



# Recovery of volatile fatty acids from fermentation of sewage sludge in municipal wastewater treatment plants



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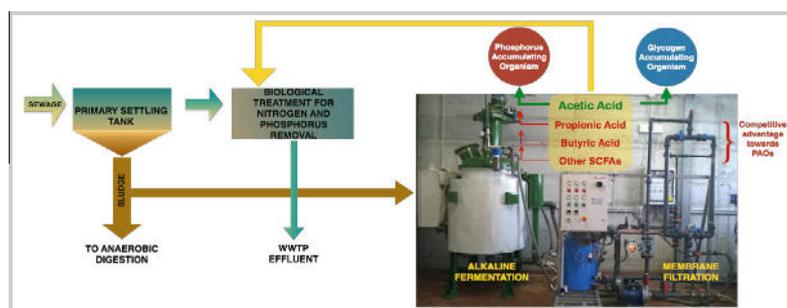
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## HIGHLIGHTS

- Wollastonite use during fermentation resulted in low nutrient release in the liquid.
- Higher SCFAs in the liquid phase with the use of caustic soda.
- Wollastonite enhanced the sludge dewatering characteristics and filterability.
- Fermentation liquid improved nutrient removal rates compared to acetic acid.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This work investigated the pilot scale production of short chain fatty acids (SCFAs) from sewage sludge through alkaline fermentation and the subsequent membrane filtration. Furthermore, the impact of the fermentation liquid on nutrient bioremoval was examined. The addition of wollastonite in the fermenter to buffer the pH affected the composition of the carbon source produced during fermentation, resulting in higher COD/NH<sub>4</sub>-N and COD/PO<sub>4</sub>-P ratios in the liquid phase and higher content of propionic acid. The addition of wollastonite decreased the capillary suction time (CST) and the time to filter (TTF), resulting in favorable dewatering characteristics. The sludge dewatering characteristics and the separation process were adversely affected from the use of caustic soda. When wollastonite was added, the permeate flux increased by 32%, compared to the use of caustic soda. When fermentation liquid was added as carbon source for nutrient removal, higher removal rates were obtained compared to the use of acetic acid.

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## 1. Introduction

Wastewater facilities are increasingly required to implement treatment process improvements to meet stricter discharge limits

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with respect to nutrients and at the same time want to maintain low operating expenses. Often commercially available organic carbon sources are used in wastewater treatment plants (WWTPs) for biological nutrient removal (BNR) from wastewater. However, the price of commercial synthetic carbon sources has significantly increased over the last years. Therefore, the use of non-conventional carbon sources seems to be an appealing alternative, considering their lower greenhouse gas (GHG) footprint compared to conventional ones. Fermenting sludge to produce short chain fatty acids (SCFAs) that can then be used in the subsequent BNR process

## Nomenclature

BNR	biological nutrient removal	soda-SFL	sludge fermentation liquid in which caustic soda is added
COD	chemical oxygen demand	sPRR	specific phosphorus release rate
CST	capillary suction time	sPUR	specific phosphorus uptake rate
DNBPR	denitrifying via nitrite biological phosphorus removal	SRT	solids retention time
FL	fermentation liquid	TMP	transmembrane pressure
GHG	greenhouse gas	TN	total nitrogen
HAc	Acetic acid	TP	total phosphorus
Hi-But	Iso-Butyric acid	TS	total solids
Hn-But	n-Butyric acid	TSS	total suspended solids
HPr	Propionic acid	TTF	time to filter
HRT	hydraulic retention time	TVS	total volatile solids
Hi-Va	Iso-Valeric acid	UF	ultrafiltration
Hn-Va	n-Valeric acid	VFA	volatile fatty acid
OFMSW	organic fraction of municipal solid waste	VSS	volatile suspended solids
OLR	organic loading rate	WAS	waste activated sludge
S/L	solid/liquid	W	wollastonite
SCFA	short chain fatty acid	W-SFL	sludge fermentation liquid where wollastonite has been added
sCOD	soluble COD	WWTP	wastewater treatment plant
SF	sludge fermentation		
SFL	sludge fermentation liquid		
sNUR	specific nitrogen uptake rate		

seems to be a sustainable process, having the additional advantage of decreasing the amount of sludge to be disposed (Li et al., 2011; Tong and Chen, 2007; Ucisik and Henze, 2008; Zheng et al., 2010). Recovering SCFAs from sewage sludge is currently a challenge in WWTPs. Depending on process conditions of the sewage sludge fermentation, the concentration of SCFAs can be satisfactory (i.e. >2 g/L), with favorable proportions of acids for the subsequent BNR process (i.e. ~40% acetic acid (HAc), ~15% propionic acid (HPr), ~25% butyric acid (HBut)) (Jiang et al., 2009; Lee et al., 2014; Li et al., 2011). The results of recent studies have shown that the use of sludge fermentation liquid (SFL) decreases the production of nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) during the BNR processes accomplished via the nitrite pathway (Zhu and Chen, 2011). Despite the extensive work on sludge fermentation, there is still a gap of knowledge about how process parameters (i.e. pH, temperature, solids retention time (SRT), hydraulic retention time (HRT)) can affect the efficiency of sludge fermentation in terms of the composition and the quantity of SCFAs. Most applications of waste-derived SCFAs still remain at laboratory scale (Lee et al., 2014). To ascertain the transferability of the process from the laboratory to the market, pilot scale studies are also required.

