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Optimization of Primary Sludge Hydrolysis for Nutrient Removal in Wastewater Treatment Plants

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Abstract. Primary sludge biological hydrolysis may be employed to produce readily biodegradable carbon, used to enhance biological nutrient removal processes applied in wastewater treatment plants. The objective of this work was to evaluate the efficiency of primary sludge hydrolysis to produce readily biodegradable organic carbon. Lab-scale units operated, as acid digesters in order to evaluate the effect of: 1) HRT, 2) SRT, 3) temperature and 4) sludge recycle on the efficiency of primary sludge hydrolysis. Primary sludge acid digesters without recycle operating within an HRT range between 2 d – 5 d may achieve a soluble COD efficiency that ranges between 5% - 8% of influent particulate COD, at ambient temperatures. The temperature dependency of solubilization rates can be described by an Arrhenius type equation with a temperature dependence coefficient θ equal to 0.073.

Primary sludge acid digesters with sludge recycling can achieve much higher efficiencies in terms of readily biodegradable COD and VFAs production even at low HRTs of 1 day. The efficiency of acid digesters with sludge recycle in terms of soluble COD production was found to be approximately 10% of the particulate COD in the influent, at ambient temperatures.

Keywords: anaerobic sludge hydrolysis, acid digester, prefermenter, readily biodegradable COD production

1. Introduction

Anaerobic degradation processes may be divided to at least four stages: disintegration, hydrolysis, acid/acetogenesis and methanogenesis. These processes are normally catalyzed by intracellular or extracellular enzymes and act on the pool of available organic material. According to the Anaerobic Digestion model No1 (ADM1) (IWA, 2002), extracellurar solubilisation which results to readily biodegradable COD production is divided into disintergration and hydrolysis. Disintergration is considered a largely non-biological step and converts composite particulate substrate to inerts, particulate carbohydrates, proteins and lipids. Hydrolysis of particulate carbohydrates, proteins and lipids to monosaccharides, aminoacids and long chain fatty acids (LCFA), respectively is an enzymatic process. Disintergration is mainly included to describe degradation of composite particulate material such as primary or waste activated sludge. The hydrolysis steps are to describe the degradation of well defined macromolecule substrates to each soluble monomer. All disintegration and hydrolysis kinetics are represented by first order kinetics. Digestion of soluble materials mediated by organisms is an intracellular process and results in biomass growth and decay (IWA, 2002).

In the hydrolysis phase, the volatile suspended solids, mainly consisting of proteins (approx. 30%), carbohydrates (approx. 40%) and lipids (approx. 30%), are hydrolyzed by means of extracellular enzymes to aminoacids, sugars and long chain fatty acids (LCFA) respectively. In acidogenesis phase the products from the hydrolysis are fermented into volatile acids and in subsequent acetogenesis phase LCFA as well as volatile fatty acids (VFA) except acetate are decomposed through β-oxidation (Brinch, *et al.*, 1994). Finally, methane is produced in the last phase by means of two groups of methanogen bacteria: a) hydrogenotrophic methanogens, and b) aceticlastic or acetotrophic bacteria.

Acid phase digestion may be employed to produce soluble organic carbon to enhance biological denitrification or biological phosphorus removal (BNR), (Pitman, *et al.*, 1992) or short-cut nitrification/denitrification process for the treatment of sludge reject water with a high NH_4-N content. Maximum production of soluble organic carbon can be achieved only when methane production has been effectively suppressed. The minimum cell residence time for methane production from lipids and volatile acids at mesophilic temperatures and normal pH values of 6.8 to 7.5 is approximately 2.5 to 4 days. However some methane is produced at much shorter detention times due to utilization of hydrogen produced during fermentation of carbohydrates and proteins to volatile acids. Minimum cell residence time for hydrogen utilizing bacteria at 37°C is 19 hours. Methane production also can be suppressed by reduction of pH below the normal range of 6.8 to 7.5 required by the methanogenic phase (Eastman and Ferguson, 1981).

Guerrero et al. (1999), reported that during primary sludge digestion an initial period between 1-10 days could be observed where hydrolysis – acidification were the controlling processes and very low methane production occurred. Following this initial period, VFA accumulation decreases and methane production becomes more important.

