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Anaerobic thermophilic treatment of cattle manure in UASB reactors

Cattle manure was characterised after filtration through a 1-mm sieve and subsequently treated in a 9-l volume UASB reactor made of transparent PVC at a thermophilic temperature (55˚C). Different Hydraulic Retention Times (22.5, 16, 10.6, 8.9 and 7.3 days) were employed and organic matter, total solids and metals were determined, as was the production of biogas. After screening, the COD of the manure subjected to anaerobic thermophilic treatment varied between values of 33,382 and 45,513 mgO_2 l^{-1}. The highest percentage of COD removal obtained was 79.7% for an HRT of 22.5 days and there was a fraction refractory to biodegradation of 11%, calculated using Chen & Hashimoto's model.

Finally, the results obtained at a thermophilic temperature were compared with those obtained at a mesophilic temperature (obtained in a previous work). The reduction in COD was slightly greater under mesophilic conditions, though the main advantage of thermophilic anaerobic treatment is the faster inactivation of viruses and bacteria.

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Introduction

Animal waste, mainly manure, has been used to maintain soil fertility for many centuries. However, intensive animal production in recent years has resulted in high concentrations of animals in small areas, producing large amounts of waste with insufficient nearby land for its application.

Asturias is an Autonomous Community located in the North of Spain, with a large population of cattle that produces milk and meat. In general, the greatest concentration of milk-producing farms (the most problematic, since the cows are usually kept in stables) is found in the areas near the coast, where the elimination of cattle manure by means of its use as a fertiliser may lead to environmental problems. In some of these municipalities, cattle-farming concentrations in the order of 2.18 units of cattle per Ha of useful farmland are reached (Castrillón *et al*. 1999).

The manure from cattle is a material containing an abundant amount of organic matter (with values of COD of around 45,000 mg O_2 l^{-1} or higher), rich in nitrogen (fundamentally ammoniacal-N), potassium, calcium and phosphorus. It also contains variable amounts of other materials, such as heavy metals, among which the principal ones are generally Fe, Mn, Zn and Cu (Marañon *et al.* 2001).

Within the field of cattle manure treatment, there is a diversity of possible solutions/treatments: agricultural use of the manure, phase separation, composting, aerobic and anaerobic treatments, etc. (Aburas *et al.* 1995; Boiran *et al.* 1996; Espona *et al*. 1995; Jungersen & Ahring 1994; Kanwar & Guleri 1994; Rulkens & Have 1994; Shyam & Sharma 1994; Wetterauer & Killorn 1996).

Currently, the most sought-after solution to the problem of manure waste involves the widespread application of anaerobic treatments. Anaerobic digestion of manure simultaneously produces biogas, an energy source that can contribute to the self-sufficiency of the farm, as well as organo-mineral fertilisers.

Anaerobic technology for industrial wastewater treatment has advanced considerably over the past decade due to the development of high-rate reactors. Although most of the treatability studies have been conducted under mesophilic conditions, thermophilic conditions are presumably more effective for the degradation of organic compounds and the killing of pathogens, thus minimising the risk of spreading pathogens (Turner *et al*. 1997).

A number of different countries use this kind of treatment at the industrial level; one of these is Denmark, where cattle manure is treated in centralised biogas plants (Danish Energy Agency, 1995). In general, the types of reactors used are stirred tanks, employing high residence times.

Various authors have studied anaerobic treatment of different farm wastes at the laboratory scale (pig manure, chicken manure, etc.), employing different types of reactors and under different operating conditions (Maibaum & Kuehn 1999; Pagilla *et al*. 2000). The major difficulty for this type of treatment is to be found in the case in which the concentration of ammonium in the farm waste is too high, and may even inhibit the process. This has in fact occurred in the treatment of pig manure (Hansen *et al.* 1999).

Among the high-rate reactors, the UASB process is the most commercially successful. Hundreds of full-scale treatments plants have been installed over the past decade for the treatment of various wastewaters (Fang & Wai-Chung 1999).