The pH is an important factor that controls the hydrolysis and acidification during sewage sludge fermentation. Alkaline conditions are expected to lead to more soluble protein and carbohydrate generation. At the same time, the methanogenic activity is inhibited resulting in enhanced SCFAs production (Wu et al., 2009). The optimum pH has been found to be in the range of 9–11 and can be maintained with the use NaOH and Ca(OH)<sub>2</sub> (Su et al., 2013; Wu et al., 2009). However, this practice is not desirable in full-scale plants, since it increases the cost and the environmental impact of the process. The addition of alkaline silicate minerals to control the pH can increase the sustainability of the fermentation process. The economic evaluation concerning the use of biowaste derived external carbon sources revealed that the organic fraction of municipal solid waste (OFMSW) fermentation liquid (FL) is a less expensive option compared to the use of synthetic HAc for the treatment of high strength nitrogenous effluents (Katsou et al., 2014). Considering the complex physicochemical nature of fermented effluents, the separation of SCFAs from fermented sludge is not a straightforward process. There are very

few studies examining the solid/liquid (S/L) separation of fermented effluents. The effective and straightforward separation of FL from the fermented sludge can enhance the sustainability of the process and can lead to reduced production of wet sludge. In previous studies, the sludge dewatering ability was negatively affected by the use of caustic soda due to the release of Na<sup>+</sup>, which impaired the separation of the FL from the fermented sludge (Su et al., 2013). One commonly applied technique for S/L separation is filtration. Nevertheless, membrane filtration is energy demanding, which limits its applications (Zhang et al., 2009). S/L separation is not always effective and the deteriorated filtration capability of the sludge makes the conventional sludge dewatering methods not practical (Tong and Chen, 2007; Yuan et al., 2006).

Within this context, the application of an efficient separation method based on membrane filtration is examined, aiming at the optimization of the whole treatment scheme. Membrane technology has been studied for the separation, isolation, recovery and utilization of volatile fatty acids (VFAs) (Zacharof and Lovitt, 2012). Membrane filtration is expected to allow the selective separation and retain the VFAs within the liquid stream, while rejecting the suspended solids. To apply this technology effectively, pretreatment of the fermented effluent is necessary since membrane fouling can be the major operational deficiency limiting the wider adoption of the process for the S/L separation.

This work studied the integration of the sewage sludge fermentation–membrane separation (SF–MS) process in order to recover SCFAs from sewage sludge and subsequently use them for nutrient bioremoval in a WWTP. The use of a suitable alkaline silicate mineral (wollastonite) was studied to enhance the performance of the fermentation process and the subsequent S/L separation stage. Finally, the feasibility of using the SFL as carbon source for enhanced BNR was assessed.

## 2. Methods

### 2.1. Source of sewage sludge and reasons for wollastonite selection

The sewage sludge used for the fermentation experiments was collected from the municipal WWTP of Carbonera (Veneto Region,

Italy). It consisted of mixed primary and secondary sludge. The use of wollastonite (Progind, Italy) to adjust the pH in the fermenter was tested as this could also lead to several advantages. SCFA production during sludge fermentation (SF) can provide the necessary acidity for dissolution of silicate minerals, resulting in the release of carbonate ion ( $\text{CO}_3^{2-}$ ) during the fermentation process which can lead to precipitation as  $\text{CaCO}_3$  and  $\text{Ca}_3(\text{PO}_4)_2$ . Since alkaline silicate minerals dissolve more rapidly at lower pH (White and Brantley, 1995), the process of anaerobic fermentation could potentially increase the dissolution rate of the mineral as a result of acid production (Salek et al., 2013; Ullman, 1996). Wollastonite (W) has also exhibited excellent ammonium adsorption (Lind et al., 2000). In combination with struvite crystallization, most of the phosphorous and potassium and 65–80% of the nitrogen could be recovered.

## 2.2. Impact of wollastonite on sludge fermentation

The impact of wollastonite dosage on the efficiency of the fermentation process, the S/L separation process and the characteristics of the produced liquid was investigated in lab scale reactors using different wollastonite concentrations (i.e. 1, 10, 20, 40 g/L). Wollastonite was added at the beginning of each experiment. The batch experiment setup was placed in an incubator, at the temperature of  $37 \pm 1$  °C. The experiments were repeated without any mineral addition to serve as a baseline (control) experiment. Samples were periodically collected from the reactors to monitor SCFAs, soluble COD (sCOD), total and volatile suspended solids (TSS, VSS), pH, the ammonium ( $\text{NH}_4\text{-N}$ ) and the phosphate ( $\text{PO}_4\text{-P}$ ) level. Under the optimum operating conditions the capillary suction time (CST) was measured (340 M CST, Triton, UK) and the time to filter (TTF) tests (Lo et al., 2001) were conducted.

## 2.3. Integrated pilot scale sludge fermentation and membrane separation system (SF–MS) scheme

The pilot plant (Fig. 1) with the characteristics shown in Table 1 was operated in the WWTP of Carbonera (Veneto, Italy). The anaerobic fermenter consists of a 500 L completely stirred reactor. The reaction temperature was maintained at  $35 \pm 1$  °C by an electric water heater. The sludge was fed to the fermentation unit directly

from the full-scale WWTP. A grid filter with an opening of 0.5 cm was installed before the fermentation unit feeding tube in order to avoid clogging of the subsequent filtration system. After the fermentation process a membrane filtration S/L separation scheme was installed to separate the FL from the sludge, so that the former than then be applied as a carbon source in the BNR process. The separation was carried out by employing two tubular cross-flow ultrafiltration (UF) membrane modules, operating in the inside–outside filtration mode (MO P13U 1 m, Berghof, Germany). The membrane modules were made of polyvinylidene fluoride (PVDF) with internal diameter of 8 mm and molecular weight cutoff (MWCO) of 15 kDa. The length of the membrane was 1 m and each module had a filtration area of 0.32 m<sup>2</sup>. The maximum pressure of the module was 600 kPa and the maximum operating temperature was 40 °C. The pressure and flow rates were controlled by a centrifuge pump, two ball-type back pressure valves and two pressure gauges (Endress + Hauser type Cerabar M) installed in the inlet and outlet of the membrane unit. The flow rates in the filtration modules were recorded by an Endress + Hauser Promag 50 flow meter, while Riels FHKU flow meter was used to measure the permeate flow rate. The fermentation liquid produced in the SF–MS process was collected and adequately stored to be used as an external carbon source for the nutrient removal. The fermentation process was operated in a semi-continuous mode, while the filtration process was operated for 10 h/day in batch mode. The concentrate was partially sent back to the fermentation and partially internally recycled in the UF module. Recirculation was regulated in order to maintain a flow rate of 50% of the feed flow rate. The membrane unit was operated in the following mode: filtration for 180 min, forward flush at high flow rates for 1 min, back flush using permeate for 1 min. Every day a certain volume of fermented sludge was wasted from the fermentation system in order to maintain the desired SRT. Both the wasted sludge and the FL removed in each filtration run were replenished with fresh sludge that was fed to the fermentation reactor. CST, TTF and step-flux tests (Le-Clech et al., 2003) were carried out periodically to evaluate the filterability and the critical flux of the fermented sludge. The following temperature correction factor was applied for permeate flux (Fan et al., 2006):

