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Investigation of the anaerobic digestion of cosmetic industrial wastes: Feasibility and perspectives

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1   **INVESTIGATION OF THE ANAEROBIC DIGESTION OF COSMETIC**

2   **INDUSTRIAL WASTES: FEASIBILITY AND PERSPECTIVES**

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11 **Abstract**

12 This study assessed the anaerobic digestion (AD) of wastes deriving from cosmetics production:

13 sludge from onsite wastewater treatment plant (sWWTP), residues of shampoo/conditioner

14 (RSC) and sludge from mascara production (MS), considered as single substrates and as

15 mixture according to the produced amounts (54 %-wt sWWTP, 31 %-wt RSC, 13 %-wt MS,

16 plus 2 %-wt food waste from the canteen, FW). Total COD (COD_T) was 624-1436 g O_2/kg $_{VS}$,

17 while soluble COD was 5-23 %-wt of COD_T. AD tests at 35 °C achieved the following biogas

18 yields: 0.10 Nm^3/kg$_{vs}$ (70 %-v/v methane) for sWWTP; 0.07 Nm^3/kg$_{vs}$ (62 %-v/v methane) for

19 RSC; 0.04 Nm^3/kg$_{vs}$ (67 %-v/v methane) for MS. The mixed substrates underwent physico-

20 chemical pre-treatments (thermo-alkaline, TA: 120 min at 50 °C; thermo-alkaline-sonication,

21 TAS: 15 min at 40 kHz and 80 °C, both based on the addition of 0.08 g NaOH per each g of

22 total solid in the substrate), reaching 64-66 % disintegration rate, and AD tests (5 %-wt dry

23 substance) at 35 and 52 °C. Biogas yields were (for TA and TAS respectively): 0.22 and 0.20

24 Nm^3/kg$_{vs}$ (62-70 % methane); 0.21 and 0.19 Nm^3/kg$_{vs}$ (66-66 % methane) at 52 °C. At both

25 temperatures, methane yields considerably improved (+71-100 %), compared to mixed

26   untreated substrates, and 5-8 %-wt total solids reductions were observed. A technical-economic

27   scale-up assessment completed the research. The energy analysis highlighted the crucial role of

28   TA pre-treatment in achieving the process energetic sustainability. The economic analysis

29   showed that the AD of the considered cosmetic waste could be sustainable anyway, thanks to

30   the savings related to the disposal of the digestate compared to current waste management costs.

31   **Keywords:** biogas, cosmetic waste, economic analysis, pre-treatment, scale-up.

32   **1.   Introduction**

33   According to the European Parliament regulation No. 1223/2009 (European Parliament, 2009),

34   cosmetic products may include "any substance or mixture intended to be placed in contact with

35   the external parts of the human body with the aim of cleaning, perfuming, protecting, keeping

36   them in good conditions". The same EU regulation bans the use of hazardous substances in

37   cosmetic products to ensure the highest protection of human health. Growing interest for the

38   sustainability of raw materials employed to manufacture cosmetic products (Bom et al., 2019)

39   has been involving in recent years the consumers, cosmetics industries and academia.

40   Nonetheless the major concern on ensuring the highest safety and sustainability of cosmetic

41   products, the European Waste Catalogue (EWC) and the list of wastes in art. 7 of Directive

42   2008/98/CE often define hazardous and mark with an asterisk the EWC codes assigned to

43   wastes deriving from the manufacturing of fats, grease, soaps, detergents, disinfectants and

44   cosmetics (a sub-chapter of wastes deriving from organic chemistry processes). Liquid and solid

45   wastes originating from cosmetic products manufacturing are usually incinerated or landfilled,

46   while wastewater is typically treated in onsite treatment plants (Demichelis et al., 2018a),

47   because of the high concentrations of chemical oxygen demand (COD), suspended solids, fats,

48   oils and detergents (Abidemi et al., 2018). Enhanced onsite wastewater treatment operations are

49   necessary in cosmetic industries to mitigate the impact of the treated effluent on the receiving

water bodies (De Melo et al., 2013). The presence of scarcely biodegradable compounds in cosmetics wastewater lead to the adoption of different treatment strategies, as:

1. *the enhancement of soluble COD to promote subsequent biological processes* through physico-chemical pre-treatments (Demichelis et al., 2018a), catalytic wet peroxide oxidation (Bautista et al., 2010) or combined light/Fe^0/H_2O_2 processes (Muszyński et al., 2019);

2. *the decrease of total COD* through flocculation/coagulation (Kim et al., 2020), electro-coagulation (Müller Tones et al., 2020), combined electro-coagulation and heterogenous photo-catalysis (Boroski et al., 2009) or advanced oxidation processes, as electro-chemical oxidation (Awad and Ghany, 2013), Fenton oxidation (Bautista et al., 2007), photo Fenton-like treatment and heterogenous photo-catalysis (De Andrade et al., 2020);

3. *the application of biological processes highly efficient towards the removal of high organic loads*, as membrane bioreactors (MBR) (Banerjee et al., 2016; Friha et al., 2014; Monsalvo et al., 2014), upflow anaerobic sludge blanket (UASB) (Puyol et al., 2011) and biofilm (Fan and Wang, 2017) reactors.

On the grounds of the performed literature survey on cosmetic industrial waste management, two issues appeared noteworthy: state-of-the-art literature exclusively focused on cosmetic wastewater treatment, leaving out any other waste; cosmetic wastewater treatment applied at full-scale only involve, to our knowledge, physico-chemical pre-treatments preliminary to active sludge processes, or MBR and UASB designs, while all other options, even if characterized by high COD removal performances, are not yet mature at full-scale and technically and economically feasible (Zhen et al., 2017). The aim of this work is to fill the gap investigating the feasibility of the AD of cosmetic waste. Compared to existing literature, this research has the two general elements of novelty: it is specifically focused on cosmetic waste and not on cosmetic wastewater; it explores the feasibility of the AD of unconventional scarcely biodegradable substrates. In details, this work investigated the treatment of the cosmetic wastes

75   (303 t/y) produced by L'Oréal Group in a plant located in Italy; specifically, sludge from the

76   onsite wastewater treatment plant (sWWTP), residues of shampoo and conditioner (RSC,

77   hazardous), sludge from mascara production (MS, hazardous) and food waste (FW) from the

78   canteen, considered singularly and as mixture according to produced amounts. At the moment

79   of this research, these waste materials were landfilled or incinerated. This work is the follow-

80   up of a previous study (Demichelis et al., 2018a), which investigated the technical feasibility of

81   different physico-chemical pre-treatments, based on chemicals (NaOH or HCl), heat (50-90 °C)

82   and sonication, and their various combinations for different times and temperatures, on the same

83   wastes. The performances of the pre-treatments were compared for the single wastes according

84   to the disintegration rate (DR, i.e., the % enhancement of soluble COD) (Li et al., 2012) and the

85   best results were obtained for thermo-alkaline (TA) treatment at 50 °C for 120 min and termo-

86   alkaline-sonication (TAS) at 80 °C for 15 min, reaching DR equal to 64 % for TA and 66 % for

87   TAS. Further AD tests at 35 °C on the waste mixture, feeding 5 %-wt dry substance after TA

88   and TAS, showed 44-48 % increase of methane production (0.13 Nm^3/kg_{VS}) and 5-7 %-wt

89   reduction of waste amounts compared to the untreated wastes. The study was concluded by a

90   preliminary analysis of the scale-up at full plant scale of TA and TAS, reaching the economic

91   feasibility (14-20 % savings compared to the adopted waste management operations), with TA

92   exhibiting lower investment and operational costs compared to TAS. Related to the described

93   previous study (Demichelis et al., 2018), the common aspects (apart of the considered cosmetic

94   wastes) with the present work are just the adoption of TA and TAS as pre-treatments and the

95   investigation of AD at 35 °C feeding 5 %-wt dry substance; the follow up presented in this work

96   has five significant improvements: 1. the characterization of the samples was enhanced; 2. the

97   investigation of AD explored mesophilic (35 °C) and thermophilic (52 °C) conditions; 3. AD

98   tests were performed on single wastes at 35 °C and on their pre-treated (TA and TAS) mixture

99   at 35 °C and at 52 °C (while the previous study considered AD tests only of the waste mixture

100   at 35 °C); 4. the performances and kinetics of the AD processes were analyzed through the

101   modified Gompertz model; 5. finally, the overall process (pre-treatment + AD) was scaled-up

102   based on energy and economic analyses, to explore the economic sustainability of the value

103   chain.

