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Integrated sewage sludge treatment for the sustainable recovery of fine-chemicals: Technical and economic analysis[☆]

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ABSTRACT

A sustainable procedure for effectively isolating grease from urban thickened sewage sludge was developed and examined. Thickened sludge underwent centrifugation, was treated with HCl and H_2O_2, heated to 353 K and then centrifuged again. Besides a pure lipid current with a FFA content of 90–92 % (with a grease yield of up to 73.3 %), an aqueous acidic current and a wet residual solid cake (TS: 31.7 ± 3.4 %) were also generated. The technical integration of this procedure in conventional sludge-treatment lines were then investigated under pilot scale. The cogenerated streams were found to be digestible under anaerobic conditions, leading to a production of biomethane higher than that foreseeable based on the biomethanogenic potential of the starting sludge. This improvement of biomethane production demonstrated that the reactive step of the grease recovery process has a favorable effect on the digestibility of the residual sludge. Concomitantly, a reduction in the volumes of final sludge to be disposed of by 20 % was also determined. Alternatively, a different scenario of integration of the grease recovery was studied for WWTP not equipped with anaerobic digesters. The residual solid cake obtained from the lipid recovery process can be efficiently dried through a low-temperature desiccator. The desiccated cake (TS: 86.0 ± 6.0 %) had a high calorific value (17 MJ/Kg) capable of producing the electric and thermal energy needed for running the lipid recovery process. For both cases, the proposed integrated sewage sludge treatments could produce economic benefits capable of making the costs of investments recoverable within three years. These results pose the proposed grease recovery as a sustainable approach for the treatment of municipal sewage sludge, while facilitating the recovery of valuable resources.

1. Introduction

The rapid industrialization and economic growth of modern society are forcing a continuous increase in the consumption of fossil fuels to meet the resulting growing demand for energy [1,2]. Oil, coal and natural gas, the primary energy resources, are decreasing due to the extensive exploitation of their non-renewable reserves [3]. In addition, the consumption of fossil fuels also poses an environmental issue due to the emission of greenhouse gasses (GHG) [4,5]. The energy crisis and the environmental risks associated with these energy resources have become a significant problem that could be mitigated by the use of alternative energy sources [6–8]. Bioproducts (e.g. biodiesel, biolubricants, biosurfactants) derived from various feedstocks such as virgin vegetable oils [9–11], represent valid alternatives to fossil-based products. However, their increasing demand faces the main obstacle of purchasing oily feedstock at reasonable prices. The industrial production of raw materials from renewable resources suffers from economic sustainability issues, as the starting feedstock accounts for approximately 80 % of the total production costs [12,13]. One of the main reasons is linked to the competition between biofuel producers and the food industry. This situation poses a threat to food security as agricultural products are increasingly utilized for non-food purposes [14]. The

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use of inexpensive and non-edible oily feedstock has recently been the subject of numerous studies. Waste cooking oils [15,16], animal fats [17,18], brown and yellow grease [19–21] have been effectively used to produce liquid fuels and high-value oleochemicals, avoiding the use of natural virgin resources and reducing production costs. In this context, urban sewage sludge is a viable lipid feedstock: it is an inexpensive resource from wastewater treatment, available worldwide and not subject to seasonal restrictions [22,23]. In Europe, the annual production of sewage sludge is estimated at around 10–13 million tonnes of dry matter [24]. Sewage sludge, if not properly treated, can pose serious environmental and health risks, both direct and indirect, to humans. Besides the conventional biological (pathogens and bacter) [25,26] and chemical pollutants (heavy metals, mineral oil, PCBs and PAH) [27], regularly monitored for the most suitable final destinations, nowadays new pollutants should have been attentioned namely viruses [28], PFAS [29], emerging pollutants (pharmaceuticals, cosmetics, drugs, endocrine disruptors, etc.) [30] and microplastics [31] which can be accumulated onto the final sewage sludge, altering the present state of the art for appropriateness of treatments and final disposal of the relevant residual sewage sludge. Several technologies have been developed for the treatment and disposal of sewage sludge, addressing legislative restrictions on direct use in agriculture, composting, incineration and landfilling [32–34]. However, utilizing this waste to recover lipids can be a sustainable and valuable option for sewage sludge management, which aligns with the modern principles of the circular economy. Although many methods have been proposed [35,36], the direct liquid-liquid extraction from wet sewage sludge with immiscible organic solvents appears to be the most effective method for lipid recovery. Hexane has already been investigated in a study that simulated an industrial-scale process with thickened [37] and dewatered [38] primary sludge, resulting in reasonable benefits. After the extraction process, however, a residual sludge contaminated by the organic solvent is produced, which makes any application difficult [39]. In addition, the process requires large reactors in relation to the high amount of hexane that needs to be added for the extraction process [38]. Bio-based solvents have also been investigated from this point of view. Ethyl esters of volatile fatty acids [40,41] have been demonstrated to be effective in extracting lipids from sewage sludge, while facilitating the rapid biodegradation of the extraction residues under anaerobic conditions, resulting in biogas production. Nevertheless, the economic advantages of this approach are compromised by the limitations associated with the composition of sewage sludge and solvent recovery [40]. Ionic liquids are considered an environmentally friendly alternative for lipid extraction due to their chemical and thermal stability and potential recoverability [42,43]. However, their cost is considerably higher than that of conventional extraction agents, limiting their industrial use. Recently, innovative extraction technologies without solvents have been developed to better meet the stringent environmental standards for this recovery step in a wastewater treatment plant (WWTP) [44]. It has been shown that only particular sludges can be processed [45]. In this work, an innovative process for separating grease from urban sewage sludge was investigated [46]. Thickened sewage sludge (as used for the anaerobic treatment in the WWTP of Lecce) was centrifuged, reacted with acid and H_2O_2, brought to 353 K and centrifuged again, obtaining the separation of a stream very rich in Free Fatty Acids (FFAs). After an initial optimization of the reaction conditions on a laboratory scale using different acids (formic and hydrochloric acid) and H_2O_2, the process was scaled up to process two cubic metres of thickened sewage sludge per hour. For the first time, the biomethane potential (BMP) of different residues was determined in order to evaluate the technical integration of this procedure in WWTP with the anaerobic treatment of sewage sludge. Alternatively, a new scenario was also investigated to evaluate the integration of this procedure in WWTP not equipped with anaerobic digesters. For the first time, the residual cake was desiccated through a low-temperature plant, evaluating the composition of the final biomass and the relevant high heating value. In both cases, the economic assessment was also investigated.

2. Materials and methods

2.1. Chemical characterization of sewage sludge

Sewage sludge used in this study was taken from the WWTP of Lecce (South of Italy, about 200.000 Population Equivalent, PE). The samples were promptly analyzed (alkalinity, Total and Volatile Solids (TS, VS), trans-esterifiable lipids and ash content [47]) and used, avoiding a long storage time (within 48 h, 277 K). Each analysis was performed in triplicate to calculate the mean value and relative standard deviations.

2.2. Lipid extraction procedure optimization

Centrifuged sewage sludge was reacted with formic or hydrochloric acid in different molar ratios with respect to the alkalinity of the sludge (0, 1, 2 and 3), and H_2O_2 (0, 5, 10 and 15 wt% with respect to TS). Reacted sewage sludge was brought to 343 K and immediately centrifuged (4000 rpm for 5 min, ALC 42 Centrifuge), by obtaining (i) a greasy layer on the top, consisting mainly of FFAs, (ii) an aqueous acidic intermediate phase and (iii) an exhausted cake. These three different phases were manually separated, quantified, dried (378 K, 24 h) and chemically characterized. The grease recovery yield was determined as follows (Eq. (1)):

$$\text{Recovery yield }(\%) = \frac{m_{Grease}{*}TS_{Grease}FFAs_{Grease}}{m_{Sludge}{*}TS_{Sludge}{*}FFAs_{Sludge}}{*}100 \tag{1}$$

where m_{Grease} and m_{Sludge} are the wet masses of separated grease and the initial centrifuged sludge, respectively, $FFAs_{Grease}$ and $FFAs_{Sludge}$ are the FFAs percentages (%) in the greasy layer and the centrifuged sludge, respectively and TS_{Grease} and TS_{Sludge} are the total solids content of the separated grease and the initial sludge.