$$J_{20} = J_T \times 1.025^{(20-T)} \quad (1)$$

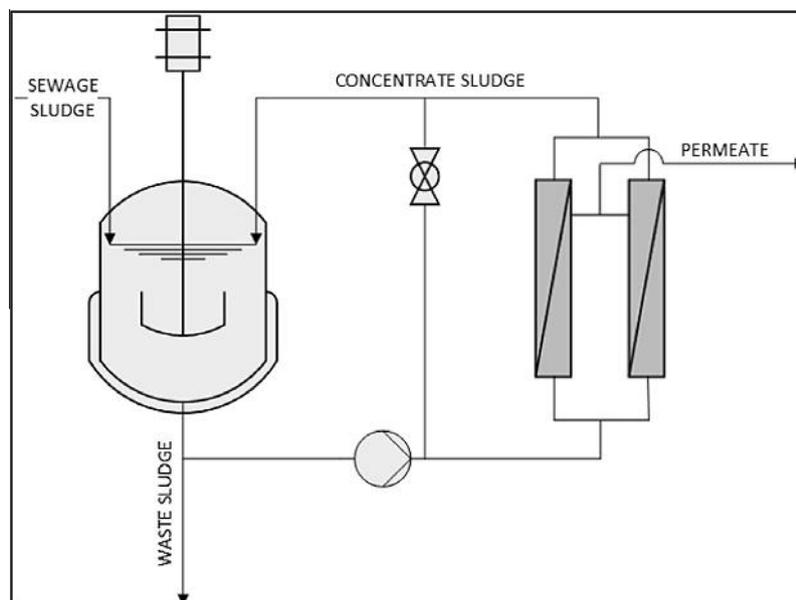


Fig. 1. Pilot scale sludge fermentation–membrane separation (SF–MS) scheme.

where  $J_{20}$  (L/m<sup>2</sup> h) is the permeate flux at 20 °C,  $J_T$  (L/m<sup>2</sup> h) is the permeate flux at the operating temperature  $T$ .

#### 2.4. Operating periods in the SF–MF pilot system

Table 1 shows the main operating conditions applied in the pilot SF–MS unit. To improve the organic loading rate (OLR), a semi-continuous configuration coupled to UF system was applied by separating and recirculating the solids fraction of the fermented sludge to the fermentation reactor. This way the SRT was maintained higher than HRT. The experimentation was divided in 5 periods. In period 1 (days 1–40) the pH was not controlled. This period of experimentation was the baseline, against which the other periods were evaluated. During period 2 (days 41–80) and period 5 (days 151–180) caustic soda was added in order to maintain the pH in the range of 9.5–10.5, while in periods 3 (81–120) and 4 (121–150) wollastonite (10 g/L) was added in order to buffer the pH and avoid the addition of chemicals in the alkaline fermentation process. During the whole experimentation the fermentation process was conducted by applying an HRT in the range of 4.6–5.9 days, based on the results obtained in batch tests. Two different SRT (5 and 14 days) were applied to assess the effect of SRT on the fermentation process. In periods 1–3 the process was conducted at high SRT = 14 days, while during periods 4–5, the SRT was kept very close to HRT (around 5–6 days).

#### 2.5. Kinetics of nutrients removal in municipal WWTPs

Ex-situ (batch) biomass activity tests were conducted to evaluate the rate of nutrient removal from municipal wastewater. The FL produced under different operating conditions was applied in batch reactors as an external carbon source to favor nutrient removal. In the specific nitrogen uptake rate (sNUR) tests, 500 mL of activated sludge were collected from the municipal WWTP of Carbonera (Italy) at the end of anoxic phase and were placed in 1 L Erlenmeyer flasks under mild agitation. The top part of the flask was covered with aluminum foil to avoid direct contact with air. Subsequently, the biomass was spiked with fixed nitrate concentration and with an external carbon source (caustic soda-SFL or wollastonite-SFL) and the nitrite, nitrate and phosphate profiles were recorded. The effect of the SFL on the specific phosphorus uptake rate (sPUR) and on the specific phosphorus release rate (sPRR) was evaluated in batch tests following the procedure of Janssen et al. (2002). To determine the sPRR, biomass was collected at the end of the anoxic period and was initially placed in mild agitation until the NO<sub>x</sub>-N was absent. Then, the biomass was placed in a sealed vial under agitation and argon gas was supplied to completely remove oxygen. Subsequently, the biomass was spiked with a known PO<sub>4</sub>-P concentration and with the carbon source (i.e. sludge fermentation liquid and acetic acid). The external carbon source was dosed at the beginning of the anaerobic

phase in order to have an initial soluble COD/PO<sub>4</sub>-P ratio in the range of 11–13 kgCOD/kgPO<sub>4</sub>-P. The variation of nitrite, nitrate, SCFAs and phosphate with time was recorded. In all batch activity tests, the temperature was maintained at 23 ± 2 °C and the pH at 7.5 ± 0.3 using NaHCO<sub>3</sub> and NaOH. Three replications were conducted for each activity test. The reported activity values have been normalized to the reference temperature of 20 °C using the Arrhenius temperature correction equation and to the VSS concentration of the mixture. The data reported were the average of measurements for three different replicates.

#### 2.6. Analytical methods

All analyses were conducted in triplicate. Total and volatile solids (TS, VS) TSS, VSS, pH, COD, sCOD ammonium, total nitrogen (TN), total phosphorus (TP), CST and TTF were determined according to standard methods (APHA AWWA WEF, 1998). The sCOD was determined by filtering the sample through Whatman 0.45 µm membrane filters and determining the COD in the permeate. For the TTF test a 1:5 dilution was applied. CST and TTF were normalized to total solids (TS). Nitrite, nitrate, and phosphate were measured by ion chromatography (Dionex ICS-90 with AG14 and AS14 columns) in samples that were first filtered through 0.20 µm Whatman membranes. SCFAs were analyzed by gas chromatography (Column: Nukol 15 m, 0.53 ID; temperature 85–125 °C, 30 °C min<sup>-1</sup>; carrier: N<sub>2</sub>, 5 mL min<sup>-1</sup>).