104   **2. Materials and methods**

105   *2.1 Substrates characterization*

106   The wastes analyzed in the research were sampled in 2016 at L'Oréal Saipo Industriale (L'Oréal

107   Group) plant located near Turin (Italy), producing shampoo and conditioner, mascara, and

108   make-up powders for the mass market in 34 countries. Waste production in 2015 was equal to

109   303 t and included: sludge from onsite biological wastewater treatment plant (sWWTP) (EWC

110   070612), residues of shampoo and conditioner production (RSC) (EWC 070608*), sludge from

111   mascara production (MS) (EWC 070601*) and food waste from the canteen (FW) (EWC

112   200108). At the moment of the research, sWWTP was landfilled, RSC and MS were incinerated,

113   and FW was sent to composting. In this work, waste samples were considered individually and

114   as mixture (in the following defined "Mix") according to the relative amounts produced in the

115   plant in 2015 (54 %-wt sWWTP, 31 %-wt RSC, 13 %-wt MS, 2 %-wt FW).

116   The characterization involved 5 samplings for each waste, along 9 months, to assess any

117   variability in composition. The measured parameters were: total solids (TS) and volatile solids

118   (VS) according to reference procedures (APHA-AWWA-WEF, 2012); pH through a pH 340

119   WTM pH-meter; total chemical oxygen demand (COD) and soluble chemical oxygen demand

120   (sCOD) according to a reference method (Raposo et al., 2008); ammonium through Nanocolor

121   Ammonium Test 1-05 reagents and a UNICAM Helios Alpha UV-vis spectrophotometer;

122   elemental analysis was performed by means of a CHNSO Thermo Fisher Flash 2000 Analyzer

123   EA 1112. Unfortunately, only one replicate was possible in the elemental analysis of RSC and

124   MS. The digestate was analyzed at the end of the AD tests measuring TS and VS and the lower

125   heating value (LHV) according to UNI EN 15170:2009 method, adopting benzoic acid as

126   reference material. LHV analyses involved 5 replicates for each sample.

127

128   *2.2. Pre-treatments*

129   The pre-treatments tests involved the mixed wastes (Mix) according to the procedures

130   optimized in a previous work (Demichelis et al., 2018a). Specifically, in both cases the NaOH

131   was added to the Mix (0.08 g/g of TS of the substrate), and the two pre-treatments were

132   performed as follows. The thermo-alkaline (TA) treatment at 50 °C for 120 min in a Julabo

133   Corio-C thermostatic bath and termo-alkaline-sonication (TAS) at 40 kHz in a VWR USC

134   300TH device at 80 °C for 15 min. Full details about the optimization of the pre-treatments and

135   the results achieved on single waste materials are available in the cited study (Demichelis et al.,

136   2018a).

137

138   *2.3. Anaerobic digestion tests*

139   AD tests were carried out at 35 °C on the single waste materials (FW excluded) and the Mix,

140   and at 52 °C on the Mix. In all cases in batch mode, feeding 5 %-wt TS and adopting substrate-

141   inoculum ratio equal to 1:1 based on VS. The inoculum was provided by two local facilities: a

142   WWTP performing mesophilic AD of the sludge and a plant performing thermophilic AD of

143   the organic fraction of municipal solid waste; before the tests, the inoculum was stored at 20 °C

144   and degassed for 7 days. The mesophilic inoculum was characterized by 1.71 %-wt TS, 75 %

145   VS/TS and pH 7.3; the thermophilic inoculum by 2.65 %-wt TS, 60 % VS/TS and pH 6.9. The

146   AD tests were performed in 0.5 L Pyrex Duran glass bottles (0.4 L working volume), connected

147   by 6 mm Teflon tubes to 2.5 L gas-tight Tedlar bags. Each reactor was purged with nitrogen for

148   1 min to remove air from the headspace. A 55 L Julabo-Corio-C thermostatic water-bath

149   allowed to control the temperature of the digesters. For each substrate (the single wastes and

the Mix), 12 reactors were engaged: 2 blanks (containing only the inoculum), 3 for biogas measurement and 3 for methane measurement. Unfortunately, only one replicate was available for methane measurement at 52 °C. During the tests, each reactor was manually shaken three times per day for 5 days per week. Biogas and methane volumes were measured 5 days per week through water displacement (10 g/L NaOH aqueous solution was employed to wash CO_2 from the reactors used for methane measurement) and referred to standard temperature and pressure (0 °C, 1 atm). The AD tests were declared completed when marginal biogas production was below 1 %.

2.4. Performance and kinetics analysis

The performance and kinetics of AD were analyzed according to Gompertz modified model (Nguyen et al., 2016) according to (eq. 1).

$$B(t) = P \exp\left\{- \exp\left[\frac{R_{max} e}{P} (\lambda - t) + 1\right]\right\} \tag{1}$$

where $B(t)$ is the cumulative methane production (Nm^3 $kgVS^{-1}$) at time t (day), P is the methane potential of the substrate (Nm^3 $kgVS^{-1}$), R_{max} is the maximum methane production rate (Nm^3 $kgVS^{-1}$ d^{-1}), λ is the lag phase (day), e is the base of the natural logarithm. The kinetic parameters were estimated using non-linear least square regression analysis by means of the SOLVER tool pack of Microsoft Excel.

2.5. Scale-up assessment: reactor design and energy balance

The scale-up of the process applied on the Mix at 35 °C in a continuously fed digester was based on two scenarios: AD without any pre-treatment (S1) and after TA pre-treatment (S2), considering the amount of waste produced at the moment of the research (303 t/y) (section 2.1). Two sub-scenarios, based on the amount of available waste, were also considered for S2: a. investigating the size of the digester necessary to process 303 t/y of waste mixture; b.

175 investigating the minimum size of the digester necessary to produce enough methane to achieve

176 energy self-sufficiency (thermal and electric energy). The reactor design parameters were

177 derived from the results of the pre-treatments and of the AD tests presented in section 3.3.

178 The energy analysis was performed to estimate the net thermal energy (TE_{net}) and the net

179 electrical energy (EE_{net}), expressed in MJ/year and considering one year of operations, as in eq.

180 1 and 2, adopting the parameters and calculations detailed in Table 1.

181

182 $TE_{net} = TE_{CHP} - TE_{pre} - TE_{AD} - TE_{loss}$ (1)

183 $EE_{net} = EE_{CHP} - EE_{mix}$ (2)

184

185 Where TE_{CHP} [MJ/year] is the thermal energy obtained from the biogas in a combined

186 heat&power (CHP) unit; TE_{pre} [MJ/year] is the thermal energy spent during the TA pre-

187 treatment; TE_{AD} [MJ/year] is the thermal energy required to heat the substrate prior to AD;

188 TE_{loss} [MJ/year] is the energy lost through the walls of the reactor. EE_{CHP} [MJ/year] is the

189 electricity obtained from the biogas in the CHP unit, and EE_{mix} [MJ/year] is the electrical energy

190 needed for the mixing.