2.3. Pilot plant scale for grease recovery from thickened sewage sludge

Fig. 1 shows the process flow diagram for the recovery of grease from thickened sewage sludge on a pilot scale. The process begins with an initial centrifugation of the thickened sewage sludge, which was performed using a Vitone V0® decanter (referred to as HD1). In this step, two streams were generated: the centrate C1, which was returned to the primary clarifier of the wastewater treatment plant and the centrifuged sludge (CS1), which was collected in a thermoregulated reactor (R). When approximately 700 kg of centrifuged sewage sludge were collected in R, a stepwise process was carried out that included the gradual addition of 50 kg of HCl (30 wt%) and then 25 kg of H_2O_2 (30 wt %). This was followed by a 15-minute period during which the reaction occurred at a temperature of 343 K, with the reactor being heated externally using a pellet boiler. After the chemical treatment, the reacted sludge (RS) was pumped into a second Vitone V0® horizontal decanter (HD2). In this step, the mixture was separated into two streams: a centrate (C2), which contained dissolved grease and other soluble components and the final exhausted cake, which represented the dewatered residual solids. C2 was then fed directly into a vertical separator (Vitone V2700, VS). In this unit, the raw grease was separated from the exhausted aqueous phase (EAP). The grease recovery was calculated according to Eq. (1).

As for the energetic consumption, the average values for electricity (53 ± 2 kWh) and heat (360 ± 10 MJ) needed for running all the operations in a single batch were monitored and considered in the final feasibility evaluation.

2.4. Bio-methane potential tests and semi-pilot digester

The final anaerobic biomethane potential of i) the initial sludges

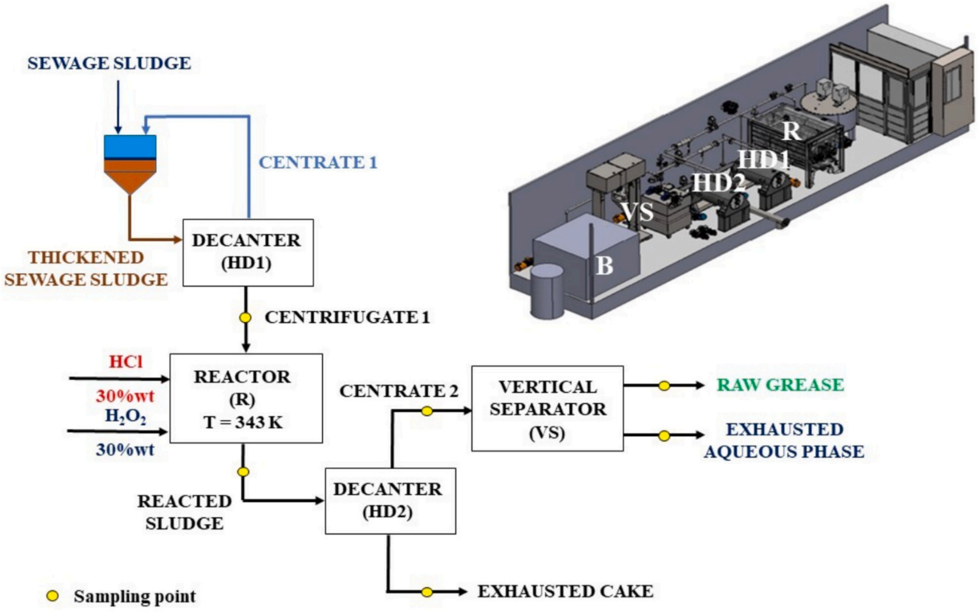

Fig. 1. Procedure scheme for the separation of raw grease from thickened sludge.

treated for lipid extraction, ii) the EAPs and iii) the final exhausted centrifuged cakes were evaluated by BMP tests using the Automated Methane Potential Test System (AMPTS-II, Bioprocess Control, Sweden) equipped with mechanically stirred and thermostated (310*K*) glass reactors of 0.5 L. Each reactor was partially filled with inoculum and substrate, maintaining an S/I ratio (substrate to inoculum) of 0.5 based on volatile solids (VS). Blank tests were performed by mixing inoculum and distilled water to account for methane production due to organic residues in the inoculum. Once sealed, the reactors were flushed with a stream of pure nitrogen to restore the anaerobic conditions. The gas produced by each bioreactor was measured online with volumetric cells equipped with an automatic data acquisition system at standard conditions (298 K; 1 atm) after the CO_2-fixation units (filled with 3 M NaOH solution). The semicontinuous anaerobic digestion (AD) test was performed under mesophilic conditions (310 K) on the final residual cake after the treatment with HCl and H_2O_2 in a 10 L stainless steel continuous stirred-tank (CSTR) bioreactor (Bioprocess Control, Sweden) [48]. The produced biogas was collected and passed through a CO_2 trap (with NaOH solution) before entering a methane detection unit (μFlow, Bioprocess Control, Sweden) with temperature and pressure compensation to normalize the gas flow rate and measurements at 273 K and 1 atm. The organic loading rate (OLR) and the hydraulic retention time (HRT) were set at 2 gVS L^{-1} d^{-1} and 30 days, respectively. After the start-up phase, the feed pH value was adjusted daily to 4.5–5 using a 3 M NaOH solution.

2.5. *Desiccation unit*

The desiccation of the final exhausted cake was carried out using a low-temperature SHINCCI unit, Model SBDD2400FL. In this desiccation unit, the sludge was heated directly by the forced recirculation of hot air, which ensured a high thermal efficiency. The drying temperature was set to 333 or 348 K. The latent heat required to evaporate the moisture from the exhausted cake was recovered by condensing the steam using a heat pump, making the drying process almost thermally self-sufficient. For this reason, the drying process mainly consumes electrical energy, which was used to drive the compressors, the fan and the motor to move the belts on which the sludge was transported in the insulated drying chamber. In test operation, a daily water removal of 2400 kg can be achieved with an electrical operating power of 26 kW.

3. Results and discussion

3.1. *Lipid extraction from sewage sludge: laboratory tests*

The process for extracting lipids from thickened sewage sludge was initially carried out on a laboratory scale. Considering that the grease content of thickened sewage sludge typically ranges from 1.60 to 8.10 g/kg, a representative sample with a relatively low lipid content of 2.76 g/kg was processed on a laboratory scale. After centrifugation at room temperature, the lipid content of the centrifuged sludge increased to 10.61 g/kg (with an alkalinity of 11,500 mg $CaCO_3$/L). The centrifuged sludge was systematically reacted with either HCl (37 wt%) or HCOOH (80 wt%), varying the molar ratios (MR) based on the alkalinity of the sludge. After an accurate stirring phase (200 rpm, 2 h), the pH of the resultant mixture was measured. The reacted sludge was then brought to 353 K and immediately centrifuged, resulting in a clear separation into three distinct phases: i) an oily layer on the top containing FFAs, ii) an aqueous suspension in the middle and iii) a wet residual cake on the bottom. The raw grease was recovered, dried and analyzed for the calculation of grease recovery. The results are shown in Fig. 2a.

During the centrifugation process without acid incorporation, no grease separation occurred, resulting solely in additional dewatering of the wet residual cake. Acidification allowed the separation of the lipid fraction with an efficiency that depended on both the nature and the amount of acid used, which in turn influenced the final pH of the mixture. At an MR of 2, lipid recoveries of 10.3 ± 0.7 % and 21.7 ± 0.5 % were obtained when employing HCOOH and HCl, respectively. Adding acids up to three times the initial sludge alkalinity improved the lipid recovery rates significantly, reaching 27.0 ± 0.5 % and 51.5 ± 0.5 %. Acidification has a dual function, which is prioritized as follows. First, it facilitates the conversion of solid calcium fatty acid soaps into FFAs. Calcium soaps usually account for more than 50 % of the original lipid component in sewage sludge [40,49] and remain solid even at high temperatures, unlike FFAs, whose melting point is between 333 and 343 K. Acidification converts the calcium soaps into FFAs, allowing their separation during centrifugation at these temperatures as an immiscible liquid with a lower density than water. The second effect is the degradation and solubilization of the suspended solids in the sewage sludge, which has a higher efficiency when using an excess of HCl. At an MR of three, the separation and recovery of grease doubled compared to work at an MR of two, despite low pH differences. A reduction in suspended

