EFFECT OF THE ADDITION OF CONDITIONING AGENTS AND OF INVERTED PHASE FERMENTATION PRETREATMENT ON THE BIOCHEMICAL METHANE POTENTIAL OF SLUDGE

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Abstract

Biodegradability tests were performed on sewage sludge to assess the effect of conditioning additives ($FeCl_3$ and cationic polyelectrolytes) on the methane yield. In addition, enzymic hydrolysis pretreatment (42 ºC, 48 hours), called "Inverted Phase Fermentation" (IPF), was also applied to the sludge as a pretreatment and biodegradability tests were performed on the concentrated solid phase obtained. The specific methane potential (SMP) of untreated (raw) sludge was 246 $LCH_4/kgVS_o$. The addition of high amounts of $FeCl_3$ (5.6 g/L sludge) caused a minor change in the SMP, yielding 242 $LCH_4/kgVS_o$. When a cationic polyelectrolyte was also added, increases of 11% and 25% in SMP were obtained depending on the flocculant. When applying IPF as pretreatment, the concentrated solid phase produced a 20% increase in SMP if the sludge did not contain $FeCl_3$, whereas a decrease of 6.8% was obtained if the sludge contained this coagulant. As IPF concentrates solids in an upper thickened layer, the addition of a cationic polyelectrolyte to the sludge inhibited this pretreatment.

Keywords

Sewage sludge, biochemical methane potential, inverted phase fermentation, $FeCl_3$, cationic polyelectrolyte

Introduction

The advantage of Biochemical Methane Potential (BMP) tests resides in the rapid information obtained regarding the biodegradability of a substrate. As these tests are performed under controlled conditions, they provide sludge managers with relevant information to implement appropriate strategies for sludge digestion. Although BMP tests do not reach the specific methane production (SMP) of continuous digestion (Davidsson et al., 2007), they do not require a long time to achieve the optimum Hydraulic Retention Time (HRT).
However, some relevant aspects of BMP should be noted:

1. The ratio $VS_{inoculum}/VS_{substrate}$ determines the feasibility of the test and the kinetics of biodegradation, its optimal value depending on the substrate and the inoculum (Raposo et al., 2006; Tomei et al., 2008; Kameswari et al., 2012).
2. Any inoculum adapted to digest a substrate is preferable to non-adapted inoculum for the same substrate. Acclimated microbiological cultures show the ability to overcome potential inhibitions (e.g. the presence of toxicants) (Chen et al., 2008).

When anaerobic digestion is performed on site, toxic xenobiotics usually come from the wastewater content. However, if anaerobic digestion is to be carried out off site, conditioning agents may be present in concentrations high enough to suppose the depletion of metabolic activity. This situation would lead to different BMP with the corresponding economic imbalance.

It is well known that raw sewage sludge presents poor SMP. This is due to the cellular occlusion of nutrients and the free occurrence of excessively high molecular weight species in the medium. The consequence is the limitation of the kinetics of methane production, in line with the idea of considering hydrolysis as the rate-limiting step of biomethanization (Skiadas et al., 2005). Effort thus focuses on enhancing this step, which is usually achieved by implementing pretreatments prior to anaerobic digestion. Pretreatments can not only accelerate the conversion of macromolecules into more edible substrates for bacteria strains, but also usually increase the amount of methane produced (Carrère et al., 2010). Müller (2001) ranked several pretreatments of sewage sludge according to operating behaviour and the subsequent sludge treatment processes. The Enzymic Hydrolysis pretreatment “Inverted Phase Fermentation, IPF” (Le et al., 2008) presents the advantage of enhanced solubilisation of the sludge coupled to its thickening without the need for reagents. In addition, this form of hydrolysis supposes a reduction in *Escherichia coli* of up to 99.9%.

