Anaerobic digestion of solid fraction of pig slurry

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Abstract: One option for managing liquid livestock waste is an efficient separation of the liquid and solid fractions, and their subsequent treatment applying the best available technology. SELCO-Ecopurin™ is a technique which effectively separates liquid and solid phases using polyacrylamide as a coagulation agent. Anaerobic digestion of the solid fraction is an attractive option on account of its agronomic and energetic values. This work studies the toxicity of polyacrylamide residues for the anaerobic process. It also determines the optimum range of total solid concentration for maximum gas production as a function of polyacrylamide concentration. The results have shown that it is feasible to apply anaerobic process to the solid fraction phase obtained from a separation process with a polyacrylamide concentration of 120 mg/kg, which is the usual dose used, producing a fraction with a 13% total solid content. Optimum gas yield has been obtained at a slightly lower total solid concentration.

Keywords: Anaerobic digestion; pig slurry; polyacrylamide; solid fraction; solid-liquid phase separation

Introduction

Modern pig production, which has a very intensive and concentrated character, generates a large pig slurry surplus that often cannot be used as agriculture fertiliser in the same geographical area. Several factors have been responsible for this increase in slurry generation, including the use of large volumes of water for cleaning purposes, that increases the volume of slurry and has an adverse effect on transportation costs. There are three possible ways of abating this problem:

1. Minimising water consumption on farms, and/or improving diets in order to minimise nitrogen and phosphorous content in the slurry.
2. Drying slurry, and thereby evaporating the water fraction and facilitating transportation.
3. Separating the solid and liquid fractions, then treating the liquid fraction prior to using it for irrigation on nearby land, and treating the solid fraction (SFPS) in order to stabilise it before transporting to areas with nutrients and/or organic matter demand.

Due to the low solid concentration in pig slurry (between 0.2% and 7%), it is very difficult to apply effective techniques of separation, treatment, management and transport of its different phases. It is also difficult to obtain high-energy potentials from these substrates through an anaerobic process. Biogas obtained through such process constitutes a renewable source of energy and contributes to sustainability.

The main fraction of organic matter found in pig slurry takes the form of small suspended particles -mainly in colloidal form- which are not easily separated applying a simple mechanical system (Hill and Tollner, 1980). The efficiency on suspended solids separation, using filters and presses, is limited, and for colloids agglutination it is necessary to apply a chemical coagulation process (Sievers *et al.,* 1994).

The SELCO-Ecopurin™ process uses biodegradable polymers and copolymers (cationic polyacrylamide), which have a high molecular weight, form long chains, are soluble in slurry, present low toxicity, with LD_{50} value greater than 5 g/kg, and provide separation efficiencies over 95% of total suspended solids (Mtnez-Almela *et al*., 2001).

The solid fraction stabilisation can be achieved by aerobic composting and/or anaerobic digestion. The second option provides a better energy balance and may be complemented by further aerobic composting for high quality end-product.

The amount of polyacrylamide added to slurry has influence on the final total solids concentration and on the final concentration of polyacrylamide residues, that could be higher than 5 g/kg. This may affect the feasibility of anaerobic digestion of the solid fraction.

On the other hand, solid concentration may affect methane yield. Bujoczek *et al*. (2000) found that for total solid concentrations above 4%, the maximum methane production rate decreased linearly with the total solids content. Itodo and Awulu (1999), in a work where different types of animal waste were used (pig, poultry and cattle manure), observed that methane production tended to decrease when the total solid content increased. In the case of pig slurry, this decrease took place for total solid values above 10%.

On the other hand, if a very dilute substrate is used, the volumetric methane production will be low. Moreover, a significant increase in volumetric methane production has been found in the literature when the applied organic load rate was increased. An increase in the organic load rate in the range 3.5–7.5 g VS/(L·day) produced an increase in the volumetric methane production, by using more concentrated substrates (Hill *et al.,* 1987) and by shortening retention time (Górecki *et al*.,1993; Hill and Bolte, 2000).

The objectives of the present work have been to characterise the solid fraction obtained when applying different doses of polyacrylamide during the solid/liquid phase separation of pig slurry and to study the anaerobic digestion of this fraction, focussing on polymer toxicity and on conditions that optimise the process, that is: polyacrylamide dosage and solid concentration.