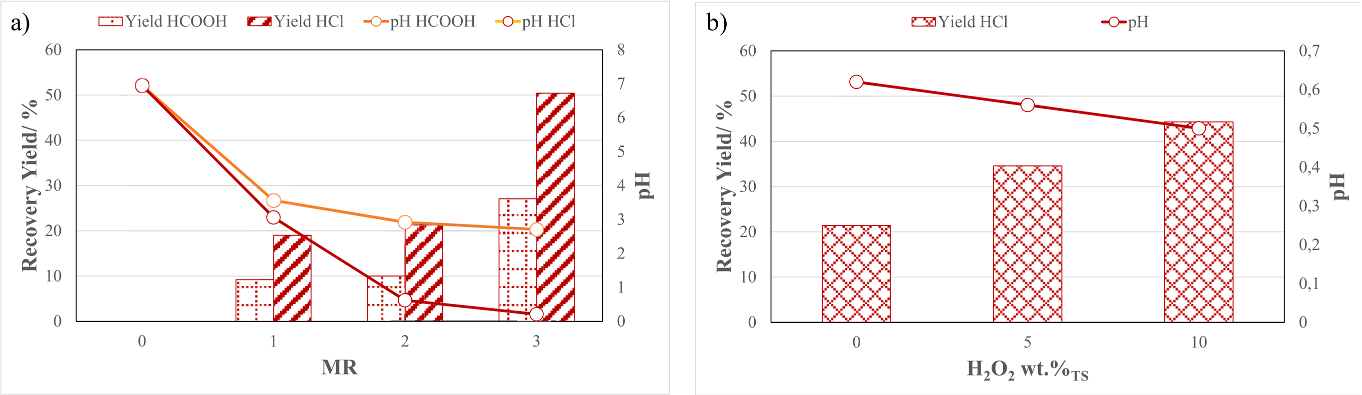

Fig. 2. a) Grease recovery yield from thickened sludge with respect to the acid:alkalinity molar ratio (MR) using HCl or HCOOH; b) H_2O_2 addition effect on the separation of grease using HCl (MR of 2).

solids improved the efficiency of grease separation from the aqueous phase. Moreover, the addition of a clean oxidizing agent was tested to boost lipid recovery by focusing on the defragmentation of colloidal solids. Specifically, the dewatered sludge was treated with HCl alongside hydrogen peroxide (H_2O_2, 30 wt%). Increasing the concentration of H_2O_2 contributed to improve lipid recovery (as illustrated in Fig. 2b). When the amount of HCl was doubled in relation to the alkalinity (MR = 2), grease recovery yields reached 32.3 ± 0.5 % and 43.6 ± 0.7 % with 5 and 10 wt% of H_2O_2 with respect to TS, respectively. Although the pH of the resultant mixture with H_2O_2 and HCl was close to that obtained with HCl alone, the presence of H_2O_2 significantly improved the recoverability of lipids by enhancing the degradation and solubilization of the suspended solids [50,51]. In the case where H_2O_2 and HCl were combined, the exhausted aqueous phase obtained after centrifugation appeared much clearer than when HCl was used alone, with the Suspended Solids (SS) content being significantly reduced (1915 and 3921 mg/L, respectively). With the aim of evaluating the possible effects of the reactive stage on the anaerobic digestibility of residual sewage sludge, a comparative study was carried out between the biomethane potentially produced from the initial centrifuged sludge used for the different experimental grease recovery tests and the total biomethane that could eventually be obtained by considering the sum of the contributions of each stream from the solvent-free separation. The BMP of the initial sludge was determined to be 135 ± 10 mL CH_4 per g_{TS}, which meant that 1053 ± 98 mL CH_4 could be produced from 100 *g* of wet centrifuged sludge (TS: 7.8 wt%). The anaerobic digestibility and BMP of each EAP and the final centrifuged cake corresponding to each specific operating condition were then singularly determined. Table 1 presents the ponderal distribution (as wet and dry solids) of grease, EAP, and final cakes produced per 100 *g* of centrifuged sludge under various reactive conditions, along with the corresponding experimental BMP values.

The biomethane related to the lipid extracts was estimated using the Buswell equation, which was restricted to the FFAs components (1000 mL per g_{FFAs}). It is worth noting that for all the reactive conditions, the total biomethane calculated as the sum of the single contributions of the final cake, the aqueous phases and the separated FFAs was almost equal to the value of the original centrifuged sludge (see the last column of Table 1). The total methane yields calculated for the tests with HCl alone were slightly lower than those calculated for the HCl/H_2O_2 combination, which is primarily due to the fact that the separation of lipids in the absence of H_2O_2 occurred through dragging of other constituents in the oily phase, whose BMP cannot be taken into account in this estimation. In fact, the use of H_2O_2 doubled the purity of FFAs in the recovered lipids compared to the values obtained with HCl alone (77.1 to 88.7 wt% vs 39.2–44.2 wt%). In each case, it was found that none of the operations performed during the solvent-free process significantly affected the initial biomethane potential of the sludge. Another critical aspect concerned the significant difference in the BMP values of the EAP, as the addition of H_2O_2 to the acid reduced the relevant methane yield, confirming the improvement in the clarification of the aqueous phase and the separability of colloidal solids.

3.2. Pilot scale tests

The process described in the previous sections was then scaled up using industrial machinery (horizontal decanters and a vertical separator) through a pilot plant assembled as shown in Fig. 1. About 25 batches were operated with thickened mixed sludge (primary and secondary) from the WWTP of Lecce, which was intercepted by the pipeline feeding the anaerobic digester. The composition of the sludge was monitored and analyzed throughout the process. In addition to evaluating the efficiency of grease separation, a detailed study was carried out on the anaerobic digestibility of the residual streams. The integration of this process was also evaluated at a pilot scale, building on the preliminary results obtained from the laboratory tests.

Table 1
Prospect of experimental data using the solvent-less recovery of lipids: wet and dry weights (in terms of g of TS/100 *g* of initial centrifuged sludge) and average BMP values (std deviation of 5 %) of final residual sludge, exhausted aqueous phases (EAPs) and recovered FFAs under the different reactive conditions reported.

Conditions		Final Residual Cake				Exhausted Aqueous phase				Lipid Extract			Tot CH_4
H_2O_2	HCl	Wet	Dry	BMP	Sub Tot CH_4	Wet	Dry	BMP	Sub Tot CH_4	Dry	FFAs	Sub Tot CH_4	mL_{CH4}/100 g
wt% TS	MR	g/100 g	g/100 g	mL_{CH4}/gTS	mL_{CH4}/100 g	g/100 g	g/100 g	mL_{CH4}/gTS	mL_{CH4}/ 100 g	g/100 g	g/100 g	mL_{CH4}/100 g	
–	1	50.8	6.9	81	559	48.7	0.7	294	205	0.5	0.2	203	967
5	1	42.3	6.3	92	580	57.3	1.2	172	211	0.4	0.3	271	1062
–	2	48.5	7.2	82	590	51.0	0.4	305	114	0.5	0.2	228	932
5	2	42.0	6.0	77	462	57.6	1.4	121	173	0.4	0.4	370	1005
10	2	43.1	6.2	75	465	56.4	1.1	82	93	0.5	0.5	473	1031
15	2	40.8	6.0	72	432	58.6	1.2	79	98	0.6	0.5	554	1084

3.2.1. Effect of co-addition of H_2O_2

First, the effect of H_2O_2 addition was investigated: Table 2 and Fig. 3 show the experimental data obtained for a batch run with HCl alone (MR of 2) and another with the combination of HCl (MR of 2) and H_2O_2 (5 wt % TS).