This paper presents the results of BMP tests on raw sludge, sludge with conditioning agents ($FeCl_3$ and the cationic polyelectrolyte “Chemifloc CH50” or “Chemifloc CH80”), sludge pre-treated by IPF, and sludge pre-treated by IPF and $FeCl_3$.

Experimental procedure

Materials

The sludge used in these experiments came from a wastewater treatment plant (WWTP) operating in a conventional manner, producing mixed sludge as a mixture of primary (thickened by gravity) and secondary (thickened by flotation) sludge. The facility has an average flow rate of 900 m^3/h, treating wastewater from 85,000 p.e., with >87% suspended solids and >90% BOD_5 removal efficiencies.

All samples of thickened mixed sludge were taken prior to dewatering (hence, without additives). $FeCl_3$ and two high molecular weight polyacrylamides (Chemifloc CH50 and Chemifloc CH80) were employed with the raw mixed sludge. Doses of these reagents were chosen to be similar to those used at WWTPs. Lime was not considered for the BMP tests as it prevents the biodegradation of sludge due to its high pH value (pH = 12.5).

The solids content, ammonium nitrogen and pH of the sludge, inoculum and polyelectrolytes are presented in Table 1.

The inoculum was mesophilic digestate from CSTR co-digesting mixtures of sewage sludge, food waste and cattle manure in our laboratory. The digestate was allowed to stand for a minimum of two days (37 ^{o}C) before being mixed with the sludge for the BMP tests. This time ensured degasification of the inoculum before making up the mixtures (Wan et al., 2011). Nonetheless, two blanks of inoculum were also monitored.

Equipment and analytical methods

NH_4-N was determined using an Orion 95-12 selective electrode for ammonium. TS and VS were determined following Method 2540 of the Standard Methods for the Examination of Water and Wastewater (APHA, 1998). pH was determined using a Crison 25 pH-meter. All analytical determinations were performed in triplicate.

Biogas composition was monitored on an Agilent 7890A gas chromatograph using a TCD detector and a Porapack N packed column plus a molecular sieve. The temperature ramp was: starting 35 ^oC (1.5 min), increasing up to 55 ^oC at a rate of 1.5 ^oC/min. Biogas volume was measured with a flow meter. All the gas volumes in this paper were converted to standard temperature and pressure (273.15 K and 101.3 kPa).

Batch experiments

All the sludge samples were characterized on reception at the laboratory and were kept under refrigeration at 4 ^oC for a maximum of two days before being used for the experiments so as to prevent biodegradation. To carry out the IPF, 25 L plastic bottles were filled with fresh sludge and an outlet hose connected the bottles to a large flask containing water to achieve anaerobic conditions. The sludge was heated to 42 ^oC and, after 48 hours, the solid phase at the top was removed and characterised (Table 1).

The mixtures of sludge (or solid phase from the IPF) and inoculum for the anaerobic biodegradability tests were made up maintaining a ratio of VS contribution from the inoculum to VS contribution from the substrate of 1:2. Subsequently, 1750 grams of the corresponding mixture were poured into glass bottles sealed with rubber stoppers and silicone. Either a coagulant (i.e. $FeCl_3$) or a coagulant plus a flocculant (Chemifloc CH50 or Chemifloc CH80) were added to test their effect on the BMP. Final conditioning agent concentrations after addition were 5.6 g$FeCl_3$/L, and 88 mL polyelectrolyte solution/L substrate (the polyelectrolyte solution being 0.6% w/v). Once capped, bottles were purged with N_2 to remove air from the headspace. Bottles were shaken any time the volume and composition of the gas was determined. Biogas was collected in Tedlar bags and measured for volume and composition.

After 25 days of anaerobic digestion at 37 ^oC, the bottles were opened and the digestates analysed. Biogas production and chemical measurements of the inoculum were proportionally subtracted in the other experiments.