Hydrolysis can be carried out in primary settling tanks, in completely mixed closed reactors or in gravity thickeners. The produced soluble organics, consisting mainly of VFA, can be elutriated from the sludge by physical or mechanical means. Sludge recycling is often employed in the case of gravity separation in order to achieve sludge retention times (SRTs) greater than hydraulic retention times (HRTs) and hence enhance “hydrolysers” population by supplying the necessary enzymes for the process. Elutriation through mechanical means is achieved more frequently by centrifugation with no sludge recycling.

The objective of this work was to evaluate the efficiency of primary sludge hydrolysis to produce readily biodegradable organic carbon. Lab-scale units operated, as acid digesters in order to evaluate the effect of: 1) HRT, 2) SRT, 3) temperature and 4) sludge recycle on the efficiency of primary sludge hydrolysis.

2. Materials and Methods

Experimental Set up and Analytical Methods

Experiments were conducted in bench scale primary sludge acid digestion systems. Each of the reactors operated at a different hydraulic retention time, submerged in a water bath for constant temperature maintenance. The anaerobic hydrolysis of primary sludge was studied at three different temperatures: 13.5, 19 and 30°C, and three different HRTs 2, 4 and 5 days. The reactors operated in a pseudo-continuous flow mechanically stirred-tank mode, without sludge recycling (HRT=SRT) or with recycle (HRT < SRT). The reactors were fed once a day with primary sludge from Psyttalia Wastewater Treatment Plant.

During all experimental periods the performance of the acid digesters units was assessed by routine measurements of temperature, pH, DO, ORP, TS, VS, total and soluble COD and NH_4-N. Total Kjeldahl Nitrogen (TKN) and volatile fatty acids (VFA) concentrations were also measured in a regular basis.

All analyses of the lab scale units were performed in accordance with Standard Methods (APHA, 2012). ORP and pH were measured daily using portable equipment (HACH, HQ40d).

Disintegration – Hydrolysis Rate Calculations

In the absence of methane production in a continuous-flow stirred-tank acid digester with constant volume V, constant inflow and outflow q, inflow dissolved and particulate constituents concentrations $S_{i,in}$ and $X_{i,in}$, and effluent concentrations S_i and X_i, the mass balance for the dissolved constituents is:

$$\frac{dVS_i}{dt} = qS_{i,in} - qS_i + Vr_i \Rightarrow$$
$$\frac{dS_i}{dt} = \frac{1}{HRT}(S_{i,in} - S_i) + r_i \qquad (1)$$

where r_i is the rate of constituent *i* production due to extracellurar solubilisation of X_i particulate. According to the ADM1 (IWA, 2002) and as shown by Efstathiou *et al*, 2003 the disintegration first order parameter effects the effluent soluble COD concentration more than the respective hydrolysis constant, as according to the model, disintegration is considered the rate limiting step for particulate COD consumption and SCOD production. Therefore the rate r_i of extracellurar solubilisation that results to soluble COD production can be determined according to the following equation:

$r_i (T) = k_{sol} (T) \text{ x } X_i$

where X_i is the concentration of particulate COD (PCOD) in the reactor that may be solubilized to produce soluble COD. The various fractions of PCOD in the CSTR were determined as follows: 10% PCOD was considered to be inert, and the rest PCOD was considered to be composite particulate material and biomass that could be solubilized to produce soluble COD.

According to the ADM1 (IWA, 2002) the influence of the temperature on the kinetic expressions (disintegration, hydrolysis, etc.) is assumed to be exponential, as shown below:

$$k_{sol} (T) \text{ x } X_i = k_{sol} (35) \text{ x } \exp[\theta (T-35)] \text{ x } X_i \qquad (2)$$

where θ is the temperature coefficient.

Therefore based on eq. (1), (2) and assuming steady state conditions, soluble COD in the effluent of the primary sludge acid digesters can be calculated according to the following equation:

$$S_i = S_{in} + k_{sol} (T) \text{ x } X_i \text{ x HRT} \qquad (3)$$

Efficiency of primary sludge acid digesters

In an acid digester when methane production is negligible, solubilization of particulate organic matter in the feed results in the production of soluble COD which is present in the effluent in terms of VFA or other minor fermentation products. The efficiency of acid digesters can be expressed as a function of soluble COD in the influent and effluent or as a function of VFA in the influent and effluent as follows: (soluble CODinf – solubleCODeff)/COD particulate inf, according to the following equations:

$$\frac{SolCOD\ eff - SolCOD\ inf}{COD\ particulate\ inf} \text{ or } \frac{VFA\ eff - VFA\ inf}{COD\ particulate\ inf}$$

3. Results and Discussion

The experiments were designed to address all three parameters that according to eq. (3) effect soluble COD production in a completely mixed primary sludge acid digester. During the 1st phase of the experiments the effect of HRT and temperature on the efficiency of primary sludge hydrolysis was evaluated. The 2nd phase of the experiments aimed to evaluate the effect of increased particulate concentration (X_i), due to sludge recycle, on soluble COD production.