191

192 **Table 1**. Parameters and calculations adopted in the energy analysis

Parameter	Calculations	Notes	Reference
net thermal energy (TE_{net}) [MJ/year]	$TE_{net} = TE_{CHP} - TE_{pre} - TE_{feed} - TE_{loss}$		
heating pre-treatment (TE_{pre})	$TE_{pre} = m_{mix} C_p (T_{pre} - T_{amb}) t \cdot 365 / \eta$	specific heat capacity (C_p): 4.18 MJ/(ton·K); efficiency of the heat exchange (η): 0.65 pre-treatment temperature (T_{pre}): 50 °C ambient temperature (T_{amb}): 15 °C; treatment time (t): 2 hours/day	Gomez-Camacho et al., 2021
heating feeding AD (TE_{AD})	$TE_{AD} = m_{mix,5\%} C_p (T_{AD} - T_{amb}) \cdot 365 / \eta$	AD temperature (T_{AD}): 35 °C; ambient temperature (T_{amb}): 15 °C	Gomez-Camacho et al., 2021
thermal loss AD (TE_{loss})	$TE_{loss} = U_{wall} A_{reactor} (T_{AD} - T_{amb}) \cdot 31.536$	natural heat convection h air: 10 W/(m²·K);	Gomez-Camacho et al., 2021

		concrete: conductivity (λ) 2.3 W/(m·K); thickness (s): 0.25 m; insulation: λ: 0.037 W/ (m·K); s: 0.08 m, U_{wall}: 0.422 W/(m²·K); surface reactor ($A_{reactor}$): 89 m²	
thermal energy from CHP (TE_{CHP})	$TE_{CHP} = Q_{CH4}\ \eta_{TH}\ LHV_{CH4}\ 365$	LHV methane (LHV_{CH4}): 35.8 MJ/m³; CHP thermal energy efficiency (η_{TH}): 0.4 methane production (Q_{CH4}) [m³/day]	Metcalf&Eddy, 2013
net electrical energy (EE_{net}) [MJ/year]	$EE_{net} = EE_{CHP} - EE_{mix}$		
electricity mixing AD (EE_{mix})	$EE_{mix} = P_{mix}\ t\ V_{reactor}\ 31536$	power input (P_{mix}): 0.02 kW/m³; reactor volume ($V_{reactor}$): 64 m³ mixing time (t): 15/60 hours	Gomez-Camacho et al., 2021
electricity from CHP (EE_{CHP})	$EE_{CHP} = Q_{CH4}\ \eta_{EL}\ LHV_{CH4}\ 365$	CHP electrical efficiency (η_{EL}): 0.4	Metcalf&Eddy, 2013

193

2.6. Scale-up assessment: economic analysis

A preliminary economic assessment was performed according to (Demichelis et al., 2018a and b; Chiappero et al., 2019) to estimate the profitability of the two scenarios detailed in section 2.5. The profitability assessment was based on the following parameters: return of investment (ROI), i.e., the ratio between the annual net profit and the initial investment; net present values (NPV), and payback time (PBT). A plant lifetime equal to 20 years and a 5 % discount rate on the future cash flows were considered. The economic assessment involved capital costs, operational costs, and revenues. The annual net profit was determined as the difference between the revenues and the operational costs; the amortization of the initial capital cost was not considered in the present analysis. The capital costs included the fixed capital costs (FCC), and the working capital costs (WCC) assumed equal to 6.5% of FCC [4]. The cost of land was not considered since the installation was placed inside the cosmetic industrial plant. The operational costs were composed by cost of the NaOH for the pre-treatment and of the water for the dilution of the Mix, by thermal and electrical energy (obtained from the energy assessment), and labor costs. The revenues derived from the surplus electricity from biogas co-combustion in the CHP

209   unit, and from the saved costs related to the disposal of the digestate (0.12 €/kg) compared to

210   the costs of the current waste disposal for sWWTP (0.15 €/kg), RSC and MS (0.31 €/kg), and

211   FW (0.11 €/kg) (Demichelis et al., 2018a).

212   **3. Results and discussion**

213   *3.1.Substrates characterization*

214   The results of the characterization of the studied cosmetic wastes (Table 2) showed that all

215   substrates could be eventually considered suitable for AD based on their physico-chemical

216   features (VS above 75 %, TS below 35 %, pH not too far from neutrality), even if the values of

217   C/N were rather lower (respectively 10.71 for sWWTP, 5.49 for RS, 5.87 for MS and 14.40 for

218   FW) than the values (20-35) usually recommended for AD (Metcalf&Eddy, 2013). Moreover,

219   the low values of COD_S/COD_T witnessed the need of pre-treatments aimed at increasing the

220   amount of soluble organic substances. sWWTP showed the highest variability in COD values,

221   which was not unexpected; in fact, the onsite WWTP was fed by wastewater deriving from the

222   washing of reactors and pipes in the productive lines of L'Oréal plant, where industrial

223   production was organized in batches of different cosmetic products.

224   The Mix (54 %-wt sWWTP, 31 %-wt RSC, 13 %-wt MS, 2 %-wt FW) was characterized by

225   14.06 % TS, 83.68 % VS/TS and C/N equal to 8.86.

226   **Table 2.** Characterization of the cosmetic wastes (*only one replicate available)

	sWWTP	RSC	MS	FW	reference
pH	6.54±0.49	6.30 ±0.17	6.69±0.79	5.08±0.34	Demichelis et al., 2018a
TS (%)	2.43±0.74	24.98±0.45	34.70±2.18	25.06 ±3.31	Demichelis et al., 2018a
VS/TS (%)	86.24±3.2	81.65± 1.51	75.46±1.28	97.17±0.95	Demichelis et al., 2018a
COD_T (mgO$_2$/g $_{VS)}$	1174.06 ±94.80	1436±23.1	1148.52±17.56	624.25±48.4	Demichelis et al., 2018a
COD_S/COD_T	5.56±0.88	51.48±1.48	6.19±0.26	23.24±1.79	Demichelis et al., 2018a
NH_4^+ [mg/g $_{VS}$]	0.29±0.06	2.54±0.34	0.02±0.01	0.02±0.02	this study

C (%)	44.69±0.57	51.60*	60.50*	45.65±4.39	this study
H (%)	7.43±0.16	2.05*	0.30*	6.76±0.58	this study
N (%)	4.17±0.44	9.40*	10.30*	3.24±1.44	this study
S (%)	1.15±0.24	0.90*	0.11*	0.05±0.07	this study
formula	$C_{13}H_{26}O_{12}N$	C_6HO_6N	$C_{24}HO_{18}N$	$C_{22}H_{40}O_{20}N$	this study
C/N	11	6	6	14	this study

227

228 *3.2. Results of the anaerobic digestion tests performed on the single cosmetic wastes*

229 The AD tests performed at 35 °C on the single cosmetic wastes (Figure 1) provided some

230 interesting insights: sWWTP exhibited the highest specific biogas production (0.10 ±0.014

231 Nm^3/kg_{vs}, 70 %-v/v methane), followed by RSC (0.07 ±0.010 Nm^3/kg_{vs}, 62 %-v/v methane)

232 and MS (0.04 ±0.001 Nm^3/kg_{vs}, 67 %-v/v methane). These results demonstrated that the

233 considered cosmetic wastes could undergo AD, even if further actions are needed to improve

234 their biodegradability and therefore biogas and methane yields. TS removal was 2.1 % for

235 sWWTP, 24.2 % for RSC and 34.5 % for MS, meaning the following reduction of the amounts

236 of "raw" (i.e. as they are produced in the plant) wastes: 18.9 %-wt for sWWTP, 3.2 %-wt for

237 RSC and 1.43 %-wt for MS. As expected from the results of the characterization, sWWTP

238 showed the highest variability in biogas and methane specific daily productions. It was also

