

1 **SOLID - LIQUID SEPARATION OF DAIRY MANURE:**
2 **DISTRIBUTION OF COMPONENTS AND METHANE**
3 **PRODUCTION.**

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61 **Abstract**

62 Chemical treatment and screening can be an effective technique for separation of dairy cattle manure
63 into a liquid fraction (LF) and a nutrient-rich solid fraction (SF). The optimum loading of a strong
64 cationic polyacrylamide was found to be 43.9 g kg⁻¹ of dry excreta. The separated SF contained 29.1% of
65 the initial mass present in the manure and the chemicals added. The Volatile Solids (VS) / Total Solids
66 (TS) ratio, which was 0.78 for the manure, rose to 0.82 for the SF and decreased to 0.63 in the LF.
67 Furthermore, the SF retained 76.1, 79.9, 59.4 and 87.4% of TS, VS, Total Kjeldahl Nitrogen and Total
68 Phosphorus, respectively. In the LF, the ratio of filtrate chemical oxygen demand (COD_{filtrate}) and COD
69 due to volatile fatty acids (COD_{VFA}) in relation to total COD (COD_T) were 0.86 and 0.76, respectively.
70 The percentage of anaerobically biodegradable chemical oxygen demand (COD_{BD}) for the LF was 83.0%.
71 Treatment of the LF in high loading anaerobic reactors would be possible due to these COD
72 characteristics. Specific methane production in terms of VS for the separated LF was 0.580 m³ kg⁻¹. For
73 dairy manure and SF, it was 0.320 and 0.258 m³ kg⁻¹, respectively.

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75 **Keywords:** dairy manure; solids removal; polyacrylamide; liquid fraction; anaerobic biodegradability.

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1. Introduction

Intensive dairy cattle farms generate vast amounts of animal slurry with a low concentration of nutrients. Land application, the traditional dairy manure management strategy, is posing serious environmental pollution problems [1, 2]. In wet climate zones, for example, the liquid fraction of manure is responsible for superficial and subterranean water pollution. These environmental problems are difficult to solve due to the high contents of organic matter and nutrients [3].

An analysis of pre-disposal conditioning treatments of cattle manure has shown that the separation of liquid and solid fractions of manure is one of the most suitable upstream operations. The size of manure storage vessels is reduced, which implies significant cost savings [4]. The separated solid fraction (SF) has relatively small volume and is suitable either for the production of compost or anaerobic dry digestion [5]. The shipping cost for stabilised solid fraction from intensive dairy farms zones to others with lack in nutrients will be diminished [6] and the liquid fraction (LF) offers the benefit of more economical and easier treatment options [7].

The analysis of particle size distribution in fresh dairy manure have shown that Total Solids (TS) and Volatile Solids (VS) are almost equally contained in particles larger than 1 mm and smaller than 0.053 mm. Usually less than 25% of the TS and VS are contained in particles smaller than 1 mm and larger than 0.053 mm [8]. It was found that 60% of TS, 86% of Total Kjeldahl Nitrogen (TKN) and 94% of Total Phosphorus (TP) were contained in particles with a size smaller than 0.5 mm [9]. Other authors consider necessary to remove all particles smaller than 0.25 mm as well as coarse particles in order to effectively control odour and reduce nitrogen and phosphorus contents of LF in manure [10].

Screens are the most extensively used separators. The performance of screen separators is basically determined by mesh size, velocity flow, solids concentration and particle size distribution in manure [11]. Smaller screen sizes achieve higher solid removal percentages, but the SF presents a higher moisture content. As manure flow increases, this effect becomes more pronounced [12]. When manure is collected by flushing, it is more dilute and it filters better through the sieve. The SF separated contained lower suspended solids and nutrients than the SF from the higher total solids manure, due to the fact that the additional water washed more fine solids and nutrients through the screen [13]. A review of the performance of manure separator devices has been described in the literature by Hjorth et al. [14]. According to these authors, centrifugation is the most effective technique for removing dry matter (DM) and Total Phosphorous (TP), whereas filtration results in lower efficiency for the removal of DM and nutrients.