Effect of HRT: Three lab-scale primary sludge acid digesters operated at HRTs equal to 2, 4 and 5 days and constant temperature of 19 – 21°C, in order to evaluate the effect of HRT on the efficiency of primary sludge solubilization. The reactors operated in a pseudo-continuous flow mechanically stirred-tank mode, without sludge recycling (HRT=SRT). The star-up of each acid digester lasted for approximately one month. Following achievement of steady state conditions the acid digesters operated for approximately another two months to collect all necessary data. The results of the steady state operation of the acid digesters for the three HRTs are summarized in Table 1, while the results of their efficiency in terms of soluble COD and VFAs production is shown in Figures 1-2.

As shown in Figures 1 and 2, within the range of temperatures, pH and residence times studied, increasing residence, results in a significant increase in effluent soluble COD. The efficiency of acid digesters in terms of soluble COD production equals 5%, 6% and 7.9% of the particulate COD in the influent for HRTs of 2 d, 4 d and 5d respectively. In addition VFAs production is also increased both as absolute value and as percent of effluent soluble COD. As shown in Table 1 VFAs production equals to 56, 94.7 and 126 mg COD_{VFA} / g VS_{inf}, for HRTs of 2 d, 4 d and 5d respectively. Approximately 80% of the soluble COD in the effluent is VFAs. The distribution of VFAs, illustrated in Figure 2, was similar in all HRTs studied and on average equals 44.5% acetate, 37% propionate, 15% butyrate and 3.5% isobutyrate. However it should be underlined that due to the relatively low pH in the acid digesters that was consistently below 6.1 and the relatively low average operating temperature that ranged between 19 – 21^{o}C the methanogenesis obtained even at HRT of 5 d, was practically negligible. Methanogenesis was estimated according to the difference between TCOD in the influent and effluent sludge samples. The difference between influent and effluent TCOD concentration was practically zero and therefore methane production was considered negligible. As shown by the ADM1 (IWA, 2002) a higher methanogenesis should be expected if operating at higher pH values and temperatures or HRTs. Therefore based on the results presented in this study it appears that the optimum HRT is approximately 4 d for pH and temperatures do not exceed 6 and 21oC respectively. For higher pHs or temperatures optimum HRTs should be lower than 4d in order to maintain methanogenesis to a minimum.

Effect of temperature: In order to evaluate the effect of temperature on the solubilization rate of particulate organic matter in primary sludge, lab-scale primary sludge acid digesters operated at a constant HRT of 2 d. Each of the reactors was submerged in a water bath for constant temperature maintenance. The anaerobic hydrolysis of primary sludge was studied at three different temperatures: 13.5, 18.5 and 30^{o}C. The total disintegration and hydrolysis rate for each temperature was calculated according to eq. (3). The average values for disintegration and hydrolysis first order parameters equal to 0.023, 0.034, 0.074 d^{-1}. estimated at various temperatures are shown in Table 2.

The temperature dependency of the solubilisation of particulate matter was evaluated using Arrhenius relationship (Figures 3) as follows:

$$k_{sol}(T) = A \times \exp[-Ea/(R\times T)]$$

where k_{sol} (T) is the solubilization rate (d^{-1}), A is a frequency factor (d^{-1}), Ea is the activation energy of the process (J mol^{-1}), R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K). In Figure 3, primary sludge hydrolysis data from a previous study (Efstathiou *et al*, 2003) are also presented that are in very good agreement with the present study. Both studies show that from the slope of the straight line the activation energy was calculated equal to 52.96 KJ mol^{-1} for the solubilization rate. These values are very close to the ones reported by Veeken and Hamelers (1999) for the hydrolysis of organic waste (64 KJ mol^{-1}). The temperature dependence coefficient θ for disintegration and hydrolysis was 0.073, which is higher than the value of 0.054 proposed by Ferreiro *et al*., (2003) for primary sludge hydrolysis.