#### 2.7. Statistical analysis

The normality of distribution of investigated parameters was assessed. All parameters in the study were distributed normally. Data were expressed as mean ± standard deviation. Two-tailed *t*-tests were used to determine whether there were significant differences in the results concerning SCFA production, filtration performance and dewatering characteristics. Analysis of variance by one way ANOVA (with Tukey's post hoc test) was used to compare mean nutrient removal rates measured with different carbon source. The results were considered as statistically significant when  $p < 0.05$ . Statistical analysis was carried out using the STATISTICA 8.0 (StatSoft Software).

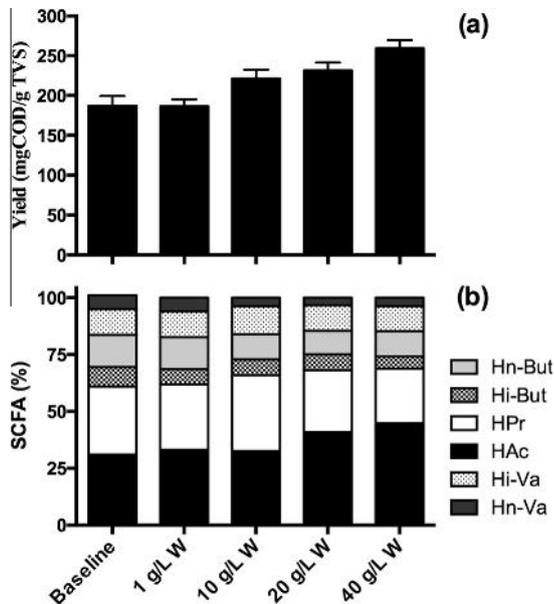
### 3. Results and discussion

#### 3.1. Sewage sludge characteristics

The main physicochemical characteristics of the sewage sludge used in the pilot and bench scale fermentation reactors are the following: pH = 6.4 ± 0.3, TSS = 19,140 ± 151 mg/L, VSS = 15,645 ± 164 mg/L, COD = 18,221 ± 855 mg/L, sCOD = 274 ± 56 mg/L, TP = 291.1 ± 49, soluble phosphorus = 12.6 ± 2.7 mg P/L, TN = 729.3 ± 121 mg N/L and soluble nitrogen = 46.1 ± 13 mg N/L.

**Table 1**  
Operating conditions of the SF–MS (average ± standard deviation) (number of samples = 15).

Parameter	Period 1	Period 2	Period 3	Period 4	Period 5
Days of operation	1–40	41–80	81–120	121–150	151–180
Mean for pH adjustment	–	Caustic soda	10 g/L wollastonite	10 g/L wollastonite	Caustic soda
pH	5.71 ± 0.45	10.1 ± 0.25	7.15 ± 0.06	7.11 ± 0.02	9.99 ± 0.32
Solids fed (gTVS/L)	7.17 ± 3.19	7.33 ± 0.41	8.54 ± 1.41	9.50 ± 0.51	9.23 ± 0.97
Solids in reactor (gTVS/L)	16.73 ± 3.95	23.51 ± 3.67	25.18 ± 1.58	14.41 ± 1.12	14.39 ± 0.69
HRT (d)	5.42 ± 1.10	5.93 ± 1.05	4.62 ± 0.51	5.13 ± 0.11	5.16 ± 0.23
SRT (d)	13.63 ± 0.58	14.17 ± 1.21	13.83 ± 0.32	6.13 ± 0.55	5.21 ± 0.60
Temperature (°C)	35 ± 1	35 ± 1	35 ± 1	35 ± 1	35 ± 1
Flow UF module (m <sup>3</sup> /h)	–	5.71 ± 0.98	7.18 ± 0.12	–	–
TMP (bar)	–	0.68 ± 0.06	0.71 ± 0.06	–	–

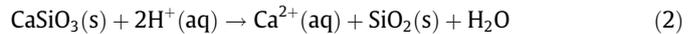


**Fig. 2.** (a) SCFA production and (b) SCFA composition in the fermentation liquid in which different wollastonite concentrations (1, 10, 20, 40 g/L, 37 °C) have been added. Control: no wollastonite addition. Error bars represent the standard deviation of triplicate samples (Hn-Va = n-Valeric acid, Hi-Va = Iso-Valeric acid, Hn-But = n-Butyric acid, Hi-But = Iso-Butyric acid, HPr = Propionic acid, HAC = Acetic acid).

### 3.2. Effect of wollastonite concentration on sludge fermentation in bench scale

Fig. 2 shows the effect of different wollastonite concentrations (1–40 g/L) on the SCFA production (Fig. 2a) and on the SCFA composition (Fig. 2b) obtained for the bench scale reactors. The increase of wollastonite concentration from 1 to 40 g/L resulted in an increase in the yield of SCFA production from 187 to 259 mgCOD/gTVS. The higher concentration of wollastonite maintained the pH of the fermentation sludge at higher levels, thus favoring the production of SCFAs. The use of elevated concentrations of wollastonite also enhanced the proportion of acetic acid and propionic acid in the SFL. HAC was the most abundant acid (35–47% of the total SCFAs) and HPr the second one (23–33%) (Fig. 2b). Fig. 3a shows the phosphorus release and Fig. 3b the pH trend measured with different wollastonite concentrations. When wollastonite was added a significantly lower phosphorus release into the liquid was observed, while nitrogen release was

similar for the examined mineral concentrations (average of 354 mg N/L). P release was very low (less than 2 mg/L) when mineral was dosed at concentrations of 10–40 g/L, while the use of the lowest wollastonite concentration (i.e. 1 g/L) did not affect the P release in the liquid (Fig. 3a). Although the mineral was only added at the first day of the fermentation process, the pH did not decrease significantly. When 20 and 40 g/L of wollastonite were added, the pH was maintained above 7 and 8 respectively the first 3 days of the process (Fig. 3b). In the presence of acids, the following reaction can occur:

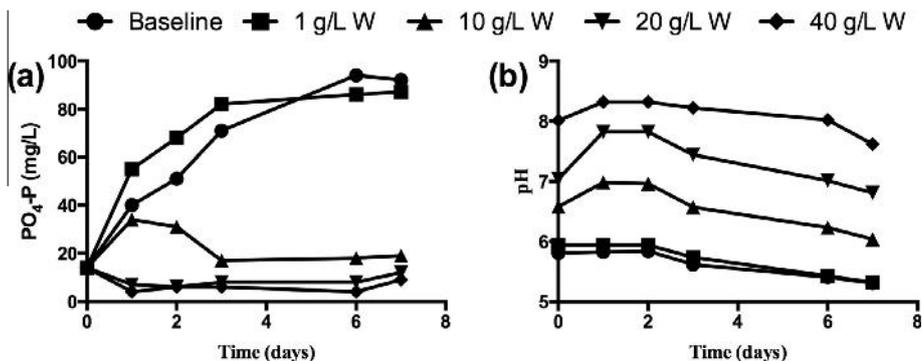


As seen in the above reaction  $\text{H}^+$  is consumed and it is thus possible to maintain a basic pH (8–9). Besides, an increasing pH results in precipitation as  $\text{CaCO}_3$  and  $\text{Ca}_3(\text{PO}_4)_2$  with a subsequent reduction of P release in the liquid phase. The production of SCFAs by alkaline fermentation is highly dependent on pH; the maximum production was obtained after 5 days. The use of alkali silicate mineral seems to be a sustainable way for buffering the pH during the alkaline fermentation process. In the pilot scheme a concentration of 10 g/L was applied, as this was the lowest mineral concentration resulting in very low release of  $\text{PO}_4\text{-P}$  in the liquid and satisfactory buffering of the pH in the reactors. At the same time 10 g/L is a realistic concentration that can be applied in full scale reactors without causing operation problems such as excessive membrane clogging and increased operating expenses.

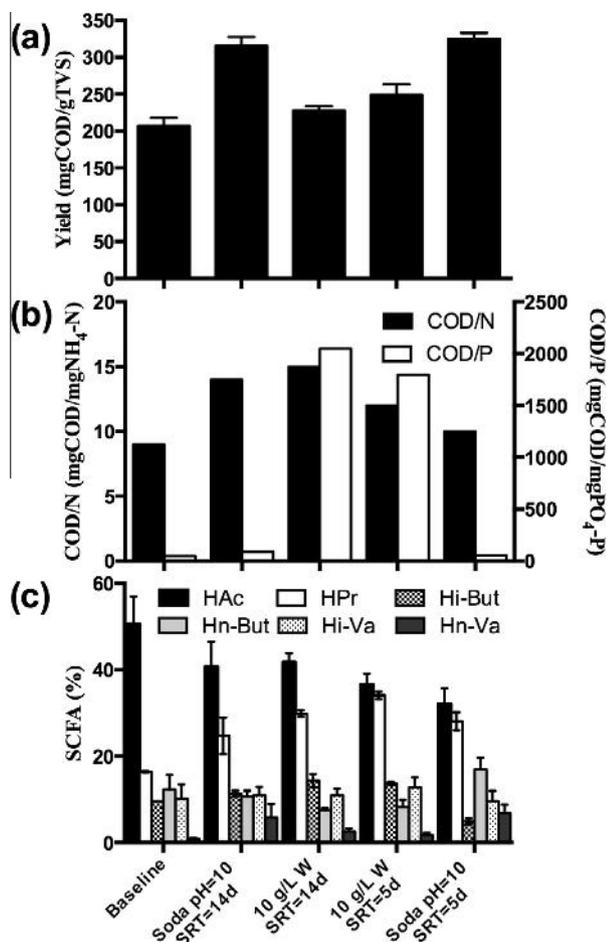
### 3.3. Pilot scale SF–MS process

#### 3.3.1. Sludge fermentation

Fig. 4a–c show the effect of wollastonite and caustic soda addition as pH buffering agents on the performance of the fermentation processes in terms of (1) SCFA production, (2) SCFA composition and (3) nutrient release. The figure also shows the impact of two different SRTs that were applied. The average total SCFAs production was 206.5, 315.6, 227.9, 248.6 and 325.0 mgCOD/gTVS for periods 1, 2, 3, 4 and 5 respectively. In period 1 (baseline period), pH adjustment was not carried out and as result, the pH in the fermentation reactor ranged between 5.3 and 6.5. The addition of NaOH (period 2) increased significantly the SCFA production yield ( $p < 0.001$ ) while the addition of 10 g/L of wollastonite (period 3) resulted in a small increase in the SCFA yield compared with the control period. Consequently, caustic soda was a more effective buffering solution than wollastonite (2nd vs 3rd column of Fig. 4a). The actual pH achieved with the use of soda was 10, while the addition of 10 g/L of wollastonite increased and stabilized the pH of the process up to 7 ( $p < 0.001$ ).



**Fig. 3.** (a) P release and (b) pH time profile during the fermentation of sewage sludge at different wollastonite concentrations (1, 10, 20, 40 g/L, 37 °C). Baseline: no wollastonite addition. The data reported are the average of triplicate samples.



**Fig. 4.** (a) SCFA yield, (b) COD/N and COD/P ratio in the liquid phase (c) SCFA composition in the different periods (W corresponds to 10 g/L of wollastonite addition). The data reported are the average of triplicate samples. Error bars represent the standard deviation of triplicate samples (Hn-Va = n-Valeric acid, Hi-Va = Iso-Valeric acid, Hn-But = n-Butyric acid, Hi-But = Iso-Butyric acid, HPr = Propionic acid, HAC = Acetic acid).