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124 Coagulation is a process of aggregating suspended (colloidal or dispersed) particles to form settleable
125 flocs through addition of electrolytes or organic polymers. Most suspended particles in wastewaters with
126 a pH greater than four have a negative charge, thus the electrolytes used are inorganic salts of multivalent
127 cations such as iron, aluminium and calcium. The flocculation process, agglomeration of coagulated
128 particles into larger, rapidly settling flocs, is effected through particle-particle interaction through
129 attachment to long-chain polymer molecules. Cationic polyacrylamides (PAM) with moderate charge
130 density are more effective than polymers with higher charge density for solids and nutrients removal [11,
131 15].

132 The conventional treatment applied to animal manures has been the anaerobic digestion process,
133 which permits the recovery of biodegradable organic matter in the form of methane in the biogas, whereas
134 the nutrients remain in the stabilised manure, except volatilised ammonia [16, 17]. If the LF obtained by
135 screening is subjected to an anaerobic digestion process in low load reactors, pump and piping operational
136 problems are lower, as well as fouling into the reactor, but organic matter removal in terms of VS did not
137 reach values higher than 45% [7, 18]. If manure is very diluted, the LF can be treated in high loading
138 anaerobic reactors, but a previous study [19] only reached 41.5% of COD removal efficiency. If higher
139 organic matter removal efficiencies are desired in the anaerobic digestion process, a LF with lower
140 suspended solids content would be necessary; in this case, screening should not be the only pre-treatment
141 performed.

142 In Cantabria, a region in northern Spain, about 350,000 dairy cows generate around 4,500,000 t per
143 year of semi-liquid manure (7-14% TS). Most of the intensive farming is operated on the coastal
144 flatlands, which are tourism areas. Manure storage capacity is limited and there is not enough land
145 available for waste disposal by direct application during those periods when the soil benefits from nutrient
146 additions, which leads to environmental damage. In humid areas, especially those with steep terrain (as is
147 the case in many parts of Cantabria), the liquid fraction of manure is responsible for part of the pollution
148 found in superficial and underground waters.

149 The development of solutions for this problem was the motivation for the present work. The overall
150 process undergone by the manure was considered: once the initial hydrolytic and acidogenic stages have
151 taken place in a controlled manure pit [20], solid and liquid fractions of manure can be separated and then
152 stabilised by means of biological treatments. In order to obtain a liquid fraction with the majority of its
153 COD in soluble and highly biodegradable form to be treated in high-load anaerobic reactors, chemical
154 reactives have to be used. Anaerobic digestion in dry fermentation batch systems is an attractive

155 alternative for the solid fraction [21]. Once this material has been digested it can be used both as a
156 fertilizer or soil conditioner. However, anaerobic treated effluents of the LF can not be discharged to
157 public water bodies without further treatment, according to present environmental regulations. Therefore,
158 additional decontaminating processes have to be applied to the effluent, alone or mixed with other
159 wastewaters.

160 The objectives of the present work are:

161 (1) To determine the optimum dose of polyacrylamide needed for achieving the separation of SF and
162 LF of dairy cattle manure.

163 (2) To determine the distribution of mass, TS, VS, TKN and total phosphorus from dairy cattle
164 manure in SF and LF.

165 (3) To determine the distribution of the methanogenic productivities of dairy cattle manure and its
166 solid and liquid fractions.

167 (4) To characterise the COD_{total} , $COD_{filtrate}$, COD_{VFA} and $COD_{biodegradable}$ of the LF with a view to the
168 possibility of treating it in high load anaerobic digesters.