Methods

The pig slurry and its associated solid fraction came from a treatment plant, in Modena, Italy, with an SELCO-Ecopurin™ solid/liquid separation system. Four different substrates identified in Table 1 were used, and anaerobically digested sewage sludge was used as inoculum.

Table 1. Identification and basic characterisation of the substrates used (average of three replications)

	TS (%)	VS (%)	VS (% TS)	COD (g/kg)	N_{TK} (g/Kg)	$N\text{-}NH_4^+$ (g/kg)	pH	Total alkalinity (g CaCO3/kg)
SFPS1	35.64	26.52	74.4	253.21	16.79	2.38	7.1	7.41
SFPS	13.61	10.04	73.73	96.36	7.71	1.89	7	6.05
SFPS0	1.37	0.72	52.45	11.23	1.88	1.54	7.4	5.19
PS	0.98	0.55	56.36	6.19	0.82	0.83	6.8	2.47
Sewage sludge	3.94	2.27	57.42	28.22	3.05	1.03	6.8	2.89

SFPS: Solid Fraction of Pig Slurry
SFPS1: SFPS obtained with 140 mg/kg of polyacrylamide
SFPS: SFPS obtained with 120 mg/kg of polyacrylamide (usual dose)
SFPS0: SFPS obtained without polyacrylamide
PS: Raw pig slurry

Polyacrylamide toxicity test

A toxicity test for polyacrylamide was carried out according to Field's methodology (Field *et al.,* 1988). The polyacrylamide concentrations used were between 0 and 6500 mg/L.

The culture medium consisted on 60 g/L of digested sewage sludge as inoculum, the corresponding polyacrylamide concentration, macro and micro-nutrients solutions (Field *et al.,* 1988) and a mixture of volatile fatty acids 3.8 g acetate/L as substrate (Field *et al.,* 1988). Batch reactors were 120 mL glass vials filled with 50 mL of culture medium, bubbled with N_2/CO_2 for air displacement, tightly closed with rubber stoppers, and a reducing solution was added (0.1 mL of 50 g Na_2S/L). The vials were kept at 35ºC during 46 days, and three times per week the amount of accumulated gas was measured by means head space analyses (Soto *et al*., 1993).

Batch anaerobic tests to compare total solid levels

Four substrate mixtures (Table 1) were prepared, in order to produce five different levels of solids and polyacrylamide, corresponding to five different treatments (Table 2). An additional "blank" treatment -water plus inoculum- was also prepared. The methodology of batch tests was adapted from Campos *et al* (2000): the batch reactors were 120-mL glass vials filled with 30 g of substrate and 3 g of inoculum, at 35ºC, and observed for 82 days.

Table 2. Characteristion of treatments used in the anaerobic digestion test (three replications per treatment)

	Substrate composition (see Table 1)			**Substrate characterisation**			
Treatment	**SFPS1 (%w/w)**	**SFPS (%w/w)**	**SFPS0 (%w/w)**	**TS (%w/w)**	**VS (%w/w)**	**TSS (%w/w)**	**COD (g/kg)**
T1	100	0	0	27.63	20.43	27.13	260.94
T2	50	50	0	20.00	14.99	17.17	193.24
T3	0	100	0	12.75	9.31	11.86	108.04
T4	0	85	15	9.59	6.91	8.74	91.71
T5	0	0	100	1.51	0.85	0.98	15.54
T6(blank)	0	0	0	0.34	0.19	0.33	4.87

A complete analytical characterisation was performed at both the beginning and the end of the experiment. The accumulated methane production was determined by periodic analysis of the headspace gas and calculation of accumulated gas production was adapted from Soto *et al*. (1993). The calculation for anaerobic biodegradability was adapted from Field *et al.* (1988). The parameters analysed at the beginning and at the end of test were: total and volatile solids (TS and VS); total and volatile suspended solids (TSS and VSS); total soluble solids (TsS); total and soluble chemical oxygen demand (CODt and CODs); total Kjeldahl nitrogen (N_{TK}), ammonia nitrogen ($N\text{-}NH_4^+$); pH; total, partial and intermediate alkalinity (TA, PA, IA); alkalinity relationship (AR) and volatile fatty acids (VFA): acetate, propionate, and iso and n isomers of butyrate and valerate.