In the case of cattle manure, the authors of the present article had previously studied its anaerobic treatment in the mesophilic range using UASB-type reactors at laboratory scale with good results, obtaining high organic matter removal rates (Marañón *et al*. 2001).

The aim of the present research work was to study the anaerobic treatment of cattle manure at a thermophilic temperature and to compare this with the previously studied treatment at a mesophilic temperature. The manure used in this study was produced on two farms, one with 25 cows and the other with 40. A continuous operation was planned in order to obtain steady-state operation data and to optimise COD removal with lower hydraulic residence times. With the aim of comparing the results at mesophilic and thermophilic temperatures, the same HRT were used for both temperatures.

Experimental

Reactor

The reactor used at a thermophilic temperature, which had previously been used at a mesophilic temperature, was

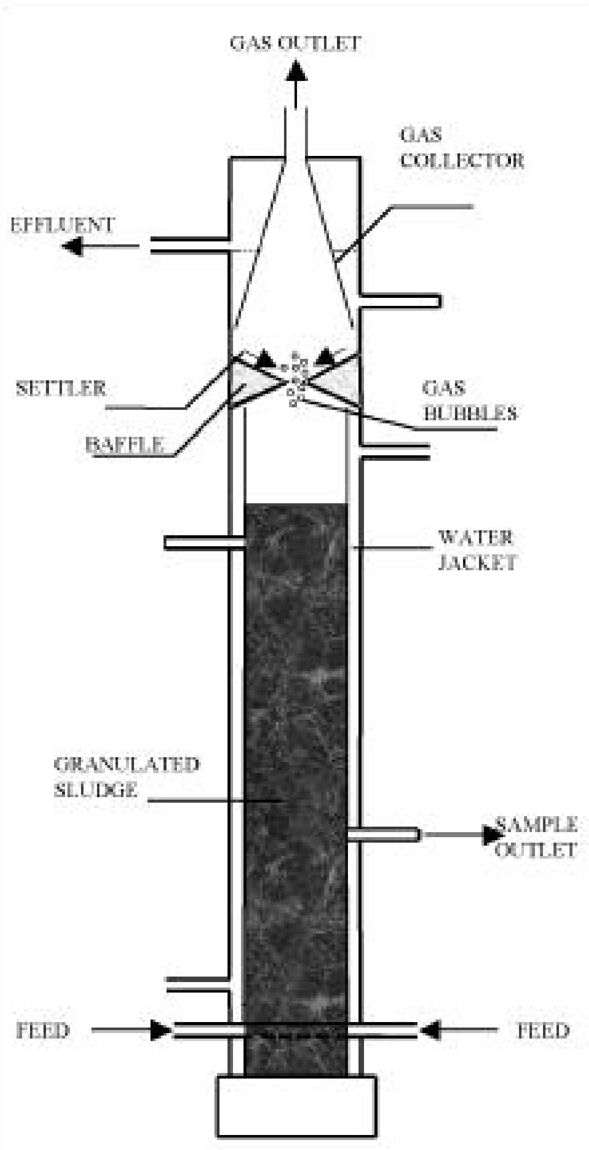

Fig. 1. UASB reactor employed in the experiments

a UASB reactor made of transparent PVC (Fig. 1). This reactor consisted of two cylindrical sections, the lower one jacketed and separated from the upper one by a deflecting ring to facilitate phase separation. The upper part had a larger diameter and contained the gas collector, as well as outlets for the effluent, recycling and other uses. Two side-outlets for samples were arranged along the lower body at two different heights. The volume of the reactor up to the triphasic separator was 9 litres.

Analytical methods

The parameters analysed in the liquid cattle manure were: COD, ammoniacal nitrogen ($N–NH_4^+$), phosphate ($PO_4^{3–}$), total solids (TS), volatile total solids (VTS), volatile acidity (VA), total alkalinity (TA), gas volume, gas composition and metals. The standard methods were employed whenever applicable (APHA, 1989).

The metals were determined by atomic absorption in a Perkin Elmer Mod. 3110 spectrophotometer.