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170 | **2. Material and methods**

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172 | **2.1. Manure collection**

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174 For this work, manure with a TS concentration of 10-14% was collected from a dairy farm in the
175 Santander area (Northern coast of Spain). There were 140 lactating cows, 40 dry cows, 80 heifers and 30
176 calves. Lactating cows had a mean age of four years, weighing between 600-700 kg. Cows diet consisted
177 in 20 kg of silage, 4 kg of lucerne and 16 kg of concentrate per cow and day. Lactating cows produced
178 about 50 kg manure per day. Manure samples were taken from the lactating cow house, directly from the
179 floor during the clean up operation (RMCH) and from the manure pit (RMP). The RMCH samples were
180 kept in a lab pit during 30 days at ambient temperature. Vessels of 25 litres were employed as controlled
181 dung pits and were provided with hydraulic closing systems in order to avoid the entrance of air, to
182 prevent volatile fatty acids (VFA) oxidation and to allow the release of generated gas to prevent an
183 excessive increase in pressure. The RMP samples were kept in similar lab pits at ambient temperature and
184 were subjected to the separation process within a maximum of five days after its collection. In some tests,
185 RMP samples were subjected to screening through a 1.5 mm mesh sieve. This operation aimed to remove

186 the larger solids, hardly biodegradable or non-biodegradable at all by natural processes. To facilitate the
187 screening operation, tap water was added to the original sample in a proportion of one litre of water to
188 four litres of manure sample. Diluted screened manure (DSM) is that resulting from having been
189 screened, after the dilution procedure outlined above, by a static laboratory screen. The mean value of the
190 TS content after screening was 60 kg m^{-3} , similar to the mean TS content obtained in farms that evacuate
191 the wastes by flushing them with water and then subjecting the slurry to mechanical screening through a
192 1.5 mm mesh sieve. The mean values of manure samples are shown in Table 1. RMCH, RMP, DSM
193 samples, as well as the solid and liquid fractions separated by flocculation and screening were kept at 4°C
194 until analytical tests were done.

195 Working with very heterogeneous samples typically leads to frequent discrepancies between the
196 results obtained in experiments and those presented in reports related to the matter [22]. The mean
197 concentrations for the RMCH samples were higher than the RMP, because of rain water dilution. The
198 VS/TS ratio was higher in RMCH than RMP because degradation of easily biodegradable organic matter
199 had started. In DSM samples, the VS/TS ratio was the lowest of all.

200

201 **2.2. Analytical methods**

202

203 Volatile fatty acids (VFA) were determined using an HP6890 GC apparatus fitted with a $2\text{m} \times 3.175 \text{ mm}$
204 glass column, liquid phase 10% AT 1000, packed with the solid support Chromosorb W-AW 80/100 mesh.
205 Nitrogen was the carrier gas and a FID detector was installed. Gas composition was analyzed on a 2m
206 Poropak T column in a HP 6890 GC System with helium as carrier gas and TCD detector. All other
207 analyses were performed following the Standard Methods for the Analysis of Waters and Wastewaters [23].
208 All analyses were done in triplicate and the data shown in this study are mean values of the three values
209 obtained. A maximum deviation of 3% was allowed between the three results and the mean. Whenever the
210 differences between the three values obtained were higher than 3% of the mean, the analysis was repeated.
211 Biodegradability of the liquid fraction was determined according to the method described by Field et al.
212 [24] for wastewaters. Volatile fatty acids (acetic, propionic, butyric, isobutyric, valeric and isovaleric)
213 concentration was converted to COD (COD_{VFA}) by using conversion factors for theoretical oxygen
214 demand: 1.066 for acetic acid; 1.514 for propionic acid, 1.818 for butyric and isobutyric acid, and 2.039 for
215 valeric and isovaleric acids. Analogously, the methane produced was converted to COD (COD_{CH_4}) by the
216 equivalence $1 \text{ kg COD} = 0.350 \text{ m}^3 \text{ CH}_4$. The calculated percentages of COD_{VFA} and CH_4 are the result of
217 dividing their respective COD values by the initial value of the total COD (COD_0).

$$\%COD_{VFA} = \frac{COD_{VFA}}{COD_0} \cdot 100$$

218

$$\%COD_{CH_4} = \frac{COD_{CH_4}}{COD_0} \cdot 100$$

219 In this method, it is assumed that:

220 *Non-VFA biodegradable Organic Matter* → *VFA + acidogenic biomass*
VFA → *CH₄ + methanogenic biomass*

$$\%COD_{acid} = \%COD_{CH_4} + \%COD_{VFA}$$

$$\%COD_{BD} = \%COD_{acid} + \%COD_{cell}$$

222 where COD_{acid} is the addition of COD due to VFA present and CH_4 produced. Biodegradable COD

