

The solubilisation of N and P during primary sludge acid fermentation and precipitation of the resultant P

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Abstract

Phosphorus (P) and ammonia (N) release, during anaerobic digestion of primary sludge for volatile fatty acid (VFA) production, was studied in laboratory batch experiments, at room temperature (daily maximum 18 to 28°C). Nutrient levels in the digester supernatant liquor averaged 0.03 mgP/mgVFA (as acetic acid) and 0.10 mgN/ mgVFA (as acetic acid), after 6 d fermentation time. The degree of solubilisation, from a fixed amount of sludge solids, was dependent on anaerobic storage time and sludge composition. Lime dosages of 60 to 400 g CaO/kg sludge solids were required to reduce the soluble phosphate levels in the sludge liquor to below 5 mg P/l. No re-release of phosphate occurred in the fermented sludge liquors after 2 d anaerobic storage time after lime dosing. Furthermore, the addition of settled sewage elutriant to fermented sludge to recover the soluble VFA, did not affect the lime dosage requirements (per kg sludge) for phosphate removal.

Introduction

Effluent from the Johannesburg waste-water purification works must comply with the 1.0 mg P/l *ortho*-phosphate discharge standard (Pitman et al., 1991). The ability of the biological nutrient removal (BNR) processes at these works to meet this standard is dependent on the characteristics of the influent waste water. Usually waste water with a high COD concentration, or in particular, low TKN/COD (0.05) and TP/COD (0.01) ratios performs well in most BNR plants. Moreover, feed waste water must have an enhanced concentration of readily biodegradable COD (RBCOD), in particular a high volatile fatty acid (VFA) fraction in the RBCOD (Barnard, 1984; Rabinowitz and Oldham, 1985; Canziani et al., 1995; Pitman, 1995). The VFAs pass readily through the cytoplasmic membrane of heterotrophic organisms present in the sewage flora of the BNR process, to be metabolised internally as a carbon or energy source (Lilley et al., 1990). Where feed sewage characteristics are not suitable, either the supernatant from high-rate anaerobic digestion of primary sludge is used to boost the VFA fraction in the feed sewage or supplementary chemical addition is required (Pitman, 1995). VFA yields averaging 0.09 mg VFA (as COD)/mg initial COD have been found, at laboratory scale, after 6 d fermentation time, for the Johannesburg waste-water treatment works primary sludges (Banister and Pretorius, 1998).

Experience has shown that the longer raw sludge undergoes acid fermentation or anaerobic digestion respectively, the greater the degree of P solubilisation (Murakami et al., 1987; Pitman et al., 1992; Skalsky and Daigger, 1995). In a survey of sludge liquors at the Johannesburg BNR works, anaerobically digested sludge liquors were found to have the highest P content (Pitman et al., 1991). This can cause additional nutrient loading on the BNR plant, but the benefits derived from VFA production during

acid digestion seem to outweigh the negative aspects of the nutrient release (Pitman, 1995). In addition, as most of the Johannesburg Waste-Water Treatment works include final sludge dewatering, special care needs to be taken to minimise P levels in sludge liquors recycled back to the inlet of the BNR reactors (Pitman et al., 1991; Jardin and Pöpel, 1996).

Chemical addition using lime, aluminium or iron salts is usually employed to precipitate the released P (Murakami et al., 1987). At present, lime addition is successfully used to precipitate P from sludge liquors, prior to dewatering, at the Johannesburg works with sludge composting facilities. It has also been found that co-aeration of raw/digested and thickened waste activated sludges under laboratory conditions, effectively reduced the lime addition requirements for P removal (Pitman et al., 1991). Efficient aeration of thickened sludges at full scale is, however, difficult to achieve.

In this paper, the solubilisation of phosphorus (P) and ammonia (N), in relation to VFA yields, during acid digestion of raw sludges, from four Johannesburg Treatment works, is quantified. Lime precipitation of phosphate in the fermented sludge liquor is evaluated and the effect of addition of settled sewage elutriant, for VFA recovery, on lime dosage requirements of fermented sludge, is assessed.