Results and discussion

Sludge sample B3 had a poorer organic content than the other two samples, with a low VS/TS ratio (0.53, Table 1). As expected, the SP presented a higher concentration in solids after the IPF pretreatment compared to the raw sludge (Le et al., 2008; Negral et al., 2011), achieving solids concentration factors of around 2 in the two sludge samples tested.

Samples of the inoculum presented the lowest concentrations in solids and also the lowest VS/TS ratios (0.39-0.48), as most of the organic biodegradable matter was mineralized during bacterial metabolism (Marañón et al., 2012).

The addition of $FeCl_3$ in such high proportions (up to 5.6 g/L in samples B2 and B3) resulted in a decrease in the effectiveness of enzymic hydrolysis during IPF. This can be assessed through the NH_4-N in the sludge and in the SPs. By way of example, when going from sludge B1 and B2 to their SPs, the increases in NH_4-N were 265% and 159%, respectively. Clearly the SP obtained from sample B2, which has a very high $FeCl_3$ content, showed the lowest increase in NH_4-N, and hence the lowest degradation of organic nitrogen compounds. Although hydrolysis and acidogenesis constitute acid steps in anaerobic digestion, enzymic inhibition may have been caused by the low pH (3.31) of the sludge with a high content in $FeCl_3$. It is not reasonable to consider inhibition by chloride, as the literature sets the threshold at 6 gCl^-/L (Appels et al., 2008).

CH_4 concentrations during the stable period ranged from 63% in sludge+$FeCl_3$ and 72% in SP. Of the negligible biogas produced by the inoculum, only 22% was CH_4. This translated as 0.01 LCH_4/gVS_o. The final SMP and daily methane production until day 20 are presented in Figure 1 for the studied substrates.

Table 1: Characterization of initial sludge samples, solid phases (SP), inoculum (I) and polyelectrolytes

Sample	TS (g/L)	VS (g/L)	VS/TS	pH	NH_4-N (g/L)	$FeCl_3$ (g/L)
Sludge						
B1	32.61	24.07	0.74	5.87	0.37	
B1 (SP)	64.31	43.78	0.68	6.30	1.35	
B2	48.93	35.90	0.73	3.31	0.06	5.60
B2 (SP)	90.68	68.89	0.76	3.13	0.15	
B3	75.11	39.61	0.53	5.16	0.12	5.60
Inoculum						
I A	25.06	9.89	0.39	7.98	0.72	
I B	21.60	9.20	0.43	7.61	0.30	
I C	19.78	9.49	0.48	7.59	0.41	
Polyelectrolyte						
Chemifloc CH50	6.70	6.06	0.90	3.14	0.07	
Chemifloc CH80	3.90	3.47	0.89	6.34	<0.01	

Table 2: Removal of solids after anaerobic biodegradation

Sludge sample	TS (%)	VS (%)
Sludge	35	50
Sludge+$FeCl_3$	14	45
Sludge+$FeCl_3$+Chemifloc CH50	12	40
Sludge+$FeCl_3$+Chemifloc CH80	14	52
SP	17	37
SP+$FeCl_3$	28	52

Untreated sludge

The degradation of solids in the sludge (Table 2 and Figure 2) remained within the usual range reported by other authors (Mottet et al., 2010). A reduction of around 50% in VS was obtained, producing 246 $LCH_4/kgVS_o$. The increase observed in NH_4-N is due to ammonification of the organic nitrogen.

Sludge with $FeCl_3$

The presence of $FeCl_3$ had no appreciable effect on methane potential or biodegradation, obtaining specific productions of 242 $LCH_4/kgVS_o$ for Sludge+$FeCl_3$. It is worth noting that the low pH in sample B2, attributable to the high concentration of $FeCl_3$ (5.6 g $FeCl_3$/L), did have a slight effect on biodegradation, VS removal being 45% instead of 50% (value obtained in the sample not containing $FeCl_3$).

The increase in NH_4-N at the end of two experiments with $FeCl_3$ was much higher than that of the untreated sludge. As previously stated, the presence of $FeCl_3$ led to a lower yield in the hydrolysis of nitrogen compounds. Hence, higher biodegration could take place in the course of the BMP test.