223 (COD_{BD}) is the sum of COD_{acid} and the COD_{cel} . This COD_{cel} takes into account the COD employed in

224 the growth of both the acidogenic and methanogenic biomass.

$$\%COD_{cell} = (\%COD_{cell})_{acid} + (\%COD_{cell})_{meth}$$

$$(\%COD_{cell})_{acid} = \frac{Y_A}{1 - Y_A} \cdot (\%COD_{acid} - \%COD_{VFA})$$

$$225 \quad Y_A = 0.196 \frac{g \text{ } COD_{cell}}{g \text{ } COD_{used}}$$

$$(\%COD_{cell})_{meth} = \frac{Y_M}{1 - Y_M} \cdot \%COD_{CH_4}$$

$$Y_M = 0.028 \frac{g \text{ } COD_{cell}}{g \text{ } COD_{used}}$$

226 where Y_A and Y_M are the estimated cellular yield coefficients for acidogenic and methanogenic bacteria,

227 respectively. The value of biodegradability after a 7-day test was considered to determine $\%COD_{BD}$.

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229 | 2.3. Experimental equipment

230

231 A lab-scale static screen with a sieve of 1.5 mm before flocculation, and 0.2 mm after flocculation, was
 232 used to separate solid and liquid fractions. To measure the anaerobic biodegradability of the LF, two
 233 cylindrical reactors, made of PVC, with an internal diameter of 22 cm, (2.5 litres total volume and 2.0 litres
 234 useful volume) were used. Stirring, at 0.33 Hz, was carried out for 20 seconds every 15 minutes by means
 235 of blade stirrers controlled by timing devices. For the methane productivity test, six reactors like those
 236 previously described were used, in this case without stirring. Two 1.0 litre bottles made of high density
 237 propylene, the tops of which were perforated in order to permit the release and recovery of biogas, were

238 used as a blank in the methane productivity test. Methane production was measured by means of a
239 displacement system using an alkaline solution in order to absorb the CO₂ produced. Methane volumes are
240 expressed at 293°K and pressure of 101.15 kPa.

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242 | **2.4. Preparation of flocculant solutions**

243

244 The polyacrylamide used has the commercial name of Praestol K144L, a registered trademark of Ashland
245 Chemicals. It is a copolymer of acrylamide (very strongly cationic). Commercial polyacrylamide (CP)
246 was supplied in solid form by the company Stockhausen Iberia, S.A. Other flocculants supplied by the
247 same company were used in previous studies, but the results obtained were worse. Although the
248 manufacturer's recommendation was a 5 kg m⁻³ solution of polymer in tap water, the polymer was added
249 to the samples as a 3 kg m⁻³ solution since it was observed that this concentration permitted an easier
250 separation of SF and LF. The dose of polymer employed will be expressed as g CP kg⁻¹ TS, where CP is
251 the solid polymer added in form of solution (3 kg m⁻³) and TS refers to the manure sample TS content.

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253 | **2.5. Separation of solid and liquid fraction**

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255 The prepared polyacrylamide solution was mixed with the dairy cattle manure using two 1000 ml beakers
256 (pouring method). This method was used due to the high solids concentration and the viscosity of the
257 manure. The mixture, composed of the polymer solution and the sample, was passed successively from
258 one beaker to the other a predetermined number of times, which depended on the solids concentration in
259 the sample. When optimal flocculation was achieved, mixing was stopped and the sample was allowed to
260 settle for 5 minutes. Then, liquid and solid fractions were separated using 0.2 mm mesh sieve, collecting
261 the flocculated solid fraction and the liquid fraction separately. Generally, the best results were obtained
262 when the volume of polymer solution was added gradually rather than all at once. Depending on the
263 solids content, air can get clogged amongst the flocs, lifting them to the top. This can be avoided by a
264 quick stirring to promote elimination of the clogged air.