The volume of gas produced was measured using a HI-TEC F101D thermal mass flow detector equipped with an electronic totaliser. The volumetric composition of the biogas was determined by means of a Geotechnical Instrument portable methanometer.

Startup and operating mode

As mentioned above, the cattle manure used in this treatment came from two farms, one with 25 cows and the other with 40. On both farms, the cows are kept in the same kind of stables: a free stall barn. Samples were taken from the liquid manure cesspit, always attempting to collect these after prior agitation of the cesspit.

The samples were kept under refrigeration after collection. The cattle manure was pre-treated by filtration through a 1-mm sieve, approximately 60% of the total filtered volume passing through this sieve, the rest being retained by the filter. With respect to solids, approximately 80% of the total solids present in the raw manure are retained by the filter, the rest passing to the filtered liquid. In some samples, it was necessary to dilute the manure before the anaerobic treatment, as shall be seen below.

Given that prior research had studied anaerobic treatment of cattle manure in the mesophilic range using two UASB reactors (Marañón *et al.* 2001), the sludge from this study was used as inoculum in the start-up of the thermophilic reactor, since mesophilic populations usually contain a certain amount of thermophilic bacteria (Schönborn *et al*. 1987). At start-up, diluted manure was added along with small amounts of methanol to assist the development of methanogenic bacteria (Durán *et al.* 1997); a period of approximately two months being needed to achieve sludge in working conditions.

The previously described parameters were determined in the manure used as feed for the reactors as well as in the effluents from the plants; the biogas generated was also characterised. Likewise, total solids and volatile solids were measured at two different points inside the reactor, with the aim of characterising the quantity of biomass inside the reactor.

Results

Characterisation of manure

Table 1 shows the average values of the composition of the influent used in the thermophilic anaerobic reactor. The COD of the majority of the samples ranged between values of around 33 000 and 45 000 mg O_2 l^{-1}. Even though the ammoniacal nitrogen content was high (its values reaching 1100 mg $N–NH_4^+$ l^{-1}), these amounts did not perturb the smooth running of the anaerobic process (Flotats *et al*. 1997, Hansen *et al*. 1999). The total solids content varied between values of 39.94 and 22.38 g l^{-1}, the majority of these being volatile solids.

Phosphate concentrations were always higher than 150 mg l^{-1}, being sufficient to be able to carry out the process adequately. The pH value was higher than 7, ranging between 7.2 and 7.7, as can be seen in Table 1.

Of the metals analysed (Fe, Mn, Cu, Cr, Zn, Cd and Pb), the major ones present were Fe, Mn, Zn and Cu. Others appeared in very low concentrations or were undetected, as is the case for Cd.

Performance of the UASB digester

The UASB digester was operated continuously for approximately one year, working with different HRT (22.5, 16, 10.6, 8.9, 7.3). The percentage of COD removed varied between 54.8 and 79.7% for HRT of 7.3 and 22.5 days, respectively; the results obtained can be seen in Table 2. Given the fact that for even a high HRT (22.5 days), the percentage of COD removed is around 79.7%, an anaerobically non-biodegradable organic fraction may possibly exist. The model proposed by Chen and Hashimoto (Chen & Hashimoto 1980) allows us to determine the value of this fraction. At the same time, the removal of volatile