It is worth noting from Fig. 3 that a recovery yield of 73.3 % of the initial FFAs was achieved when H_2O_2 was co-used in the reactive step, compared to 47.6 % when only HCl was used. EAPs were richer in FFAs when HCl alone was used, resulting in a higher grease loss (19.4 % vs 3.8 %). Another interesting aspect, already confirmed in the laboratory experiments, was the purity of the FFAs, which was higher in the case of H_2O_2/HCl (>92 %) than with HCl alone (<80 %). On the other hand, the percentage distribution of total solids of the starting dewatered sludge in the final cakes was quite similar: 59.9 % and 52.5 % of the initial total solids were collected in the final exhausted cake when the HCl/H_2O_2 combination and HCl alone were used, respectively, with a very high solids content (32.6 ± 0.5 and 30.4 ± 0.6 %, Table 2). As with the samples deriving from lab-scale tests, the methane yields of the initial centrifuged sewage sludge and the corresponding residual flows resulting from the two different reactive conditions were determined through dedicated BMP tests. Specifically, the BMP for the initial sludge yielded 210 ± 15 and 340 ± 28 mL CH_4/g TS for the centrifuged sludge treated in batch mode with HCl alone and in the presence of H_2O_2, respectively, corresponding to a potential biomethane production of 35.70 and 70.38 Nm^3 per ton of initial dewatered sludge. Batch operation with HCl alone resulted in a total potential CH_4 production of 38.20 (vs 35.70) Nm^3 per ton of initial wet dewatered sludge as the sum of the contributions from lipids, EAPs and final residual sludge. For batch operation with a H_2O_2/HCl combination, the three potential contributions of biomethane amounted to 83.24 Nm^3 of CH_4 per ton of initial wet sludge, compared to 70.38 Nm^3 of CH_4 per ton of initial wet sludge. According to these data, the balances resulted in a biomethane potential even improved with respect to the starting value determined for the initial sludge. This improvement could be explained as a further result of the reactive step in the solvent-less process for the recovery of lipids, which not only did not generate possible inhibitory species for anaerobic digestion, but could even exploit the original potential of the sewage sludge by demolishing complex structures, accelerating the process and generating significantly higher values of biomethane yield.

Table 2
Chemical composition of the incoming and outgoing streams from the pilot plant for the recovery of the lipid component from sewage sludge.

Samples	pH	TS (% wt)	Alkalinity mg $CaCO_3$ L^{-1}	Composition (%wt_{TS})	
				Esterifiable lipids	Volatile solids
Reaction with HCl					
Thickened sewage sludge	5.7	2.2 ± 0.1	2878 ± 408	19.0	77.4
Centrifuged sewage sludge	5.2	17.0 ± 0.2	16,936 ± 629	19.2	75.0
Reacted sewage sludge	3.4	16.4 ± 0.6	–	16.8	74.2
Final exhausted cake	3.0	30.4 ± 0.6	–	9.7	74.1
Exhausted aqueous phase	2.2	5.7 ± 0.1	–	13.0	66.4
Extracted lipids	–	97.7 ± 0.8	–	79.9	99.9
Reaction with HCl/H_2O_2					
Thickened sewage sludge	5.5	3.5 ± 0.1	3949 ± 125	24.2	79.2
Centrifuged sewage sludge	5.3	20.7 ± 0.4	19,760 ± 285	32.0	79.5
Reacted sewage sludge	1.9	21.0 ± 0.3	–	31.5	79.7
Final exhausted cake	2.6	32.6 ± 0.5	–	13.6	80.0
Exhausted aqueous phase	1.7	7.0 ± 0.1	–	5.8	50.5
Extracted lipids	–	95.8 ± 0.7	–	>95	>99.9

3.2.2. Experimental run of the pilot plant for the solvent-less recovery of lipids

Based on the above experimental results, the solvent-less grease recovery procedure using the optimized H_2O_2/HCl combination was investigated in the pilot plant. The lipid content in the thickened sewage sludge ranged from 2.04 to 7.79 g/kg with an average value of 4.8 ± 1.5 g/kg. On a laboratory scale, the use of a benchtop centrifuge (ALC 42 Centrifuge) for the pre-centrifugation of the thickened sewage sludge led to an increase in the initial lipid content from 2.76 to 10.61 g/kg (see Section 3.1). In contrast, the use of a horizontal decanter in the pilot scale experiments allowed a further dewatering of the thickened sewage sludge, achieving a final lipid content of about 30 ± 15 g/kg. This indicates that lipid recovery could be economically viable with appropriate scaling and process optimization. Once HCl (MR of 2) and H_2O_2 (5 wt% TS) were added, the reacted centrifuged sludge was brought to 343 K and centrifuged again, using a horizontal decanter and a vertical separator in succession. Fig. 4a shows the recoverability of raw lipids from sewage sludge in relation to the lipid concentration in the initial centrifuged sludge.

It is worth noting that the recovery yield of raw grease was greater for batches with a higher initial lipid content. From samples with an initial lipid content of 66.2 g/kg, a raw grease recovery of 73.3 % was achieved. However, the average grease recovery yield for the above batches was 41.4 ± 15.1 %. The variability in lipid recovery can be attributed to significant fluctuations in the initial lipid content of the sludge. In particular, when the initial lipid content is lower (15–20 g/kg), the recoverability decreases significantly, reaching around 25–30 %. These variations affect the efficiency of the recovery process, resulting in the observed variations in yield between batches. This grease was analyzed in detail and the composition of the different batches was very stable. As it was mainly composed of FFAs whose profile was rich in saturated palmitic and stearic acid (together over 65 %), while oleic acid was the most abundant unsaturated acid (less than 20 %), this raw grease seems to be a promising feedstock for the production of stable biolubricants and renewable diesel or drop-in fuel with limited hydrogen consumption. In addition to obtaining lipids with a very high FFAs purity, exhausted cakes and aqueous phases were also produced. Fig. 4b shows the profile of total solid content (31.7 ± 3.4 wt %) and the relevant residual FFAs content (11.0 ± 1.2 wt%$_{TS}$), which were very stable and reproducible despite the wide variability of the initial composition in the thickened and centrifuged sewage sludge. The average amount of lipids lost in the exhausted cake was 31.2 ± 7.4 %, while 22.5 ± 13.3 % of initial grease was dispersed in the EAP.

3.3. Integration of the solvent-less recovery of lipids process in conventional WWTPs

The current scenario for treating urban wastewater encompasses a wide range of different sludge treatment configurations, which depend heavily on the resulting size of WWTPs. Anaerobic digestion of sewage sludge is the most profitable treatment, but is rarely used in small plants with a capacity of 30,000 People Equivalent (PE) or less. Aerobic digestion of sewage sludge is more often used to stabilize the final sludge, which is a very costly and energy-intensive process. For this reason, two different layouts for the integration of the proposed technology were studied, based on the actual sludge treatment lines that could be active in a WWTP. Fig. 5a shows the scheme of a WWTP treating sewage sludge anaerobically, where the solvent-less recovery of grease has been inserted in the process lines between the thickening of the mixed sewage sludge and the anaerobic digester. Fig. 5b shows the case in which the technology was applied in a WWTP without an

