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Production of carboxylates from high rate activated sludge through fermentation

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HIGHLIGHTS

- pH of 7 and 35 °C were found as optimal parameters for A-sludge fermentation.
- Fermentative inoculum presence enhances carboxylate production from A-sludge.
- A-stage sludge produces more VFA compared to waste activated sludge values.
- Iron content is directly proportional to CH_4 but not to carboxylate production.

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ABSTRACT

The aim of this work was to study the key parameters affecting fermentation of high rate activated A-sludge to carboxylates, including pH, temperature, inoculum, sludge composition and iron content. The maximum volatile fatty acids production was 141 mg C g^{-1} VSS_{fed}, at pH 7. Subsequently the potential for carboxylate and methane production for A-sludge from four different plants at pH 7 and 35 °C were compared. Initial BOD of the sludge appeared to be key determining carboxylate yield from A-sludge. Whereas methanogenesis could be correlated linearly to the quantity of ferric used for coagulation, fermentation did not show a dependency on iron presence. This difference may enable a strategy whereby A-stage sludge is separated to achieve fermentation, and iron dosing for phosphate removal is only implemented at the B-stage.

1. Introduction

For domestic and industrial wastewater the focus for reuse has been on the water itself as well as the energy contained within the organics (Verstraete and Vlaeminck, 2011). Domestic sewage could also be a source of products such as nutrients or volatile fatty acids (VFAs) that can be used as building blocks for the production of valuable products such as medium and long chain fatty acids, alcohols and Polyhydroxyalkanoates (PHA) (Agler et al., 2011; Kleerebezem et al., 2015; Lee et al., 2014) among the others. However, the typical issue with domestic wastewater is its low organic concentration which impedes to obtain an economically feasible production process.

Several concentration technologies allow recovery of the clean water and increase the amount of organic matter for further processing (Meerburg et al., 2015; Verstraete et al., 2009). Best known is the "Adsorption-Belebungsverfahren" process (AB process, generally translated as Adsorption – Biodegradation or Adsorption – Bio-oxidation) (Boehnke et al., 1997), also termed "high-rate activated sludge". The AB process is a two-stage treatment system where the first stage, the highly loaded biological adsorption stage or A-stage, is a modification of the conventional activated sludge system (CAS) (Constantine et al., 2012). CAS is typically performed with, loadings of 0.25 kg BOD kg^{-1} VSS d^{-1} (PaDEP, 2014), high aeration and SRT of 8–20 days, with a low digestion efficiency of the sludge (waste activated sludge (WAS)) due to the high aeration and high sludge age. (Bolzonella et al., 2005). The A-stage is operated with high loadings (2–10 kg BOD kg^{-1} VSS d^{-1}), low hydraulic retention time (HRT 15–30 min) and solid retention time (SRT) between several hours and 1 day (Boehnke et al., 1998). These

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conditions determine bioflocculation with high biomass yields and minimal CO_2 formation, complemented with sorption and storage mechanisms that remove COD (Meerburg et al., 2015). The A-sludge is highly biodegradable and easily digested to biogas (Boehnke et al., 1998). The subsequent B-stage ensures polishing of the wastewater to meet discharge standards. Typically, the A-stage has a COD removal efficiency of 26–52% (De Graaff and Roest, 2012), and 80% of the excess sludge of the overall plant is withdrawn from the A-stage. The excess B-sludge is combined with the excess A-sludge before digestion to achieve energy neutrality at the facility level. The process is applied at full scale in several municipal wastewater treatment plants (WWTPs) and industrial plants (Boehnke et al., 1997). The limited experience to date does lead to considerably different operational approaches and hence different sludge properties (De Graaff and Roest, 2012).

Thus far the sludge valorization has been investigated through anaerobic digestion either as a single substrate (Huoqing et al., 2013; Meerburg et al., 2015) or in co-digestion with other organic waste streams (De Vrieze et al., 2013; Verstraete and Vlaeminck, 2011). In recent years, another route has come to the fore, the carboxylate platform, whereby mixed populations are used to ferment organic matter carboxylates that are the end product instead of biogas (Agler et al., 2011; Angenent et al., 2004). As past studies on hydrolyzed secondary sludge have shown that it is possible to ferment it although to a limited extent (Morgan-Sagastume et al., 2011; Pratt et al., 2012), the highly degradable A-sludge could be a more suitable source. The main interest in A-sludge fermentation is that VFA can be used as perfect additional carbon source to enhance biological nitrogen and phosphorous removal in waste water treatment plants (Lee et al., 2014), with no requirement of previous extraction from the sludge, avoiding acetate or methanol expenses for wastewater's with low carbon content. The fermentation can then be followed by anaerobic digestion for removal of unfermented organics. The potential of the A-sludge for carboxylate production in terms of conversion efficiencies and product outcomes, and how this could relate to residual digestion has not been yet explored.