Analytical methods

The analytical methods were adapted from (AWWA/APHA/WEF, 1995). Alkalinity was analysed according to method proposed by Hill and Jenkins (1989). Volatile fatty acids (VFA) were measured using a ThermoInstruments Trace 2000 gas chromatograph fitted with a FFAP capilar column (0.25 mm ID and 30 m long) and a FID. Helium was used as the carrier gas with a flow rate of 1 mL/min. Methane and carbon dioxide concentrations in the biogas were measured using a ThermoInstruments GC8000 Top gas chromatograph fitted with a Porapak N packed column (2 mm ID and mesh size 80-100) and a TCD. Helium was used as the carrier gas with a flow rate of 20 mL/min.

Statistical methods

Regression analyses were done using the Levemberg-Marquardt algorithm. Means separation tests were performed using statistical analysis software (SAS) and by applying a Duncan test with a significance level of 5%.

Results and discussion

Effect of polyacrylamide over substrate characteristics

The basic characterisation of the different substrates - shown in Table 1- was carried out prior to the anaerobic test. The solid fraction of pig slurry obtained from a usual dose of polyacrylamide (120 mg/kg) had a total solid concentration higher than 13%. A slight increase in the polyacrylamide dose, from 120 to 140 mg/kg, led to a very significant increase in the total solid concentration in the solid fraction, which surpassed 35% of the total weight. The separation efficiency of Kjeldahl nitrogen, and particularly its organic nitrogen content, was greater than for other separation technologies (Moller *et al*., 2000).

Polyacrilamide toxicity study

Results of methane production from vials at different polyacrylamide levels, between 0 to 6500 mg/kg, did not show significant differences (see Figure 1), indicating that the polymer compound was not toxic for anaerobic microorganisms at the studied concentrations.

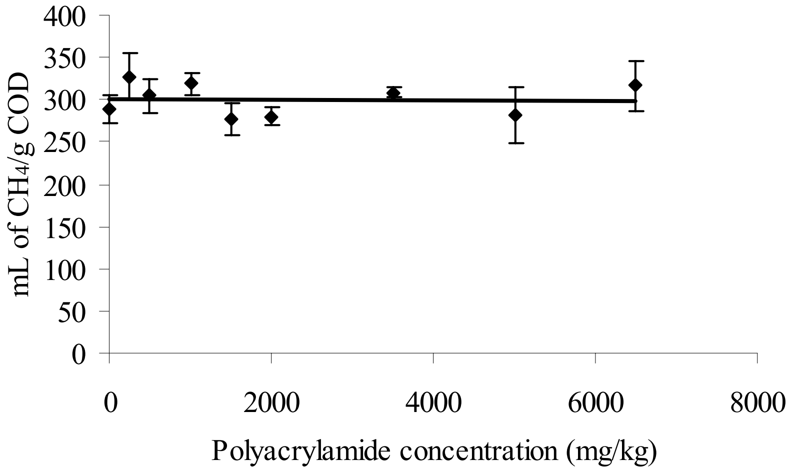

Figure 1. Obtained methane production as a function of polyacrylamide concentration

Study of the initial total solid concentration effect

T2 treatment rendered the absolute maximum gas production (Figure 2). T1 treatment, with 100% SFPS1, provided very low values for all gas production parameters, especially methane yield per gram of initial organic matter. Treatments T3 and T4, corresponding to 120 and 102 mg/kg of polyacrylamide respectively, gave similar values of methane production, with T3 being slightly greater than T4 (Table 3 and Figure 2). With the exception of treatment T1, volumetric gas production per gram of substrate (M) increased with TS concentration (Table 3 and Figure 2). Methane yield (B) respect to initial organic matter showed the opposite tendency (Table 3 and Figure 3), with higher values of methane yield for the most diluted treatments.