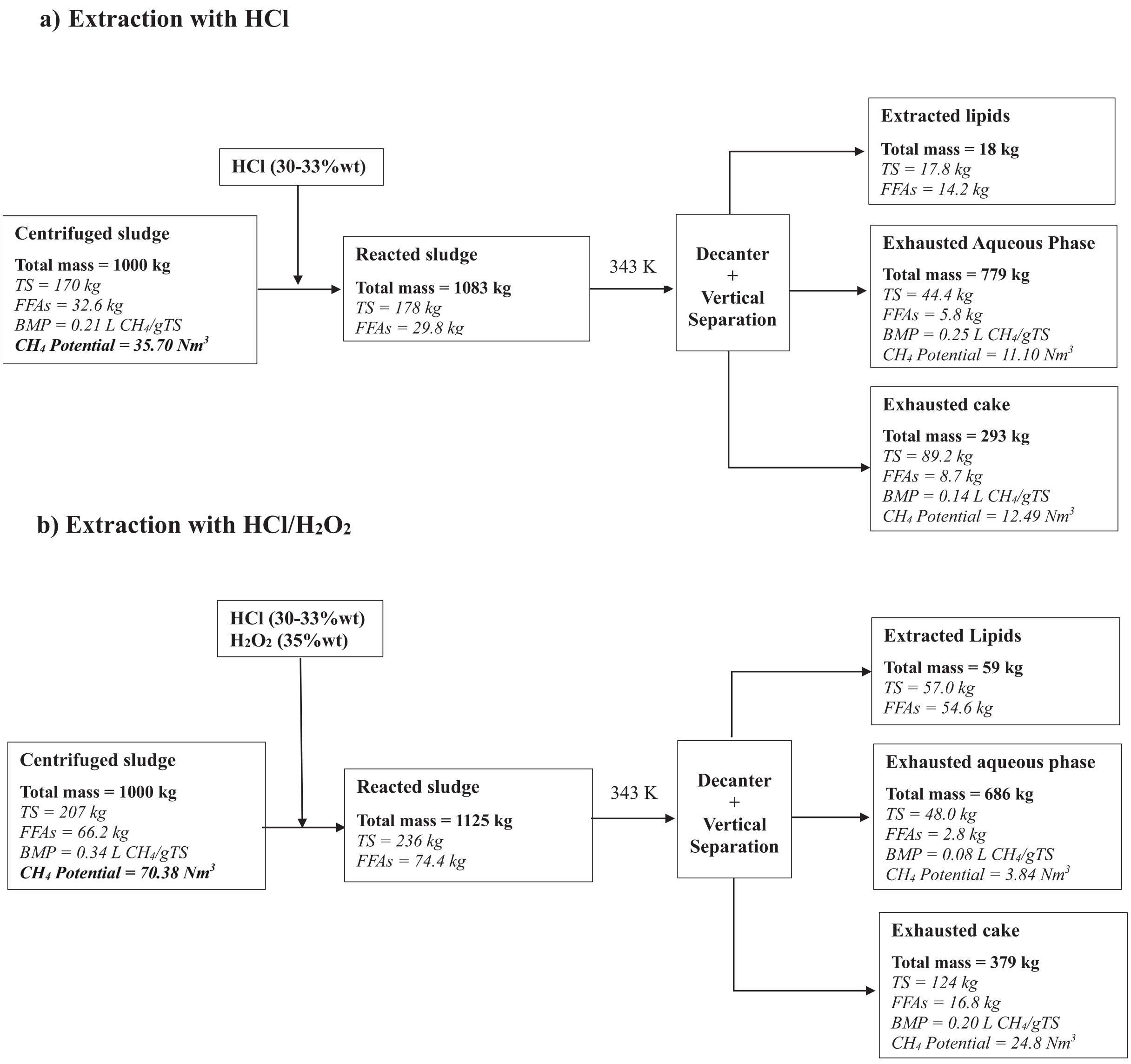

Fig. 3. Scheme of the lipids recovery from sewage sludge under different reactive conditions: masses, composition and BMP values.

anaerobic digester. The two different approaches are discussed in detail in the following sub-sections, together with the corresponding pilot-scale investigations.

3.3.1. WWTP with anaerobic treatment of sewage sludge

The integration of the solvent-free recovery of grease in a WWTP with a conventional configuration and anaerobic sludge digestion was investigated. A specific batch sample with a composition close to the average value was selected. Fig. 6a shows the profile and the scheme of the ponderal balances with the main representative values: a dewatered sludge with a TS of 18.1 % (whose VS were 80.7 %) and a grease content of 25.9 g/kg was reacted with an HCl/H_2O_2 combination, heated to 353 K and processed as described above, obtaining a recovery yield of FFAs of about 47.9 %. According to this recovery prospect, the removal of the initial volatile solids from the dewatered sewage sludge was about 10 %.

The corresponding residual streams, namely the EAP and the final exhausted cake, were collected, mixed according to the balance shown in Fig. 6a and anaerobically digested in a 10 L anaerobic reactor. Feeding the reconstituted sludge (TS = 11.8 ± 0.03 %; VS = 9.4 ± 0.1 %, Table 3) over a period of approximatively 85 days resulted in an average cumulative methane yield of 0.203 ± 0.005 Nm^3/kg_{VSfed} (Fig. 6b), with a concomitant VS removal during the steady state of 54 ± 3 %.

In this case, an overproduction of biomethane compared to the assumed value per ton of the initial dewatered sludge was determined due to activation of starting substrates in the reactive step. A BMP of 138 ml/g_{TS} was determined for the starting sludge, resulting in a potential total CH_4 production of 25 m^3 per ton. In contrast, according to the productivity experimentally obtained by the anaerobic digester under semicontinuous conditions from the residues produced for the batch under study, 36.3 Nm^3 were eventually produced (24.1 coming from the residues and 12.2 Nm^3 potentially coming from the FFAs separated). The production of 24.1 Nm^3 of biomethane from the residues, which would be the volume effectively available, has a potential energy of 959.18 MJ (39.8 MJ per Nm^3 of CH_4). The use of a cogeneration unit, considering a yield of energy conversion of 90 % and repartition of electrical energy and heat cogenerated of 30 % (287.75 MJ, namely 80 kWh) and 60 % (575.51 MJ), respectively [52], could make the energetic consumption related to the extraction process to be covered by burning the biogas generated from the anaerobic digestion of the relevant residues. Another direct consequence of integrating the solvent-free process in a WWTP with an anaerobic digester is the improvement in VS reduction, which increases from 50 % for a typical and optimal value of VS removal in conventional anaerobic digestion of sewage sludge to over 65 %, as

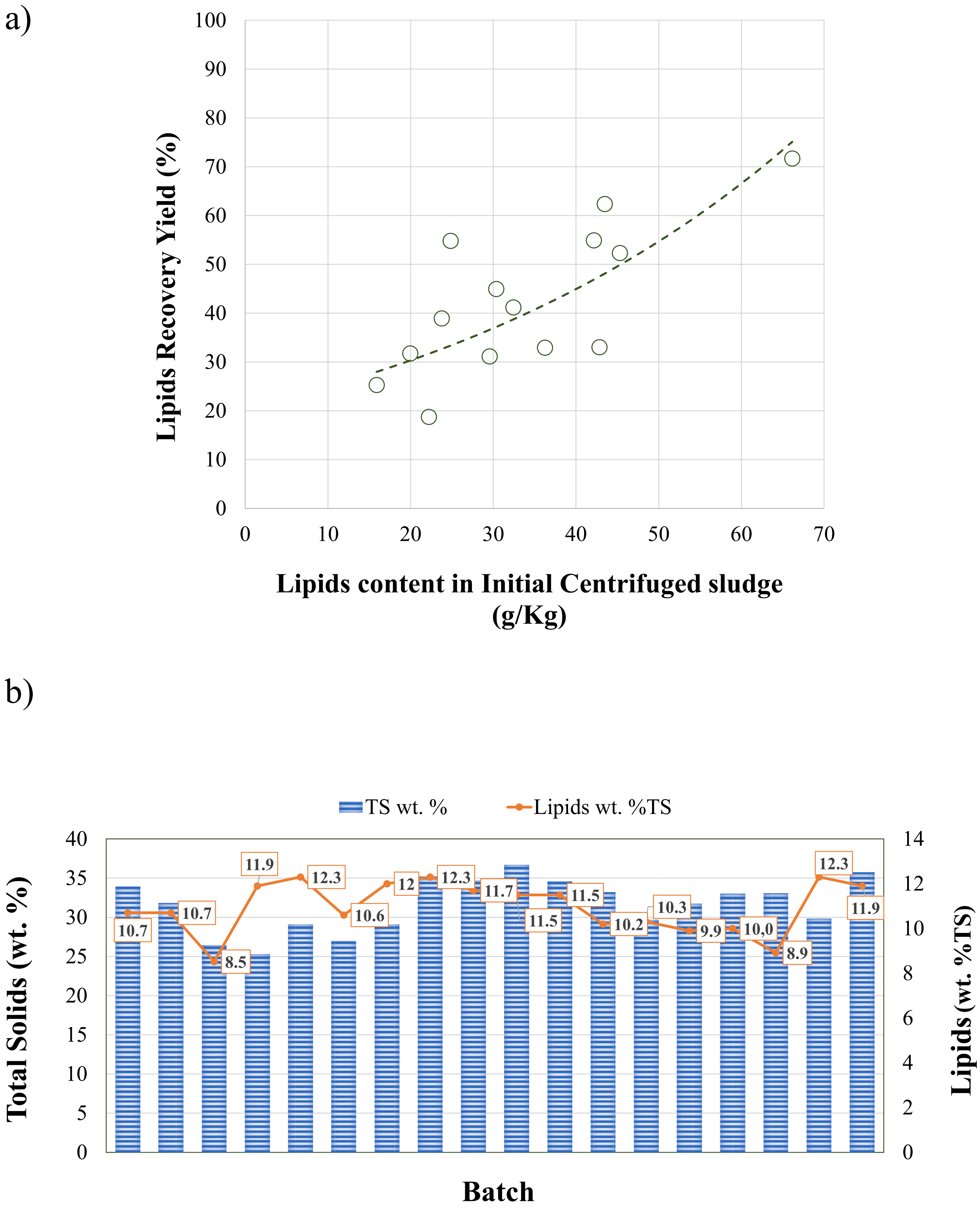

Fig. 4. a) Recovery yield of raw grease with respect to initial composition; b) Composition profile of the final exhausted cakes.

