POLITECNICO DI TORINO
Repository ISTITUZIONALE

Pre-treatments aimed at increasing the biodegradability of cosmetic industrial waste

Original
Pre-treatments aimed at increasing the biodegradability of cosmetic industrial waste / Demichelis, F., Fiore, S., Onofrio, M.. - In: PROCESS SAFETY AND ENVIRONMENTAL PROTECTION. - ISSN 0957-5820. - STAMPA. - 118:(2018), pp. 245-253. [10.1016/j.psep.2018.07.001]

Availability:
This version is available at: 11583/2710822 since: 2018-07-13T10:18:14Z

Publisher:
Elsevier

Published
DOI:10.1016/j.psep.2018.07.001

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

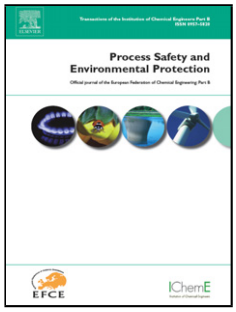
Publisher copyright
Elsevier postprint/Author's Accepted Manuscript

© 2018. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
http://creativecommons.org/licenses/by-nc-nd/4.0/.The final authenticated version is available online at:
http://dx.doi.org/10.1016/j.psep.2018.07.001

(Article begins on next page)

28 November 2026

Accepted Manuscript



Title: Pre-treatments aimed at increasing the biodegradability of cosmetic industrial waste

Authors: Francesca Demichelis, Silvia Fiore, Maurizio Onofrio

PII: S0957-5820(18)30428-2
DOI: https://doi.org/10.1016/j.psep.2018.07.001
Reference: PSEP 1442

To appear in: *Process Safety and Environment Protection*

Received date: 27-3-2018
Revised date: 11-6-2018
Accepted date: 3-7-2018

Please cite this article as: Demichelis, Francesca, Fiore, Silvia, Onofrio, Maurizio, Pre-treatments aimed at increasing the biodegradability of cosmetic industrial waste.Process Safety and Environment Protection https://doi.org/10.1016/j.psep.2018.07.001

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

ACCEPTED MANUSCRIPT

PRE-TREATMENTS AIMED AT INCREASING THE BIODEGRADABILITY OF COSMETIC INDUSTRIAL WASTE

Francesca Demichelis, Silvia Fiore*, Maurizio Onofrio

DIATI (Department of Engineering for Environment, Land and Infrastructures), Politecnico di Torino. Corso Duca degli Abruzzi 24, 10129 Torino, Italy

* Corresponding author: prof Silvia Fiore, DIATI Politecnico di Torino, Corso Duca degli Abruzzi 24 - 10129 Torino, Italy; email: silvia.fiore@polito.it. tel +39 011 0907613

Highlights

- The enhancement of biodegradability of cosmetic industrial waste was investigated
- The performances of different physic-chemical pre-treatments were compared
- The increase of soluble COD was employed as reference parameter
- Best results were achieved from thermo-alkaline pre-treatment
- Methane yield increased of 50% after pre-treatments reaching 0.14 Nm^3/kg_{VS}

Abstract

This work investigated physic-chemical pre-treatments aimed at improving anaerobic digestion (AD) of cosmetic industrial waste produced by a plant belonging to L'Oréal Group. A mixture designed according to relative abundances of waste was considered: sludge from internal wastewater treatment plant (54%-wt), residues of shampoo/conditioner (31%-wt), mascara sludge (13%-wt), food waste (2%-wt). The mixture had 80% VS/TS and COD equal to 1240 mg $O_2/g_{VS;}$ soluble fraction of COD was 22%. Investigated pre-treatments were: chemical, thermal, sonication

ACCEPTED MANUSCRIPT

and various combinations; their performances were assessed through the disintegration rate (DR, the increment of soluble COD due to the pre-treatment compared to the unaltered sample). Best results were achieved from TA - thermo-alkaline (120 min at 50°C) with DR 64.4 % and TAS - thermo-alkaline-sonication (15 min at 80°C and 40 kHz) with DR 66.1%. The benefits of AD on pre-treated waste mixture were: 50% increase in methane yield (0.14 Nm^3/kg_{VS}) and 5-7%-wt reduction of waste amount. From technical, energy and economic viewpoints, the proposed technical solution can provide an interesting perspective, fully consistent with Circular Economy principles.

Keywords: biogas, cosmetic, economic analysis, industrial waste, pre-treatment

1. Introduction

Nowadays, society and industrial world are encouraged to adopt sustainable production criteria. The depletion of non-renewable resources and social-political pressure drive industrial world towards green resources, such as biomass and waste, to achieve environmental, economic and social outcomes.

Usually, cosmetic wastes are incinerated or treated through coagulation/flocculation or pressure-flotation (Moggio, 2000). These processes imply environmental, energy and economic outlays and they are performed prior landfilling the waste. However, current regulations concerning industrial and hazardous waste promote the adoption of innovative and sustainable technologies (EU Parliament, 2016).

Anaerobic digestion (AD) is a mature technology for waste-to-energy production. Organic fraction of municipal solid waste, manure, crops and waste activated sludge from wastewater treatment (Linke et al., 2013; Rico et al., 2011) were extensively studied as substrates. Suitable AD feedstock should have: almost neutral pH, at least 75%-wt volatile solids and 20-30:1 carbon to nitrogen ratio (Dihoa, 2003).

ACCEPTED MANUSCRIPT

This study investigated the management of waste materials from cosmetics production through anaerobic digestion and particularly the feasibility of pre-treatments aimed at increasing biogas yields. We considered the waste (303.3 t in 2015) produced by a plant belonging to L'Oréal group located in NW Italy. Four materials, combined in a mixture according to their relative abundances, were studied: sludge from internal wastewater treatment plant (sWWTP), residues of shampoo and conditioner (RSC), sludge from mascara production (MS) and food waste (FW) from the canteen. In 2015 RSC and MS (corresponding to 44%-wt of total waste) were destined to incineration as hazardous waste because of their high organic carbon content.

Waste materials deriving from cosmetics production are usually characterized by high COD (624÷1436 mg/g_{VS}), suspended solids, fats, oils and detergents contents, mostly non-readily biodegradable compounds which make harder the application of conventional biological processes (Puyol et al., 2011). Thus, the focus of this study was to increase the available organic matter of the considered substrates through physic-chemical pre-treatments. It is important to underline that pre-treatments here investigated on cosmetic waste materials are based on studies referred to conventional AD substrates, such as wastewater sludge (Kim et al., 2013; Carrere et al., 2010), crops (Bondesson et al., 2013), rice (Bak et al., 2010) and macro-algae (Karray et al., 2015).

All pre-treatment configurations were designed considering temperature as key parameter. Thermal treatment is one of the most studied pre-treatments and it is implemented at industrial scale (Carrere H. , et al., 2010). A crucial factor of thermal pretreatment is the capability to reduce or completely remove pathogenic substances, present in personal care and cosmetic waste as antimicrobial and anti-mildew. Other positive effects of thermal pre-treatments are related to AD process, as the reduction of digestate viscosity, with subsequent enhancement of digestate handling (Carrere H. , et al., 2010).

Thermo-sonication pre-treatments are considered able to process recalcitrant components and heterogeneous substrates (Karray et al., 2015; Hernoux et al., 2013). Generally sonication treatments are more effective for substrates mixed with water (Rodriguez et al., 2017) and the

ACCEPTED MANUSCRIPT

optimal frequency range for cavitation and disruptions of cell structures is 20-40 kHz (Benabdallah El-Hadj et al., 2007). Possible drawback of sonication pre-treatment is the loss of volatile organic materials during cell disruption by ultrasounds (Tsapekos et al., 2015). Thus, proper combination of temperature, chemicals and sonic power has to be found.