Studying the correlation between methane yield (B) and initial TS (Figure 4), it is possible to observe a clear linear decrease associated with the increase on substrate total solid content. Other authors have observed this tendency; Bujoczek *et al*. (2000) found that for total solid concentrations above 4%, maximum methane production rate decreased with total solid content, following a linear tendency; Itodo and Awulu (1999) observed that methane yield tended to decrease when total solid content increased for different types of animal waste. In the case of pig slurry, this decrease only took place for total solid values above 10% (Itodo and Awulu, 1999).

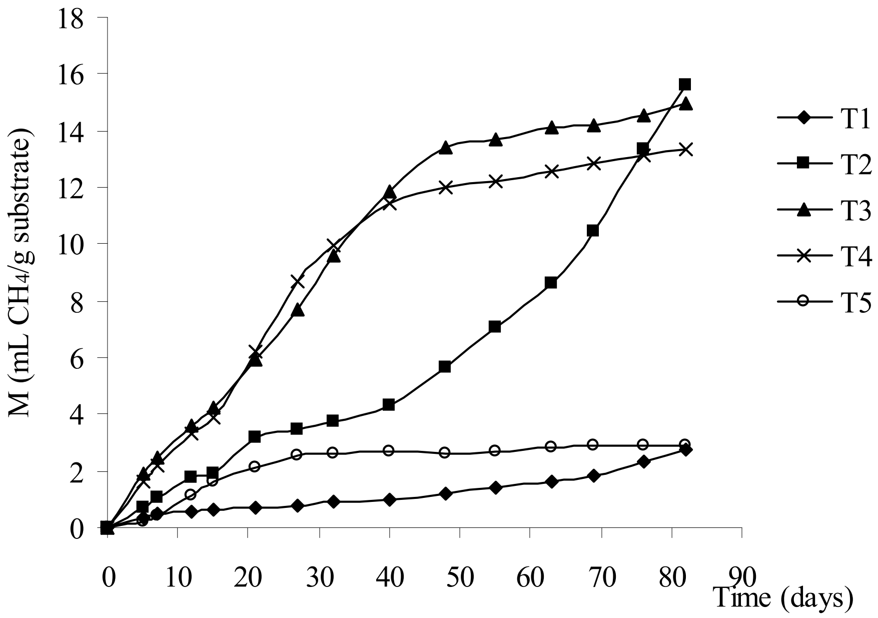

Figure 2. Accumulated methane production per gram of substrate for batch anaerobic test

Table 3. Accumulated production of biogas and methane

Treatment	Biogas production (mL/g sub)	CH_4 production (M) (mL/g sub)	CH_4 Yield (B) ($mLCH_4/gVS$)	CH_4 Yield ($mLCH_4/gCOD$)
T1 (31% TS)	7.01 B	2.77 A	8.83 A	10.17 A
T2 (21% TS)	24.49 E	15.62 D	74.37 B	77.83 B
T3 (13.6% TS)	21.87 D	14.93 C	109.70 C	154.96 D
T4 (9.9% TS)	19.73 C	13.37 B	135.42 D	157.19 D
T5 (1.34% TS)	3.76 A	2.927 A	218.19 E	132.77 C

Different letters indicate significant differences among Duncan test means with a significance level of 5%, by columns