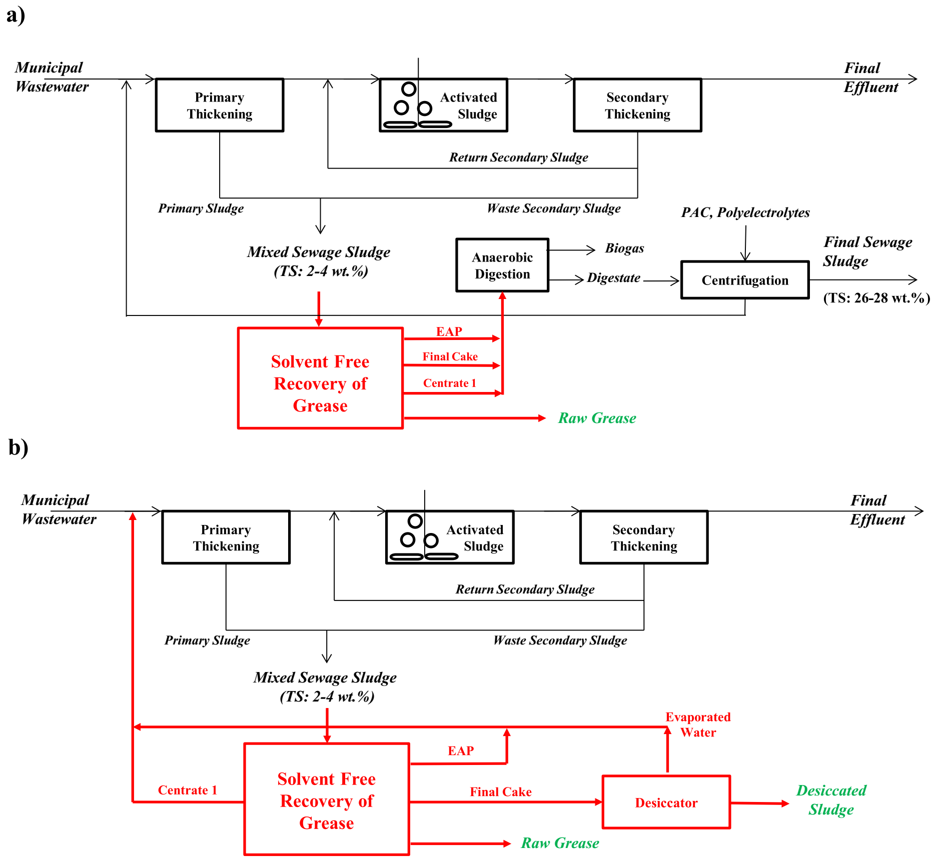

Fig. 5. a) Scheme of integration of the solvent-free recovery of lipids procedure in a WWTP with anaerobic digestor and b) with an alternative configuration.

observed in this case. This increase in VS removal could significantly reduce the final total amount of sludge to be disposed of. Considering that an average value of VS of 79.7 ± 2.5 % was determined in this specific WWTP, about 20 % less sludge would be expected to be produced with respect to the direct anaerobic digestion of initial sewage sludge, supposing an analogous final dewaterability.

3.3.2. Desiccation of final sludge

The integration of the process for the recovery of grease from sewage sludge in a WWTP which is not equipped with an anaerobic digester was also studied (Fig. 6b). In this scenario, a desiccation unit for the final exhausted cake was considered. The C1 obtained from the first dewatering of thickened sludge, the EAP and the recondensed water from the desiccation unit were sent back to the water treatment systems. The operating principle of the dryer used in this work was based on the removal of humidity from the sludge by evaporation through the forced passage of heated air, which is blown onto a mesh belt that transported the exhausted cake for drying. The only parameter that could be acted upon to reduce the cake's humidity was the speed of the carpet. By reducing the belt speed, the dwell time of the cake in the dryer was extended so that a better desiccated sludge was obtained at the exit of the plant. With an electrical power consumption of the dryer of 53–55 kWh (average value taken during the working period), an internal temperature of the dryer of 333–343 K was achieved when processing about 300 kg of final exhausted cake. As regards the value of the percentage of dryness in the cake to be dehydrated, upon entry from the dryer, it was on average 31.7 ± 3.4 wt% compared to that upon exit from the dryer, which was 86.0 ± 6.0 wt%. It is also worth noting that the organic content in the resulting desiccated cake was found to be 80.5 ± 1.9 wt%, which was quite similar to the VS content determined on the initial dewatered sludge (79.3 ± 2.5 %). The heat of combustion of 17.0 ± 1.3 MJ/kg, the low value of free chlorides (0.2 %) and organic chlorine compounds (0.06 ± 0.01 %) would allow a safe and potential use of this desiccated cake as a solid biofuel that could be burnt in situ for sustaining the electric and heat demands to run the process of separation of grease while reducing waste production. According to the ponderal prospect reported in Fig. 6a, over 130 Kg of desiccated cake could be produced per ton of initial dewatered sludge, with a potential energy content of 2340 MJ (doubling the value of the anaerobic digestion), which would enable energy sustainability to be achieved. 585 MJ, namely 162.5 kWh of electricity and 1404 MJ of heat [53], would broadly provide the energy required to operate the pilot plants. As already mentioned, another significant advantage of this option was the considerable reduction in the volume of final sludge to be disposed of: if only desiccation was considered, around 35 % of the expected sludge obtained by conventional treatment could be produced. Otherwise, if the desiccated cake was combusted in situ, the final residue would be reduced to a further one-fifth (ashes), namely 7 % of the usual sewage sludge production.

3.4. Economic feasibility and general impact of the application of the solvent-free grease recovery technology

The energy balances discussed in the previous sections have shown that the residual streams cogenerated during the application of the solvent-free grease recovery process can provide sufficient electricity and heat to run all processes without external efforts. These figures simplified the preliminary economic balance of the process by limiting the costs to the reagents (HCl and H_2O_2), while the benefits included the production of raw grease, a final reduction of the sewage sludge to be disposed of and polyelectrolytes saved for the final dewatering of the sewage sludge. In the case of a WWTP that processes sewage sludge anaerobically, the capital costs are related approximately to the grease recovery plant unit alone (it is assumed that the cogenerator was already