The aim of this work was to design a pre-treatment procedure to allow the effective management of cosmetic waste though anaerobic digestion. Our approach was based on three pillars: technical, energetic and economic. Technical analysis investigated the possibility of treating cosmetic waste through a biological process and it consisted of three main steps: 1) chemical and physical characterisation to define the amount and availability of organic matter; 2) assessment of the performance of pre-treatments about the increase of available organic matter; 3) evaluation of the biodegradability of the pre-treated substrates through AD, with the double goal of biogas production and reduction of the amount of the waste. Energy analysis evaluated the energy consumption of pre-treatments and consequent anaerobic digestion. Economic analysis considered investment and operational cost and revenues deriving from biogas exploitation. Finally, a technical/energetic/economic combined analysis evaluated the profitability and sustainability of the implementation of pre-treatments on cosmetic waste at industrial scale. To complete the economic investigation, a comparison between the new proposed process (pre-treatments + anaerobic digestion) and the current cosmetic waste management, was made.

2. Materials and methods

2.1. Substrates origin and characterization

The waste materials analysed in the research were produced in 2016 at L'Oréal Saipo Industriale plant, located near Turin (Italy) and belonging to L'Oréal Group. The plant produces shampoo and conditioner, mascara and make-up powders for the mass-market segment in 34 countries. Waste production in 2015 was equal to 303.3 t: sludge from internal biological wastewater treatment plant

ACCEPTED MANUSCRIPT

(sWWTP) (54%-wt), residues of shampoo and conditioner production (RSC) (31%-wt), sludge from mascara production (MS) (13%-wt) and food waste from the canteen (FW) (2%-wt).

Qualitative characterisation of the waste materials estimated: Total Solids (TS) and Volatile Solids (VS) according to a reference procedure (EPA, 2001); pH through a pH 340 WTM pH-meter; total chemical oxygen demand (COD) and soluble chemical oxygen demand (**s**COD) according to a reference method (Raposo, 2008). Characterization analyses involved 3 replicates for each substrate.

2.2. Pre-treatments

The operative conditions of the pre-treatments investigated at laboratory scale are outlined in Table 1. Two series of pre-treatments were performed: the first on a limited amount of substrate (0.5-1 g depending on VS content) to pre-screen the most promising pre-treatment; the second series was tested on the same amount of waste (7-65 g of sample depending on VS content) employed for AD tests feeding 5% TS in a 500 mL batch reactor, to achieve consistency. Pre-treatment analyses were performed only on sWWTP, RSC and MS, since FW was considered easily biodegradable. Alkali and acid pre-treatments were carried out at 25 °C for 24 h with NaOH (Carrere et al, 2010) and HCl (Navarotto, 2012). Physical pre-treatment consisted in thermo-sonication at 40 kHz through a VWR Ultrasonic cleaner USC 300TH at 50-90 °C with reaction times of 15, 30 and 120 min. Hybrid pre-treatments were thermo-chemical (in a Julabo Corio-C thermostatic bath) and thermo-chemical-sonication.

Table 1. Pre-treatments configuration

Pre-treatment	conditions	Time [min]	Temperature [°C]
chemical	0.08 g NaOH /g_{TS} 0.5 % TS HCl	120	25
physical	Thermal-Sonication	15, 30, 120	50, 70, 90
combined	Thermo-chemical: 0.08 g NaOH/g_{TS} 0.5 % TS HCl	15, 30, 120	50, 70, 90
	Thermo-chemical-		

ACCEPTED MANUSCRIPT

	sonication: 0.08 g NaOH/g $_{TS}$ 0.5 % TS HCl		

The performance of pre-treatments was evaluated in terms of COD solubilisation (see Eq. 1) and disintegration rate (DR) (Li et al., 2012) (see Eq. 2):

$$COD\ solubilisation\ [\%] = \frac{sCOD_{\ pre-treat}}{COD} \cdot 100 \quad (1)$$

$$DR\ [\%] = \frac{sCOD_{\ pre-treat} - sCOD}{COD - sCOD} \cdot 100 \quad (2)$$

where, COD, $COD_{\ pre-treat}$, $sCOD$ and $sCOD_{\ pre-treat}$ mean total and soluble COD respectively before and after pre-treatments.

2.3 Anaerobic digestion tests

AD tests were carried out in 0.5 L Pyrex glass bottles (Duran, Germany) connected by 6 mm Teflon tubes (PTFE, Germany) to 2.5 L Tedlar gas-bags. Methane was measured inserting a 2L bottle (Duran, Germany) filled up with 1.8 L water, 50 mL ethanol, 20 g NaOH and 0.5 g phenolphthalein between the reactor and the gas-bag to remove carbon dioxide and hydrogen sulfide. Methane was measured through water displacement. AD tests were performed in batch mode feeding 5% TS and adopting 1:2 inoculum to substrate ratio (Parra-Orobio et al., 2018). Incubation was carried out in a Julabo Corio-C water bath at 35 °C. AD batch reactors were manually shaken every 2 hours during working hours. Three replicates for methane measurements from the samples plus two replicates for the control (inoculum), were carried out for each test. Digestion process was declared concluded when marginal methane production was below 1%.

2.4 Energy requirements

ACCEPTED MANUSCRIPT

After the technical evaluation, the performances of pre-treatments and AD were investigated in terms of energy consumption (EC) (see Eq. 3)

$$EC\ [kWh/kg_{TS}] = \frac{P \cdot t}{TS} \cdot 100 \qquad (3)$$

where P [W] is the absorbed power input, t [s] is the process time and TS [kg] is the feed. The energy demand of thermostatic and ultrasounds baths were respectively 32 W/L and 226.7 W/L.

2.5 Economic assessment

Economic analysis evaluated AD scale up to treat all the wastes produced in L'Orèal plant, in comparison with costs and revenues of present waste management operations. The economic analysis didn't account the cost of substrates production. AD process considered investment (construction of digester and gasometer) and operational (energy, water, labors and waste disposal) costs and revenues as thermal and electric energy produced through biogas (see Table 2). For the investment cost was assumed amortization, calculated through 5 years with an interest of 1.5 % (see Eq. 4).

$$A = C_0 \cdot \frac{i \cdot (1+i)^n}{(1+i)^n - 1} \qquad (4)$$

where A is the amortization cost, C_o is the initial capital cost, i is the interest and n is the number of years on which amortization is extended.

The costs of the actual waste management operations are as follows: sWWTP 0.15 €/kg, RSC and MS 0.31 €/kg, FW 0.11 €/kg. These values are strictly linked to northwest Italian context.

Table 2. Investment and operational costs considered for economic assessment

	item	unit	cost	Reference
investment costs	reactor construction	[€/ m^3]	550	(Arnò et al, 2017)
	interest	[y]	5	
	tax of interest	[%]	1.5	

ACCEPTED MANUSCRIPT

operational costs	thermal energy	[€/kWh]	0.20	(Eurostat, 2017)
	electric energy	[€/KWh]	0.22	(Eurostat, 2017)
	diesel	[€/l]	1.10	(Eurostat, 2017)
	digestate treatment	[€/kg]	0.01	(EcoPiemonte, 2017)
	labours	[€/y]	45000	(ISTAT, 2017)
	NaOH	[€/kg]	0.27	
	water	[€/m^3]	1.37	(SMAT, 2017)
revenues	thermal energy from biogas	[€/kWh]	0.20	(Eurostat, 2017)
	thermal energy from biogas	[€/kWh]	0.20	(Eurostat, 2017)

3. Results

3.1 Substrates characterization

The four substrates had pH values between 5.08 and 6.9, VS/TS values above 75% and COD higher than 624.25 mg/g_{VS} (see Table 3). Further investigation was performed through the evaluation of sCOD, which represents the readily available organic matter. The ratio sCOD/COD ranged between 5 and 51%, witnessing a low biodegradability of the considered materials, leading to the necessity to explore pre-treatments.

