Comparison between the conventional anaerobic digestion of sewage sludge and its combination with a chemical or thermal pre-treatment concerning the removal of pharmaceuticals and personal care products

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Abstract Many novel treatment technologies, usually representing a pre-treatment prior to the biological degradation process, have been developed in order to improve the recycling and reuse of sewage sludge. Among all the methods available, a chemical (alkaline) and a thermal treatment have been considered in this study. The behaviour of 13 substances belonging to different therapeutic classes (musks, tranquillisers, antiepileptic, anti-inflammatories, antibiotics, X-ray contrast media and estrogens) has been studied during the anaerobic digestion of sewage sludge combined with these pre-treatments (advanced operation) in comparison with the conventional process. Two parameters have been analysed: the temperature (mesophilic and thermophilic conditions) and the sludge retention time. While organic matter solubilization was higher with the alkaline process (55–80%), no difference between both pre-treatments was observed concerning volatile solids solubilization (up to 20%). The removal efficiencies of solids and organic matter during anaerobic digestion ranged from 40–70% and 45–75%, respectively. The higher removal efficiencies of pharmaceuticals and personal care products were achieved for the antibiotics, Naproxen and the natural estrogens (>80%). For the other compounds, the values were in the range 20–70%, except for Carbamazepine, which was not removed at any condition tested.

Keywords Anaerobic digestion; chemical pre-treatment; pharmaceuticals; personal care products; sewage sludge; thermal pre-treatment; thermophilic

Introduction

Sludge treatment and disposal is becoming an important issue. Traditionally, sludge from sewage treatment plants (STPs) was applied on farmland as fertiliser and soil amendment. However, legislation concerning application of sludge on farmland is likely to be tightened, which will limit this disposal route in the future. Therefore, the interest in methods to reduce the volume and mass of biosolids is growing.

Due to their high organic fraction, anaerobic digestion is one of the fundamental processes in sewage sludge treatment for reducing and stabilising the organic solids. Reduction of sludge solids is not the only objective of this process, but production of energy in the form of biogas, improvement of dewaterability and a high quality final product are achieved. Significant inactivation of pathogens also occurs during the anaerobic digestion, depending on the process temperature and technological layout. The main disadvantage of this process is the quality of the supernatant from sludge thickening and dewatering, which contains high concentrations of solids, organic matter, ammonia nitrogen and other compounds. This stream is normally recycled to the inlet of the STP, thus increasing the inlet loads of solids, oxygen demand and nutrients. Besides, the efficiency and the digestion rate are limited by the hydrolysis of solids (Pavlostathis and

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Gosset, 1986). Therefore, several approaches have been considered in order to improve the anaerobic digestion process, with the aim of minimising the disposed sludge amounts and maximising the digested sludge quality.

Many pre-treatment methods can be used to improve the biodegradability of sludge, such as chemical addition, thermal treatment, mechanical or ultrasonic disintegration, and oxidative, enzymatic or microbial pre-treatment. By means of an efficient pre-treatment, the substrate can be made better accessible for the anaerobic bacteria, optimizing the methanogenic potential of the waste to be treated, and thus improving the rate and degree of degradation. Other processes in sludge treatment are also enhanced with these pre-treatments, such as stabilisation, bulking and foaming, conditioning, dewatering and final disposal (Müller, 2000).

Among the several disintegration methods available, two have been investigated in this study: a chemical and thermal process. Chemical treatment causes the destruction of complex organic compounds by means of strong mineral acids or alkalis. Alkaline hydrolysis (Chiu *et al.*, 1997) refers to a process in which the sludge pH is increased up to 12 by adding an alkali and it is maintained during 24 hours. The thermal hydrolysis is able to split and decompose a remarkable part of the sludge solid fraction into soluble and less complex molecules and to contribute significantly to pathogen destruction. In this process, the sludge is heated to 130–180 °C for 30–60 minutes (Machenbach and Odegaard, 1998). Both pre-treatments followed by the anaerobic process lead to an increase in biogas production and degree of solids degradation. However, some possible secondary effects must be considered, such as the increase in pollutants concentration, the generation of hardly degradable organic compounds and odours, and the worsening of the dewatering properties.

