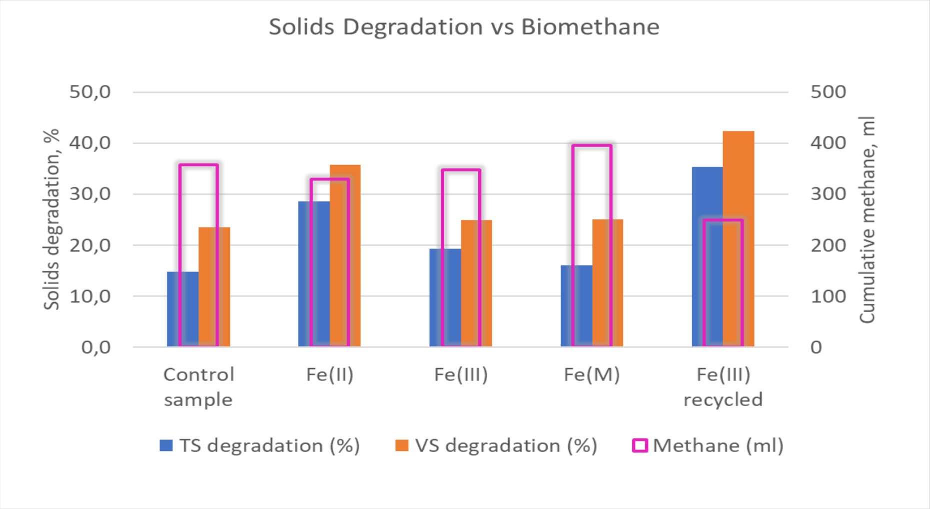






Biomethane potential

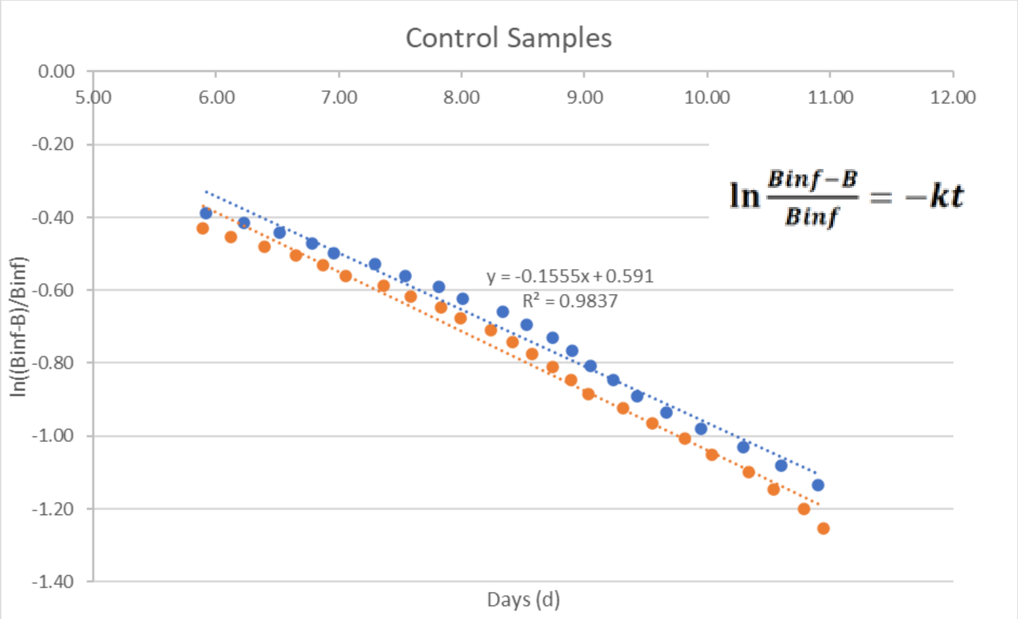




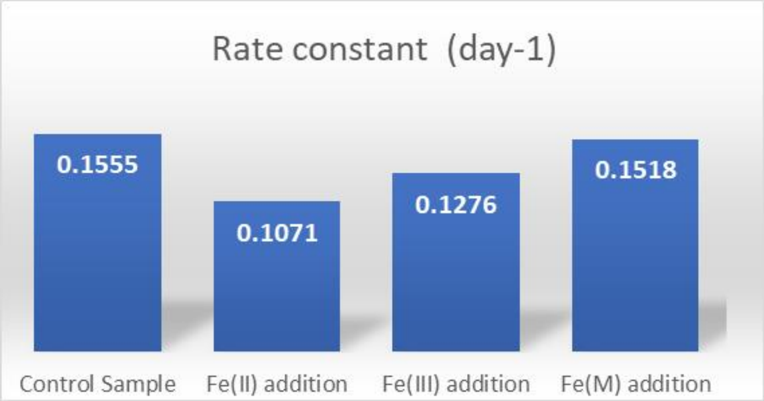
BMP is the normalized methane volume
ml CH_4/g VS