Table 3. Characterization of the considered waste materials

	sWWTP	RSC	MS	FW
pH	6.54±0.49	6.30 ±0.17	6.69±0.79	5.08±0.34
TS [%]	2.43±0.74	24.98±0.45	34.70±2.18	25.06 ±3.31
VS/TS [%]	86.24±3.20	81.65± 1.51	75.46±1.28	97.17±0.95
COD [mg O_2/g_{VS}]	1174.06 ±94.80	1436±23.10	1148.52±17.56	624.25±48.4
sCOD [mg O_2/g_{VS}]	65.55±13.49	739.68±24.3	71.08±3.24	145.34±18.75

3.2 Pre-treatments

Two series of pre-treatments were carried out. The first was performed with two main folds: 1) evaluation of the enhancement of organic matter availability in the substrates through COD

ACCEPTED MANUSCRIPT

solubilization values and 2) investigation of the most promising pre-treatment through disintegration rate (DR) values.

3.2.1 Pre-screening of pre-treatments: COD solubilisation

The first series of pre-treatments were: chemical, physical (thermal-sonication) and combined (thermo-chemical and thermo-chemical-sonication). COD solubilisation values witnessed the increase of available organic matter in the substrates after pre-treatments (see Table 4). The sCOD/COD ratio of untreated substrates was about 6% for sWWTP and MS, and around 50% for RSC. COD represents the indirect measure of organic matter and it is composed of biodegradable and non-biodegradable fractions; biodegradable COD is divided into fast and slowly biodegradable COD (Metcalf and et al., 2013). sCOD is made of all the above-mentioned components. COD solubilization value of RSC was the highest because of its high amount of surfactants. Due to their different composition, the three substrates reacted differently to the various pre-treatments, however all exhibited an increment of sCOD/COD after all pre-treatments. The percent increase of COD solubilization values of treated and untreated substrates (see Table 5**)** ranged between:

- for sWWTP: 51.49 (50 °C, 40 kHz, 15 min) and 91.46% (0.08 gNaOH/g_{TS}, 90 °C, 120 min),
- for RSC: 44.75 (0.05 %TS HCl, 90°C, 120 min) and 44.77% (0.08 gNaOH/g_{TS}, 50°C, 40 kHz, 15 min)
- for MS 1.61 (0.08 gNaOH/g_{TS}, 70 °C, 120 min) and 81.20% (0.05 $\%_{TS}$ HCl, 80 °C, 40 kHz, min)

The lowest increase of COD solubilisation was achieved by RSC, since the sCOD/COD ratio of un-treated RSC was already around 50%.

Table 4. Evaluation of pre-treatments through COD solubilisation

ACCEPTED MANUSCRIPT

		sCOD/COD		
Pre-treatment		sWWTP [%]	RSC [%]	MS [%]
none		5.58	51.51	6.19
Chemical	0.08 $gNaOH/g_{TS}$, 25°C, 24h	18.90	95.66	19.47
	0.05 $\%_{TS}$ HCl, 25°C, 24h	32.76	94.57	27.51
Physical thermo-sonication	50°C at 40 kHz, 15 min	11.51	93.73	20.00
	50°C at 40 kHz, 30 min	24.10	95.29	7.62
	80°C at 40 kHz, 30 min	65.37	95.29	8.63
Combined				
thermo-alkaline	70°C, 120 min	35.86	97.03	6.29
	90°C, 120 min	47.57	97.03	8.73
thermo-acidic	70°C, 120 min	45.15	93.62	21.55
	90°C, 120 min	41.60	93.24	18.71
thermo-alkali-sonication	50°C 40 kHz, 15 min	15.92	98.62	15.85
	50°C 40 kHz, 30 min	28.20	97.49	11.39
	80°C 40 kHz, 15 min	28.39	97.49	11.39
thermo-acidic-sonication	50°C 40 kHz, 15 min	41.82	93.35	16.15
	50°C 40 kHz, 30 min	35.49	94.11	20.04
	80°C 40 kHz, 15 min	35.58	94.20	32.91

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 5. Percent increase of COD solubilization of sWWTP, RSC and MS according to the type of pre-treatment

Pre-treatment		sWWTP [%]	RSC [%]	MS [%]
none		5.6	51.5	6.2
Chemical	0.08 gNaOH/gTS, 25°C, 24h	70.5	46.2	68.2
	0.05 %TS HCl, 25°C, 24h	8.0	45.5	77.5
Physical thermo-sonication	T=50°C, 40 kHz, 15 min	51.5	45.0	69.1
	T=50°C, 40 kHz, 30 min	76.8	45.9	18.7
	T=80°C, 40 kHz, 30 min	91.5	45.9	28.3
Combined				
thermo-alkaline	70°C, 120 min	84.4	46.9	1.6
	90°C, 120 min	88.3	46.9	29.1
thermo-acidic	70°C, 120 min	87.6	45.0	71.3
	90°C, 120 min	86.6	44.8	66.9
thermo-alkali-sonication	50°C, 40 kHz, 15 min	64.9	47.8	61.0
	50°C, 40 kHz, 30 min	80.2	47.2	45.7
	80°C, 40 kHz, 15 min	80.3	47.2	45.7
thermo-acidic-sonication	50°C, 40 kHz, 15 min	86.6	44.8	61.7
	50°C, 40 kHz, 30 min	84.3	45.3	69.1
	80°C, 40 kHz, 15 min	84.3	45.3	81.2

3.2.2 Pre-screening of pre-treatments: disintegration rate

Considering RSC, DR value for alkali pre-treatment (38.76%) was higher than from acid one (22.00%); for sWWTP and MS acid pre-treatment were more promising than alkali ones (see Figure 1 A, B). MS persisted in an insoluble form after all chemical pre-treatments. sWWTP after an alkali pre-treatment for 24 h at 25 °C achieved DR 13.13%; DR equal to 20% was reported for a civil wastewater sludge (Carrere et al, 2010).

Thermo-chemical pre-treatments were carried out at 70 ° and 90 °C. After thermo-alkali pretreatments (see Figure 1C) sWWTP and MS exhibited the same trends: highest DR values were reached at 90 °C, with respectively 43.92% and 2.7%, while RSC reached the highest DR at 70 °C (89.36%). Still, temperatures of 70 °-90 °C were not able to solubilize MS. After thermo-acidic pretreatments (see Figure 1D), all substrates achieved the highest DR at 70 °C. To sum up thermo-

ACCEPTED MANUSCRIPT

chemical pretreatments performances: thermo-acidic pre-treatment at 90 °C was the most efficient for MS, since hydrochloric acid addition enhanced the solubilisation of the substrate; thermo-alkali at 70 °C was the most promising pre-treatment for RSC (DR=89.36%), because RSC, high in surfactants, saponified with NaOH addition. Thermo-alkali pre-treatment at 90°C and thermo-acidic pre-treatment at 70 °C for sWWTP reached the same DR, around 40%. After thermo-alkali-sonication pre-treatments (see Figure 1E), all substrates achieved the same DR in the two configurations: 30 min at 50 °C and 15 min at 80 °C: 23.32% for sWWTP, 66.87% for RSC and 5.55 % for MS. RSC and MS reached the highest DR in themo-alkali-sonication configuration at 15 min at 50°C, respectively 84.00% and 10.29%, while sWWTP reached the highest DR at 50 °C for 30 min. After thermo-acidic sonication pre-treatments (see Figure 1F), RSC and MS achieved the best DR in the configuration of 15 min at 80 °C, respectively 16.43% and 22.00%, while sWWTP reached the highest DR at 50 °C for 15min: 37.80%. Comparing thermo-chemical-sonication pre-treatments, it is possible to observe that sWWTP reached the highest DR with thermal acid sonication for 15 min at 50 °C, RSC achieved the highest DR for thermal alkali sonication for 15 min at 50°C (84.00%) and MS reached the best DR for thermal acid sonication pre-treatment for 15 min at 80°C (22.00%). Thermal-sonication pre-treatments (see Figure 1G) were performed at 40 kHz and 50 °C for 15 and 30 min and at 80 °C for 15 min. The most promising configuration for sWWTP was at 80 °C for 15 min, with DR equal 62.86%, for RSC were at 50 °C for 30 min and at 80 °C for 15 min, respectively achieving 33.00% and 33.13%. DR accomplished by RSC with thermo-sonication pre-treatment were in agreement with 30% DR reached with pharmaceutical waste (Pei, et al., 2015).