Table 1. Average composition of the manure used for different HRT

	HRT (days)				
Parameter	22.5	16	10.6	8.9	7.3
pH	7.3	7.2	7.2	7.7	7.3
$N–NH_4^+$ (mg l^{-1})	1082	1008	653	964	783
TA (mg $CaCO_3$ l^{-1})	7454	6617	4767	7582	6968
VA (mg CH_3COOHl^{-1})	2749	4107	2997	3077	1714
COD (mg O_2l^{-1})	37527	45513	33382	37421	37034
Total solids (g l^{-1})	29.16	31.85	22.38	28.07	39.94
Inorganic solids (g l^{-1})	11.09	9.98	7.10	9.69	16.12
Volatile solids (g l^{-1})	18.07	21.87	15.28	18.38	23.82
% Volatile solids	62.0	68.7	68.3	65.5	59.6
Fe (mg l^{-1})	50.87	80.21	60.43	79.33	71.52
Mn (mg l^{-1})	7.70	8.54	9.60	1.50	2.84
Zn (mg l^{-1})	4.96	3.25	13.40	21.50	17.32
Cu (mg l^{-1})	1.74	3.14	2.08	2.17	1.94
Pb (mg l^{-1})	0.26	0.39	0.39	0.36	0.32
Cr (mg l^{-1})	0.08	0.31	0.25	0.28	0.28
Cd (mg l^{-1})	n.d.	n.d.	n.d.	n.d.	n.d.

fatty acids decreases with decreasing HRT, good correlations existing with respect to the COD. Although in some cases the total volatile acidity in the effluent exceeds the value of 500 mg l^{-1}, the fact that the values of alkalinity were high (Table 3) leads to this acidity being neutralised without presenting problems of acidification in the reactor.

For values equal to or less than 10.6 days, it was not possible to work with manure that presented COD higher than 40 000 mg O_2 l^{-1}, since flotation of the sludge took place within the reactor. It was therefore necessary to dilute the manure until the values of the concentrations were lower than this value. This circumstance was not observed when working in the mesophilic range (Marañón *et al*. 2001).

This situation might perhaps be solved by recirculating the liquid effluent, which would lead to dilution of the influent. However, this recirculation was not carried out, since the high values of pH presented by the effluent (between 8.0 and 8.3, as can be seen in Table 3) would entail the addition of hydrochloric acid so as to decrease the pH.

Table 2. COD and VA removal for the different HRT and OLR (mean values)

HRT (days)	COD Influent, mg l^{-1}	OLR kg COD m^{-3} d^{-1}	% COD removed	% VA removed
22.5	37527	1.67	79.7	86.7
16	45513	2.84	74.9	84.7
10.6	33382	3.15	68.1	83.8
8.9	37421	4.16	61.2	78.8
7.3	37034	5.06	54.8	54.2

As mentioned above, determination of the content of total solids (TS) and volatile solids (VS) was carried out both in the filtered manure (in some cases diluted) used as influent for the reactor, as well as in the effluents generated. Likewise, the concentration of total and volatile solids inside the reactor was also carried out, employing the two samples outlets located at different heights. Due to the difficulties encountered in filtering the manure through a 0.45 µm filter, determination of suspended volatile solids, considered to be indicative of the microbial concentration, was not carried out. Table 4 presents the results obtained.

To determine the solids inside the reactor, weekly samples were taken in the order of 100 ml at the lower exit and 75 ml at the upper exit, which allowed the growth of the biomass throughout the reactor to be controlled. This operation served at the same time to carry out purging of the sludge. When the concentration of solids was very high, the volume of sludge to be purged at the lower sampling outlet was increased, thus impeding excessive accumulation of inorganic solids inside the reactor.

As can be observed, the concentration of total solids

Table 3. Values of total alkalinity and pH of the effluent for each HRT

HRT (days)	22.5	16	10.6	8.9	7.3
TA influent (mg$CaCO_3$ l^{-1})	7454	6617	4767	7582	6968
TA effluent (mg $CaCO_3$ l^{-1})	3783	4877	4184	5671	5526
pH effluent	8.2	8.3	8.1	8.0	8.0

Table 4. Average concentration of the solids in the influent manure, the effluent and inside the reactor for the different HRT (mean values)