Solids degradation vs Biomethane production

First-order modeling of experimental data



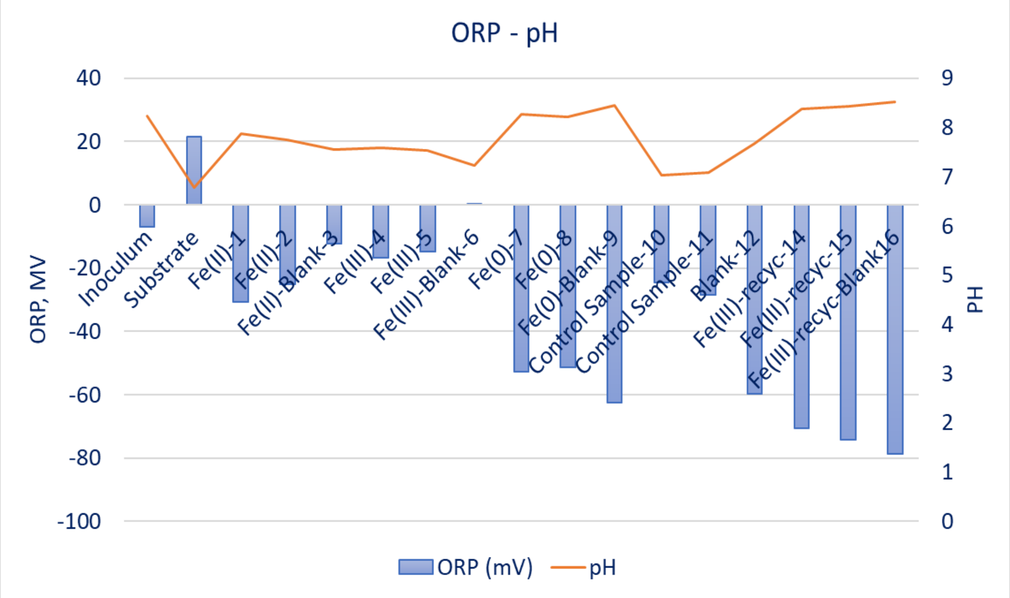
$$\ln \frac{Binf - B}{Binf} = -kt$$



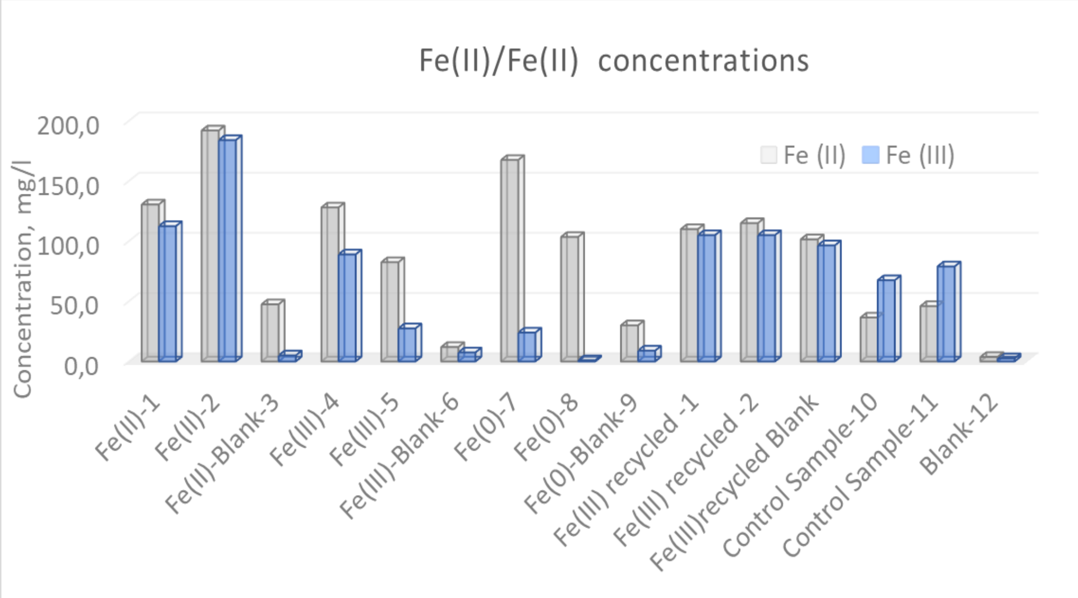
Hydrolysis constant rate

First-order kinetic modelling, assuming that hydrolysis is the limiting factor in the anaerobic conversion process