239 noteworthy the duration of the AD processes: 21 days for sWWTP, 15 days for RSC and 27
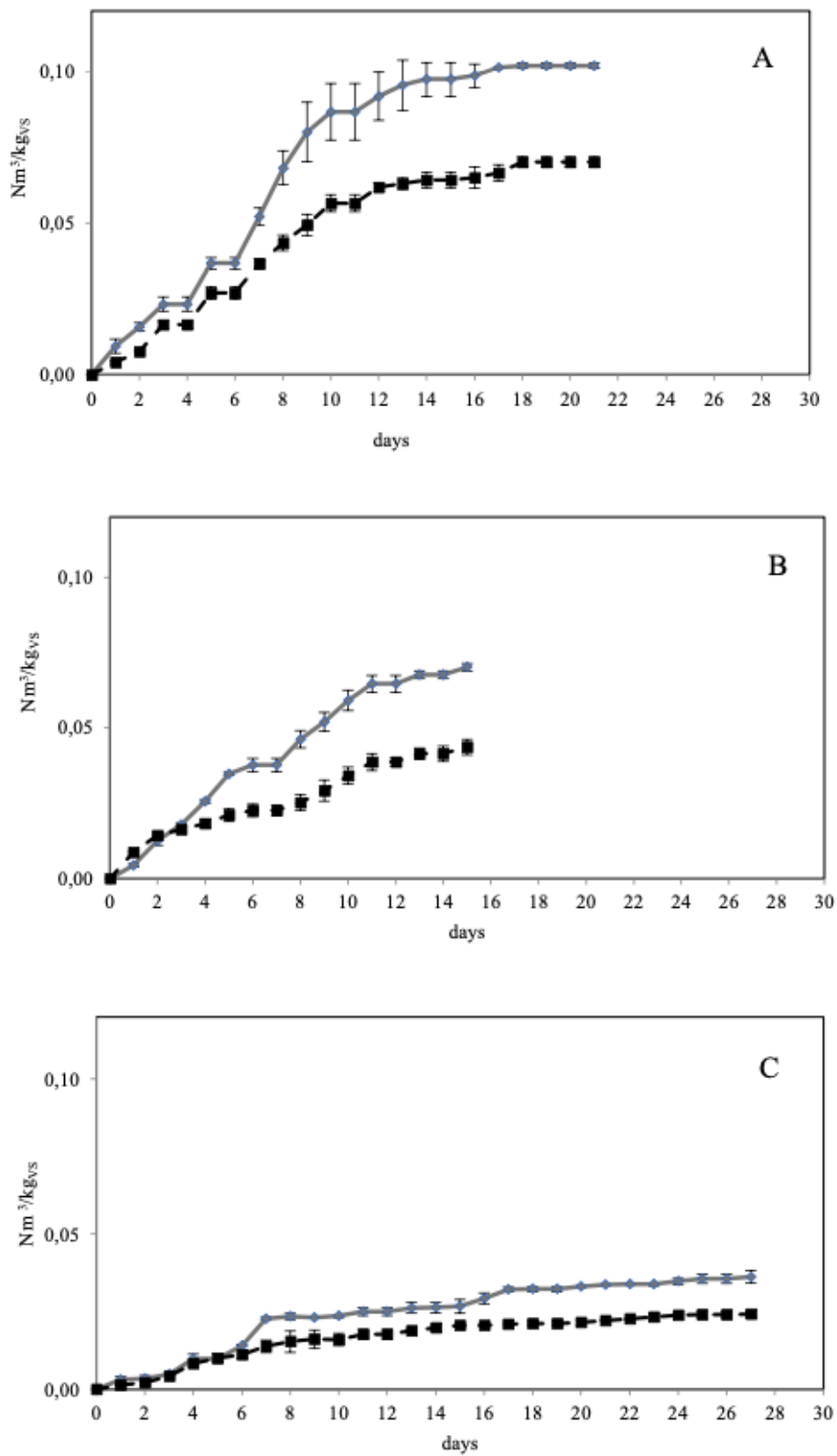
240 days for MS.

Figure 1. Results of AD tests at 35 °C on (A) sWWTP, (B) RSC and (C) MS (specific biogas production in grey; specific methane production in black)
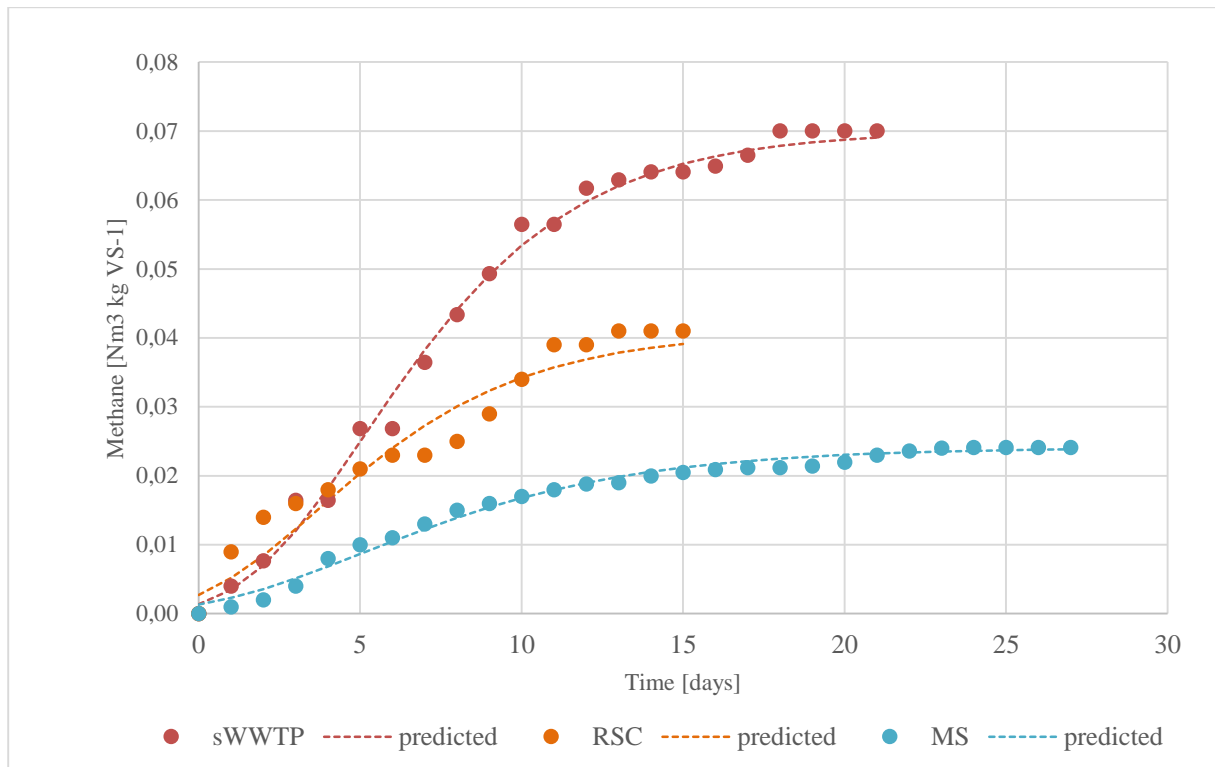
244

Figure 2. Results of the modeling of experimental methane production from the single cosmetic

wastes at 35 °C through the modified Gompertz model

247

Table 3. Performance and kinetic parameters of the AD at 35 °C of single cosmetic wastes

obtained through the modified Gompertz model (P: methane potential of the substrate; R_{max}:

maximum methane production rate; λ: lag phase)

	P	R_{max}	λ	R^2
	(Nm^3 kgVS^{-1})	(Nm^3 kgVS^{-1}d^{-1})	(days)	(-)
sWWTP	0.070	0.007	1.385	0.993
RSC	0.041	0.004	0.000	0.933
MS	0.024	0.002	0.302	0.986