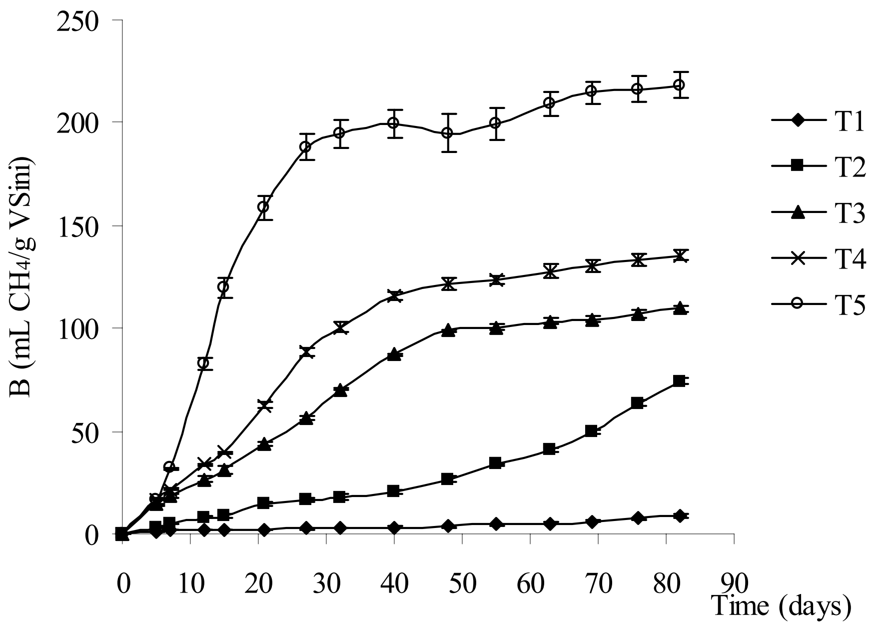

Figure 3. Accumulated methane yield per gram of initial volatile solids

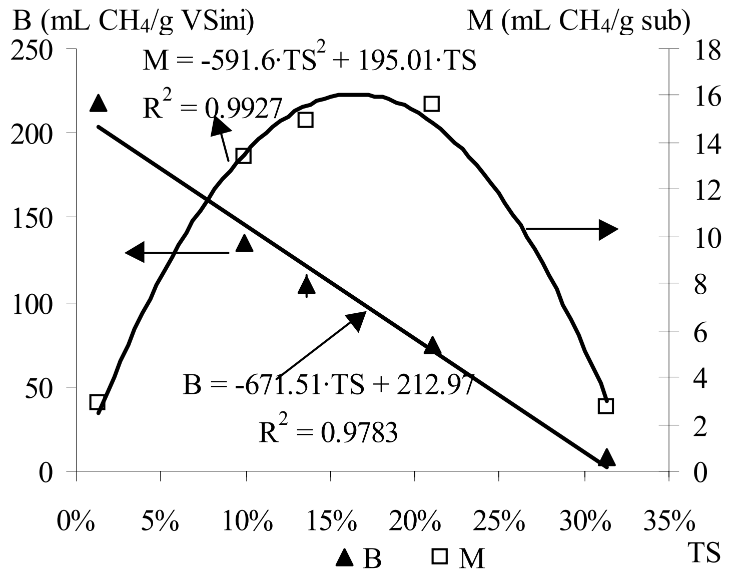

Figure 4. Correlation between total solid content and methane production with respect to initial VS (B) and initial substrate (M).

As polyacrylamide toxicity was not demonstrated (Figure 1), the explanation for the lower methane production in the most concentrated treatments could be the limitation to external transport due to colloidal aggregation, or possibly an inhibiting phenomena.

In most of the treatments, ammonia nitrogen concentration increased towards the end of the process (Table 4) due to protein hydrolysis. In treatments T1 to T4, ammonia nitrogen concentration practically doubled, and reached extremely high levels: above 6 g N/kg. This increase in ammonia nitrogen and pH throughout the process caused a significant increase in free ammonia at the end of the process. The recorded values were greater than those described as inhibitory by some authors (Hashimoto, 1986; Gallert *et al.*, 1998), although below those proposed for thermophilic temperatures by others (Angelidaki and Ahring, 1993; Hansen *et al.,* 1998).

Table 4. Nitrogen form content at the beginning and at the end of anaerobic batch tests.

	N_{TK} (average initial-final) gN/kg	$N\text{-}NH_4^+$ (gN/kg)		NH_3 (mgN/kg)	
		Initial	**Final**	**Intial**	**Final**
T1 (31% TS)	15.59	3.07	6.47	90.52	286.23
T2 (21% TS)	11.65	2.19	4.96	48.10	387.89
T3 (13.6% TS)	7.87	2.46	3.57	248.91	337.70
T4 (9.9% TS)	6.42	1.78	3.29	36.23	328.97
T5 (1.34% TS)	2.02	1.37	1.63	57.68	246.31
T6	0.37	0.25	0.20	2.86	9.93

The high concentration of acetate at the end of the process in T1 (Table 5) together with the ammonia concentration (Table 4), over 6 g $N\text{-}NH_4^+$/L at the end of digestion process, could indicate the inhibition of acetoclastic methanogenic microorganisms by free ammonia. The other VFAs were also accumulated, but at lower levels than acetate. The accumulation of acetate could also have caused the accumulation of other longer chain acids, since a high concentration of acetate may inhibit the acetogenic process (Ahring and Westermann, 1988).