Experimental

The primary sludge used in this study was obtained from four major BNR plants in Johannesburg, namely Northern Works (NRAW), Goudkoppies (GRAW), Olifantsvlei (ORAW) and Bushkoppie (BRAW). The sludge was collected from the underflow lines of the primary sedimentation tanks. Settled tank effluent (STE) was collected from the overflow lines of the primary clarifiers. Anaerobic batch reactors, with a liquid volume of 5 l, were used, each equipped with a central stirring shaft connected to a 90 W output, 36 r·min⁻¹ motor. The reactors were filled with fresh primary raw sludge and the experiments were run at room temperature. Daily maximum temperatures ranged from 18 to 28°C.

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Quantification of N and P release in different sludges

Several batch tests (Batches 1 to 4) were run to evaluate the acid fermentation characteristics of the four Johannesburg primary sludges. In Batches 1 and 2, four reactors were run concurrently for each batch test, i.e. the reactors were filled with NRAW, ORAW, GRAW and BRAW respectively, with total solids (TS) concentrations ranging between 0.5 to 5.5 % (m/v), and then allowed to ferment for a period of 10 d.

In Batches 3 and 4, two reactors were run concurrently i.e. the reactors were filled with ORAW (3.8% TS) and NRAW (1.2% TS) for Batch 3, and NRAW (0.98% TS) for Batch 4, and fermented for a period of 6 d. Retention times were reduced from 10 d to 6 d since little more is gained in VFA yield after 6 d, as well as the increased possibility of methanogenesis occurring in the sludge after 6 d (Lilley et al., 1990; Banister and Pretorius, 1998).

The effects of acid fermentation on these batch tests, specifically VFA levels, soluble and total chemical oxygen demand (COD), nitrogen (NH_3/N), *ortho*-phosphate (*o*- PO_4/P), were monitored for each sludge type on a daily basis. Total and volatile solids (TS and VS) concentrations were determined every third day. All the analytical tests, were conducted in accordance with *Standard Methods* (1995) (i.e. method numbers 5220C; 4500- N_{org} ; NH_3/P ; 2540B and E respectively), except the VFA analysis.

The VFA content was measured using a headspace-gas chromatography system (Perkin Elmer HS40 - Hewlett Packard 5890), equipped with a flame ionization detector (FID). A 25 m, 5% phenyl-methylsilicon column was used.

Headspace parameters: Sample temperature, 75°C; needle and transfer temperature, 130°C; thermostat time, 31 min; GC Cycle time, 22 min; pressurisation time, 5 min; injection time, 0.1 min.; withdrawal time, 0.2 min.

Gas chromatography (GC) parameters: Initial temperature, 35°C, initial time, 1 min; rate 1, 10°C/min; final temp 1, 95°C; rate 2, 50°C/min; final temp 2, 230°C; final time, 5 min, helium 10 psi. Detector and injector temperature, 250°C.

Esterification method: 10 ml of sample, 0.5 ml concentrated sulphuric acid and 1 ml ethanol were pipetted into a headspace vial and capped. The vial was boiled in water for 30 min and placed in the headspace sampler. Samples were prepared in duplicate. The GC column was calibrated by injecting from a standard VFA solution (prepared as for sample) in a headspace vial.

Lime dosing of fermented primary sludge

At the end of the 10 d fermentation period (Batches 1 and 2), commercial ground unslaked lime (SABS 459, Type 1, Grade 11) was dosed in the range of 0 and 5.0 g lime/l, (0.88% available CaO) to a 200 ml aliquot fermented sludge sample. The sample was stirred gently for 15 min and the pH measured. The sample was then allowed to settle and the supernatant filtered through GF-C filters and analysed for *o*- PO_4/P , NH_3/N , alkalinity and VFAs. In the case of the thicker sludges e.g. ORAW, the sample was centrifuged (Hitachi Refrigerated Centrifuge) at 10 000 r·min⁻¹ for 10 min, the supernatant decanted and then filtered for analysis.