Characteristics of the digested samples

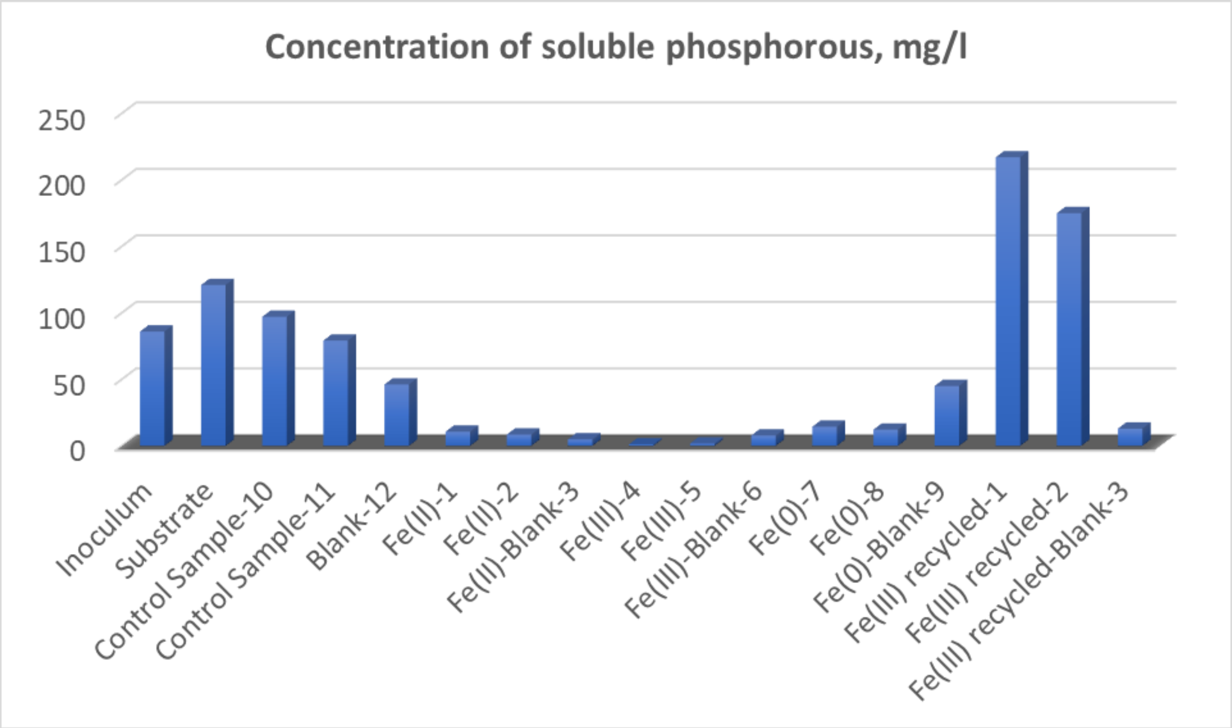


ORP potential – pH of the digested samples



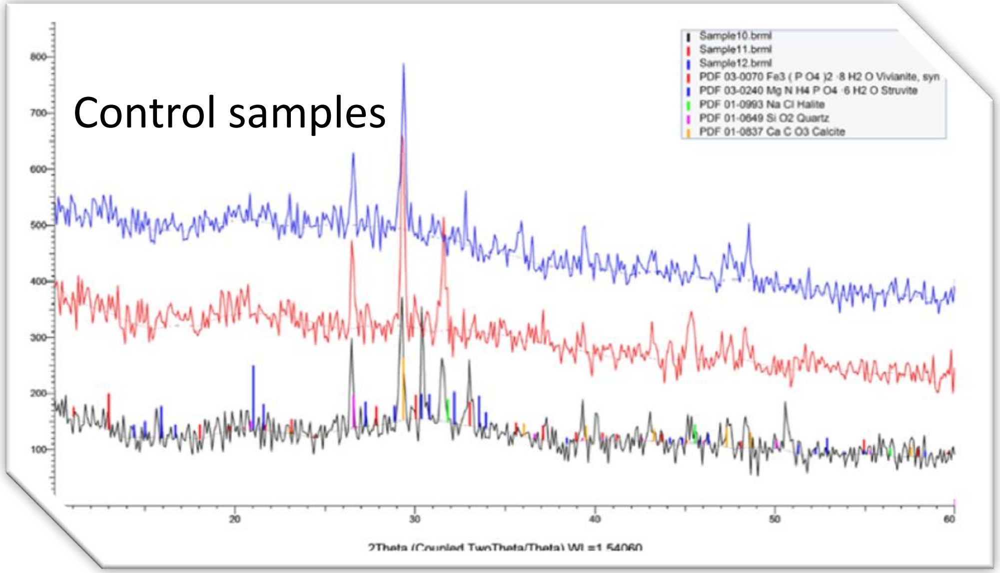
Fe (II) and Fe (III) concentrations after acid extraction of digested samples