265

266 | **3. Results and discussion**

267

268 | **3.1. Evaluation of the optimal dose of CPE in solid-liquid separation tests**

269

270 A set of preliminary tests was run to roughly determine the optimal dose of CP. From these results, the
271 necessary dose was estimated according to the TS concentration of the samples. Later experiments were
272 carried out, using a slightly lower or higher dose than that calculated previously, with the aim of
273 accurately determining the optimum dose with the least possible number of tests. Mean values for TS and
274 VS in the samples analysed during these experiments are shown in Table 1. The volume of each sample
275 was 200 cm³. In this case the concentration of the CP solution was 5 kg m⁻³.
276 Table 2 shows the experimental values obtained in the separation of LF and SF for the RMP samples. The
277 polymer dose is expressed as milligrams of solid polymer per gram of TS in manure samples (mg CP g⁻¹
278 TS). The results obtained in the separation of LF and SF as TS removal percentages for the three kinds of
279 samples analysed in this work were adjusted according to a Logistic Function. For TS, the equation of the
280 model is given as a function where “x” is the flocculant dose, as g CP kg⁻¹ TS.

$$281 \quad TS_{removed} = \frac{a}{1 + b \exp^{-cx}}$$

282 Values obtained for constants are shown in Table 3. Figure 1 shows the removal percentages of TS Vs
283 CP dose for RMCH. The optimum doses were 42.8, 43.9 and 43.6 g kg⁻¹ for DSM, RMP and RMCH
284 samples, respectively. The values for the optimum dose were very similar for RMP and RMCH samples,
285 which had a similar TS content. For the DSM sample, the optimum dose was a little lower; this sample
286 type was also the one with the lowest TS level. The TS removal efficiencies for the samples whose CP
287 doses equal or surpass the optimum were 84.0% ± 0.2; 89.3% ± 0.5 and 93.3% ± 0.1 for DSM, RMP and
288 RMCH, respectively.

289 In Figure 1, when the polymer dose is lower than the optimum, the TS removal percentage increases
290 fast with growing doses; when dose value is close to the optimum, the removal percentage slows down
291 and when the optimum dose is reached, it keeps constant. Comparing the results obtained with the
292 different types of manure, a linear correlation (Figure 2) is observed between solids concentration in the
293 sample to be treated and the removal percentage of TS using flocculant doses equal to or higher than 45 g
294 kg⁻¹.

295

296 | 3.2. Trial of separation process

297

298 A dairy manure sample, taken from the cow house of the farm, was kept in a lab-scale manure pit for 30
299 days at laboratory temperature (293-296°K). Previous experiments showed that after 30 days of storage at

300 ambient temperature, VFA concentration had increased; however, no methanization had occurred [20].
301 Thus, only the development of the hydrolytic and acidogenic stages were allowed. For this experiment, 10
302 kg of the stored dairy manure sample were subjected to a flocculation process with the reactive Praestol
303 K144L, using a concentration of 3 kg m^{-3} . The minimum volume of polymer solution for which the
304 separation of manure in solid and liquid fractions took place was determined. This dose was 19.8 g kg^{-1} of
305 TS in manure. A lab-scale stationary screen like that described in Material and Methods (above) was used
306 for dewatering the SF. The results of the separation process for 1.0 kg of raw dairy manure from the lab-
307 scale manure pit can be seen in Table 4.

308 The mass of the SF separated was 29.1% of the mass of the original dairy manure and the polymer
309 solution. The SF contained the majority of the TS (76.1%), VS (79.9%), TKN (59.4%) and TP (87.4%) of
310 the initial content of the dairy manure. The rest of the initial components of the manure remained in the
311 liquid fraction. The VS/TS ratio was 0.78 for dairy manure, 0.82 and 0.63 for SF and LF. The SF had a
312 higher percentage of organic matter content than the dairy manure.

313 The percentage of TS, TKN and TP removed are in the same range as those reported, after
314 coagulation-flocculation and screening operations, for 1.5% TS flushed dairy manure [10]. Removal
315 percentages are higher than those obtained, without previous flocculation, by centrifugation [25].