From the pre-screening of pre-treatments, the most promising were the following:

- for sWWTP: thermal-sonication at 80 °C for 15 min (DR 62.86%) and thermo-alkaline pre-treatment at 90°C for 120 min (DR 43.92%);
- for RSC: thermo-alkaline pre-treatment at 70 °C for 120 min (DR 89.36%) and thermo-alkaline-sonication at 50 °C for 15 min (DR 84.00%)

ACCEPTED MANUSCRIPT

- for MS: acidic pre-treatment (DR 22.63%) and thermo-acidic-ultrasonic pre-treatment at 80°C for 15 min (DR 22%).

3.2.3 Pre-treatments scale up

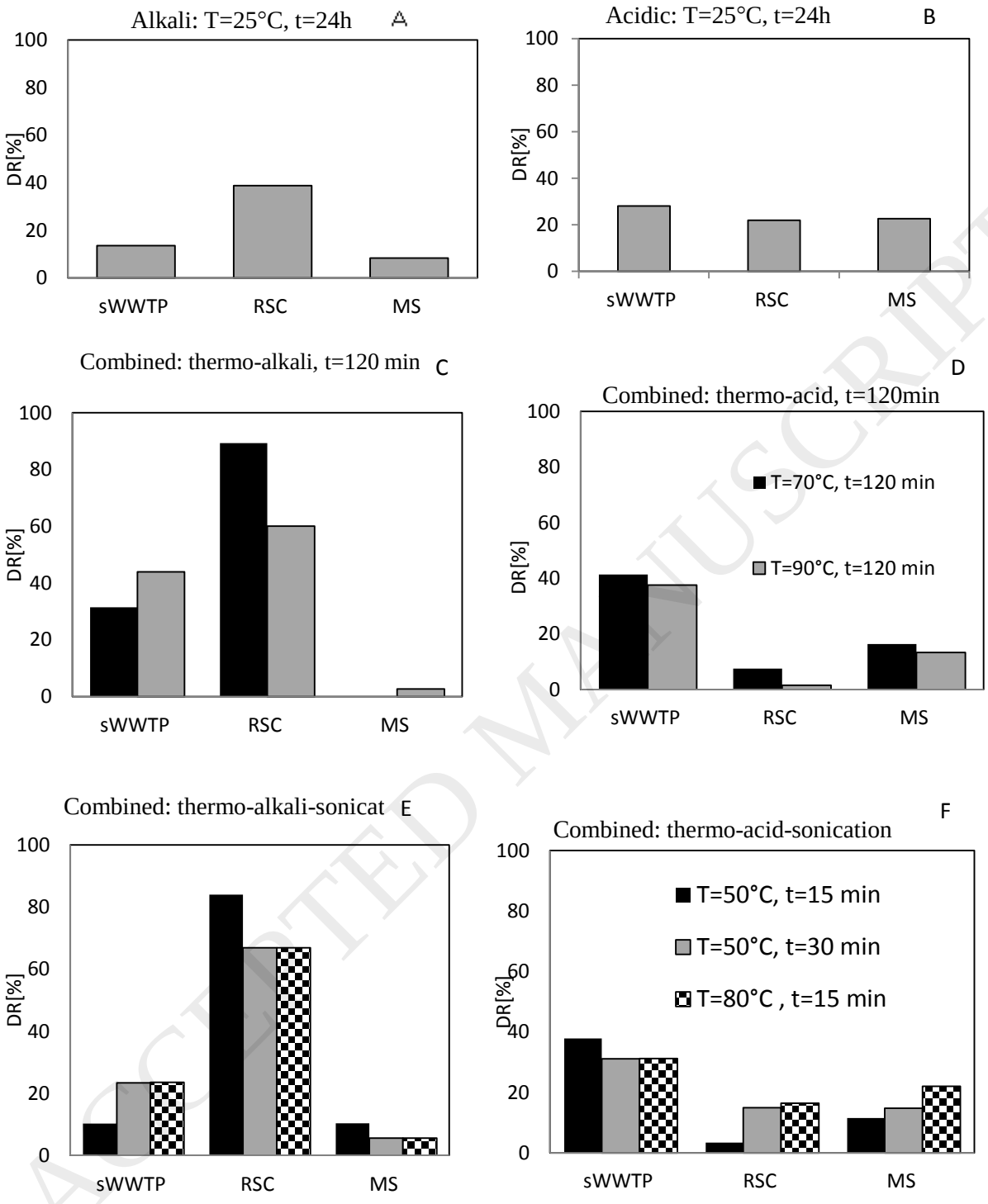
Afterwards the pre-screening of pre-treatments, a deeper investigation was carried out only on the most abundant substrates: sWWTP and RSC. To gain consistency, sWWTP and RSC pre-treatment tests were performed on the same amount of waste employed for 5% TS fed AD process (see section 2.2).

Even if the pre-treatments in the bullet list of section 3.2.2 were the most promising for sWWTP and RSC, to compare the different pre-treatments we chose 50° and 80° C with reaction times of 15, 30 and 120 min. For sWWTP, the evaluated pre-treatments were: thermal, thermo-alkaline, thermo-sonication and thermo-alkaline-sonication, while for RSC were thermo-alkaline and thermo-alkaline-sonication. For a complete assessment of pre-treatments, a comparison between first and second series of pre-treatments is provided in Table 6.

sWWTP exhibited a consistent scale effect, while RSC reached in both series of pre-treatments DR values of the same magnitude order. Specifically, increasing the amount of sWWTP, after thermo-sonication (80 °C for 15 min) DR decreased of 66.17%, while after thermo-alkaline-sonication (50°C for 15 min) DR increased of 74.63% (see Table 6). For RSC, after thermo-alkaline (50 ° C for 120 min) and thermo-alkaline-sonication pre-treatments (50 C for 15 min) scale effects respectively of 11.29% and 8.04 % were detected.

ACCEPTED MANUSCRIPT

Figure 1. Pre-screening of pre-treatments in terms of disintegration rate (DR)



ACCEPTED MANUSCRIPT

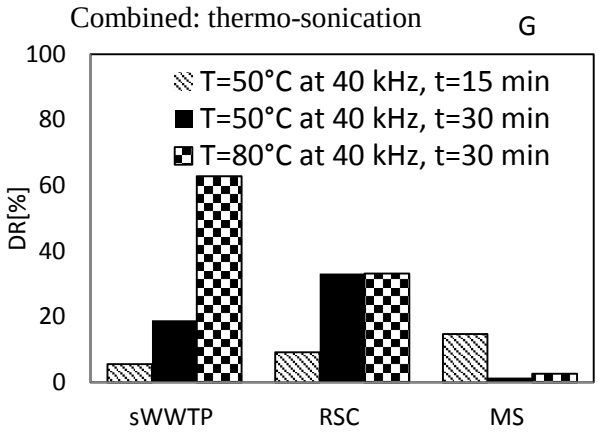


Table 6. Evaluation of the pre-treatments performed on sWWTP and RSC (*first set of tests; **second set of tests).