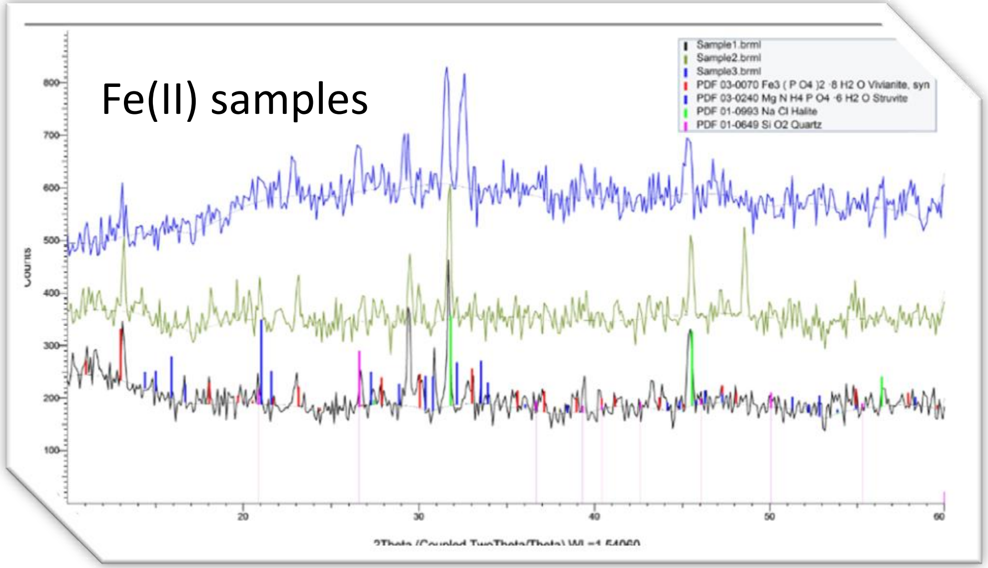
Characteristics of the digested samples

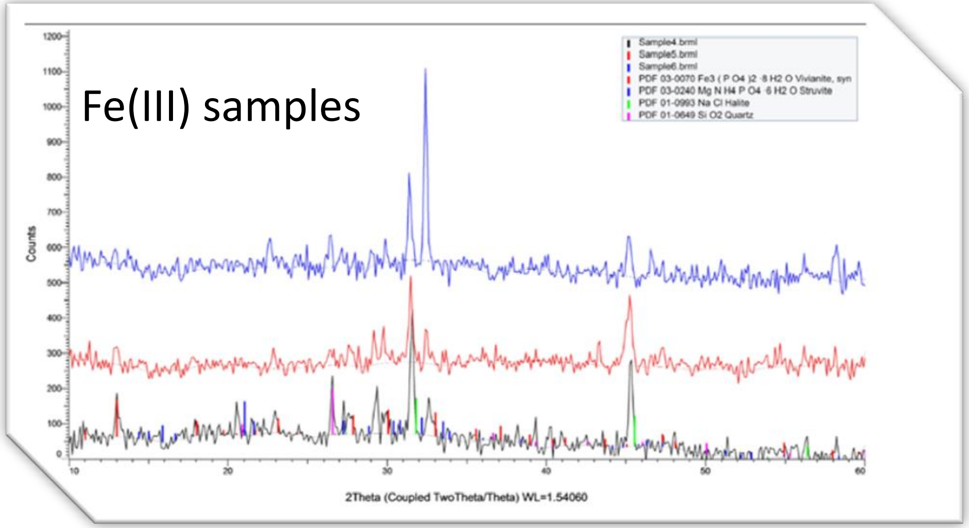


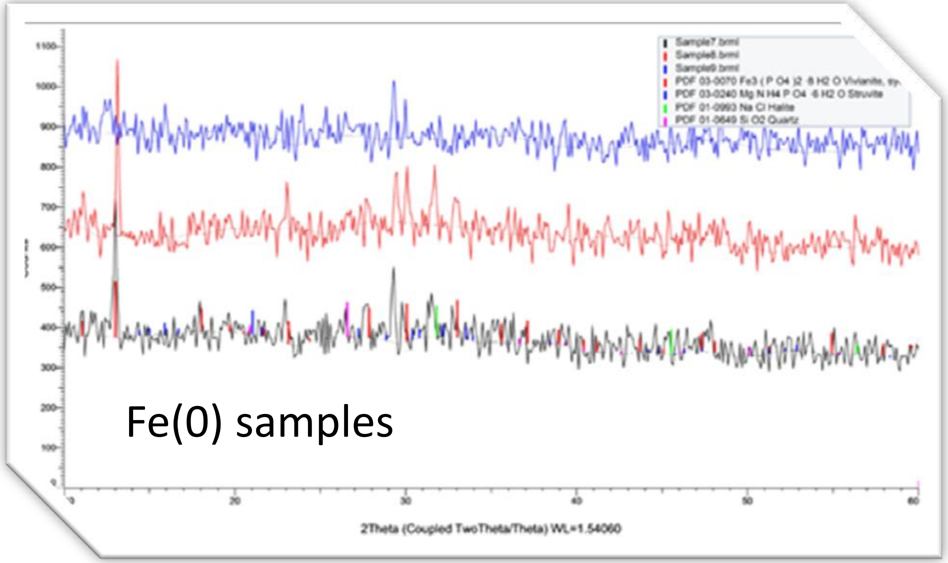
Concentration of soluble phosphorous in Inoculum, Substrate, and Digested Samples