When the wollastonite was used to buffer the pH, the SFL obtained had lower PO<sub>4</sub>-P concentrations compared to the baseline period ( $p < 0.001$ ) due to precipitation as struvite crystals and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. The content of NH<sub>4</sub>-N and PO<sub>4</sub>-P concentration in the fermentation liquid is critical for its further use in the BNR. As witnessed by the high ammonium and phosphate concentration in the fermentation liquid of the baseline experiment, the fermentation process causes significant organic nitrogen and phosphorus release in the liquid as ammonia/ammonium and phosphate respectively. In several studies the nitrogen and phosphorus that was released could be effectively recovered through struvite crystallization by adding magnesium (Benisch et al., 2009; Yuan et al., 2009). However, this process is sustainable only when the ammonium to phosphate molar ratio is adequately balanced in the fermentation liquid in order to be removed as struvite.

**Table 2**

Nutrient removal kinetics obtained with the use of different carbon sources during ex situ biomass activity tests (average ± standard deviation of triplicate experiments). Numbers with different symbols are significantly different ( $p < 0.05$ ). Symbols shared in common between the numbers of the same parameter would indicate that they are not significantly different. The comparison is always made between the numbers of the same parameter.

Parameter	Wastewater	Acetic acid	Soda-SFL	Wollastonite-SFL
sNUR (mg N/g VSS h)	1.12 ± 0.22	3.54 ± 0.31*	4.46 ± 0.41**	4.36 ± 0.30**
sPRR anaerobic (mg P/g VSS h)		1.24 ± 0.23*	1.98 ± 0.46**	1.83 ± 0.49**
sPUR aerobic (mg P/g VSS h)		1.31 ± 0.27*	1.97 ± 0.41**	2.06 ± 0.26**
sPUR anoxic (mg P/g VSS h)		0.35 ± 0.15	0.35 ± 0.12	0.42 ± 0.20

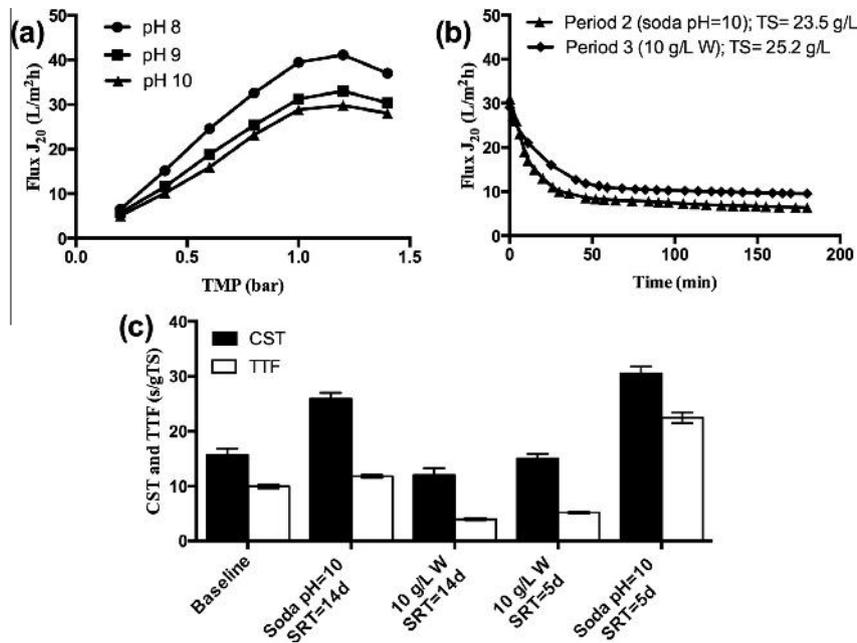
The influence of caustic soda, wollastonite and SRT on the composition of SCFAs is shown in Fig. 4c. The increase of SRT from 5 to 14 d resulted in an increase in the proportion of HAC and in a decrease of HPr both in the cases where wollastonite and caustic soda were added with sufficient statistical significance ( $p < 0.05$ ) while the proportion of the other SCFAs remained relatively stable. It also seems that when wollastonite is used, SFL is characterized with higher amount of HPr ( $p < 0.05$ ).

### 3.3.2. Filtration performance and dewatering characteristics

The fermented sewage sludge was separated in the solid and the liquid stream through membrane filtration in order to obtain a liquid stream with low suspended solids and very high SCFAs. The high temperature maintained in the fermentation unit (35 °C) is expected to favor the subsequent filtration process. The filtration performance decreased with time due to the deposition of soluble and particulate matter on the membrane surface. The filterability of the caustic soda fermentation effluent was evaluated by the step-flux filtration test (Fig. 5a). The increase in permeate flux resulted in a linear increase of TMP. However, above a certain TMP value the permeate flux decreased. Moreover, the increase of pH negatively affected the permeate flux, confirming that the sludge dewatering characteristics and the separation process are adversely affected from the addition of caustic soda (Su et al., 2013). Another factor that impacted on the dewatering characteristics of the fermented effluent is the type of the agent/additive that is used during the fermentation process. Fig. 5b shows the permeate flux versus time of a typical filtration run for periods 2 and 3. The average flux measured for soda-fermented sludge was 9.5 L/m<sup>2</sup> h. Compared to soda, the flux increased by 32% (12.5 L/m<sup>2</sup> h) when wollastonite-fermented sludge was used ( $p < 0.001$ ). The fermented sludge filterability was evaluated through CST and TTF tests. When wollastonite was added, the average CST and TTF decreased by 51% and 59% respectively. The addition of 10 g/L of wollastonite resulted in more favorable dewatering characteristics with a confidence interval higher than 95% (Fig. 5c). However, during the whole operation of the UF unit clogging phenomena in the membrane module and in the feed pumps frequently occurred due to the presence of fibrous materials in the sewage sludge. When these problems occurred a sudden drop of membrane permeability was recorded. The implementation of an effective pre-treatment step is essential. The use of grinding, upstream of the fermentation, could eliminate the occurrence of this problem.