316 Table 5 shows the characteristics of the liquid fraction. TS concentration was reduced from 101.2 kg
317 m^{-3} for the dairy manure to 19.46 kg m^{-3} for the liquid fraction. After the flocculation process, the COD
318 total (COD_T) concentration was 21.53 kg m^{-3} , and 18.50 kg m^{-3} was the value of $\text{COD}_{\text{filtrate}}$, due to
319 organic matter in the soluble fraction obtained after filtering the LF. The percentage of COD_T due to
320 $\text{COD}_{\text{filtrate}}$ was 85.9% after the flocculation treatment. Elimination of VFA is not desirable through the
321 coagulation-flocculation process since they are biodegradable compounds transformable to methane.
322 Regarding COD_{VFA} , in the LF this value was 75.5% of the COD_T . This high percentage of COD_T due to
323 VFA leads us to expect a high percentage of COD removal and its conversion to methane in a posterior
324 anaerobic treatment. There were three main VFA which contribute to COD_{VFA} : acetic acid, 45.3%;
325 propionic acid, 22.6% and butyric acid, 17.8%. These percentages are in accordance with those found in
326 the bibliography [26].

327 On the other hand, as data in Tables 4 and 5 shows, TKN and TP concentrations in the liquid fraction
328 decreased from 4.18 and 0.81 kg m^{-3} in dairy manure to 1.48 and 0.07 kg m^{-3} in the liquid fraction
329 respectively. This decrease in nutrient concentration in the LF is advantageous for anaerobic digestion
330 since the removal of nitrogen and phosphorous nutrients is minimal during anaerobic process, which is

331 only due to cellular synthesis, struvite (MgNH_4PO_4) precipitation and NH_3 stripping, owing to a pH
332 increase.

333 The TS content of the SF, shown in Table 4 is lower than the optimum (40-50%) for the development
334 of the composting process [27]. Thus, it would be necessary to mix the SF with other wastes that contain
335 higher solids content, such as straw and sawdust, to make treatment by the conventional aerobic
336 composting process possible. Another option for this solid fraction is the semi-liquid anaerobic process in
337 either batch or continuously fed systems.

338 For an industrial application with a decanter centrifuge, conducting a pre-screening process before
339 flocculation would considerably diminish the polymer consumption to remove solids from the RMCH for
340 two main reasons: on one hand the removal of solids in the process of screening, about 50% according to
341 Rico et al. [7], and on the other hand the screened liquid fraction obtained would have a lower TS content,
342 which means lower dose of polymer required. Carrying out the flocculation process with previous
343 screening would allow a solid-liquid separation process with lower reactive consumption, and a resulting
344 decrease in costs. In this work, the farm where manure was taken was equipped with an industrial manure
345 separator that only could process the manure from the pit. Fresh manure daily removed from the cow
346 house during cleaning operation could not be directly pumped to the separator. For anaerobic
347 biodegradability and methanogenic productivity tests it is recommendable to use fresh manure. However
348 laboratory scale is a very laborious task of screening, and the solid fraction obtained presents high
349 moisture content.

350 Depending on the origin of the manure, time and conditions of storage, some differences in the
351 composition and distribution may appear after solid-liquid separation. The longer the time and higher the
352 temperature, the greater the amount of organic matter that would be in soluble form, organic nitrogen that
353 would be converted into ammonia and biodegradable organic matter that would be transformed into VFA.
354 If methanization takes place, VFA in the liquid fraction will decrease as the result of CH_4 formation.

355

356 **3.3. Methane production**

357

358 A set of batch assays were performed to determine the methane productivity of the manure, the solid
359 fraction and the liquid fraction. Six reactors of 2.5 L, as described above, were employed and the
360 experiments, carried out at 35°C, were run in duplicate. 300 g of stabilised manure were put, as
361 inoculums, with 1000 g of manure, SF or LF into each reactor. Two 1.0 L bottles, as described above,
362 loaded with 300 g of the same stabilized manure and 0.5 L of tap water were used as blanks. The eight

363 reactors were placed in two thermostatic baths, four into each one, in order to achieve a temperature of
364 35°C in the reactors. In all the cases, air was removed from the reactors by passing biogas through them.
365 During 90 days, the biogas produced in each reactor was collected in a gas meter as described above. The
366 results reported are the mean values from the two reactors with the same kind of sample, subtracting the
367 mean value of biogas blank production.