XRD analysis of digested samples

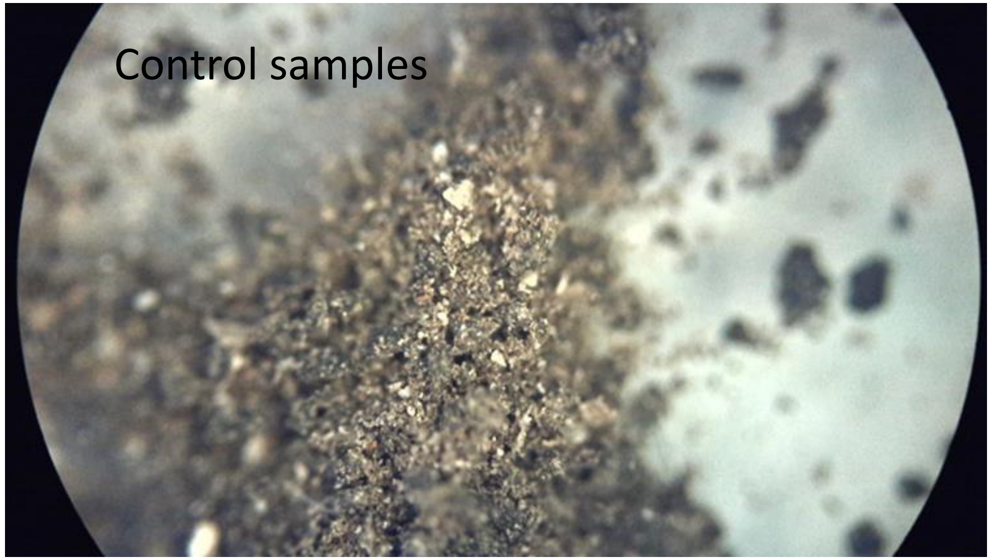


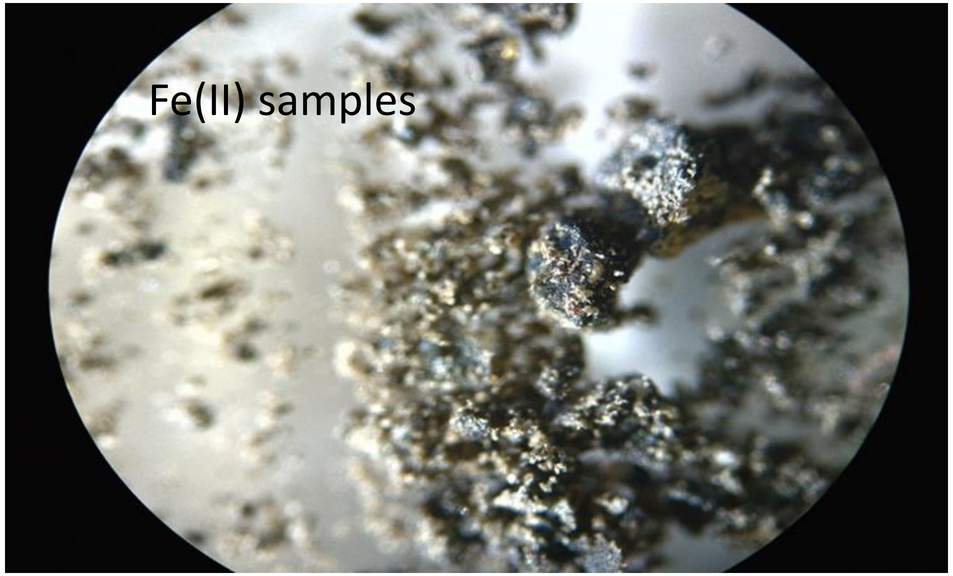


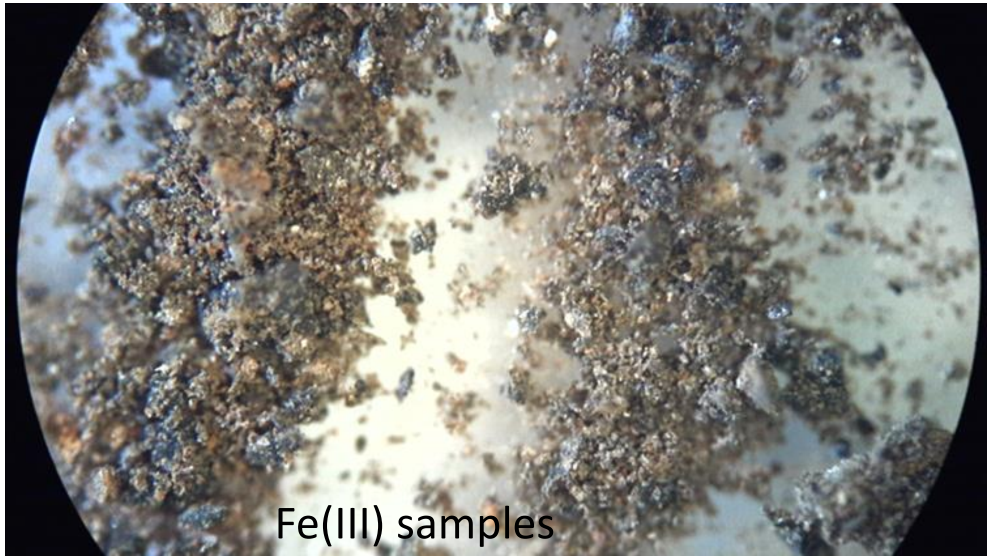


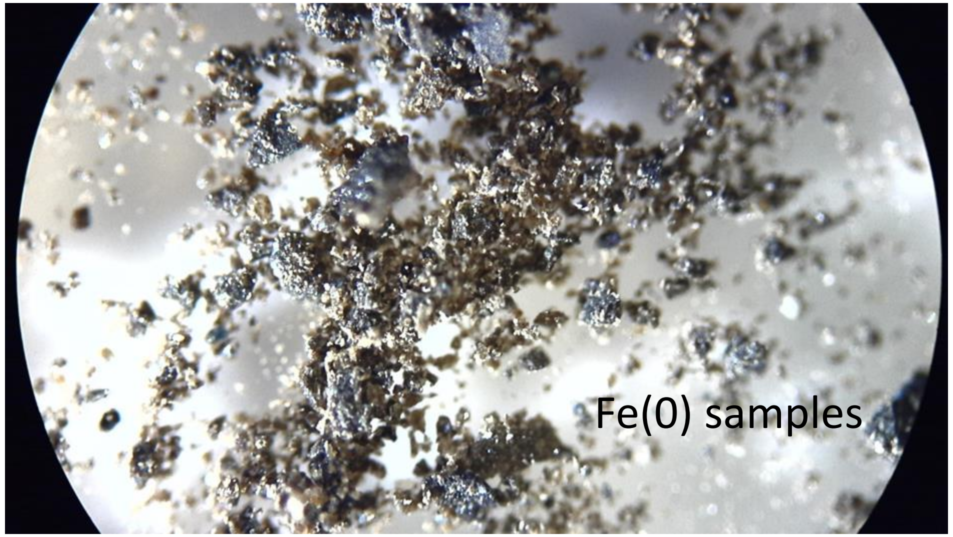


Optical Microscope analysis of digested samples









Theoretical scenario for estimating the electricity generation and vivianite production

Samples	Biomethane $m^3/t_{VS\ substrate}$	Biogas[1] $m^3/t_{VS\ substrate}$	Electric power [2] $kWh/t_{VSsubstrate}$
Control Sample	87,1	134	287
Fe (II)	64,3	99	212
Fe (III)	60,9	934	201
Fe (M)	99,8	154	329
Fe(III) recycled	70,1	108	230
Vivinite production[3]	190 kg/t Dry sludge		

[1] Considered that 65% of biogas is methane [2]Considered that 1 m^3 of biogas produces 2.14 kWh

[3]Considered that 90% of Total P is converted to Vivianite

Conclusions

Conclusions

- Iron is an element that is commonly found in Wastewater Treatment Plants and can be added at different stages of WW treatment for COD and phosphorous removal.

