## Phosphorus recovery and VFAs production from sewage sludge fermentation

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Modern wastewater treatment, driven mainly by limited natural resources, emerged the need to change the focus from treating wastewater and sludge only for their safe disposal to recovering the valuable resources such as energy and nutrients from these wastewater streams. In this regard, sewage sludge represents an important source of carbon and nutrients, mainly phosphorus ( $PO_4^{3-}$ -P), that can be recovered and/or transformed to valuable products such as struvite, volatile fatty acids (VFAs), cellulosic fibres, enzymes (Healy *et al*, 2015). Among them, VFAs have been demonstrated that can be used as readily biodegradable carbon source to enhance the biological phosphorus removal (EBPR) or for the production of more advanced final products, such as biopolymers polyhydroxyalkanoates (PHAs). VFAs can be obtained from the fermentation of sewage sludge, and its final use depends on the VFA composition in fermented sludge (Singhania *et al*, 2013; Lee *et al*, 2014). Moreover, the recovery and subsequent reuse of phosphorus contributes simultaneously to the conservation of the mineral phosphorus reserves and eutrophication prevention. The crystallisation of struvite (MgNH4PO4·6H2O) could be a sustainable alternative to recover phosphorus from the fermented sludge. This crystallisation process is not only used for recovering phosphorus but also generates a product with commercial value as a fertilizer (de-Bashan and Bashan, 2004). Thus, the aim of this work was to study the fermentation of primary sludge (PS), secondary sludge (WAS) and a mixture of PS and WAS (PS&WAS) in order to maximise the production of VFAs as well as the recovery of PO4<sup>3-</sup>-P by struvite crystallisation.

For this work fresh thickened sewage sludge was collected once a week from the municipal WWTP of Verona (Veneto Region, Italy). Here the PS and the WAS are thickened up to 30-58% total solids (TS) by a gravity belt thickening (Klein Technical Solutions) and a screw drum (Huber, Screw Thickener RoS 2), respectively. The sludge was stored in a fridge at 2°C of temperature. Besides separate testing of PS and WAS, even the mixture of PS and WAS was prepared in the laboratory based on a ratio of 1:1 v/v. A sequencing batch fermentation reactor (SBFR) with a working volume of 4 litres was operated under three main periods, based on the sludge types fed: WAS, WAS&PS and PS. The reactor was equipped with a blade stirrer installed in the bottom, while the temperature was maintained constant at  $37\pm1$  °C by a thermostatic bath, and without pH control. The HRT was kept at 4 days by the daily discharge <sup>1</sup>/<sub>4</sub> of the reactor and replacing the same volume with fresh sewage sludge. Samples were periodically taken from the fermentation reactor in order to determine the concentrations of PO<sub>4</sub>-P, NH<sub>4</sub>-N, VFAs, soluble chemical oxygen demand (soluble COD), total solids (TS), volatile solids (VS) and pH. Once the operation of SFBR was stable, PO<sub>4</sub><sup>3-</sup>-P recovery from sludge fermentation liquid (SFL) by struvite crystallisation was studied. Mg(OH)<sub>2</sub> was used as Mg<sup>2+</sup> and alkali sources to promote struvite crystallisation. The crystallisation pH was fixed at 8.5. The experimental time was 60 min. The concentration of PO<sub>4</sub>-P was determined during the experimental time. All the samples were centrifuged and filtered through cellulose membrane filters.