Effect of sludge recycle: Sludge recycling in primary sludge acid digesters may be employed in a WWTP if the acid digester is followed by a gravity thickener of primary sludge. Applying sludge recycling achieves sludge retention times (SRTs) greater than hydraulic retention times (HRTs) and enhances acid digestion efficiency by recycling necessary extracellular enzymes and by increasing particulate COD concentration in the reactor.

In order to evaluate the effect of sludge recycling, three lab-scale primary sludge acid digesters operated at a constant SRT of 4 d, in a pseudo-continuous flow mechanically stirred-tank mode. Two digesters operated with sludge recycle and HRTs equal to 1 d and 2 d, respectively. The third digester operated without recycle and thus HRT was equal to 4 d. All reactors operated at a constant temperature between 21 – 23^{o}C and were fed once a day with primary sludge from Psyttalia Wastewater Treatment Plant.

The results of the steady state operation of the three acid digesters are summarized in Table 2. Their efficiency in terms of soluble COD production is shown in Figure 4. The data illustrate that sludge recycling significantly increases the efficiency of primary sludge hydrolysis and soluble COD production. The efficiency of acid digesters, in terms of soluble COD production, equals to approximately 9.5 – 10% of the particulate COD in the influent for the two acid digesters with recycle whereas for the system without recycle is equal to 6%. The higher efficiency of the two digesters with recycle is even more evident if one calculates soluble COD production per m^3 of reactor per day. Soluble COD production for digester 1 and 2 with recycle equals to 2.64 kg $COD_{so}l/m^3$-d and 1.26 kg $COD_{so}l/m^3$-d, respectively whereas for the digester 3 without recycle is limited to 0.42 kg $COD_{so}l/m^3$-d. Similar, higher efficiencies are obtained for VFA production. It should be underlined also that no significant difference in the efficiency between the two digesters with recycle was observed. Therefore the digester with the lower HRT (HRT = 1 d) appears the most cost effective solution for primary sludge hydrolysis for readily biodegradable COD production.

Table 1: Primary sludge acid digesters operating with no recycle at various HRTs and effluent values (average values ±standard deviation).

Parameter	**Influent**[1]	**Effluent**	**Effluent**	**Effluent**
		HRT = 2 d	**HRT = 4 d**	**HRT = 5 d**
pH	6.35±0.21	6.2±0.2	5.9±0.2	7.87±0.3
T (^{o}C)		18.7±2.2	21±1.7	21.2±1.5
TS (g L^{-1})	21.5±9.8	17.6±8.8	17.6±6.6	25.0±4.7
VS (g L^{-1})	15.1±7.0	12.9±6.5	12.8±4.9	16.4±5.6
COD total (g L^{-1})	29.0±14.7	23.5±0.07	28.0±10.3	34.0±7.7
COD sol (g L^{-1})	1.61±0.81	2.40±1.20	3.3±1.0	4.4±0.7
NH_4-N (mg L^{-1})	111±30	201±114	233±50	298±57
Redox (mV)		-198±18	-206±26	-171±26
VFA (mg COD L^{-1})	1114±576	1854±926	2694±816	3880±616
Sol COD production (mg CODsol/ g VS_{inf})		72.5	116	143
Sol COD production (%) (CODsol/ COD $partic_{inf}$)		5.0	6.0	7.9
VFA production (mg COD_{VFA} / g VS_{inf})		56	94.7	126
NH_4-N production (mg NH4-N increase/ VS_{inf})		7.1	9.0	9.3

[1] influent data are average values that cover all the period of the experiments of all three digesters

Table 2: Primary sludge acid digesters operating at constant SRT equal to 4 d with and without recycle - influent and effluent values (average values ±standard deviation).