Pharmaceutical and personal care product (PPCP) ingredients (Daughton and Ternes, 1999) constitute a group of persistent organic compounds, which are present in municipal wastewaters as a result of their domestic application. Most pharmaceuticals or their metabolites are excreted into urban wastewaters and eventually make their way to the STPs. The removal of these substances through the STP depends not only on the profile of the wastewater treatment (conventional activated sludge, biofilter, nitrification–denitrification systems) but also on the physico-chemical properties of the compounds. In this way, the sorption capacity will be the most important parameter which determines the distribution of the compound between the liquid and solid phases. For those PPCPs with high solid–water distribution coefficients (K_d), the amount present in the sludge will be significant, being the total amount sorbed function of the solids content and the PPCPs concentration in the aqueous phase. Depending on the efficiency of each sludge treatment technology, these compounds will be recycled with the supernatant or disposed of with the sludge.

A recent review published by the UK Environment Agency noted that no quantitative data were found on concentrations of pharmaceuticals in sewage sludge although this is a potential route for lipophilic substances to the terrestrial environment (Ayscough *et al.*, 2000). Principal reasons for the lack of such data are likely the inherent difficulties associated with the analysis of sludge samples.

Those PPCPs not readily biodegradable during STP treatment enter in the receiving waters as dissolved pollutants via STP discharges or in agricultural fields via digested sludge. Effects of some PPCPs, e.g. endocrine disrupters and antibiotics, in the aquatic environment are well documented (Petersen *et al.*, 1997; Jobling *et al.*, 2002), but not much is known about the behaviour of these compounds in soils. Intake by plants, leaching into the groundwater and negative impact on the terrestrial organism are not excluded.

Another interesting question is whether the presence of these micropollutants in sewage sludge has an adverse effect on the anaerobic digestion process used for its stabilization. Methanogens are generally considered to be the most sensitive microorganism group participating in the anaerobic process and their activity is usually the rate-limiting step of the process (Speece, 1983). Thus, it is possible that PPCPs may affect methanogens' physiology and growth and eventually lead to a process being less efficient. The PPCPs' impact on anaerobic digestion has not been studied sufficiently. Hilpert *et al.* (1981) studied the sensitivity of methanogens to 28 antibiotics (by the agar diffusion test), stating that methanogens are sensitive to some antibiotics.

The objective of this work is to study the influence of a thermal and alkaline pretreatment on the PPCPs' behaviour during the anaerobic digestion of sewage sludge, with the aim of determining the final amounts being discharged with the treated sludge.

Materials and methods

Raw sewage sludge

Raw sewage sludge used in this work was collected from an urban STP corresponding to a population of approximately 100,000 inhabitants located in Galicia (NW Spain). A mixture (70:30, v/v) of primary and biological sludge collected from the thickener and flotator, respectively, was used as feeding of the anaerobic digestion pilot plant. The main characteristics of this feeding are indicated in Table 1.

PPCPs

Thirteen substances belonging to different therapeutic classes have been considered in this work: musks (Galaxolide and Tonalide), antiepileptic (Carbamazepine), tranquillizer (Diazepam), anti-inflammatories (Ibuprofen, Naproxen and Diclofenac), X-ray contrast medium (Iopromide), antibiotics (Sulfamethoxazol and Roxithromycin) and estrogens (Estrone, 17β-estradiol and 17α-ethinylestradiol). Several spiking solutions containing the different substances were added to the sludge mixture before feeding the anaerobic digesters in order to ensure the presence of these compounds in the raw sludge. The spiked concentrations of PPCPs ranged between 4 and 400 μg/L.

Anaerobic digestion pilot plant

The anaerobic digestion pilot plant consists of two lab-scale (10 L) anaerobic digesters (Figure 1). One of them is operated in the mesophilic range (37 °C) and the other one under thermophilic conditions (55 °C). The temperature is maintained by hot water circulation through the external jacket of both digesters. The feeding, common for both reactors, is stored at 4 °C, from where it is pumped to each digester. In order to maintain the high sludge retention time (SRT) required for sludge digestion (10–30 d), both pumps are programmed to feed the digesters three times per day. Simultaneously, the digested sludge is pumped out and collected in tanks.

Four parameters are controlled online: temperature, pH, stirring speed and biogas production. Besides, solids and organic matter content, alkalinity, volatile fatty acids (VFA) and biogas composition are monitored twice per week.