HRT (days)	Influent TS, g l^{-1} (%VS)	Reactor Lower sampling outlet TS, g l^{-1} (%VS)	Reactor Upper sampling outlet TS, g l^{-1} (%VS)	Effluent TS, g l^{-1} (%VS)	Ratio VS Effluent VS Influent
22.5	29.16 (62.0)	47.94 (55.7)	18.00 (55.7)	11.91 (49.8)	0.31
16	31.85 (68.7)	42.60 (60.1)	43.50 (60.9)	15.37 (56.7)	0.36
10.6	22.38 (68.3)	40.50 (59.9)	28.90 (61.8)	10.98 (67.2)	0.42
8.9	28.066 (65.5)	43.57 (60.7)	33.40 (61.4)	14.66 (55.4)	0.43
7.3	39.94 (59.6)	45.70 (55.6)	32.37 (52.8)	22.69 (54.3)	0.52

decreases with the height inside the reactor, with the exception of the 16-day HRT, in which this concentration presents very similar values. Increasing the HRT diminishes the content in volatile solids in the effluent.

Table 5 shows the metals content in both the influent and the effluent of the reactor. It can be seen that the metal found in the highest proportion is iron, followed by Zn, Mn and Cu. We can also see that after anaerobic treatment, a reduction in the metals content is produced, due on the one hand to their precipitation as sulphides or hydroxides, and on the other, to adsorption processes of the metals in the sludge (Artola *et al*. 1997). The metals removed to the greatest extent are those found at higher concentrations. No relationship was observed between the percentage removal and the operating HRT.

In anaerobic processes, the microorganisms consume organic matter and transform this into a gas composed mainly of methane and carbon dioxide. The values of maximum production attained were 0.30 m^3 CH_4 Kg^{-1} COD removed for the lowest HRT, close to the theoretical value of 0.35 m^3 CH_4 Kg^{-1} COD. The percentage in volume of methane in the biogas varied between 67.7% and 56.0%.

Kinetic model

If the ratio S/So (concentrations of effluent and influent, expressed as COD) is plotted against the HRT (Fig. 2), a concordance for all points can be observed (regression values of 0.998). The Chen and Hashimoto model (ST = R + (1-R) K / qmm- 1 + K, q = HRT) was applied to the experimental data with the following results for the different parameters:

Kinetic constant, K = 0.595

Specific growth rate, mm = 0.266 day-1

Refractory fraction, R = 0.11

Table 5. Average metals content in the influents and the effluents for the different HRT

HRT (days)	Metal (mg l^{-1})	Fe	Mn	Zn	Cu	Pb	Cr	Cd
22,5	Influent	50.87	7.70	4.96	1.74	0.26	n.d.	n.d.
	Effluent	18.32	1.98	1.38	0.68	0.18	n.d.	n.d.
	% Removal	64.1	74.2	71.2	60.8	30.7	–	–
16	Influent	80.21	8.54	3.25	3.14	0.39	0.31	n.d.
	Effluent	36.76	4.44	1.56	1.92	0.22	0.21	n.d.
	% Removal	50.4	48.0	51.8	38.7	44.2	32.2	–
10.6	Influent	60.43	9.60	13.40	2.08	0.39	0.25	n.d.
	Effluent	27.93	4.25	7.37	1.19	0.24	0.14	n.d.
	% Removal	53.8	35.6	45.0	43.0	39.0	42.4	–
8.9	Influent	79.33	1.50	21.50	2.17	0.36	0.28	n.d.
	Effluent	30.04	1.31	7.99	1.30	0.17	0.13	n.d.
	% Removal	62.1	12.9	62.8	39.9	72.8	54.3	–
7.3	Influent	71.52	2.84	17.32	1.94	0.32	0.28	n.d.
	Effluent	32.87	2.04	5.83	0.97	0.20	0.24	n.d.
	% Removal	54.0	28.3	66.3	49.9	37.5	15.0	–