Sludge with $FeCl_3$ and Chemifloc CH50

The addition of Chemifloc CH50 led to a higher SMP in the sludge, increasing from 242 to 269 $LCH_4/kgVS_o$. Chu et al. (2003) reported that the addition of cationic polyelectrolytes in similar amounts to those added in this study accelerated CH_4 production in the initial stages. The upgrade in CH_4 production due to adding coagulants and flocculants was somewhat surprising, as these additives produce super-structures which, *a priori*, are less available to bacteria. In other words, the contact between substrate and bacteria/enzymes would be hindered in an initial stage. On the other hand, the formation of floccules may enable nutrients to come into contact with bacteria/enzymes. Additives would thus enhance the "transport" of nutrients to the bacteria. In fact, El-Mamouni et al. (1998) observed that flocculants added to an upflow anaerobic sludge blanket favoured granulation, with the known benefits for biogas production (Hulshoff Pol et al., 2004).

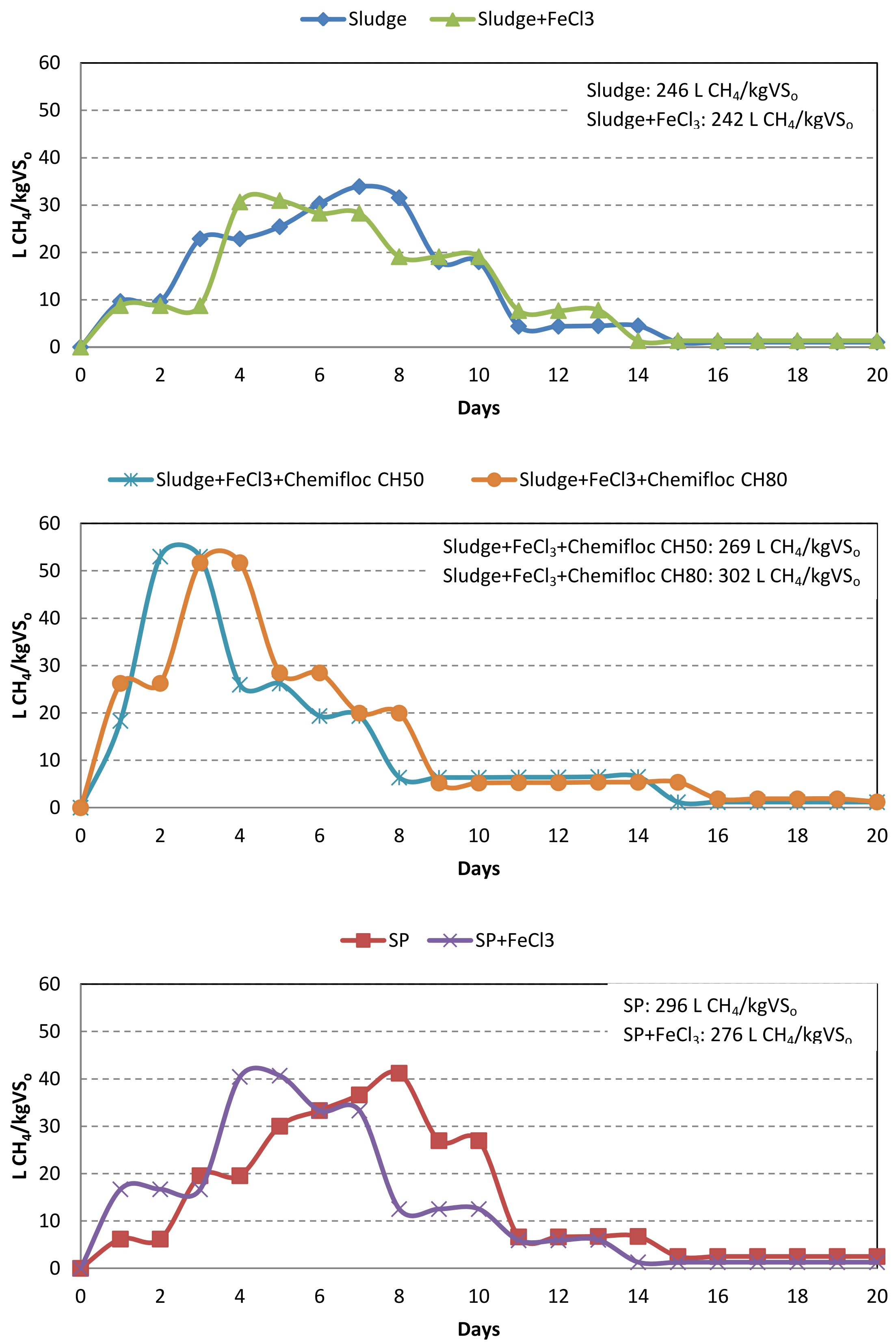

Figure 1. Specific methane potential (SMP) of raw sludge, with additives, and Inverted Phase Fermentation (SP=Solid Phase)