Substrate	Pre-treatment	T [°C]	t [min]	DR [%]*	DR [%]**
sWWTP	Thermal	80	15		9.36
			30		33.76
			120		13.85
	Thermo-alkaline	80	15		36.90
			30		53.45
			120		25.26
		50	15		39.03
			120		57.10
	Thermo-sonication	80	15	62.86	21.26
			30		42.75
			120		32.32
	Thermo-alkaline-sonication	80	15		50.45
			30		46.81
			120		41.25
		50	15	10.25	40.41
RSC	Thermo-alkaline	50	15		5.82
			30		21.09
			120	84	74.51
	Thermo-alkaline-sonication	50	15	89.36	82.13
			30		32.53
			120		17.27

ACCEPTED MANUSCRIPT

After the evaluation of scale effect, our attention was focused on the pre-treatments performed on the amount of sWWTP and RSC employed for AD at 5% TS. For sWWTP, thermal and thermo-sonication pre-treatments at 80 °C provided the highest DR for a reaction time of 30 min, respectively 33.76% and 42.75%; although 15 and 120 min were respectively insufficient and excessive reaction times. Comparing thermo-alkaline and thermo-alkaline-sonication pre-treatments with physical pre-treatment, the addition of NaOH provided an increase of DR (see Table 6). In accordance with literature (Bahera et al., 2014), during alkaline pre-treatment saponification reactions took place causing the decrease of polymerization and cristallinity degrees. From thermal to thermo-alkaline pre-treatments at 80°C for 30 min, DR increased of 19.69%, while from thermo-sonication to thermo-alkaline-sonication pre-treatments at 80 °C for 15 min, DR increase of 29.19%. Thermo-alkaline pre-treatments at 80 °C were effective in terms of DR for 30 min reaction time, while thermo-alkaline pre-treatments carried out at 50 °C were promising for working time of 120 min. Thus, higher solubilisation can be achieved with lower temperatures but longer treatment times. This trend is in agreement with the kinetics laws, since kinetics rate is faster with the increase of temperature and consequently the reaction time decreases. However, the combination of high temperature and long reaction times does not necessarily provide a synergistic effect, as physical pretreatment of the present study demonstrated, because possible toxic or inhibitory secondary products may occur. After thermo-alkaline pre-treatments, decreasing the temperature from 80 to 50 °C and increasing the reaction time from 30 to 120 min, DR increased of 6.40%.

High temperature had a drawback: loss of volatile organic compounds, which resulted in the reduction of DR and potentially in methane production (Ariunbaatar et al., 2014). Nevertheless, the difference between the two proposed thermo-alkali pre-treatment configurations (80°C for 30 min and 50 °C for 120 min) was less than 6.40%. Thus, the evaluation of the two configurations considered not only DR values but also the cost of thermal energy to support the process and the reaction time. Decreasing temperature from 80 to 50 °C implied two main advantages: reduction of energy and of equipment requirement in industrial scale-up perspective. Thermo-alkaline-sonication

ACCEPTED MANUSCRIPT

pre-treatment at 80 °C was more effective for a reaction time of 15 minutes than for 30 and 120 min. This trend was due to a higher availability of organic matter after sonication than after thermal pre-treatment. Consequently sonication required shorter reaction time. Sonication didn't change chemical mechanisms of the pre-treated substrates, but the reaction kinetics was boosted up (Lou et al., 2014).

For RSC, thermo-alkaline pre-treatment achieved the highest DR by increasing reaction time from 15 to 120 min at 50 °C, DR increased from 5.82 to 74.51%. Opposite trend was depicted with thermo-alkaline-sonication pre-treatment (see Table 6), which reached the highest DR by decreasing the reaction time from 15 to 120 min at 80 °C; DR value decreased from 82.13 to 17.27%. Long thermal chemical treatments combined with other pre-treatments could produce inhibiting substances, reducing the benefit of the pre-treatments (Talebnia et al., 2008). Thus, the most effective pre-treatments for the RSC were: thermo-alkaline treatment (at 50 °C for 120 min) and thermo-alkaline-sonication pre-treatment (at 50 °C for 15 min).

3.2.4 Pre-treatments investigation on waste mixture

Thermo-alkaline and thermo-alkaline-sonication pre-treatments were the most promising pre-treatments for sWWTP and RSC. Since sWWTP and RSC were the most abundant substrates, the above-mentioned pre-treatments were performed on a mixture made up according to relative abundances of waste materials (54% sWWTP, 31% RSC, 13% MS and 2% FW), in the following named "Mix". The amount of Mix employed for pre-treatment test was the same used for AD process at 5% TS. Thermo-alkaline (TA) and thermo-alkaline-sonication (TAS) pre-treatments were performed on the Mix and compared with the pre-treatments carried out on sWWTP and RSC (see Figure 2).

For all thermo-alkaline pre-treatments (50 °C for 15-120 min and 80 °C for 30 min) the Mix reached DR higher than 40% in accordance with general DR values of alkaline and combined alkaline pre-treatments higher than 30% (Carrere et al, 2010). The Mix achieved DR values similar

ACCEPTED MANUSCRIPT

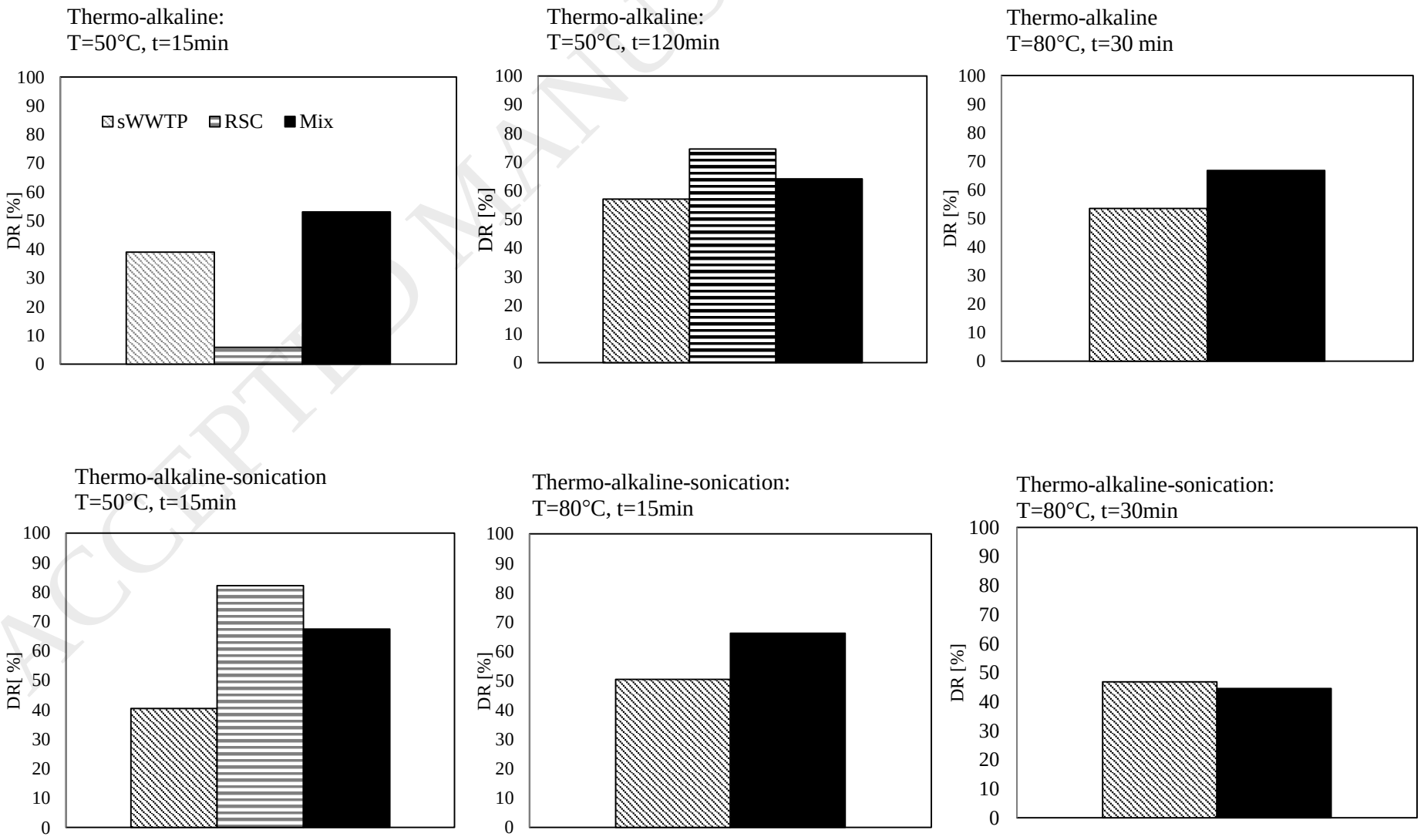
for thermo-alkaline pre-treatments performed at 50 °C for 120 min and at 80 °C for 30 min, respectively 64.10% and 66.74%. Since DR values of the two configurations were similar, the choice was evaluated in terms of environmental, energy and economic perspectives, considering if it was more convenient a process with low temperature and long reaction time (50 °C and 120 min) or with high temperature and short reaction time (80 °C and 30 min). In an industrial contest, treatments at 50 °C are easier to realize and maintain than treatments at 80° C, in terms of energy and equipment demand (Bahera et al., 2014). Among the three configurations of thermo-alkaline-sonication pre-treatments, the one performed at 80 °C for 30 minutes was the least advantageous in terms of DR. Whereas thermo-alkaline-sonication pre-treatments performed at 50 °C for 15 min and 80 °C for 15 min reached similar DR values for Mix and RSC, but for sWWTP the highest DR was achieved at 80 °C for 15 min with 50.45%. Among the explored pre-treatments the most promising for the Mix were: 1) thermo-alkaline (50 °C for 120 min) for which a synergistic interaction between sWWTP and RSC took place, since DR value was an average of DR reached by sWWTP and RSC individually and 2) thermo-alkaline-sonication (80 °C for 15 min at 40 kHz).