Table 1 Main characteristics of the raw sludge (g/L)

	TS	VS	TSS	VSS	COD_t	COD_s
Prim. sludge	50–145	25–85	50–125	25–70	45–120	1–8
Biol. sludge	15–40	10–35	10–35	10–30	10–50	1–7
Mixture	35–110	25–65	30–95	20–60	30–110	1–8

Figure 1 Anaerobic digestion pilot plant

The pilot plant was started up with 20% of methanogenic sludge coming from an anaerobic mesophilic reactor and 80% of sewage sludge. The whole start-up period lasted around three months. Afterwards, the digesters started to be fed with sludge previously spiked with PPCPs and two stages of operation have been performed in each digester with (advanced) and without (conventional) pre-treatment. The mesophilic digester was operated with a SRT of 20 and 10 days; while the thermophilic one was run at 10 and 6 days.

In each operational stage, once the steady-state was achieved (after a period corresponding to 1 or 2 SRT), 2–4 samples of digested sludge were taken for PPCP analysis. All the samples were taken as 5-day composite samples preserved by refrigeration (4 °C) and with the addition of hydrochloric acid to pH < 2 in order to stop biological activity.

Alkaline and thermal pre-treatment

The chemical pre-treatment was carried out by adding lime (CaO) to the stirred sludge until the pH was over 12, checking this value after 24 hours. The sludge was neutralised with hydrochloric acid before being fed in the anaerobic digesters.

The thermal pre-treatment was carried out in an autoclave at 130°C for 60 minutes, followed by a cooling until room temperature before being stored in the fridge.

Analytical methods

Solids, organic matter, VFA and alkalinity were analyzed according to *Standard Methods* (APHA-AWWA-WPCF, 1999). The biogas production was measured as water displacement (Veiga *et al.*, 1990) and its composition was analyzed by a gas chromatograph (HP 5890) equipped with a thermal conductivity detector.

PPCPs' soluble content. The concentrations of musks, anti-inflammatories, antibiotics, estrogens, neutral pharmaceuticals (Carbamazepine and Diazepam) and X-ray contrast medium in aqueous phase were determined according to García-Jares *et al.* (2002), Rodríguez *et al.* (2003), Hirsch *et al.* (1998) and Ternes (2001), respectively.

PPCPs' sorbed amount. The PPCP concentrations in the sludge were determined according to Ternes *et al*. (2002) for estrogens and Ternes *et al*. (2005) for the other substances.

Calculations

In order to develop the PPCPs' mass balances during the anaerobic digestion of sewage sludge, it is important to know the different factors which must be considered in the calculations.

Background content. Most of PPCPs studied in this work have been detected in the STP considered, and therefore they were already present in the sludge. Their concentrations in the raw sludge were calculated from those in the aqueous phase, using the K_d values (Ternes *et al*., 2004). The total background concentration (C_{raw}) is the sum of the liquid and sludge contributions of both primary and biological sludge.

Inlet concentration. The total inlet concentration (C_{in}) of each PPCP is the sum of the background (C_{raw}) and the spike (C_{spike}).

Outlet concentration. Since the digesters are completely stirred, their outlet comprises the digested sludge and the aqueous phase. This effluent was centrifuged in order to simulate a high efficiency solids separation step and two streams were obtained: the liquid (supernatant), which is usually recycled to the primary treatment (water line) of the STP, and the digested sludge, which is finally disposed. Both must be considered in the calculation of the total outlet concentration (C_{out}) of each PPCP.

Removal efficiency and accuracy analysis. Removal efficiencies for all PPCPs were calculated as the difference between the inlet and outlet concentrations. A statistical selection of the results obtained was performed according to the following criteria: (i) consistency of the measurements in liquid and sludge phases, and (ii) consistency in the K_d values calculated for digested sludge.

Results and discussion

Pre-treatment effectiveness

The pre-treatment effectiveness was analyzed in terms of volatile solids and organic matter (COD) solubilization (increase of soluble COD and decrease of VSS) and mineralization (removal of total COD and VS). Table 2 shows the results obtained.