Stability of phosphate precipitate in fermented sludge after lime dosing

In a separate batch test (Batch 5), 6-d-old fermented NRAW (1.6% TS) was dosed with ground unslaked lime, to a pH of 9.5, for P precipitation (Pitman et al., 1991). The sludge was then mixed gently for 2 d after dosing. Aliquot samples were removed, prior to dosing and then twice a day after dosing, and analysed as described above.

Effect of the addition of settled sewage elutriant on lime dosage

In Batch 6, NRAW (0.8% TS) was fermented in a batch reactor for 6 d and then split in half. To one half settled tank effluent (STE) was added in the ratio of NRAW:STE 1:2. The other half was left undiluted. Ground unslaked lime was added to the two mixtures to increase the pH to 9.5 for P removal and then mixed gently for 30 min. Aliquot samples were removed prior to dosing and after lime dosing and mixing. Each aliquot was analysed as described above.

Results and discussion

The levels of VFA (approximately 10% of the total influent COD), achieved during the course of these experiments, indicate that favourable conditions for the growth and maintenance of a healthy population of acid-producing micro-organisms had been established (Rabinowitz and Oldham, 1985; Lilley et al., 1990; Skalsky and Daigger, 1995). The acid fermentation characteristics of the different sludges from these Johannesburg works and optimisation strategies for fermentation are presented in a separate paper (Banister and Pretorius, 1998).

Quantification of N and P release in different sludges

Acid fermentation, of the four primary sludges, resulted in significant increases in soluble P (Fig. 1) and ammonia as N (Fig. 2). The level of P or N in the sludge liquor would appear to depend on retention time, and waste-water solids concentration and composition (Figs. 1 and 2). Maximum levels of P and N were reached within 3 to 6 d retention time, while ORAW, at 5.5% TS, showed the highest levels of nutrient release in contrast to BRAW, at 0.5% TS, respectively. This is in agreement with the findings of Pitman et al. (1992) who reported an increase in the potential for P release at higher suspended solids concentrations in the sludge liquor.

Furthermore, the upward slope of these nutrient production curves (Figs. 1 and 2), mimics the slopes of the VFA generation curves (Fig. 3), linking it to the hydrolysis of particulate organic matter in the sludge (Eastman, 1977). Solubilisation of N and P begins immediately with each sludge type and appears to follow first order kinetics (Figs. 1 to 3). Similar first-order kinetics have been reported for VFA production in sludge (Lilley et al., 1990; Skalsky and Daigger, 1995; Jardin and Pöpel, 1996; Banister and Pretorius, 1997). Deviations from the curve are most likely due to analytical error and the heterogeneous nature of primary sludge. Solubilisation of P and N in primary sludge was in the order of 0.002 to 0.008 mg P/mg initial COD and 0.005 to 0.018 mg N/mg initial COD, after 6 d. Results were calculated for 6 d, since it is unlikely that retention times, at full-scale, will extend beyond 6 d, due to the tankage cost implications and the increased