n.d. not detected

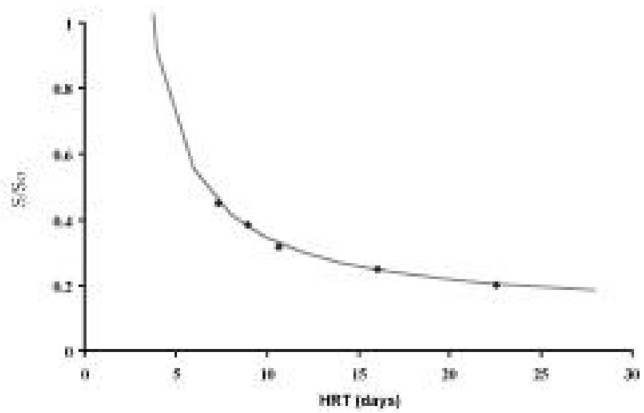

Fig. 2. Ratio COD effluent/influent versus HRT

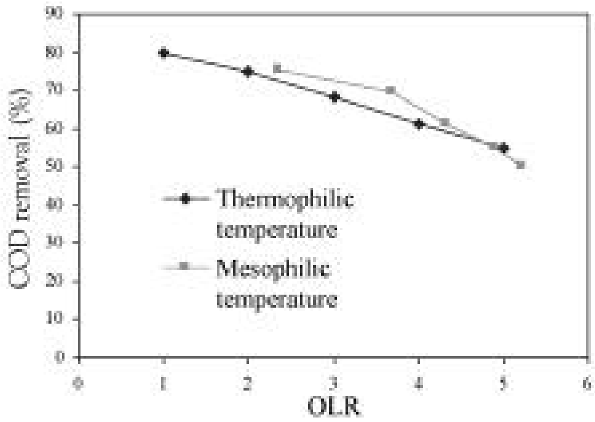

Fig. 3. Percentages of COD removal versus OLR

The fraction refractory to biodegradation (R) was found to be about 11%, which means that at a thermophilic temperature a fraction that is refractory to anaerobic treatment exists in cattle manure that is mainly made up of lignocellulosic material not digested by the animal. According to this values, if we consider the highest COD removal obtained (79.7%), there is still a fraction of about 9% that may possibly be removed by operating at higher HRT.

Comparison between mesophilic and thermophilic anaerobic digestion

To compare anaerobic treatment at mesophilic (more detailed data can be found elsewhere, Marañon *et al.* 2001) and thermophilic temperatures, the percentage of COD removed and the content of material that was refractory to degradation were analysed. The fact that, as mentioned above, it was not possible to work in the thermophilic range with COD higher than 40 000 mg O_2 L^{-1} for HRT of 10.6 days or less meant that the organic loading rates used in the thermophilic range were lower than those used in the mesophilic range, even though the same HRT had been used in both temperature ranges. This consequently impeded the comparison of the removal capacity achieved as a function of the HRT. In the comparative study, the percentage removal achieved was therefore studied as a function of the Organic Loading Rate (OLR) of the influent.

Fig. 3 presents the average percentages of COD removal for both types of digestion as a function of the OLR. As can be observed, the values are generally slightly lower at the thermophilic temperature. Thus, from this point of view, the use of thermophilic treatment is not advantageous in the case of anaerobic treatment of cattle waste. However, when faced with the choice of one temperature range or the other, other factors must be considered, amongst these the possible inactivation of bacteria and viral pathogens, for which the results are more positive in the case of working at a thermophilic temperature (Turner & Burton 1997).

The percentage of material refractory to anaerobic biological degradation coincides for both temperature ranges; thus the amount of organic matter that may be removed would be similar.

Conclusions

Anaerobic treatment may be applied to the liquid cattle manure studied, resulting in a high percentage of COD removal. However, the COD level of the effluent is still high. This fact, together with that of the high amounts of ammoniacal nitrogen present, points to the need to use this method in combination with others: aerobic and/or physico-chemical methods.

The fraction that is refractory to biodegradation (R) was determined to be about 11%.

The percentages of COD removal achieved in the thermophilic range are generally slightly lower than those obtained in the mesophilic range. If we solely take into consideration this parameter, anaerobic treatment in the thermophilic range will therefore not be advantageous, as it consumes more energy to heat the reactor. However, thermophilic treatment achieves a greater removal of the pathogenic microorganisms that may be present in the manure. This could also be achieved by subjecting the manure to pasteurisation prior to anaerobic treatment.

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