368 On day 90 the mean methane volumes accumulated were 25.21, 33.47 and 7.08 L kg⁻¹ for dairy
369 manure, solid and liquid fractions, respectively. The results from both assays were coherent, reaching a
370 maximum difference of 2% for the solid fraction. In Figure 3, the evolution of the specific methane
371 production for each sample can be seen. These values were calculated from the accumulated methane
372 volumes and the VS values in Table 4. The final values were: 0.320, 0.258 and 0.580 m³ kg⁻¹ of VS for
373 dairy manure, solid and liquid fractions, respectively. The liquid fraction was the sample with the highest
374 specific methane production due to its high biodegradability. The manure reached an intermediate value,
375 while the solid fraction presented the lowest one, since the majority of the hardly biodegradable
376 compounds ended up in this fraction.

377 The methanogenic productivity found in this assay for dairy manure (0.320 m³ kg⁻¹ of VS) is higher
378 than others found in the bibliography [24]. It must be taken into account that when VS content is
379 measured in dairy manure, there is a high fraction of volatile organic components such as VFA. The VS
380 measurement includes drying (105°C) and incineration (550°C). During drying operations, VFA losses
381 can be expected for dairy manure depending on sample pH values. This means that only 25% of the VFA
382 present could have been included in the VS measurement [28]. In addition, methane production was
383 minimised in the controlled manure pit. For these reasons, the specific levels of methane production for
384 these samples of dairy manure, solid and liquid fraction were higher. The specific methane production
385 increased for the liquid fraction because the easily biodegradable components were not removed by the
386 physical-chemical treatment.

387 Figure 4 represents the methane production from 1 kg of manure, 25.21 dm³. It is worth taking into
388 account that 1 kg of manure, after the flocculation treatment, resulted in 0.485 kg of SF and 1.168 kg of
389 LF. The solid and liquid fractions derived from 1 kg of manure yielded 16.24 and 8.27 L of methane
390 respectively, which results in 24.51 L, a 2.8% less than non separated manure. This small difference can
391 be attributed to experimental errors. That represented 64.4% and 32.8% for solid and liquid fractions
392 respectively, with regards to methane production from 1 kg of manure. So, approximately two thirds of
393 methane yield were produced by the solid fraction whereas liquid fraction produced the third part of the
394 methane yielded by non-separated manure.

395 Separation of liquid and solid fractions by means of coagulation-flocculation decreased the total
396 production of methane per mass unit for the separated liquid fraction. However the specific methane
397 production considerably increased. On the other hand, for the solid fraction the methane production per
398 mass unit increased but the specific methane production decreased. The important issue is the fact that
399 now the time required to convert the biodegradable organic matter into methane for the liquid fraction
400 diminished as the majority of the hardly biodegradable organic matter was removed. The liquid fraction
401 had yielded 90% of the final methane production after 21 days, whereas the manure and the solid fraction
402 required 48 and 52 days to reach this percentage, respectively.

403 The methane yield also depends on the origin of the manure, time and conditions of storage, pre-
404 treatments and the amount of seeding employed in methanogenic production assays. Raising active
405 seeded biomass increases organic matter employed in biochemical methanogenic reactions and
406 diminishes the organic matter used in cell synthesis processes.

407

408 **3.4. Biodegradability of liquid fraction**

409

410 The same liquid fraction obtained by the treatment of 10 kg of dairy manure from the lab-scale manure pit
411 was subjected to an anaerobic biodegradability test at 35°C. In this way, the percentage of anaerobic
412 biodegradable COD for the liquid fraction was determined.

