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

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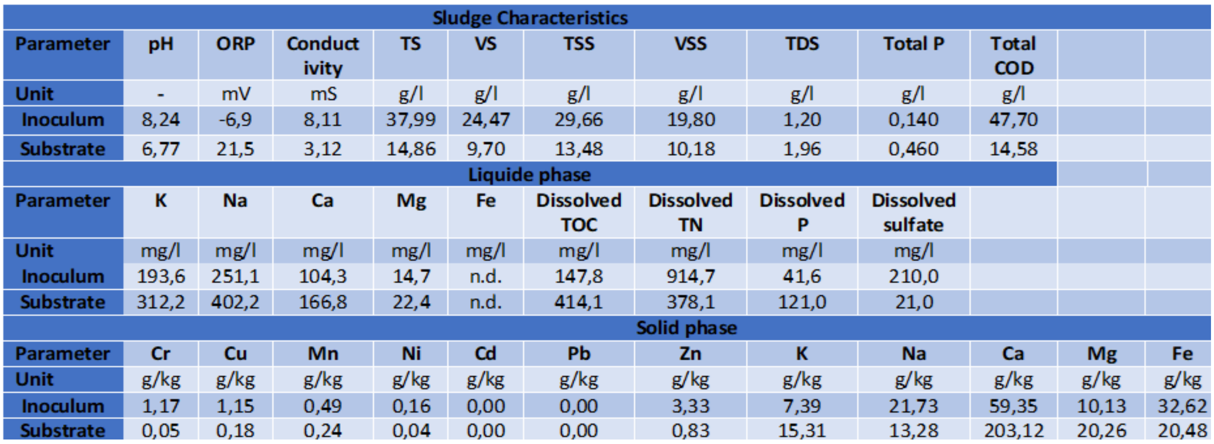
Phosphorus is an essential nutrient for all living organisms and is a key element for global food production as it is widely used as fertilizer (Childers et al. 2011). Since the start of the intensification of agriculture in the 1960s, the mineral fertilizer use increased by more than 700%, due to the global population growth as well as the changes in food consumption habits over the years (Schipanski and Bennett, 2012; van der Salm et al., 2009). Phosphorus is recognized by the European Union as a critical raw material (CRM). So, it is of paramount importance to exploit secondary sources of phosphorus like sewage sludge (Ohtake et al. 2019) for its sustainable use based on the principles of the circular economy. 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. The formation of Vivianite ($Fe^{2+}Fe^{2+}{}_2(PO_4)_2 \cdot 8H_2O$), a hydrated insoluble iron phosphate mineral, could increase the share of recoverable P in sludge by higher Fe dosing (Wilfert et al. 2018).

The present study focuses 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. Biogas production is a key parameter for the energy autonomy of a Wastewater Treatment Plant (WWTP), and can provide the plant with heat and electricity. The main objectives of the current study are to identify the parameters that affect the production of biogas and vivianite and to identify a possible symbiotic link between a WWTP 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.

Activated sludge samples were obtained from excess sludge (Larnaca WWTP) before mechanical thickening by a screw thickener. 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 according to Angelidaki et al., 2009. 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. The digestion period was approximately 20 days. The amount of added iron is calculated based on the stoichiometrically molar ratio of Fe:P= 1.5 required for vivianite formation. The calculated amount of iron source added is based on the iron content of the source, and the total P and S content of the sludge. Iron first binds the sulfur in the sludge to form FeS, so more iron is likely needed (Prot et al., 2020).

Table 1. Presents characteristics of the Inoculum and activated sludge used in the batch experiments. All parameters are determined according to Standard Methods (APHA, 2020).

Table 2. Characteristics of the Inoculum and activated sludge used in the batch experiments



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		
Liquide 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	0,83	15,31	13,28	203,12	20,26	20,48

Figure 1 presents typical methane production during anaerobic digestion of samples with excess of $FeCl_2$ 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 is observed and the 18th day methane production nearly stops. The initial linear methane production increase may be attributed to the consumption of readily biodegradable organic material firstly, and then the remaining biodegradable organic fractions. 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. 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. On the other hand, the highest solids degradations (Fig.3) are observed in the samples with these iron sources which may indicate that the production of CO_2 is favored over biomethane. Vivianite formation with the characteristic peak at $2\theta \cong 13^o$ 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).

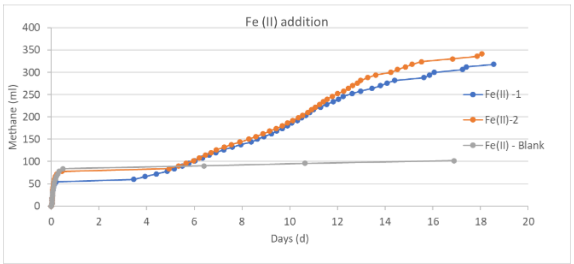


Figure 1: Methane production during anaerobic digestion of samples with an excess of Fe (II) source

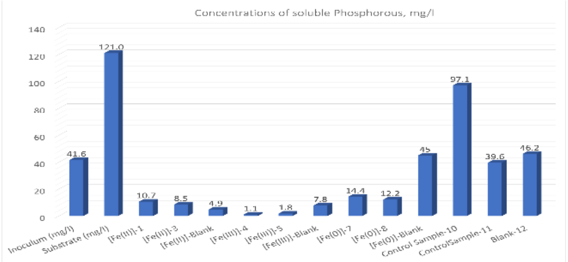


Figure 2: Concentration of soluble phosphorous before and after anaerobic digestion

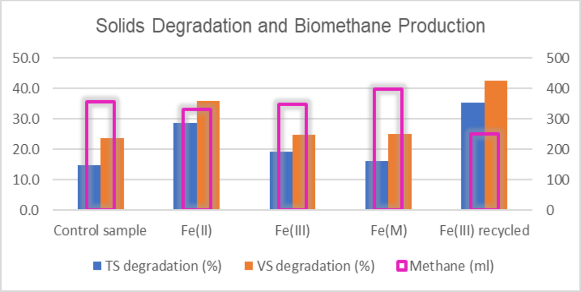


Figure 3. Solids degradation and Biomethane production per category iron source added

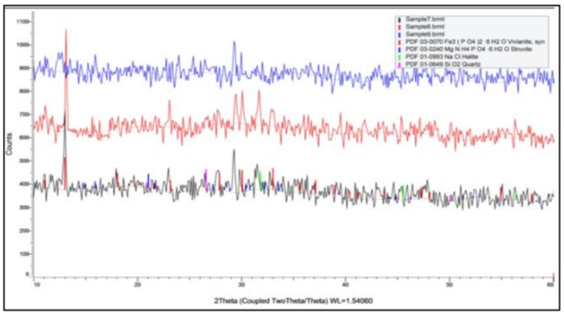


Figure 4: XRD analysis of samples with additional metallic iron

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