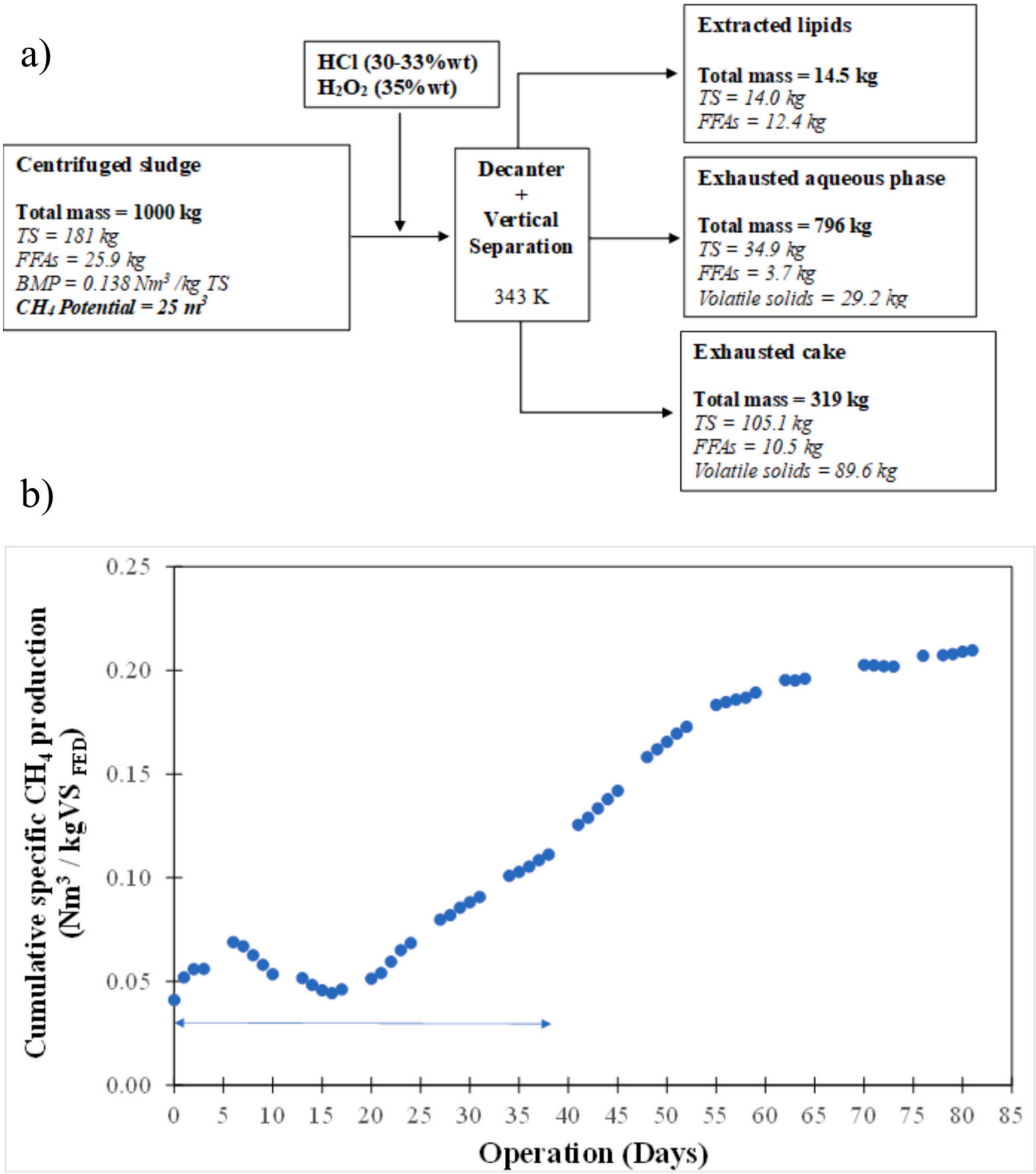

Fig. 6. a) Ponderal distribution and composition of currents generated from the pilot plant for a batch having a representative composition; b) biomethane production profile recorded using as a feed, the recomposed slurry obtained from EAP and the exhausted cake as obtained from the abovementioned batch.

present). These costs were highly dependent on the size of the first centrifuge, which is correlated to the daily volume of thickened sludge that needs to be treated. Table 4 reports the cost estimates for the WWTPs designed for 100,000, 300,000 and 1000,000 PE (300, 450 and 800 kEuro, respectively).

As far as operating costs were concerned, the consumption of reagents (HCl and H_2O_2) was calculated taking into account the corresponding dosages used in the experimental tests reported in this work. The annual amount of sludge produced was calculated assuming 50 g of sludge (as dry solids) are generated per day per capita [54], whose 79.7 ± 2.5 % were VS. The amount of sewage sludge saved was calculated considering that, as a baseline, a consumption of 50 % of the initial VS for the conventional anaerobic process is typically obtained [54] vs a consumption of 65 % determined for the investigated integrated process. This reduction in residual solids was also used to estimate the amount of polyelectrolytes saved, assuming that 15 kg of polymer is added per ton of digested sludge and that commercially available formulations have a polymer content of 45 %. An average TS value of 17.0 ± 3.5 % was determined for the sewage sludge after preliminary centrifugation, and an average value of 18.5 ± 5.9 % for the lipid content, for which an average recoverability yield of 41.4 ± 15.1 % was achieved. According to these figures, 1384 tons of grease could be annually recovered from WWTP designed for 1000,000 PE. Assuming a final price of 800 Euro/ton for raw grease, a value absolutely coherent and competitive to the present market, an annual revenue of 62.5, 187.7 and 626 kEuro could be obtained for 100,000, 300,000 and 1000,000 PE, respectively, with a total recovery of the CAPEX investment in less than three years for medium-big WWTPs. The economic scenario was less favorable for relatively small plants (100,000 PE), as about 5 years are required to cover the initial costs of the plants. For smaller WWTPs with a capacity

Table 3
Chemical composition of the slurry obtained by recombination of EAP and the final exhausted cake recovered from a batch of centrifuged sludge with an average composition.

Composition	wt%
TS	11.8
VS	9.4

TS composition	$wt\%_{TS}$
FFAs	10.1
EHS	3.2
Proteins	30.0
Cellulose	15.1
LHC	14.5
Ashes	19.1
Total	92.0

of 50,000 PE, besides the plant cost of 200 kEuro related to the grease-recovery unit, a desiccation unit (150 kEuro) and a solid fuel cogeneration unit (200 kEuro) would contribute to a total CAPEX investment of 550 kEuro. Under the same conditions defined above, 55 ton of grease could be annually recovered, consuming 123.65 kEuro in reagents (HCl and H_2O_2), but saving almost the entire annual costs of polyelectrolytes (about 17 kEuro) and obviously, the final sewage sludge to be disposed of (over 400 kEuro). According to these figures, the value of plants could be recovered in less than two years. The recovery of grease from urban sewage sludge, if applied on a large scale, could significantly improve the current market for oily feedstock. Over one-tenth of the present continental demand for biodiesel [22] and/or drop-in fuel [48–50] could be satisfied in Europe. In addition, this raw grease could be either used for the production of biolubricants [55] and bio-surfactants [56], enriching the Circular Economy scenario with several new positive developments [57] by substituting the impacting virgin oily feedstock nowadays used. As for the environmental aspect, the containment of waste up to an almost zero-waste discharge associated with desiccation-combustion in situ could definitely solve the problem of sewage sludge management while producing fine chemicals and energy in different forms. This approach would further benefit from the containment of polyelectrolytes in emulsion consumption, allowing new products to open and assess proficient resource recovery. Ashes obtained at the end of the combustion should be rich in precious minerals such as metals and phosphorus that could contribute to solving the scarcity of primary critical feedstocks. In addition, this scheme of operations could directly address modern problems related to contaminants, such as organic emerging pollutants and micro- and nano-plastics, which are ubiquitous and rarely degraded through biotreatments, making the use of final sludge in agriculture more complicated. In this direction, improving the primary precipitation of sludge [4,58], including the use of chemical enhancer additives for the relevant treatment, could serve as a new virtuous action towards modern concepts of water depuration [59]. Such an improvement in sedimentation may act as an effective treatment for removing pollutants from water, which could then be treated and destroyed in a WWTP without the need for costly technologies to be applied to the water lines.

3.5. Recovery of grease from sewage sludge: economic and environmental impacts comparison between solvent-free and solvent-based technologies

The evaluation of the economic and environmental sustainability of recovering lipids from sewage sludge represents a crucial aspect while comparing solvent-free and solvent-based technologies. Before proceeding with this comparison, a key premise should be considered. These two technologies are positioned at different maturity levels. To the best of our knowledge, the extraction of lipids from sewage sludge using organic solvents has only been investigated at the laboratory scale, with industrial projections based on simulators that utilize these experimental findings. The evaporative recovery of solvent, as well as the final properties of the relevant sewage sludge after lipid extraction, would need to be experimentally tested on a larger scale to obtain more reliable data to be used for a correct comparison with the solvent-free procedure, which was run on a pilot scale. Several organic solvents have been tested for the recovery of grease from sewage sludge due to their effectiveness in solubilizing lipids. However, only the use of hexane for lipid extraction from wet sewage sludge, is a well-established method that has been thoroughly investigated for its high efficiency in lipid recovery (yield >80 %) at competitive costs [38]. The solvent extraction on desiccated sludge was overlooked, as desiccation has a further economic and energetic impact [60]. The economic analysis for the recovery of grease from wet sewage sludge using hexane was recently studied (i) directly operating on thickened sewage sludge or (ii) after preliminary centrifugation, depending on the WWTP's dimensions [38]. CAPEX has a significant impact on the economic evaluation, as it encompasses extractive reactors and additional equipment and unit operations (such as separators, evaporators, and condensers) for the hexane recovery and recycling. This makes the extractive process with hexane economically viable only for large WWTPs, dimensioned for 1000,000 PE, for which a selling price of the recovered grease of 800 Euro/ton can guarantee a return on investment after 1.8 years, which is comparable to the figures related to the solvent-free procedure described in this work. On the other hand, for WWTPs ten times smaller, namely 100,000 PE, the final selling price for grease recovered through a solvent-based

Table 4
Prospect of costs and economic benefits derived from the integration of the lipid recovery procedure in a WWTP equipped with an anaerobic digester.