The high concentration of propionate and the high value for the propionate/acetate (P/A) relationship (Table 5) at the end of treatment T2, showed that the process –and especially the acetogenic microorganisms- had been strongly inhibited, although the biogas and methane volumetric production achieved the maximum value for this treatment (Table 3). The most probable reason for this fact was an organic overloading. This would also explain the shape of the accumulated methane curve, with longer lag phase duration than in the most dilute treatments (Figure 2).

The other treatments (T3 to T6) showed much lower levels of VFA, and in many cases only acetate was detectable, showing that non inhibitory effect on methanogenic phase were present.

Table 5. Volatile fatty acids concentration at the beginning and at the end of the batch experiments (units in mM)

Treatment	Acetate	Prop.	Iso-but.	N-but.	Iso- val.	N-val.	T-VFA	P/A ratio
Initial								
T1 (31% TS)	75.48	5.84	6.99	3.43	10.96	0.35	103.05	0.08
T2 (21% TS)	62.87	14.38	4.81	4.85	7.48	0.96	95.33	0.23
T3 (13.6% TS)	50.23	22.91	2.63	6.27	3.99	1.57	87.60	0.46
T4 (9.9% TS)	42.53	17.38	2.05	4.97	3.12	1.21	71.25	0.41
T5 (1.34% TS)	42.33	9.55	1.39	4.42	1.87	1.04	60.61	0.23
T6 (Blank)	0.70	0.28	0.18	0.06	0.01	0.07	0.71	0.63
Final								
T1 (31% TS)	206.23	54.72	27.00	39.53	39.49	2.12	369.08	0.27
T2 (21% TS)	8.13	77.58	12.55	0.16	18.98	0.19	117.61	9.53
T3 (13.6% TS)	1.45	0.09	0.06	0.00	0.08	0.00	1.68	0.07
T4 (9.9% TS)	1.03	0.00	0.01	0.00	0.33	0.00	1.37	0.00
T5 (1.34% TS)	0.13	0.00	0.00	0.00	0.00	0.00	0.13	0.00
T6	0.17	0.07	0.00	0.00	0.00	0.00	0.00	0.00

The organic content, measured as volatile solids (total-VS- and suspended-VSS-) and as total COD, were much higher in concentrated treatments than diluted, with significant differences among all treatments. It was also observed that in almost all treatments, VSS constituted a high percentage of VS, thus indicating the lack of soluble and easily accessible substrate for microorganisms.

The maximum of the curve M (Figure 4) provides the value of total solids concentration that produces the maximum of methane volume per unit of raw substrate. This maximum is obtained with a low methane production per unit of VS, and it poses the question on what is the optimal level of total solids. An approximation to the level of total solids for optimal methane production could be done assuming that this must provide the maximum of the product M·B. Adjusting M experimental data to a 3rd degree polynomial model, and B to a linear model, the total solids level that maximised the M·B product has been 11.2%. If a 4th degree polynomial model is considered, the optimal solids concentration will be slightly lower. These values must be considered as indicative as a first approximation.

Conclusions

The Selco-ECOpurin™ process is very sensitive to polyacrilamyde concentration: an increase from 120 to 140 mg/kg is capable of almost tripling the total solid content of the solid fraction.

The use of a polyacrilamyde concentration greater than 120 mg/kg is not recommended for further anaerobic treatment due to the effect of the high total solid concentration: symptoms of inhibition by ammonia nitrogen and organic overloading have been found in the most concentrated treatments. The polyacrilamyde toxicity effect has not been demonstrated for the tested levels.

A proposed optimal polyacrylamide concentration for the anaerobic digestion process is that which yields a total solid concentration of around 11.2%. The process is perfectly viable for a concentration of 13% corresponding to a polyacrylamide concentration of 120 mg/kg that is usually used at industrial scale.

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