The percentage of COD solubilization is higher with the alkaline (55–80%) than with the thermal pre-treatment (55–62%); while no differences were observed concerning solids solubilization (up to 20%). In contrast, the mineralization percentages of both solids and organic matter were higher in the thermal process.

Table 2 Effectiveness (%) of the alkaline and thermal pre-treatments

		Alkaline	Thermal
Volatile solids	Solubilization	0–13	0–20
	Mineralization	0	0–5
CODr	Solubilization	55–82	55–62
	Mineralization	0–4	0–12

Anaerobic digestion process

The operational characteristics of the mesophilic and thermophilic digesters are shown in Tables 3 and 4, respectively.

The removal efficiencies of solids ranged from 50 to 70% and from 40 to 65% for the mesophilic and thermophilic processes, respectively. In both digesters, the elimination of solids increased when they were run at higher SRT. The operation at higher temperature (thermophilic) led to better solids removal in the conventional and advanced operation with thermal pre-treatment; however, when applying the alkaline process, the reduction was similar in both digesters or slightly higher in mesophilic conditions.

The elimination of COD_t and COD_s varied between 50–75% and 60–80%, respectively, in the mesophilic range, and between 45–70% and 20–65%, respectively, in the thermophilic one. Similarly to solids, better organic matter removal efficiencies were achieved at higher SRT. The elimination of COD_S increased with the advanced operation, regardless of temperature, SRT and type of pre-treatment. The same pattern was observed for COD_t in the mesophilic process; however, in the thermophilic range, higher removal of COD_t was achieved in the conventional operation. The operation at higher temperature (thermophilic) led to higher COD_t removal, but lower COD_s reduction.

The biogas production was slightly higher in thermophilic conditions, whereas the methane content was similar in both digesters (60–65%).

PPCPs' behaviour

A summary of PPCPs' behaviour during conventional and advanced sludge treatment by anaerobic digestion is shown in Table 5 (average value and standard deviation of 2–3 samples). Since transformations between Estrone and 17β-estradiol occur naturally, both substances were considered together in the mass balance calculations.

It should be pointed out that removal means no presence in the effluent of the digesters, either in the liquid supernatant or in the digested sludge. Therefore, sorption onto sludge is not the mechanism responsible for PPCPs' elimination. Taking into account that volatilization seems to be negligible for these substances due to their low Henry coefficients ($\approx 10^{-5}$) and that sorption to the digester's walls could occur only at the beginning of the experiment (an equilibrium should have been achieved after long-time operation), the PPCPs' removal efficiencies indicated in Table 5 appear to be due to transformation/degradation processes during sludge anaerobic digestion.

All substances were removed to some extent during anaerobic treatment of sewage sludge, except Carbamazepine, which was not eliminated at any condition tested. Moreover, PPCPs' removal was similar in both digesters, with the exception of Diazepam,

Table 3 Performance of conventional and advanced operation of mesophilic digester

	Conventional		Advanced			
			Alkaline		Thermal	
	20 d	10 d	20 d	10 d	20 d	10 d
Biogas characteristics						
G (m^3/m^3d)	1.0 ± 0.2	1.9 ± 0.4	1.1 ± 0.2	2.5 ± 0.1	1.4 ± 0.4	3.2 ± 0.3
$\%CH_4$	59 ± 4	62 ± 2	62 ± 3	64 ± 2	61 ± 3	60 ± 3
Removal efficiencies						
VS	64 ± 2	51 ± 9	61 ± 11	64 ± 1	69 ± 5	62 ± 3
VSS	61 ± 5	50 ± 6	66 ± 5	61 ± 3	69 ± 6	56 ± 10
COD_t	62 ± 9	51 ± 8	70 ± 5	50 ± 3	75 ± 4	64 ± 6
COD_s	65 ± 11	57 ± 14	82 ± 4	82 ± 6	81 ± 4	74 ± 8

Table 4 Performance of conventional and advanced operation of thermophilic digester