251

The performance and kinetic parameters estimated from daily methane production and methane

yield of the single cosmetic wastes at 35 °C through the modified Gompertz model (Table 3,

Figure 2 and Appendix) showed that sWWTP exhibited the highest methane potential

(experimental values) and maximum methane production rate values, compared to RSC and

256 MS, even if with greater lag phase. The fitting of the experimental data through the modified

257 Gompertz model was in all cases satisfactory, achieving coefficient of determination values

258 between 0.93 and 0.99. Comparing the estimated biodegradability of the different waste

259 materials, the highest methane production rate was ascribable, accordingly to the methane

260 potential, in the order sWWTP>RSC>MS; on the contrary, the lag phase length followed the

261 sequence sWWTP>MS>RSC. The highest lag phase estimated for the sWWTP may be due to

262 the already mentioned high concentrations of COD, suspended solids, fats, oils and detergents

263 in the cosmetic industry wastewater (Abidemi et al., 2018) that concentrate in the related waste

264 activated sludge. However, the fact that sWWTP achieved the highest methane potential and

265 production rate values, compared to the other considered samples, demonstrated that this

266 specific waste is anyway biodegradable.

267

268 *3.3. Results of the anaerobic digestion tests performed on mixed cosmetic wastes*

269 The positive effect of the pre-treatments (DR was 64 % ± 0.01 after TA and 66 % ± 0.01 after

270 TAS) was appreciated from the results of the AD tests involving the Mix (Table 4 and Figure

271 3). The cumulative biogas/methane production curves showed analogous ultimate yields and

272 different durations of the AD process: 22 days at 35 °C and 17 days at 52 °C, with a faster

273 process in thermophilic conditions, compared to mesophilic, according to literature (among the

274 others, Chi et al., 2010; Ge et al., 2011; Gebreeyessus and Jenicek, 2016).

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276

277

278

279 **Table 4.** Results of the AD tests performed on the Mix at 35 and 52 °C and after TA and TAS

280 pre-treatments (SBP: specific biogas production; SMP: specific methane production. *only one

281 replicate was available for SMP at 52 °C)

	Mix		TA Mix		TAS Mix	
T (°C)	35	52	35	52	35	52
AD duration (d)	22	17	22	17	22	17
SBP (Nm^3/kgvs)	0.10 ± 0.01	0.11 ± 0.002	0.22 ± 0.02	0.21 ± 0.005	0.20 ± 0.004	0.19 ± 0.01
SMP (Nm^3/kgvs)	0.08 ± 0.01	0.07*	0.14 ± 0.01	0.14*	0.14 ± 0.03	0.12*
CH_4 (% v/v)	77	67	62	66	70	65
SMP increment (%)	/	/	75	100	75	71

282

283
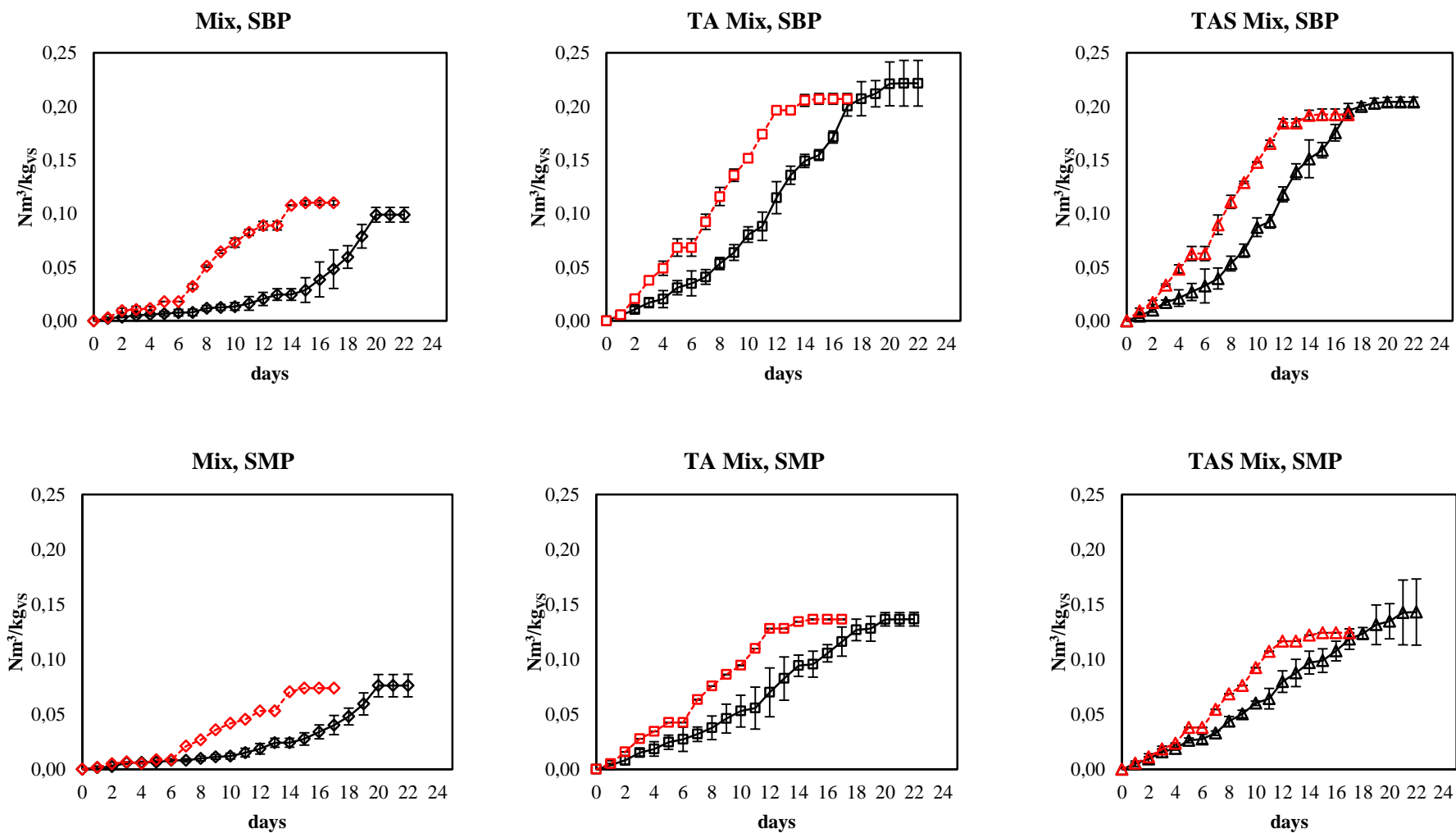
Figure 3. Results of AD tests performed at 35 °C (black) and 52 °C (red) on mixed cosmetic wastes (Mix) unaltered and after TA and TAS pre-

treatments (SBP: specific biogas production; SMP: specific methane production). Only one replicate was available for SMP at 52 °C

286 Even if the cosmetic waste materials considered in this work are largely different from any other

287 substrate already studied, a comparison with state-of-the-art literature related to the application

288 of pre-treatments to improve AD of sewage sludge (e.g., the most similar substrate in available

289 literature) could be beneficial anyway. Methane production from sewage sludge resulted

290 improved after thermal (40 %), alkaline (83 %) and ultrasounds (35-95%) pre-treatments (Zhen

291 et al., 2017); industrial active sludge exhibited 90 and 104 % methane production increments

292 after thermal and ultrasound pre-treatments respectively (Carrère et al., 2010).