For each experimental period, operational pH remained stable and it was around 7.1±0.4, 5.3±0.3 and 5.1±0.3 for the fermentation of WAS, PS&WAS and PS, respectively. Figure 1 shows the concentration of VFAs and its composition in the fermented sludge for the whole experimental time. The production of VFAs from the cofermentation of WAS & PS was higher than from the fermentation of PS and WAS. Besides, as expected, the production of VFAs from WAS fermentation was lower than for the fermentation of PS. The average production of VFAs was 159.1±32.4, 209.6±11.0 and 222.0±19.2 mg COD/gVSfed for WAS, PS&WAS and PS fermentation, respectively. Regarding the composition of VFAs, acetate and propionic acids were the dominant VFAs in the SFL for all sludge fermentations. For WAS fermentation, mainly acetic (24-50% of the total VFAs) and propionic acids (15-31%) were produced, while n-butyric and n-valeric constituted approximately 14-28% and 8-30% of the total VFAs, respectively. Total VFAs contributed about 44.9% of the soluble COD in the fermented WAS, indicating that the presence of large amounts of organic soluble compounds in this fermented sludge. Meanwhile, acetic (35-39% of the total VFAs) and propionic acids (40-44%) were the most prevalent VFAs in the SFL of fermented PS. Also, n-butyric (11-15%) and n-valeric (6-13%) acids were detected. Total VFAs contributed to about 60.2% of the soluble COD in fermented PS. For PS&WAS fermentation, acetic acid was the dominant VFAs in the liquid fraction (35-46%) and propionic acid was the second one (30-36%). The percentage of n-butyric with n-valeric acids over total VFAs varied between 6% and 20%. VFAs represented around 45.9% of the soluble COD in the fermented PS&WAS. From the aforementioned results it can determined that the ratio of propionic acid to acetic acid for secondary sludge fermentation was higher than for primary sludge fermentation. The ratio of propionic/ acetic acids was 0.6, 0.8 and 1.2 for WAS, PS&WAS and PS fermentation, respectively. Thus, the fermentation of PS allows to obtain high percentages of acetic and propionic acids over total VFAs. From these results it was determined that the sludge type used affects the composition of VFAs produced during the fermentation process.

On the other hand, the release of  $PO_4^{3-}P$  and  $NH_4^{+}-N$  was observed during the operation of SBFR, significant amounts of these nutrients were obtained for all sludge fermentation periods. In contrast to the production of VFAs, the highest release of  $PO_4^{3-}P$  and  $NH_4^{+}-N$  was observed from the fermentation of WAS, achieving average release of  $NH_4^{+}-N$  and  $PO_4^{3-}P$  of 32.6±8.5 mg  $NH_4^{+}-N/g$  VS<sub>fed</sub> and 1.6±0.4 mg  $PO_4^{3-}-P/g$  VS<sub>fed</sub>. While the average release of nutrients from WAS+PS fermentation was 21.1±3.3 mg  $NH_4^{+}-N/g$  VS<sub>fed</sub> and 1.3±0.4 mg  $PO_4^{3-}-P/g$  VS<sub>fed</sub>. The average concentration of released  $PO_4^{3-}P$  and  $NH_4^{+}-N$  from the SFL of PS was 7.5±1.6  $NH_4^{+}-N/g$  VS<sub>fed</sub> and 1.0±0.2 mg  $PO_4^{3-}-P/g$ VS<sub>fed</sub>. The average concentration of  $PO_4^{3-}-P$  in these SFLs was between 60.2 and 72.8 mg  $PO_4^{3-}-P/L$ . Meanwhile the average concentration of  $NH_4^{+}-N$  was between 440 and 1170 mg  $NH_4^{+}-N/L$ . So, struvite crystallization experiments were developed in order to determine the feasibility of  $PO_4^{3-}-P$  recovery from these SFLs. For all struvite crystallisation experiments,  $PO_4^{3-}-P$  was the limiting factor in this crystallisation process and the concentration of  $PO_4^{3-}-P$  was measured to estimate the efficiency of struvite crystallisation from the SFL. The highest  $PO_4^{3-}-P$  recovery percentage, 96%, was obtained from the SFL of co-fermentation of PS&WAS. While, the recovery percentages of  $PO_4^{3-}-P$  obtained from the SFL of PS and WAS fermentations were 89.0% and 81%, respectively. Thus, the efficiency of  $PO_4^{3-}-P$ recovery from the fermented sludge was higher than 81.0%. From the aforementioned results it can be concluded that it is feasible to recover phosphorus from sewage sludge fermented by struvite crystallization.

Therefore, the fermentation of sewage sludge could be a suitable source of VFAs and  $PO_4^{3-}P$ , in which it is possible to recover  $PO_4^{3-}P$  by struvite crystallisation and then it could be used as carbon source for other biological processes, such as biological nutrients removal or PHAs production.

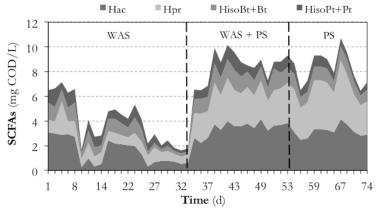


Figure 1. VFAs concentration and its composition in the sludge fermentation liquid for WAS, WAS&PS and PS.

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