In details, the pH values achieved after thermo-alkaline (50 °C for 120 min) and thermo-alkaline-sonication (80 °C for 15 min) pre-treatments on the Mix were respectively 7.20 and 7.43.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Figure 2. Investigation and comparison of pre-treatments on sWWTP, RSC and Mix



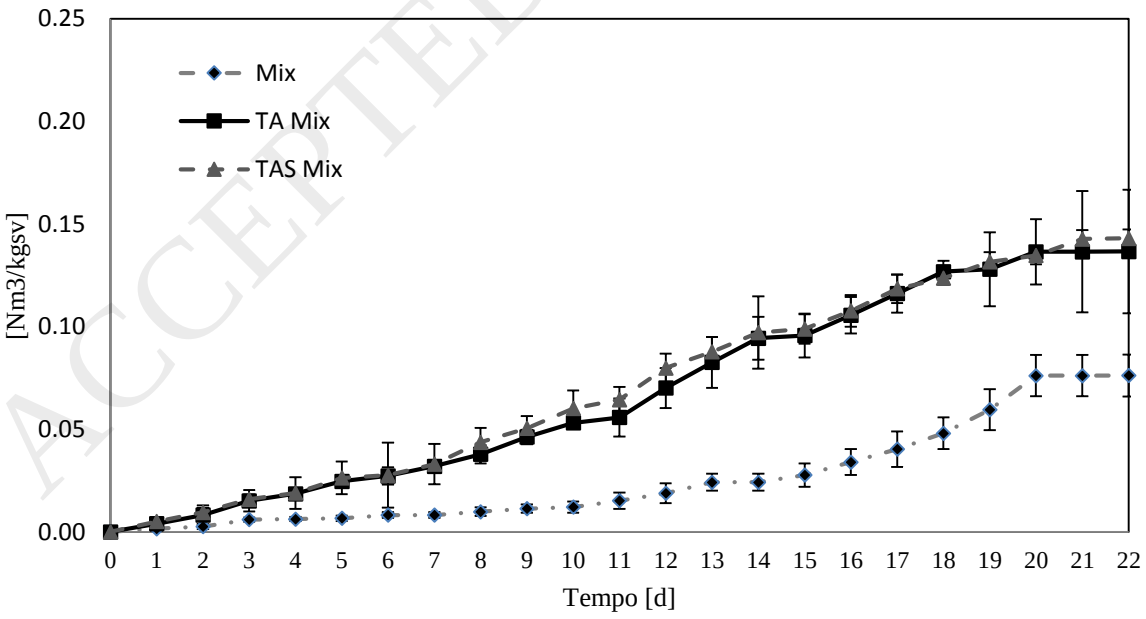
ACCEPTED MANUSCRIPT

3.3 Anaerobic digestion tests

The biodegradability of the unaltered and pre-treated Mix was tested within anaerobic co-digestion. Co-digestion was performed for two main reasons: first of all to evaluate and compare the biodegradability of the unaltered and pre-treated substrates and second to optimise the current management of the substrates. According to section 3.2.4 the most promising pre-treatments were: thermo-alkali (TA) performed for 120 min at 50 °C and thermo-alkali-sonication (TAS) for 15 min at 80 °C and 40 kHz. Thus, anaerobic co-digestion was performed on: Mix, TA Mix (mixture after TA pre-treatment) and TAS Mix (Mix after thermo-alkali-sonication pre-treatment). AD tests accomplished net methane yields (see Figure 3) equal to 0.07 Nm^3/kg_{VS} from the Mix, to 0.14 Nm^3/kg_{VS} from TA Mix and TAS Mix, witnessing the efficiency of the proposed pre-treatments.

The pH values of the digestate coming out from the anaerobic co-digestion tests performed on Mix, TA Mix and TAS Mix were respectively: 7.44, 7.60 and 7.65.

Figure 3. Specific net methane production of the untreated waste mixture (Mix) Mix after thermo-alkali pre-treatment (TA Mix) and Mix after thermo-alkali-sonication pre-treatment (TAS Mix)



ACCEPTED MANUSCRIPT

Pre-treatments, in accordance with literature (Bolado-Rodriguez et al., 2016) increased methane production. Further important benefits of anaerobic co-digestion were: 1) reduction of TS thus reduction of substrates to dispose and 2) reduction of organic matter in the substrates, thus reduction of hazardous nature. In details, after anaerobic co-digestion Mix, TA Mix and TAS Mix reached a TS reduction respectively of 5.25%, 7.28% and 5.68%.

3.4 Energy consumption

A basic energy evaluation considered the consumption of the equipment and time required to perform AD and pre-treatments processes. The values were provided as kWh/kg of TS treated (see Table 7). The analysis considered three key parameters: 1) kW consumed by single operation, 2) process length and 3) amount of treated substrates. TAS and TA pre-treatments enhanced methane yields of 50% with an increase of energy consumption respectively of 1.1, in accordance with literature (Ning et al., 2016). AD process represented the highest energy item consumption, since it lasted 22 days while TA and TAS respectively only 2h and 0.25 h.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Table 7. Energy consumption of anaerobic digestion of Mix, TA Mix and TAS Mix

					Energy consumption percentage weight of the single operation	
Process	Substrate treated [kg TS]	Pre-treatment [kWh/kg ST]	AD [kWh/kg]	Energy consumption [kWh tot/kgST]	Pre-treatments [%]	AD [%]
AD Mix	0.0175	0	168.9	168.9	0	100.0
AD of TA Mix	0.0175	1.8	168.9	170.8	1.1	98.9
AD of TAS Mix	0.0175	3.1	168.9	172.0	1.8	98.2