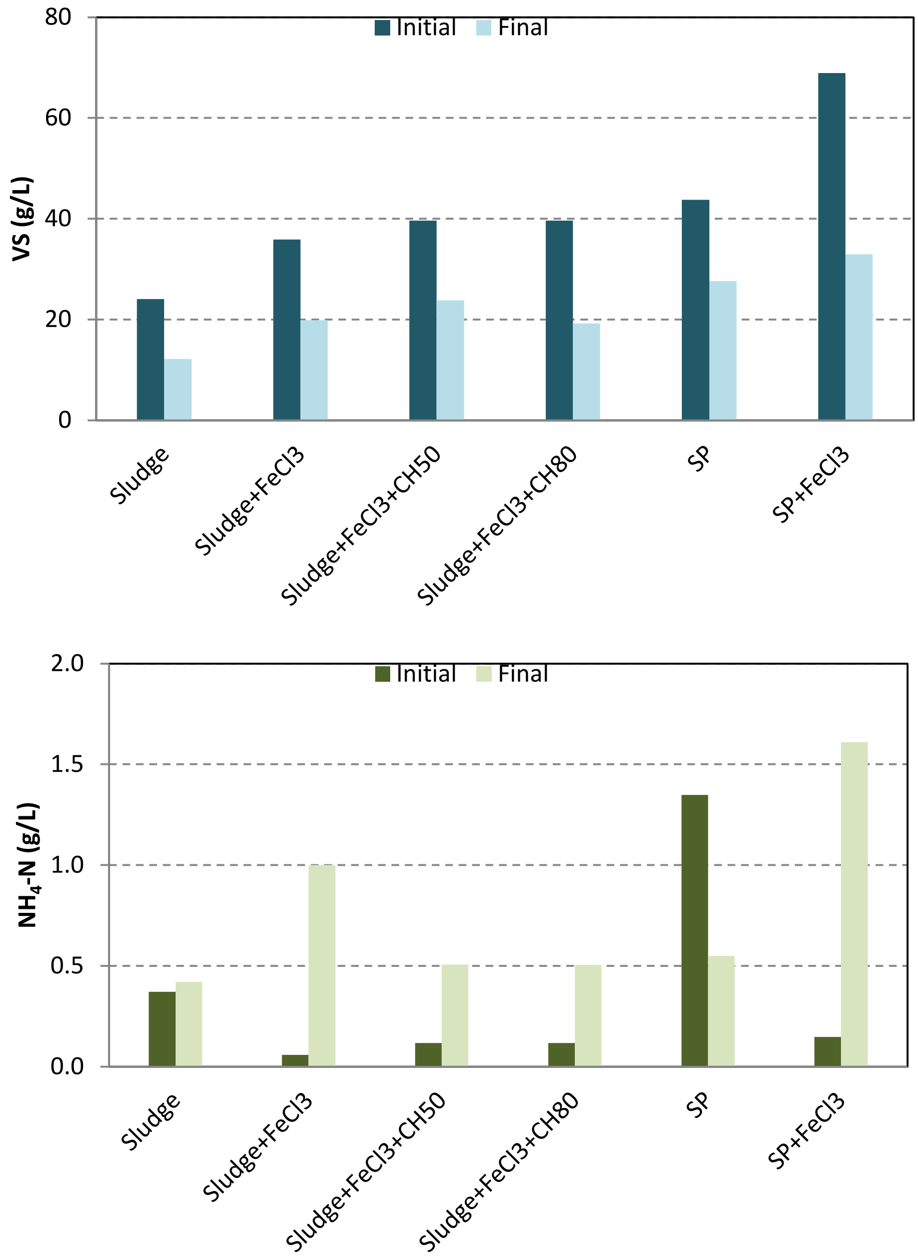

Figure 2. Solids and NH_4-N at start-up and after the biodegradadation tests

Sludge with $FeCl_3$ and Chemifloc CH80

The addition of Chemifloc CH80 led to an increase in both VS degradation (from 45% to 52%) and specific methane production (from 242 to 302 $LCH_4/kgVS_o$).

Solid Phase from Inverted Phase Fermentation

Although the solids degradation achieved in the SP was lower than in the untreated sludge, the CH_4 yield was higher, increasing from 246 to 296 $LCH_4/kgVS_o$.

Note that this result considered only the SP as the substrate. However, a Liquid Phase, rich in volatile fatty acids, is also obtained after IPF. Therefore, the enzymically hydrolysed sludge would produce an even better methane yield than sludge.

Contrary to what occurs with the sludge, in the SP there is a decrease in NH_4-N after the biodegradation test. This decrease could not be justified by the modest removal as NH_3 under a slightly basic pH at the end of the test (pH = 7.90). Sun et al. (2011) reported anaerobic ammonium oxidation in anaerobically digested sewage sludge. This process resulted in N_2 production in the absence of the nitrification-denitrification process.

Solid Phase (IPF) from sludge with $FeCl_3$

Although the addition of $FeCl_3$ led to higher degradations in solids, the SMP decreased slightly from 296 to 276 $LCH_4/kgVS_o$, as also occurred with the non enzymically pre-treated sludge.