293

294 **Table 5**. Performance and kinetic parameters of AD at 35 °C and 52 °C of mixed cosmetic

295 wastes (Mix) before and after TA and TAS pre-treatments obtained through the modified

296 Gompertz model (P: methane potential of the substrate; R_{max}: maximum methane production

297 rate; λ: lag phase)

	P	R_{max}	λ	R^2
	(Nm^3 $kgVS^{-1}$)	(Nm^3 $kgVS^{-1}d^{-1}$)	(days)	(-)
35 °C				
Mix	0.076	0.007	9.4	0.915
TA Mix	0.137	0.010	4.0	0.972
TAS Mix	0.143	0.010	3.5	0.983
52 °C				
Mix	0.074	0.009	4.8	0.975
TA Mix	0.136	0.014	2.1	0.975
TAS Mix	0.124	0.014	2.7	0.981

298

299 The performance and kinetic parameters estimated from methane production deriving from the

300 Mix before and after TA and TAS through the modified Gompertz model (Table 5, Figure 4,

301 and Appendix) showed that TA and TAS pre-treatments were able to improve the methane

302 production rate and lag phase. Comparing the pre-treatments, at 35 °C TA Mix exhibited lower

303 methane potential (experimental values) and equal maximum methane production rate values,

compared to TAS Mix, and higher lag phase; at 52°C, TA Mix exhibited higher methane potential (experimental values) and equal maximum methane production rate values, compared to TAS Mix, and shorter lag phase. The modified Gompertz model fitting of the experimental data was in all cases satisfactory, achieving coefficient of determination values between 0.92 and 0.98.
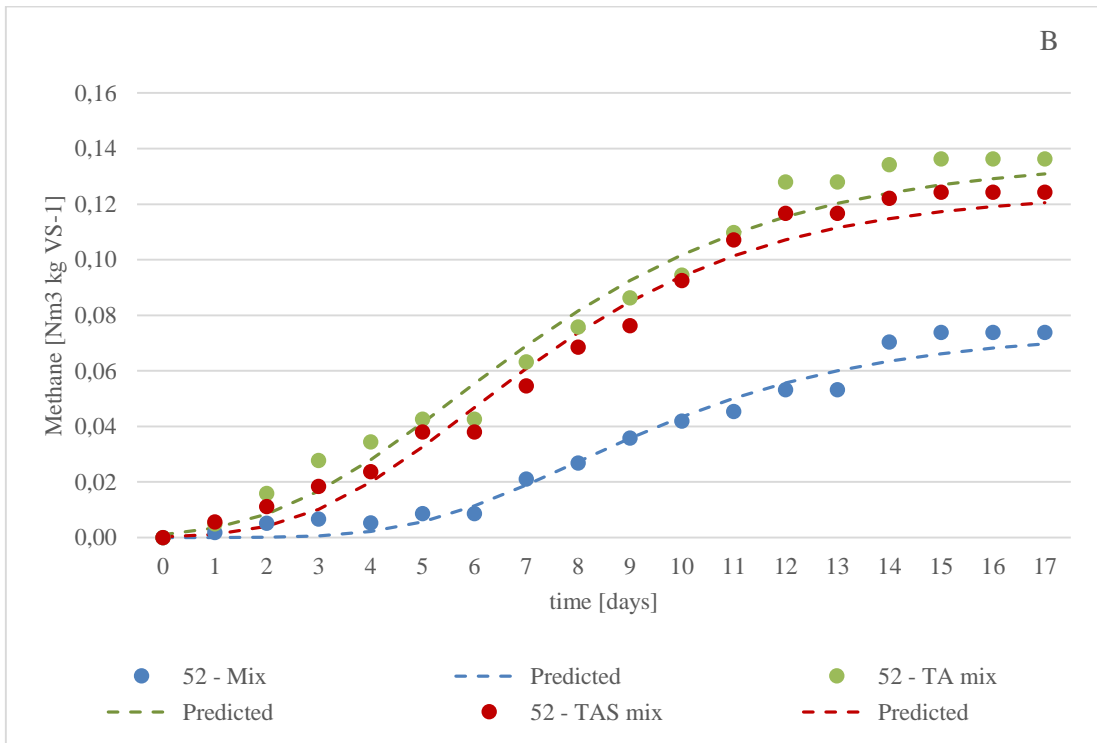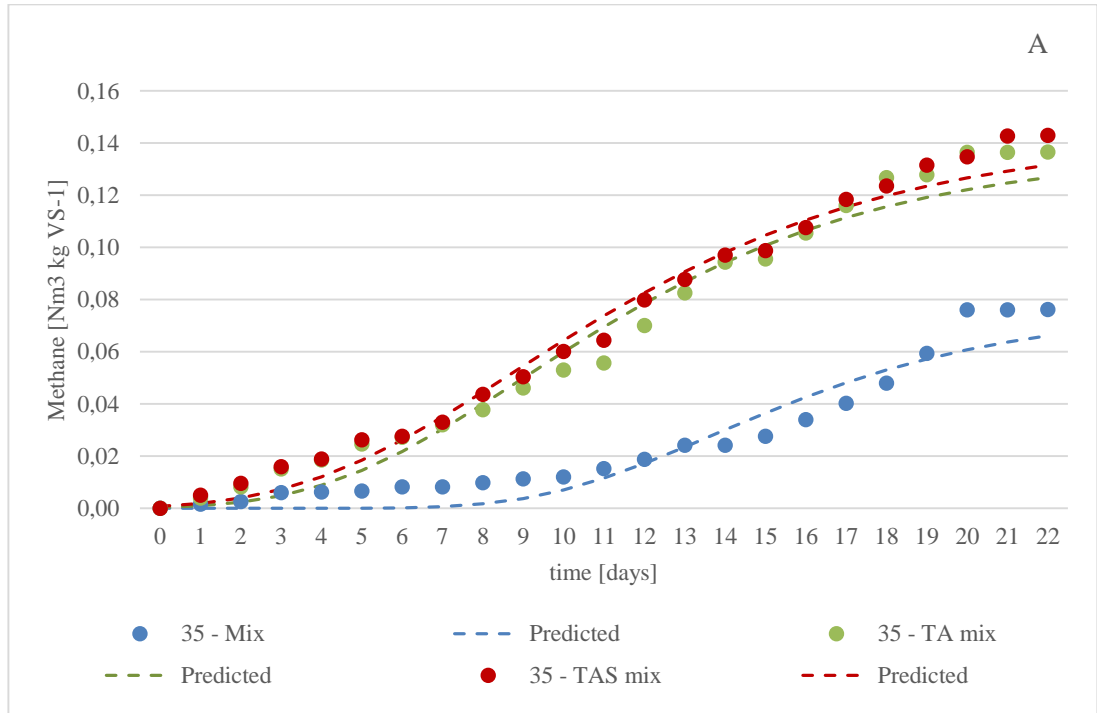
311   **Figure 4**. Results of the modeling of experimental methane production from the mixed cosmetic

312   wastes at 35 (A) and 52 °C (B) through the modified Gompertz model

313   *3.4. Results of digestate characterization*

314   The digestate samples deriving from the AD tests performed on the Mix were characterized

315   with the aim of a preliminary investigation of their thermal valorization. A main critical issue

316   is obviously represented by their high moisture content (95 %-wt), which requires a dehydration

317   treatment before the thermal valorization. The LHV values of the cosmetic waste samples were

318   as follows (values expressed in MJ/kg$_{TS}$): 20.16±1.01 for sWWTP; 25.97± 1.24 for RSC;

319   25.87±1.30 for MS.