- It has been demonstrated that adding various sources of iron, such as ferrous, ferric, metallic, and recycled ferric iron, during anaerobic digestion can facilitate Vivianite formation.

- The presence of Vivianite in digested samples is confirmed by XRD and Optical Microscope analysis which shows that Vivianite exists as free particles, potentially binding all of the phosphates in the sludge.

Conclusions

- Concerning biomethane potential, it seems that extra iron addition has some impact on it.
- Samples containing excess ferrous and ferric iron show a reduction of approximately 30% in Biomethane potential (60 and 70 ml CH_4 /g VS) compared to control samples and samples with metallic iron (90 and 100 ml CH_4 /g VS)
- Additionally, the kinetic analysis showed that the control samples and samples with metallic iron had also higher hydrolysis rate constants (0.15 day^{-1}), compared to samples with ferrous and ferric iron (0.11 day^{-1}).
- In terms of energy production, a hypothetical scenario considering the production of biomethane in a wastewater treatment plant revealed that metallic iron addition upon sludge digestion can provide the highest electricity reaching 330 kWh/t $VS_{substrate}$ while also recovering 190 kg of Vivianite per ton of Dry sludge.
- These findings suggest that separating Vivianite from the sludge could be a promising avenue for recovering valuable phosphates and energy. This aligns with the circular economy and nutrient recovery targets of future wastewater treatment plants.

Conclusions

- In summary, the recovery of valuable resources from wastewater treatment plants through the use of iron and sludge digestion can be a good example of the circular economy in action.
- It also contributes to the goals of the European green deal by reducing pollution, and nutrient losses, improving water quality and promoting sustainability

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