	Conventional		Advanced			
			Alkaline		Thermal	
	10 d	6 d	10 d	6 d	10 d	6 d
Biogas characteristics						
G (m^3/m^3d)	2.0 ± 0.3	3.7 ± 0.6	1.6 ± 0.2	4.1 ± 0.3	3.5 ± 0.2	3.7 ± 0.2
$\%CH_4$	58 ± 3	67 ± 3	62 ± 4	64 ± 2	59 ± 4	66 ± 6
Removal efficiencies						
VS	61 ± 7	56 ± 7	56 ± 8	50 ± 13	64 ± 4	48 ± 7
VSS	61 ± 5	53 ± 8	59 ± 8	53 ± 13	61 ± 6	39 ± 5
COD_t	65 ± 4	56 ± 2	59 ± 15	49 ± 4	69 ± 4	43 ± 6
COD_s	56 ± 6	16 ± 10	64 ± 10	60 ± 16	60 ± 11	51 ± 12

which was better eliminated in mesophilic conditions. Very high removal (>80%) was obtained for Naproxen, Sulfamethoxazole, Roxithromycin and estrogens (after sludge adaptation), in both digesters. Musks, Galaxolide and Tonalide, and Diclofenac (after sludge adaptation) were also reduced to an important degree, around 65%, while the elimination of Diazepam and Ibuprofen only accounts for 50 and 40%, respectively. Iopromide was the substance with the lowest removal efficiency, around 20%.

No influence of temperature, SRT and pre-treatments was observed on PPCPs' removal, except for Ibuprofen and Roxithromycin. In the mesophilic range, the alkaline process affected negatively the removal of Roxithromycin, while the thermal treatment increased the elimination of Ibuprofen. It should be pointed out that if differences up to 20% in the results are not significant due to the inherent errors of the overall mass balance performance, these effects would be more doubtful.

Literature dealing specifically with PPCPs' removal during anaerobic digestion of sewage sludge is very scarce. The few data available are referred to either estimations from the physico-chemical properties or rough calculations from mass balances. Furthermore, the results found are not clear and even contradictory, since some authors (Khan and Ongerth, 2002; Andersen *et al.*, 2003; Stamatelatou *et al.*, 2003) stated that PPCPs exhibit some resistance to anaerobic biodegradation, while others (Van de Plassche and Balk, 1997; Holbrook *et al.*, 2002; Kupper *et al.*, 2004) reported the opposite.

Table 5 Average removal efficiencies (%) of PPCPs during conventional and advanced anaerobic pilot plant operation in mesophilic and thermophilic conditions

	Mesophilic	Thermophilic	Observations
Galaxolide	65 ± 15	67 ± 16	–
Tonalide	60 ± 8	67 ± 15	–
Carbamazepine	0	0	–
Diazepam	60 ± 18	38 ± 21	Higher removal with pretreatments. Sludge adaptation
Ibuprofen	40 ± 15	47 ± 10	Influence of thermal pre-treatment
Naproxen	87 ± 5	91 ± 5	–
Diclofenac	60 ± 18	73 ± 9	Removal occurred after sludge adaptation
Iopromide	23 ± 15	23 ± 11	–
Sulfamethoxazole	99 ± 1	99 ± 1	–
Roxithromycin	85 ± 15	95 ± 5	Influence of alkaline pre-treatment
Estrone + 17β-estradiol	85 ± 10	85 ± 5	Increasing removal with sludge adaptation
17α-ethinylestradiol	85 ± 5	75 ± 15	Removal occurred after sludge adaptation

Conclusions

The alkaline pre-treatment of sewage sludge led to higher COD solubilization percentages compared to the thermal process. However, no difference in terms of solids solubilization was observed between both treatments.

The use of the sludge pre-treatments prior to the anaerobic digestion process led to higher biogas productions and organic matter removal efficiencies in both mesophilic and thermophilic conditions. In contrast, the elimination of solids was similar to that obtained in the conventional operation. No significant differences were observed between the results obtained with the alkaline and the thermal process.

Concerning PPCPs' behaviour during anaerobic digestion of sewage sludge, the following conclusions could be stated: i) very high removal (>80%) of Naproxen, Sulfamethoxazole, Roxithromycin and estrogens (after sludge adaptation); ii) high removal (>60%) of musks (Galaxolide and Tonalide) and Diclofenac (after sludge adaptation); iii) medium removal (around 50%) of Diazepam and Ibuprofen; iv) low removal (around 20%) of Iopromide, and v) no removal of Carbamazepine. In general, no significant influence of the SRT, temperature and type of pre-treatment used was observed.

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