### 3.4. Nutrients removal from wastewater

The fermentation liquid produced during periods 2–3 was tested as carbon source in ex situ biomass activity tests to evaluate and compare the rate of nitrogen and phosphorus removal against that achieved with acetic acid use (Table 2). Similar rates were obtained with the use of SFL produced with caustic soda and wollastonite. Compared to synthetic HAC the use of SFL increased the nutrient removal kinetics of nitrogen (21% and 19%) and phosphorus (37% and 39%) ( $p < 0.05$ ). The presence of high concentration of propionic acid in the alkaline fermentation liquid can explain



**Fig. 5.** (a) Permeate flux versus TMP for different pH values of the soda fermented effluent (20 °C, TS = 14.2 g/L); (b) permeate flux variation with time for fermentation effluent in which caustic soda and wollastonite have been added (constant TMP = 0.7 bar); (c) CST and TTF of the fermented effluent for the different experimental periods. The data reported are the average of triplicate samples. Error bars represent the standard deviation of triplicate samples.

the higher removal of phosphorus compared to the one obtained when HAC was applied. Furthermore, higher nitrogen removal rate has been demonstrated in cases where HPr together with HAC were contained in the carbon source used for the BNR process (Frison et al., 2013a).

### 3.5. Mass balances SF–MS

The mass balance obtained for the SF–MS system is reported in Fig. 6. When caustic soda was added in the fermentation process (Fig. 6a), more effective hydrolysis took place compared to the use of wollastonite (Fig. 6b). As a result, higher dissolution of particulate COD was observed and the SFL contained more soluble COD and soluble nutrients compared to the SFL in which wollastonite was added. Furthermore, the use of caustic soda resulted in a smaller amount of COD loss as biogas compared to that lost when wollastonite was added, since at pH 10 the activity of methanogenic bacteria was inhibited to a higher extent. The addition of wollastonite in the fermentation process resulted in more phosphorus removal as waste sludge and much less in the fermentation liquid (Fig. 6b), since a significant amount of soluble phosphorus precipitated.

### 3.6. Comparison of alternative fermentation conditions and post-treatment options

Table 3 summarizes the characteristics of the SFL produced at different operating conditions. Table 4 compares the results of this study with existing literature. The fermentation of sewage sludge resulted in the production of SFL with total SCFA concentration of 3–8 gCOD/L and yields up to 316 mgCOD/gTVS. The alkaline conditions (with dosage of caustic soda and wollastonite) increased the SCFAs production. The application of high pH (10 with caustic soda) led to higher hydrolysis of particulate matter, and thus higher SCFAs in SFL. However, this was also associated with a higher nutrients release in the liquid phase, with the ammonium reaching a concentration up to 512 mg N/L and the phosphate

82 mg P/L. The use of wollastonite reduced P concentrations to 1–2 mg P/L, resulting in a more favorable COD/N/P ratio. HAC and HPr were the most abundant acids in the SFL, consisting of 60–70% of total SCFAs. Differences in the acids composition of the SFL did not influence significantly the kinetics of N and P removal from wastewater.

Compared to the use of caustic soda, the alkali silicate minerals may enhance the economical and environmental sustainability of the fermentation process, together with the S/L separation properties of the fermented sludge. When comparing the benefits of sludge fermentation liquid against commercially available carbon, usually this analysis does not consider the concept of sustainability or GHG emissions, particularly from methanol and acetic acid production. These issues are becoming more prominent in the decision-making processes of many utilities and it can be a positive factor when deciding for the implementation of sludge fermentation at a wider scale.

### 3.7. Future perspectives for sludge alkaline fermentation

In the short-cut biological nutrient removal, the simultaneous denitrifying via nitrite biological phosphorus removal (DNBPR) offers the possibility to integrate phosphorus and nitrogen removal in a robust process. In this process ammonium is oxidized to nitrite under aerobic conditions, while under anoxic conditions denitrification and phosphate uptake via nitrite occur when an adequate carbon source is supplied (Frison et al., 2013b). The addition of commercially available acids increases not only the WWTP carbon footprint, but also the operating expenses of liquid treatment and sludge processing, since sludge production will increase as well (Yuan et al., 2009). On the other hand, the use of an internal carbon source (i.e. coming from fermentation of primary sludge or/and WAS generated in WWTPs) seems a more attractive option. This way sludge becomes a resource to be used in the WWTP as an inexpensive organic substrate for SCFAs production.