320   Considering the digestates deriving from the Mix, all gave back LHV values similar to wood

321   (12-19 MJ/kg$_{TS}$) (Green and Perry, 2007). Comparing the LHV values obtained from the Mix

322   after AD at 35 and 52 °C (Figure 5), the thermophilic conditions produced lower LHV values

323   than the mesophilic conditions, in agreement with literature (Gebreeyessus and Jenicek, 2016;
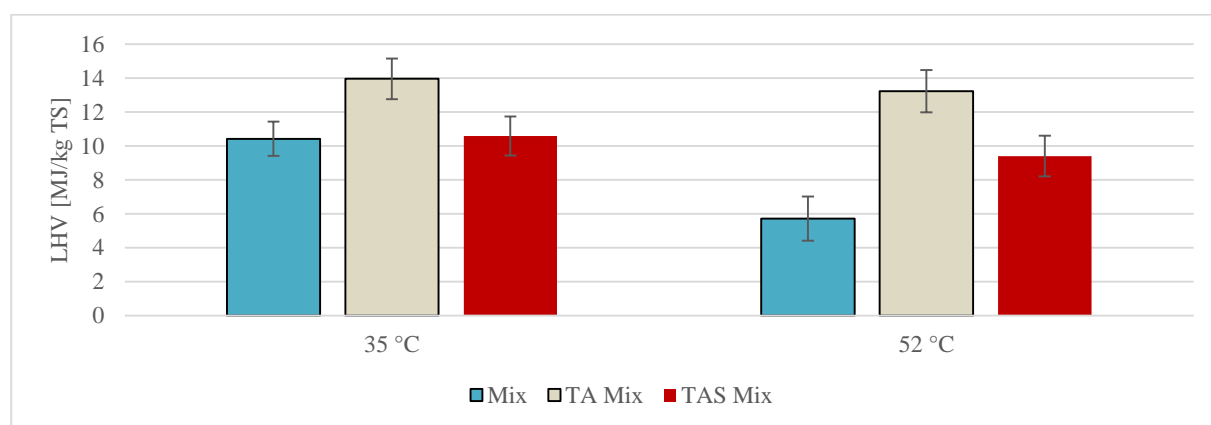
324   Khemkhao et al., 2012).

325

326

327   **Figure 5.** LHV values of digestate samples deriving from the AD tests of the Mix at 35 °C and

328   52 °C

3.5. Scale-up and economic assessment

330 The design parameters (Table 6) adopted in the scale-up analysis (section 2.5) considered AD

331 in continuous mode, feeding 5 % dry substance, and achieving the performances reported in

332 section 3.3. The analysis envisioned two scenarios: AD of the Mix "as it was" (S1) and after

333 TA pre-treatment (S2). Two sub-scenarios, based on the amount of available waste mixture,

334 were also considered for S2: the amount of waste produced at the moment of the research (a)

335 and the amount of waste necessary to achieve energy self-sufficiency (b) (section 2.5). The

336 scale-up assessment based on the amount of waste mixture produced in the plant led for

337 scenarios S1 and S2.a to a 64 m^3 digester, with methane production from the pre-treated Mix in

338 scenario S2.a (13.7 Nm^3/d) almost double than without any pre-treatment in scenario S1 (7.8

339 Nm^3/d). Scenario S2.b led to a 113 m^3 digester corresponding to 24.1 Nm^3/d methane

340 production.

341

342 Table 6. Design parameters considered for the scale-up assessment (Mix: waste mixture; TA:

343 thermo-alkaline pre-treatment with NaOH at 50 °C for 120 min; HRT: hydraulic retention time;

344 OLR: organic loading rate; Q: flow rate)

Parameter [measure unit]	S1 (Mix)	S2 (TA Mix)
TA temperature (T_{TA}) [°C]	-	50
dose of NaOH [g/g$_{TS}$]	0	0.08
temperature (T_{AD}) [°C]	35	35
HRT [days]	22	22
Total solids of the mix [kg/m^3]	140.6	140.6
Volatile solids of the mix [kg/m^3]	117.7	117.7
Total solids of the diluted mix [kg/m^3]	50	50
Volatile solids of the diluted mix [kg/m^3]	41.8	41.8

		a	b
OLR [kg$_{VS}$ /(m^3 day)]	1.90	1.90	
specific methane yield [Nm^3/kg$_{VS}$]	0.080	0.140	
Total solids removal [%]	5.25	7.28	
Q NaOH [kg/day]	0	9.3	16.5
Q Mix [m^3/d]	0.8	0.8	1.5
Q water [m^3/d]	1.5	1.5	2.7
Q diluted Mix [m^3/d]	2.3	2.3	4.1
methane production (Q$_{CH4}$) [Nm^3/day]	7.8	13.7	24.1
working volume, 80 % [m^3]	51	51	91
volume of the reactor [m^3]	64	64	113

345

346 The energy analysis (Table 7) showed that in scenarios S1 and S2.a surplus thermal energy was

347 required to heat the digester. In details, considering 303 t/y of waste mixture, TE$_{net}$ was negative,

348 indicating that TE$_{CHP}$ could just partly cover the thermal energy requirements; instead, EE$_{net}$

349 was positive. The energy surplus needed was larger for the Mix (- 59704 MJ/year) than TA Mix

350 (- 4073 MJ/year). Instead, scenario S2.b was designed to achieve E$_{tot}$ equal to zero, i.e., energy

351 self-sufficiency based on methane production.

352

353 Table 7. Results of energy analysis (Mix: waste mixture; TA: thermo-alkaline pre-treatment

354 with NaOH at 50 °C for 120 min)

	S1 (Mix)	S2 (TA Mix)	
		a	b
Net thermal energy (TE$_{net}$) [MJ/year]	- 92479	- 67507	-111786
Heating pre-treatment (TE$_{pre}$)	0	- 5689	- 10025

Heating feeding AD (TE_{AD})	- 109693	- 109693	- 193305
Thermal loss AD (TE_{loss})	- 23665	- 23665	- 34527
Thermal energy from CHP (TE_{CHP})	+ 40880	+ 71540	+ 126071
Net electrical energy (EE_{net}) [MJ/year]	+ 32774	+ 63434	+ 111786
Electricity mixing AD (EE_{mix})	- 8106	- 8106	- 14284
Electricity from CHP (EE_{CHP})	+ 40880	+ 71540	+ 126071
Total energy (Etot) [MJ/year]	- 59704	- 4073	0

Despite the waste production at the moment of the research was not sufficient to reach the energetic self-sustainability of AD at 35 °C, TA pre-treatment could be the key towards the process energetic sustainability by significantly enhancing the specific methane yield (from 0.080 Nm^3/kg_{vs} to 0.140 Nm^3/kg_{vs}). In fact, investigating the energy demand as a function of the amount of waste mixture undergoing AD at 35 °C (Figure 6), E_{tot} was negative for any values of waste production (Figure 6a), and E_{tot} even decreased by enhancing the waste production. Therefore, the energetic self-sustainability couldn't be reached for without TA pre-treatment. Instead, in case of the AD of the TA mix at 35 °C (Figure 6b), E_{net} was positive for waste production larger than 534 t/year.

Figure 6. Total energy, net thermal energy, and net electrical energy as a function of the waste production: (a) AD at 35 °C of the Mix, (b) AD at 35 °C of the TA pre-treated Mix.