WWTPs Dimension			PE	100,000	300,000	1000,000
Costs of Plants (CAPEX)			kEuro	300	450	800
Operative Costs Balance	Operative Costs	HCl (33 %)	Ton	766.8	2300.4	7668.2
			kEuro[a]	99.7	299.1	996.9
		H_2O_2 (35 %)	Ton	383.4	1150.2	3834.1
			kEuro[b]	147.6	442.8	1476.1
	Benefits	Final Sludge saved	Ton	839.1	2517.4	8391.5
			kEuro	184.6	553.8	1846.1
		Polyelectrolytes saved	Ton	7.3	21.8	72.7
			kEuro[c]	14.5	43.6	145.5
		Grease	Ton	138.4	415.3	1384.3
			kEuro	110.7	332.2	1107.4
	Revenues		kEuro	62.5	187.7	626
Time required for the recovery of CAPEX investiment			Years	4.8	2.4	1.3

[a] https://www.chemanalyst.com/Pricing-data/hydrochloric-acid-61;

[b] https://www.chemanalyst.com/Pricing-data/hydrogen-peroxide-1169;

[c] Polyectrolytes costs was assumed to be 2 kEuro/ton.

process was found to rise to over 2500 Euro/ton to guarantee a reasonable return on investment within 5 years, differing from what was calculated for the proposed configuration discussed in this work, which guarantee the return on investment in 5 years while mantaining a competitive price of 800 Euro/ton of grease. In addition, the proposed scheme of integrated technologies for even smaller WWTPs (PE $<$ 50,000), including desiccation, the in situ combustion of desiccated sludge and cogeneration, enables a competitive selling price to be maintained (€800/ton) while ensuring a very short time to return on investment (less than three years). These economic advantages towards the solvent-less procedure could be even further improved if the recent economic fluctuations related to the quotation of hexane were taken into consideration. A hexane cost of 480 Euro/ton, defined in 2021 [38], was used for running the aforementioned economic comparison. However, in the last five years, such a cost has even doubled to over 1100 Euro/ton, making the solvent-based extraction economically less convenient than the solvent-free process, also for large WWTPs.

To assess the preliminary environmental impact related to these two processes, two environmental descriptors could be introduced: the Process Mass Intensity (PMI) and the Energy Intensity (EI) [61,62]. PMI is an environmental indicator that reports the amount of reactants, including solvents, required to produce one kilogram of final products, specifically sewage grease. The larger this value, the higher the associated environmental impact [62]. As for EI, it represents the total energy required per unit of the final product.

Regarding the use of chemicals, it is essential to note that the extraction of lipids with hexane, in any case, requires a preliminary acidification. According to our findings, the solvent-less procedure requires twice the amount of HCl typically required for extraction when operated with hexane. However, this significantly larger amount of acid, which consists of 35 L of HCl per ton of centrifuged sludge, actually replaces over 1000 L of hexane per ton of sludge, necessary for operating a solvent-based extraction. Despite the recovery yield using the solvent being approximately 80 %, the corresponding PMI is 118.19 kg of total reactants per kilogram of product, compared to 86.8 kg of reactants per kilogram of grease in the solvent-free process, making this procedure less impactful.

As for the energetic balance, the solvent-based process has an EI of 9.45 $\mathrm{kWh/kg_{Grease}}$ vs 10.1 $\mathrm{kWh/kg_{Grease}}$ determined for the solvent-free process. These two values, corresponding to 34.02 $\mathrm{MJ/kg_{Grease}}$ and 36.36 $\mathrm{MJ/kg_{Grease,}}$ respectively, demonstrate that both processes are convenient from an energetic point of view, as the final product (namely sewage grease, which is prevalently composed of free fatty acids) has a higher heat of combustion (about 39 MJ/kg). The slight difference in the advantage of the solvent-based process stems from considering the pessimistic scenario, in which, in the solvent-less process, the recoverability of grease from reacted sludge remains the same as experimentally determined with the pilot unit defined in this work, even with larger centrifuges. The use of an industrial centrifuge dimensioned for 1000,000 PE is reasonably expected to achieve recoveries that exceed 50 %, with a corresponding decrease in EI. In addition, this evaluation of EI focused solely on the extractive phase; however, it could significantly change if the overall WWTP configuration is considered, including energy production from residue management. Unlike the solvent-free process, which can satisfy the energetic needs by processing the residual streams, the residual sludge obtained from a hexane-based extraction will contain less lipid, resulting in potentially less biogas obtainable from anaerobic digestion, with a reduction of the energy produced from its combustion. This could require an external source of energy to run the solvent-based extraction, making it less convenient from an energy perspective.

Finally, the use of hexane poses significant environmental problems. As it is a flammable and toxic organic solvent, its use carries the risk of leakage and emissions into the environment, potentially having harmful effects on biodiversity and human health [63]. Safety systems for handling flammable solvents and distillation processes for hexane recovery further increase operating hazard risks. According to recent guidelines for designing greener processes, working in an aqueous phase without the use of organic solvents is preferable over using organic solvents [62]. For this reason, the combined use of HCl and H_2O_2 can generally be considered more sustainable, as they are both aqueous reactants that guarantee the aqueous phase is maintained, without any risk of volatile organic emissions. In addition, it is worth emphasizing that for both cases, the use of reactants/extractants must be conducted under controlled conditions in closed reactors to prevent any form of direct gaseous emissions. On the other hand, the final effluents related to these two different processes could have very different properties and impacts. The residual sludge obtained from the solvent-based process may contain up to 6500 ppm of hexane, resulting in the effective emission of a harmful solvent into the environment. In contrast, the acidity in the residual aqueous and sludge streams derived from the solvent-free process could be neutralized using calcium-based compounds (CaO or $Ca(OH)_2$), resulting in the formation of calcium chloride, mitigating any possible impact related to the excess of HCl. In detail, the neutralized aqueous stream could have potential as a coagulant enhancer in primary sedimentation, improving the separation of suspended solids from sewage, with indirect operational benefits in biological oxidation, thereby minimizing the energy effort required for water depuration [64].

In the future, a comparative Life Cicle Assessment study will be run to determine more specific environmental indicators for these different processes. However, according to this preliminary investigation, the solvent-free process presents clear advantages from both economic and environmental perspectives when compared with the solvent-based process.

4. Conclusions

This study presents a novel and effective solvent-free process for the extraction of grease from municipal sewage sludge. The process was successfully optimized on a laboratory scale and then scaled up, proving its practical applicability. The recovered lipids, which mainly consist of high-purity free fatty acids (FFA), show promising potential for the production of biolubricants, renewable diesel and drop-in fuels. The integration of this lipid recovery process into existing WWTPs, both those with and without anaerobic digestion, proved to be feasible without compromising the efficiency of water purification. The reactive step not only facilitated lipid separation but also enhanced the anaerobic digestion of residual sludge, resulting in a higher biogas yield and increased energy production. Besides the recovery of grease, the resulting dewatered cake and the exhausted aqueous phases showed high anaerobic digestibility, which was confirmed by the corresponding BMP tests. In particular, biomethane production from sludge residues improved when the lipid extraction process was combined with anaerobic digestion, achieving a potential yield of over 80 $\mathrm{Nm^3}$ per ton of initial sludge, thereby contributing to energy self-sufficiency. Alternatively, the residual cake can be efficiently desiccated, producing a valuable solid biofuel. Economically, the proposed procedure offers attractive advantages. It can recover significant amounts of grease at competitive market prices, reduce sludge disposal costs and improve the overall sustainability of the plant. The capital costs are offset by the short payback period (less than three years for medium-big WWTPs) and by the added value of the recovered bioproducts and energy. From an environmental perspective, this approach supports the principles of the circular economy by adding value to waste streams, reducing dependence on petroleum resources, and potentially mitigating issues related to emerging pollutants, plastics and micropollutants. In conclusion, this innovative, solvent-free lipid extraction method, when integrated into wastewater treatment processes, represents a sustainable, economically viable, and environmentally friendly approach for treating sewage sludge. It not only improves biogas production and energy recovery but also converts waste into valuable bioproducts, thus contributing to resource efficiency and environmental protection, in total agreement with the EU targets defined for WWTPs of the future [65].

CRediT authorship contribution statement

Luigi di Bitonto: Writing – original draft, Investigation, Formal analysis, Data curation. **Vito Locaputo:** Validation, Investigation, Formal analysis, Data curation. **Agata Gallipoli:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Camilla M. Braguglia:** Writing – original draft, Validation, Supervision, Investigation, Formal analysis, Data curation, Conceptualization. **Anjie Li:** Writing – original draft, Funding acquisition, Formal analysis, Data curation. **Ahmad Mustafa:** Writing – original draft, Formal analysis, Data curation. **Carlo Pastore:** Writing – original draft, Validation, Supervision, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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