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

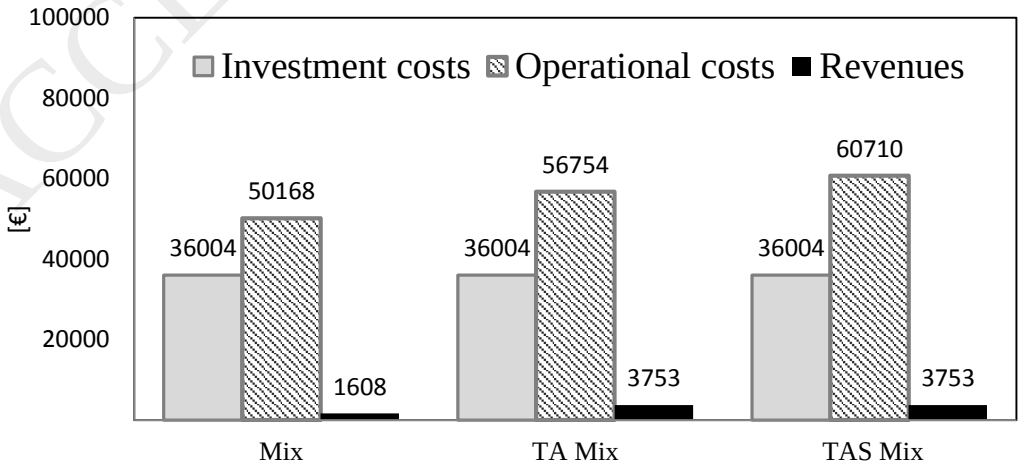
3.5 Economic assessment

A preliminary economic assessment completed the research, considering the scale up of AD to treat all the wastes produced by the plant in 2015. Table 8 depicts the technical conditions while Figure 4 describes the investment and operational costs and revenues coming from AD of unaltered and pre-treated substrates.

Table 8. Technical evaluation of AD scale up at industrial scale

		Mix	TA Mix	TAS Mix
AD feedstocks	Substrates production [t/y]	303.00	303.00	303.00
AD operative conditions	HRT [d]	22.00	22.00	22.00
	H_2O [m^3]	4.48	4.48	4.48
	Inoculum[t]	339.13	339.13	339.13
	Reactor working volume [m^3]	38.97	38.97	38.97
	Reactor volume [m^3]	43.30	43.30	43.30
AD out-puts	Digestate [t]	381.17	372.44	379.88
	CH_4 [Nm^3]	1.018.40	2.376.26	2.376.26
AD energy required	Thermal Energy for AD [MWh]	36.78	36.78	36.78
	Sonication power [MWh]	/	/	98.47
	Thermal treatment [MWh]	0	59.12	0
AD reagents	NaOH [t]	0	2.59	2.59

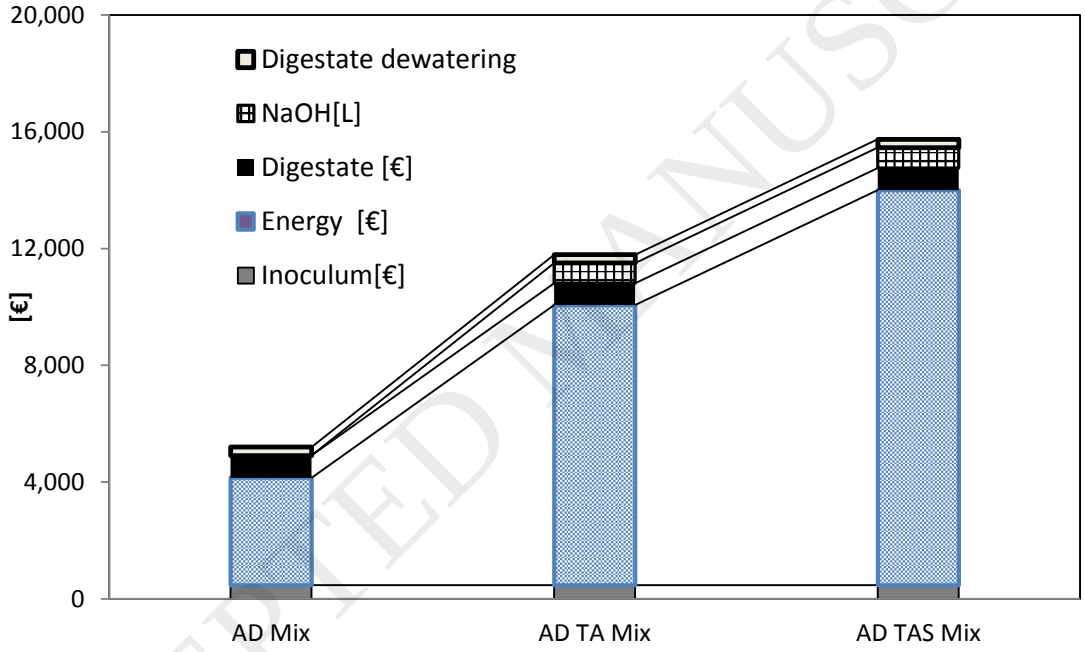
Figure 4. Investment and operational costs and revenues from AD of unaltered (Mix) and pre-treated (TA Mix and TAS Mix) mixture of substrates.



ACCEPTED MANUSCRIPT

The investments costs (construction of AD reactor and gasometer), were the same for all the three proposed solutions, since the same volume of substrate was treated. AD of TA and TAS Mix required operational costs higher than Mix (see Figure5), because TA and TAS pre-treatments at the industrial scale required respectively 62.00% and 73.00% energy and NaOH cost addition. On the other side, AD of unaltered Mix had 2% higher cost for digestate treatment, since TS reduction was 5.25% compared to 5.68% and 7.28% of pre-treated Mix. However, according to literature (Passos et al., 2017) from an economic perspective, AD without pre-treatment beats pre-treated AD.

Figure 5**.** Details of operational costs of AD process at industrial scale (labors costs not considered)



AD of TA and TAS Mix reached revenues higher than unaltered Mix, because methane content improved. However, the enhancement of organic matter reduction (5.68-7.84%) and methane production (3.1-11.4%) after TA and TAS pre-treatments didn't reach the economic sustainability. Nevertheless, comparing the current operations with the proposed waste management (see Table 9), an economic saving of 26.9 %, 20.2% and 14.3% respectively with AD of Mix, TA Mix and TAS Mix were reached, corresponding to a saving of up to about 18,000 €/year in case of unaltered Mix and around 14,000 €/y in case of thermo-alkali pre-treatment.

ACCEPTED MANUSCRIPT

Table 9: Comparison between current waste management and AD process.

	New waste management			Current waste management
	Mix	TA Mix	TAS Mix	
Management costs= Operational –Revenues [€]	48560	53002	56957	66450
Decrease waste management costs [%]	26.9	20.2	14.3	/

4. Conclusions

This research investigated the enhancement of available organic matter in cosmetic waste through pre-treatments testing the biodegradability through anaerobic digestion. The study concerned a mixture of cosmetic waste materials, which had high organic content but not ready biodegradable. The most promising pre-treatments were: thermo-alkaline TA (50 °C for 120 min) with DR=64.4 % and thermo-alkaline-sonication TAS (80 °C for 15 min at 40 kHz) with DR= 66.1%. TAS and TA pre-treatments enhanced methane yield of 50-% increasing energy consumption of only 1.1%. However, process conditions need further optimization to reach economic sustainability at full-scale.

Acknowledgements

All authors directly participated in the planning, execution and analysis of the research. The authors gratefully acknowledge L'Oréal Saipo Industriale SpA for the financial support for the conduct of the study. The authors declare to have no interest in the research.

References

ACCEPTED MANUSCRIPT

(1) Ariunbaatar, J., Panico, A., Esposito, G., Pirozzi, F., Lens, P. (2014). Pretreatment methods to enhance anaerobic digestion of organic solid waste. Appl. Energy, Vol.123, pp 143-156.