22

(a)

(b)
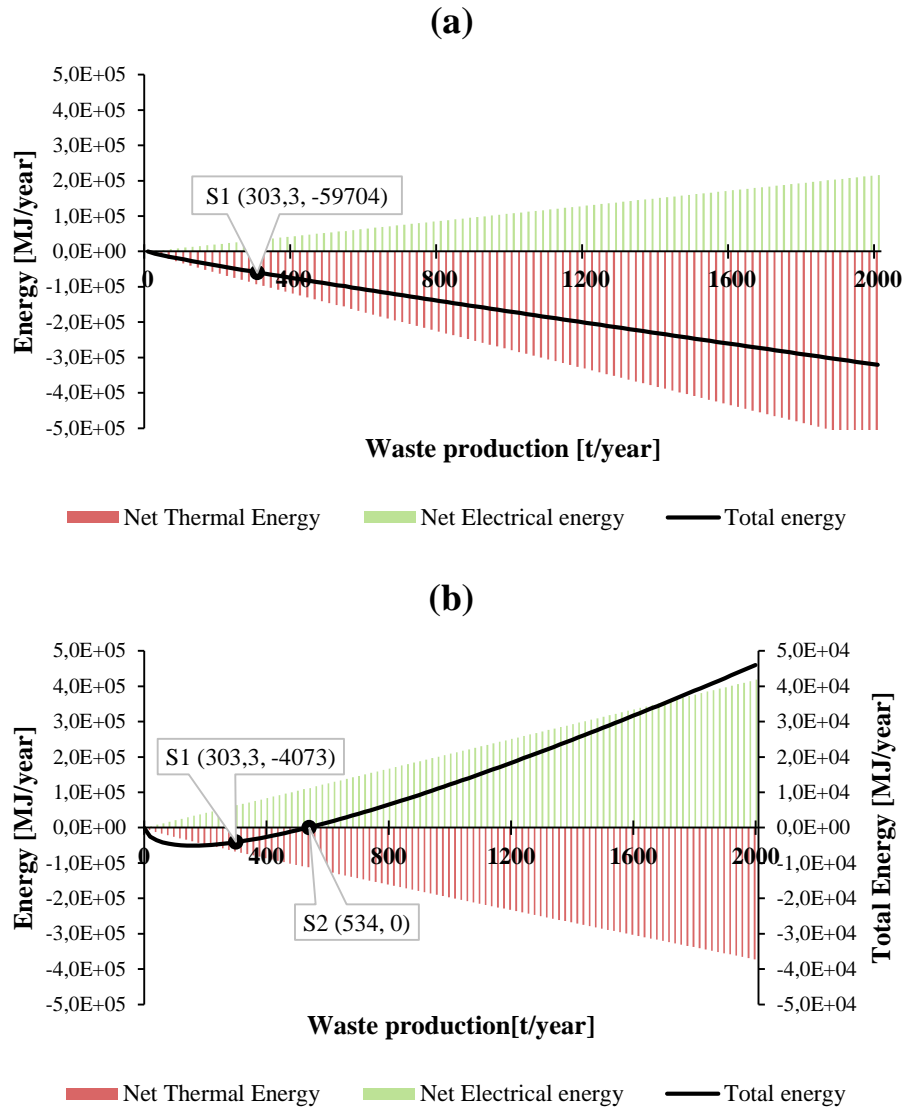
368
369

370   The results and details of the economic analysis (Table 8) showed that both the Mix and TA

371   Mix options could be profitable with the current waste production (scenarios S1 and S2.a), with

372   promising NPV and ROI of 108,694 € and 13.1 % for the Mix, and 112,936 € and 13.3 % for

373   TA Mix. In both cases the payback time of 10 years was reasonable. Despite both scenarios

374   didn't reach the energetic sustainability (natural gas was hypothesized as thermal energy

375   source), they showed promising economic performances. This is not surprising, since the major

376   contribution to the total revenues (Table 8) didn't come from the sale of electricity (representing

377   4.5 % of total revenues for the Mix and 7.6 % for TA Mix), but from the savings related to the

378 disposal of the digestate compared to the current waste management (95.5 % of total revenues

379 for the Mix and 92.4 % for TA Mix). Considering S2.b, the profitability was larger than in other

380 scenarios, with NPV of 270,294 €, ROI of 15.2 % and payback time of 9 years.

381

382 Table 8. Results of the economic analysis: operational costs, revenues, total investment costs,

383 return of investment (ROI), net present value (NPV), payback time (PBT).

	S1(Mix)	S2 (TA mi)		Notes	References
		a	b		
Total operational costs [€/year]	9182	9910	11744		
NaOH [€/year]	0	921	1623	NaOH: cost 0.27 €/kg; dose 0.08 g/gTS	Demichelis et al., 2018a
water [€/year]	753	753	1327	water cost: 1.37 €/m^3	Demichelis et al., 2018a
Net thermal energy [€/year]	717	523	866	non-household consumers - natural gas cost average EU-27 (2nd half 2020): 0.0279 €/kWh	Eurostat, 2021
Electricity [€/year]	282	282	498	non-household consumers - electricity cost average EU-27 (2nd half 2020): 0.1254 €/kWh	Eurostat, 2021
Labour [€/year]	7430	7430	7430	labour cost average EU-27: 28.5 €/hour; 1 worker; 1 hours/day; 5 days/week	Eurostat, 2021
Total revenues [€/year]	31633	32701	57626	electricity cost average EU-27 (2nd half 2020): 0.1254 €/kWh	Eurostat, 2021
Save costs for waste disposal [€/year]	30209	30209	53235	waste disposal: sWWTP: 0.15 €/kg; RSC and MS: 0.31 €/kg; FW: 0.110 €/kg; digestate: 0.120 €/kg	Demichelis et al., 2018a

Electricity [€/year]	1424	2492	4391	electricity cost average EU-27 (2nd half 2020): 0.1254 €/kWh	Eurostat, 2021
Total investment cost [€]	171087	171087	301495	FCC: Cost digester construction: 2500 €/m^3 WCC: 6.5 % of FCC	Chiappero et al., 2019
ROI [%]	13.1	13.3	15.2		Chiappero et al., 2019
NPV [€]	108694	112936	270294	lifetime (n): 20 years; discount rate (i): 5 %	Chiappero et al., 2019
PBT [years]	10	10	9		Chiappero et al., 2019

384

385 **4. Conclusions**

386 The management of the industrial wastes deriving from cosmetic products manufacturing is

387 challenging from the technical and economic viewpoints: wastewater, rich of scarcely

388 biodegradable organic compounds, is typically treated in onsite treatment plants that are highly

389 efficient in COD reduction; other wastes, including the wastewater sludge, are usually landfilled

390 or incinerated. While the available literature on cosmetic waste management only offers few

391 data on the AD of wastewater, this work was aimed at investigating the technical feasibility of

392 the AD of different cosmetic wastes deriving from one of the largest plants of L'Oréal Group

393 in Europe.

394 A first set of AD tests at 35 °C concerning the single waste materials provided encouraging

395 results (up to 0.10 Nm^3/kg$_{vs}$ of biogas, 70 %-v/v methane). Further AD tests involved a mixture

396 (according to the amounts produced in the plant) of the wastes at 35 and 52 °C. Considering the

397 low ratio between soluble and total COD, the wastes underwent physico-chemical pre-

398 treatments (thermo-alkaline and thermo-alkaline-sonication). The main findings of this research

399 were as follows: pre-treatments considerably increased (up to 100 %) methane yields compared

to untreated mixed wastes, with better performances for the thermo-alkaline pre-treatment; no significant differences were observed comparing the performances of the AD of pre-treated mixed wastes in mesophilic and thermophilic conditions, achieving in all cases biogas yields around 0.2 Nm^3/kg_{VS} and 62-70 % methane; after AD, 5-8 %-wt total solids reductions were observed; even if a dewatering process will be necessary, the thermal valorization of the digestate could be investigated in the future.

On the grounds of the technical and economic assessment of the feasibility of the scale-up of the overall process, TA pre-treatment exhibited a key role in achieving the process energetic sustainability. The economic analysis showed that with the current waste production AD of the considered cosmetic waste could be sustainable. In fact, even if the energetic sustainability wasn't achieved (natural gas was hypothesized as thermal energy source), the major contribution to the total revenues derived from the savings related to the disposal of the digestate compared to the current waste management. In conclusion, considering the lack of literature on the anaerobic digestion of cosmetic wastes, this study would like to provide an insight on the topic and stimulate further exploration of alternative management options for cosmetic wastes.

424 and writing-original draft writing and manuscript review; M. Onofrio: conceptualization,

425 methodology and writing-manuscript review.

426

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