Therefore, the goal of this study was to identify key parameters affecting fermentation of an A-sludge (here temperature and pH, inoculum addition and retention time) and subsequently assess the fermentation potential of A-sludge originating from different sites and to correlate this to different operational approaches. A prime example of a variable parameter is the iron content. Indeed considerable differences in iron concentration were found in the samples collected from the four WWTPs object of this study. Iron content was also different between the two time frames considered. In these sites salts of Fe(II) or (III) such as $FeSO_4$ and $FeCl_3$ are added in different concentrations to precipitate phosphates as $Fe_3(PO_4)_{2(s)}$ or $FePO_{4(s)}$ and to enhance the flocculation, coagulation and sedimentation of the A-sludge (Jiang and Graham, 1998). Furthermore, iron is important as coenzyme or cofactor in several enzymes involved in the anaerobic digestion process (Zandvoort et al., 2006). Methanogens require iron for their metabolic activity, and their capability to continue producing methane is strictly dependent on the presence and availability of the metal (Demirel and Scherer, 2011). The presence of iron in the sludge flocs can have a key impact for the methanogenesis, as the process is limited at low iron concentrations (Schattauer et al., 2011; Zandvoort et al., 2006). It is as yet unknown how this would impact fermentation. Similarly, A-sludge will vary in their BOD content and BOD/COD ratio, due to day-by-day variances at WWTPs level and in dilution and content of the domestic wastewater. Thus we measured key characteristics of different A-sludge and subjected them to fermentation and digestion.

2. Materials and methods

2.1. A-sludge collection

Auto-fermentation test without inoculum (see Section 2.2.1) were performed with A-sludge from Nieuwveer WWTP (Breda) in 11/2013 (COD 11.3 ± 0.5 g L^{-1}, TSS 9.1 ± 0.4 g L^{-1}, VSS 6.7 ± 0.3 g L^{-1}). In 1/2014 new sludge was collected (COD 4.3 ± 0.4 g L^{-1}, TSS 3.7 ± 0.5 g L^{-1}, VSS 2.8 ± 0.4 g L^{-1}) to ferment in the presence of an inoculum (Section 2.2.2). To compare the fermentative capacity of different A-sludge (Section 2.2.3), they were collected during two different time frames (2/2014 and 7/2014) from four WWTPs in the Netherlands: Nieuwveer WWTP (Breda), Dokhaven WWTP (Rotterdam), Utrecht WWTP (Utrecht) and Garmerwolde WWTP (Groningen). The characteristics of the A-sludge on those two sampling points are summarized in Table 1. To determine the effect of iron on the fermentation (Section 2.2.4), A-sludge was collected from Nieuwveer WWTP (Breda) in 10/2015 (COD 5.3 ± 0.5 g L^{-1}, TSS 2.2 ± 0.3 g L^{-1}, VSS 1.7 ± 0.0 g L^{-1}, Fe 171 ± 2 mg L^{-1}). Waste activated sludge (WAS) was collected from Dendermonde WWTP in 8/2015 (TS 58.7 ± 7.1 g kg^{-1}, VS 32.4 ± 7.3 g kg^{-1}, COD 45.1 ± 5.9 g L^{-1}).

2.2. Fermentation batch tests

All tests were performed in triplicate in serum flasks (120 mL) sealed with a rubber stopper and aluminum sealer. Headspace was flushed with N_2 at day 0 of all experiments which were kept temperature controlled and shaking at 120 rpm for a period of 7 or 14 days. Liquid and gas samples were taken periodically decreasing the frequency over the experiment. Biogas production was monitored for every sampling point. Chemical analysis procedures are defined in supplementary information.

2.2.1. Determination of key parameters during auto-fermentation

Eight conditions with combination of different pH (4.5, 5, 6, 7) and temperatures (35 °C and 55 °C) were carried with only 80 mL A-sludge. Control tests without pH control were performed for each temperature tested for both A-sludge and WAS from Dendermonde WWTP. The pH was adjusted to the desired value by adding 1 M NaOH or 1 M HCl after each sampling time.

2.2.2. Determination of the inoculum impact

Mixed culture inoculum from a fermenter (CSTR) treating diluted molasses (HRT 5 days, pH 5.5, T 35 °C, obtained after a stable working period of 110 days) for VFA production was previously acclimated to A-sludge as substrate at either mesophilic or thermophilic conditions. The tests were prepared by mixing 10 mL of inoculum, 30 mL of substrate and 40 mL of a pH buffer. Controls with only inoculum or only substrate by replacing either one of them with water were performed to normalize the final results. Batch tests were run combining pH (6 or 7) and mesophilic (35 °C) or thermophilic (55 °C) temperatures. pH control was carried out by means of a pH buffer (strength 200 mM H^+), prepared in tap water (pH = 6: 24.3 mg $NaH_2PO_4{\cdot}H_2O$ L^{-1} and 6.4 mg $Na_2HPO_4{\cdot}7H_2O$ L^{-1}; pH = 7:11.7 mg $NaH_2PO_4{\cdot}H_2O$ L^{-1} and 30.9 mg $Na_2HPO_4{\cdot}7H_2O$ L^{-1}).

2.2.3. Comparison of different A-sludge fermentative capacity

A-sludge from four different WWTP obtained either during the winter (February 2014) or the summer period (July 2014) were evaluated. The tests consisted of a mixture of substrate, inoculum and pH buffer as defined in Section 2.2.2. Controls with only inoculum and only substrate were also included. The tests were run at 35 °C and pH 7.