(2) Arnò, P., Fiore, S., Verda, V. (2017). Assessment of anaerobic co-digestion in areas with heterogeneous waste production densities. Energy, Vol. 122, pp.221-236.

(3) Bahera, S., Arora, R., Nandhagopal, N., Kumar, S. (2014). Importance of chemical pretreatment for bioconversion of lignocellulosic biomass. Renew Sustain. Energy Rev., Vol.36, pp 91-106.

(4) Bak, J., Kim, M., Choi, L., Kim, K. (2010). Biological pretreatment of rice straw by fermenting with Dichomitus squalens. New Biotec, Vol.27, pp 4242-434.

(5) Benabdallah El-Hadi, T., Dosta, J., Màrquez- Serra. (2007). Effect of ultrasound pretreatment in mesophilic and thermophilic anaerobic digestion with emphasis on naphthalene and pyrene removal. Water Res, Vol. 21, 87-97.

(6) Bolado-Rodríguez, S., Toquero, C., Martín-Juárez, J., Rodolfo , T., Antonio-Garcia-Encina, P. (2016). Effect of thermal, acid, alkaline and alkaline-peroxide pretreatments on the biochemical methane potential and kinetics of the anaerobic digestion of wheat straw and sugarcane bagasse. Bioresour. Technol., Vol.201, pp.182-190.

(7) Bondesson, P., Galbe, M., Zacchi, G. (2013). Ethanol and biogas production after steam pretreatment of corn stover with or without the addition of sulphuric acid. Biotchnol. Biofuels, pp 6-11.

(8) Carrere, H., Dumas, C., Battimelli, A., Batsone, D., Delgenes, J., Steyer, J. (2010). Pretreatment methods to improve sludge anaerobic degradability: a review. J Hazard Mater, 183, pp 1–15.ioha, I. N. (2003,). Effect of carbon to nitrogen ratio on biogas production. International research journal of natural science, Vol.3, pp. 1-10.

(9) EcoPiemonte. (2017). URL http://www.ecopiemonte.it/smaltimento/. *in Italian*. Last access: 12/20/2017

(10) EPA (2001). METHOD 1684 Total, Fixed, and Volatile Solids in Water, Solids, and Biosolids. U.S. Environmental Protection Agency Office of Water Office of Science and Technology Engineering and Analysis Division (4303) 1200 Pennsylvania Ave. NW Washington, DC 20460. https://www.epa.gov/sites/production/files/2015-10/documents/method_1684_draft_2001.pdf

ACCEPTED MANUSCRIPT

(11) EU Parliament (2016). Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on Cosmetic Products.

(12) Hernoux, A., Léveque, J., Lassi, U., Molina Boisse. (2013). Conversion of non-water soluble potato starch waste into reducing sugars under non conventional technologies. Carbohydr. Polym., Vol.92, pp 2065-2074.

(13) ISTAT, i. n. (2017). https://www.istat.it/it/archivio/retribuzioni. Last access: 12/20/2017 https://www.istat.it/it/archivio/retribuzioni

(14) Karray, R., Hamza, M., Sayadi, S. (2015). Evaluation of ultrasonic, acid, thermo-alkaline and enzymatic pre-treatments on anaerobic digestion of Ulva rigida for biogas production. Bioresour.Technol, Vol.187, pp. 205-213.

(15) Kim , J., Yu , Y., Lee, C. (2013). Thermo-alkaline pretreatment of waste activated sludge at low-temperatures: Effects on sludge disintegration, methane production, and methanogen community structure. Bioresour. Technol, Vol.144 , pp. 194–201.

(16) Li,, H., Li, C., Liu, W., Zou, S. (2012). Optimized alkaline pretreatment of sludge before anaerobic digestion. Bioresour. Technol., Vol.123, pp189–194.

(17) Linke, B., Muha, I., Wittum, G., Plogsties, V. (2013). Mesophilic anaerobic co-digestion of cow manure and biogas crops in full scale German biogas plants: A model for calculating the effect of hydraulic retention time and VS crop proportion in the mixture on methane yield from digester and from digestate. Bioresour. Technol., Vol.130 pp. 689-695.

(18) Lou, J., Fang, Z.,Smith, R. (2014). Ultrasoundsound-enhanced conversion of biomass to biofuels- a review. Prog. Energy Combust. Sci., Vol.41, pp 56-93.

(19) Metcalf, N., Eddy, A., Tchobanoglous, G., Stensel, H., Tsuchihashi, R., Burton, F. (2013). Wastewater Engineering: Treatment and Resource Recovery. MC Graw Hill.

(20) Moggio, G. (2000). Pre-treatment implementation for industrial effluents from a cosmetic industry [Impianto di pretrattamento di effluenti industriali per una industria cosmética]. Tecnol. Chim., 3, pp 60-64.

(21) Navarotto. (2012). Scelte tecnologiche per massimizzare la produzione di biogas. SolarExpo. *In Italian*

ACCEPTED MANUSCRIPT

(22) Ning, J., Chunquan , L., Dajing, L., Zhongyuan, Z., Zhifang, Y., Yongyun, Z. (2016). Effect of thermosonic pretreatment on drying kinetics and energy consumption of microwave vacuum dried Agaricus bisporus slices. J. Food Eng., Vol. 177, pp 21-30.

(23) Parra-Orobio, B.A., Angulo-Mosquera, L.S., Loaiza-Gualtero, J.S., Torres-Lopez, W.A., Torres-Lozada, P. (2018). Inoculum mixture optimization as strategy to improve the anaerobic digestion of food waste for the methane production. J. Env. Chem. Eng., Vol. 6 (1), pp. 1529-1535.

(24) Passos, F., Ortega, V., Donosco-Bravo, A. (2017). Thermochemical pretreatment and anaerobic digestion of dairy cow manure: Experimental and economic evaluation. Bioresour. Technol., Vol.227, pp. 239-246.

(25) Pei, J., Yao, H., Wang, H., Shan, D., Jiang, Y., Ma, L. (2015). Effect of ultrasonic and ozone pre-treatments on pharmaceutical waste activated sludge's solubilisation, reduction, anaerobic biodegradability and acute biological toxicity. Bioresource technology, Vol.192, pp.418-423.

(26) Puyol, D., Monsalvo, V., Mohedano, A., Sanz, J., & Rodriguez, J. (2011). Cosmetic wastewater treatment by upflow anaerobic sludge blanket reactor. *Journal of Hazardous Materials*, 185, pp 2-30.

(27) Raposo, F. (2008). Assessment of a modified and optimised method for determining chemical oxygen demand of solid substrates and solutions with high suspended solid content. Talanta, Vol. 76 pp.448-453.

(28) Rico, C., Rico, J., Tejero, I., Munoz, M., Gomez, B. (2011). Anaerobic digestion of the liquid fraction of dairy manure in pilot plant for biogas production: Residual methane yield of digestate. Waste Manag., Vol.31, pp 2167-2173.

(29) Rodriguez, C., Alaswad, A., Benyounis, K., Olabi, A. (2017). Pre-treatment techniques used in biogas production from grass. Renew. and Sustain. Energy Rev. Vol. 68, pp 1193-1204.

(30) Talebnia, F., Karakashev, D., Angelidaki, I. (2008). Production of bioethanol from wheat straw: an overview on pretreatmen, hydrolysis and fermentation. Bioresour. Technol., Vol.99, pp.5261-5269.

ACCEPTED MANUSCRIPT

(31) Tsapekos, P., Kougias, P., Angelidaki, I. (2015). Biogas production from ensiled meadow grass; effect of mechanical pre-treatments and rapid determination of substrate biodegradability via physicochemical methods. Bioresour. Technol., Vol 182, pp. 329-335.

ACCEPTED MANUSCRIPT