Parameter	**Digester 1**	**Digester 2**	**Digester 3**
	with recycle	**with recycle**	**without recycle**
HRT (d)	1	2	4
pH	5.96±0.31	6.14±0.25	5.9±0.2
T (^{o}C)	23±1.5	21±2.5	21±1.7
Influent TS (g L^{-1})	21.4±8.4	20.0±13.3	20.9±10.6
Influent VS (g L^{-1})	15.3±6.1	14.7±9.3	14.6±7.7
Influent COD total (g L^{-1})	26.5±12.2	28.1±16.3	29.8±16.3
Influent COD sol (g L^{-1})	1.55±0.64	1.37±1.0	1.63±1.0
Reactor TS (g L^{-1})	37.0±6.8	20.0±13.3	17.1±6.6
Reactor VS (g L^{-1})	25.8±5.3	14.7±9.3	12.8±4.9
Reactor COD total (g L^{-1})	50.2±11.3	37.0±11.3	28.0±10.3
Reactor COD sol (g L^{-1})	4.20±1.24	3.91±1.22	3.3±1.0
Effluent NH_4-N (mg L^{-1})	235±50	202±42	233±50
Redox (mV)	-127±18	-140±27	-206±26
VFA (mg COD L^{-1})	1854±926	2542±793	2694±816
Sol COD production (mg CODsol/ g VS_{inf})	173	170	116
Sol COD production (%) (CODsol/ COD $partic_{inf}$)	10.0	9.5	6.0
VFA production (mg COD_{VFA} / g VS_{inf})	125	111	94.7
NH_4-N production (mg NH4-N increase/ gVS_{inf})	7.2	7.0	9.0

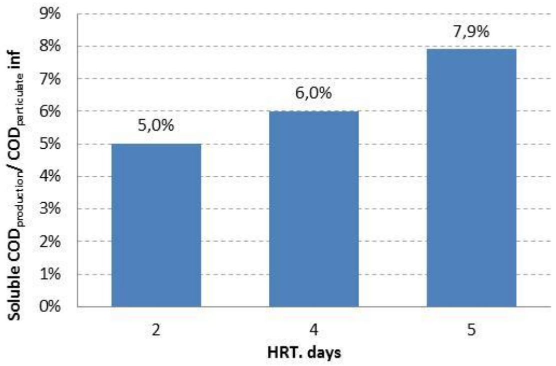

Figure 1: Effect of HRT on soluble COD production

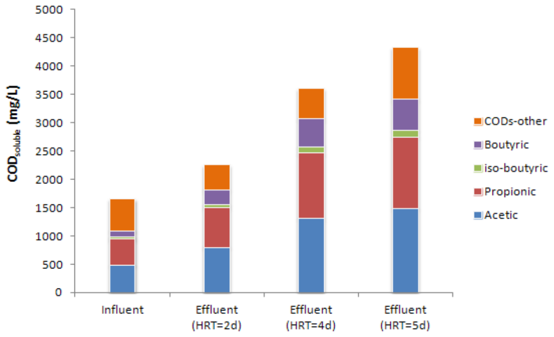

Figure 2: Effect of HRT on VFAs production and distribution

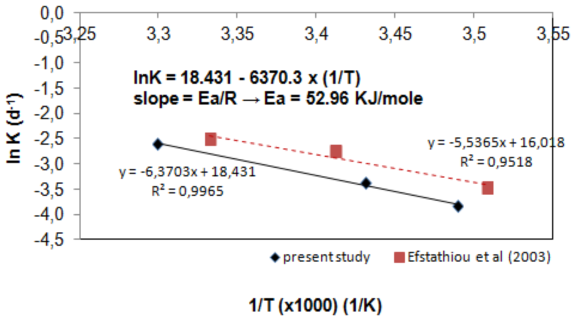

Figure 3: Effect of temperature on solubilization rate: Arrhenius plot with corresponding activation energy calculation.

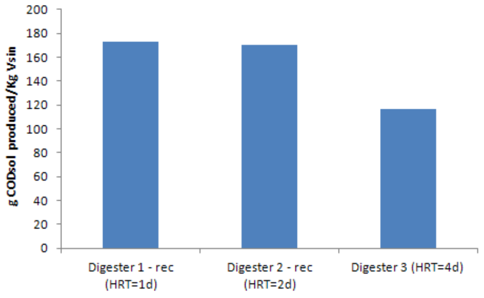

Figure 4: Effect of sludge recycling on primary sludge solubilization in acid digesters.

4. Conclusions

According to the results presented, primary sludge acid digesters without recycle operating within an HRT range between 2 d – 5 d may achieve a soluble COD efficiency that ranges between 5% - 8% of influent particulate COD, at ambient temperatures. The temperature dependency of solubilization rates can be described by an Arrhenius type equation with a temperature dependence coefficient θ equal to 0.073. Primary sludge acid digesters with sludge recycling can achieve much higher efficiencies in terms of readily biodegradable COD and VFAs production even at low HRTs of 1 day. The efficiency of acid digesters with sludge recycle in terms of soluble COD production was found to be approximately 10% of the particulate COD in the influent, at ambient temperatures.

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