With respect to NH_4-N, the high increase observed (even higher than that in the sludge with $FeCl_3$), point to an intensification of the biodegradation of the organic nitrogen throughout the course of the BMP test.

Conclusions

The addition of $FeCl_3$ had very little effect on the SMP, varying from 246 to 242 $LCH_4/kgVS_o$ in the sludge with a very high concentration of $FeCl_3$ (5.6 g/L).

The addition of Chemifloc CH50 led to an increase in SMP of 11%. An increase of 25% was achieved when adding Chemifloc CH80. It seems clear that no negative impact on off-site anerobic digestion can be expected with the addition of cationic polyelectrolites for sludge conditioning.

When applying IPF as a pretreatment, a 20% increase in SMP was observed in the sludge not containing $FeCl_3$. However, a decrease of 6.8% was observed when $FeCl_3$ was added to the sludge. It should be noted that VS degradation decreased (from 50% to 37%) in the SP obtained after IPF pretreatment, as the soluble and more biodegradable VS are present in the Liquid Phase. Conversely, if $FeCl_3$ was present during IPF, VS degradation was enhanced (from 37% to 52%).

Neither $FeCl_3$ nor polyelectrolytes worsened the degradation of organic nitrogen compounds in the sludge at the end of the BMP tests. An increase in NH_4-N was usually obtained at the end of the tests.

The presence of polyelectrolytes in the sludge inhibited IPF.

Acknowledgements

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