413 Two reactors were used to test the anaerobic biodegradability of the liquid fraction. One reactor
414 operated as a blank (300 g of biomass and 1 litre of tap water). The other was the treatment reactor (300 g
415 of biomass and of 1 litre of liquid fraction). Biomass from a UASB lab-scale reactor, treating leachates
416 from a composting plant (operating at 35°C), was used as seed biomass. The main characteristics of these
417 leachates were the high concentrations of VFA and $\text{NH}_4^+\text{-N}$. A VS concentration of 62.5 g kg^{-1} and a
418 specific methanogenic activity in terms of COD_{CH_4} at 35°C of 590 g $\text{kg}^{-1} \text{d}^{-1}$ of VS were observed for this
419 biomass. Air was removed from reactors by passing biogas through them. To measure the biogas
420 produced, two gas meters of the type described in material and methods section were used. On days 4 and
421 7, samples were withdrawn to measure COD_{T} , $\text{COD}_{\text{filtrate}}$ and the COD_{VFA} , calculating, as well, the COD
422 equivalent to the methane produced (COD_{CH_4}). Corrected values were obtained from the data of the
423 treatment reactor minus the data of the blank reactor. On day 8, one litre of supernatant was withdrawn
424 from the treatment reactor and another litre of liquid fraction was added to the reactor. The
425 biodegradability test was carried out again.

426 To determine the percentage of COD_{BD} , the corrected values obtained on day 7 were considered. The
427 percentage of COD_{CH_4} values were 83.0 and 83.5% in the first and second assay, respectively. The mean
428 value for the percentage of COD_{CH_4} was 83.3%. For the liquid fraction, the percentages of anaerobic
429 COD_{BD} were 87.2 and 87.8%, respectively.

430 Table 6 shows corrected data from the reactor corresponding to the test that resulted in a percentage of
431 COD_{BD} of 87.2. Taking into account the high methanogenic activity of the biomass used as seed (11.2 g
432 $\text{COD}_{\text{CH}_4} \text{ d}^{-1}$), the calculated theoretical percentage of COD_{cel} could not be considered, giving a more
433 conservative value, 83.0 for % COD_{BD} . Taking into account the relation between the mass of the treated
434 liquid fraction and biomass in the anaerobic biodegradability test, it is very probable that this liquid
435 fraction could be satisfactorily treated in high load reactors, like UASB, operating with HRT shorter than
436 two days.

437 Volumes of methane produced in both kinds of liquid fraction tests, methane production and
438 anaerobic biodegradability, were coherent. In biodegradability tests, a mean value of 6.94 L $\text{CH}_4 \text{ kg}^{-1} \text{ LF}$
439 was produced, whereas, in the methanogenic production assays, the mean value was 7.08 L $\text{CH}_4 \text{ kg}^{-1} \text{ LF}$.
440 The methane production in the methanogenic production test was a bit higher than that obtained in the
441 anaerobic biodegradability test, perhaps due to the different amount and origin of biomass used or the
442 different duration of the two kinds of tests.

443

444 | **4. Conclusions**

445

446 Flocculation of dairy cattle manure with TS concentrations up to 140 g kg^{-1} by additions of a strong
447 cationic polyacrylamide flocculant allows the elimination of up to 90% of total solids, using optimum
448 doses of approximately 43.9 g kg^{-1} of TS. Elimination percentages increase in a linear way with solid
449 concentrations. The solid fraction retained 29.1% of total initial mass, as well as 76.1% of TS and 79.9%
450 of VS. In addition, 59.4 and 87.4% of TKN and TP respectively, were retained in the solid fraction.

451 Methane production from the untreated manure was 0.320 $\text{m}^3 \text{ kg}^{-1}$ of VS. Liquid and solid fractions
452 yielded 0.580 and 0.258 $\text{m}^3 \text{ kg}^{-1}$ of VS, respectively. Due to its higher VS contents, the solid fraction
453 yielded twice the amount of methane than the liquid fraction. The anaerobic biodegradability of the liquid
454 fractions obtained was 83.0%, considerably higher than the value corresponding to manure (around 50%).
455 Taking into account these properties, the LF could be subjected to anaerobic process in high load reactors.

456

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458

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463 **6. References**

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