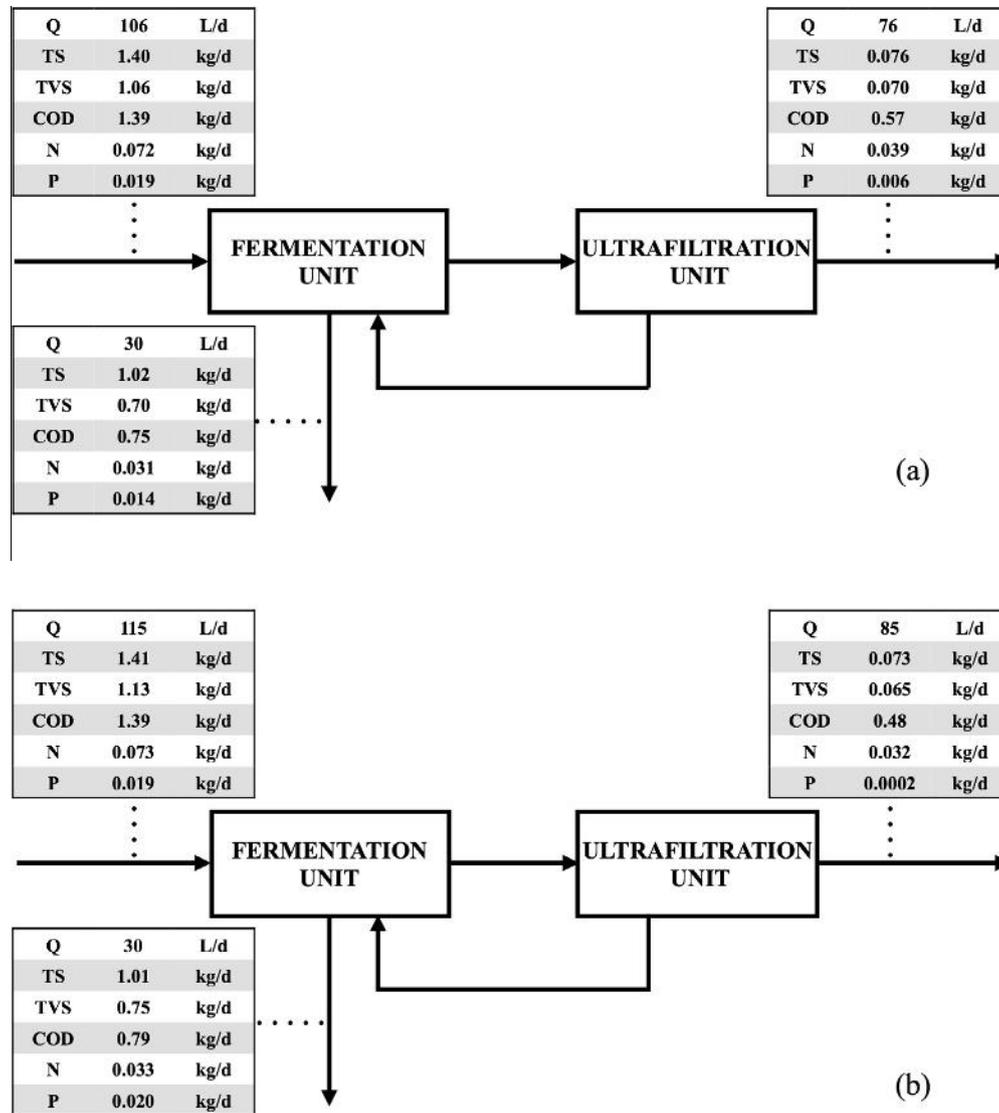


Fig. 6. Mass balances for the SF-MS process for (a) period 2 with the use of caustic soda and (b) period 3 with the use of wollastonite.

Table 3

Comparison of the characteristics of the SFL produced with the use of caustic soda and 10 g/L wollastonite and its impact on nutrient removal (average  $\pm$  standard deviation) (number of samples = 28).

Parameter	Period 1 (SFL)	Period 2 (soda-SFL)	Period 3 (W-SFL)	Period 4 (W-SFL)	Period 5 (soda-SFL)
SCFAs (mgCOD/L)	3389 $\pm$ 1320	7453 $\pm$ 1092	5596 $\pm$ 448	3738 $\pm$ 411	3184 $\pm$ 219
Hac (mgCOD/L)	1064 $\pm$ 421	2961 $\pm$ 494	2333 $\pm$ 187	1572 $\pm$ 210	1605 $\pm$ 94
HPPr (mgCOD/L)	959 $\pm$ 396	1803 $\pm$ 407	1675 $\pm$ 160	1129 $\pm$ 56	522 $\pm$ 41
Hbut (mgCOD/L)	778 $\pm$ 154	1299 $\pm$ 169	830 $\pm$ 71	603 $\pm$ 74	306 $\pm$ 51
Alkalinity pH 5.7 (mg CaCO <sub>3</sub> /L)	883 $\pm$ 121	1338 $\pm$ 86	1095 $\pm$ 188	1160 $\pm$ 113	1605 $\pm$ 34
Alkalinity pH 4.3 (mg CaCO <sub>3</sub> /L)	3150 $\pm$ 314	3363 $\pm$ 50	2568 $\pm$ 146	2082 $\pm$ 58	2325 $\pm$ 39
NH <sub>4</sub> -N released	330 $\pm$ 128	512 $\pm$ 25	372 $\pm$ 22	236 $\pm$ 12	326 $\pm$ 34
PO <sub>4</sub> -P released	72.2 $\pm$ 34	81.8 $\pm$ 5.3	2.1 $\pm$ 1.9	1.8 $\pm$ 0.7	59.8 $\pm$ 11
COD/N/P (gCOD/gN/gP)	47/4.6/1	91.1/6.3/1	2664/180.3/1	1876/125.9/1	53.2/5.4/1
Flux (L/m <sup>2</sup> h)		9.5 $\pm$ 1.6	12.5 $\pm$ 1.8		
CST (s/gTS)	15.64 $\pm$ 2.9	25.89 $\pm$ 3.1	12.03 $\pm$ 1.5	15.06 $\pm$ 1.1	30.48 $\pm$ 2.3
TTF (s/gTS)	9.94 $\pm$ 1.1	11.77 $\pm$ 1	3.94 $\pm$ 0.30	5.19 $\pm$ 0.4	22.44 $\pm$ 2.1
sPUR (mg P/g VSS h)	–	1.97 $\pm$ 0.41	2.06 $\pm$ 0.26		
sNUR (mg N/g VSS h)	–	4.46 $\pm$ 0.41	4.36 $\pm$ 0.30		

**Table 4**  
Comparison of sludge fermentation – S/L separation efficiency obtained in this work with literature.

Main conditions of fermentation	Post-treatment	Efficiency (mgCOD/gTVS)	SCFAs (mgCOD/L)	COD/N/P (gCOD/gN/gP)	CST/TTF (s/gTS)	References
pH = 10; NaOH; T = 35 °C	Membrane (UF)	316	7453	91.1/6.3/1	CST = 25.8 TTF = 11.7	Current study
pH = 7.1; 10 g/L W; T = 35 °C	Membrane (UF)	228	5596	2664/180.3/1	CST = 12.1 TTF = 3.9	Current study
pH = 10 NaOH or Ca(OH) <sub>2</sub> ; HRT = 8d; T = 25 °C	Struvite/dewatering	–	2765/2480	709/6.8/1 4133/78.6/1	CST < 100 s	Li et al. (2011)
pH = 10 NaOH	–	–	2606	18.9/1.9/1	–	Jiang et al. (2009)
NaOH and Ca(OH) <sub>2</sub>	–	303	1800	–	CST = 80 s	Su et al. (2013)
pH = 11; T = 60 °C	Struvite	259	2437	661/6.9/1	–	Mengmeng et al. (2009)
		(mgTOC/gVSS)				

#### 4. Conclusions

The long-term operation of the pilot scale alkaline sludge fermentation-membrane separation unit was examined. The use of 10 g/L wollastonite was beneficial as it maintained the pH above 7.0, increasing the SCFAs production, enhancing filterability and limiting the release of nutrients in the SFL. The sludge dewatering characteristics and the separation process were adversely affected from the use of caustic soda. The addition of wollastonite during fermentation was beneficial for filterability as the flux increased from 9.5 to 12.5 L/m<sup>2</sup> h. When fermentation liquid was applied to wastewater, the nutrient removal kinetics were improved compared to the use of acetic acid alone.

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