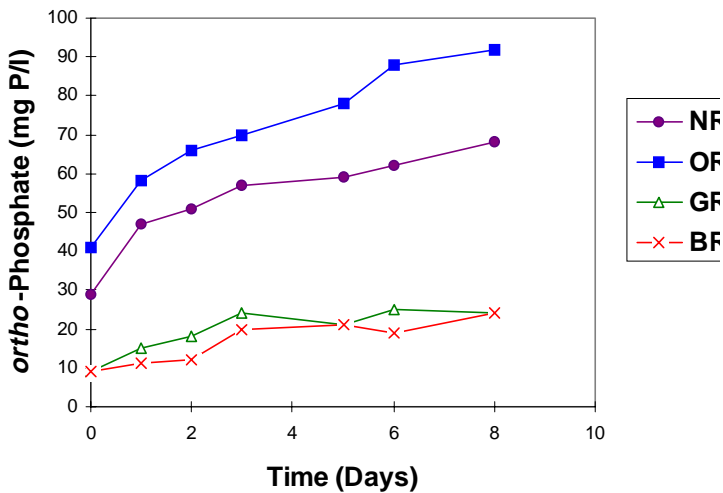


Figure 1
Solubilisation of ortho-P during acidogenic fermentation

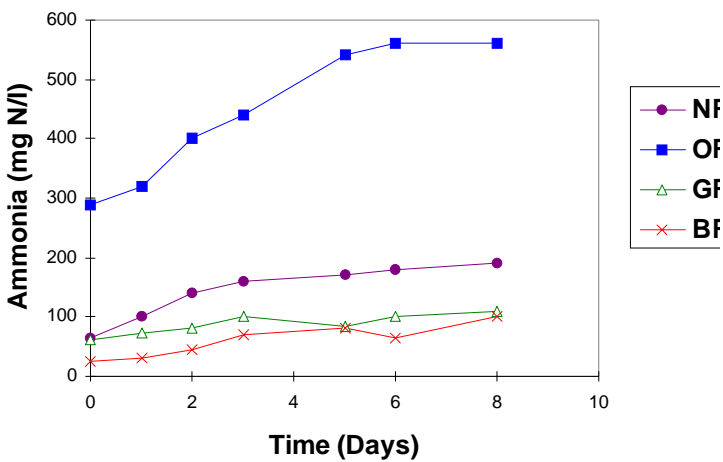


Figure 2
Solubilisation of ammonia as N during acidogenic fermentation

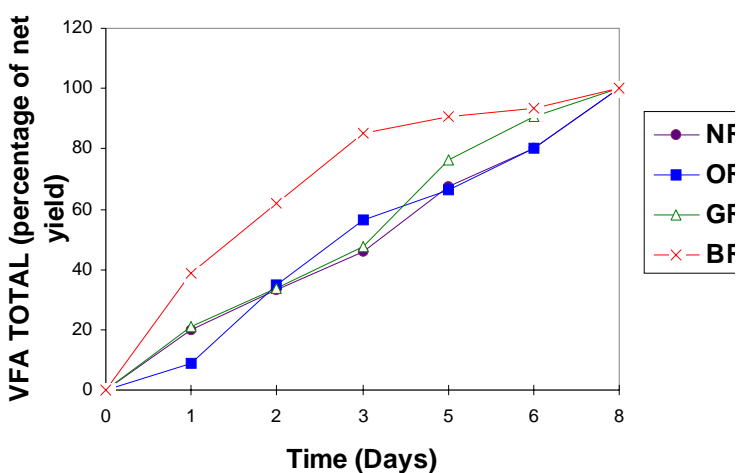


Figure 3
Normalised VFA production curves calculated as a percentage of the total VFA production after 8 d retention time

possibility of methanogenesis occurring with resultant loss of VFA (Lilley et al., 1990; Skalsky and Daigger, 1995). The results from several batch tests are shown in Table 1. Ammonia levels are generally higher in view of the fact that particulate nitrogenous materials are readily degraded during the acid phase of anaerobic digestion (Eastman, 1977).

Table 1 also shows the amount of P released in terms of the amount of VFA produced. The average P-release figure, for the primary sludges in this study, was 0.035 mg P/mg VFA (as acetic acid), 0.47 to 5.6% TS (see Table 1). Skalsky and Daigger (1995) reported a slightly higher average figure of 0.05 mg P released/mg VFA at 14 to 23°C, 0.43 to 2.6 % solids. Any difference is most likely due to primary sludge composition, since temperature was higher (maximum temperature 28°C) in our batch studies, increasing the hydrolysis rate (Eastman, 1977; Gupta et al., 1985) and solids concentrations were similar (Skalsky and Daigger, 1995; Banister and Pretorius, 1998).

At full scale, P-release could therefore impact significantly on the nutrient load of BNR plants when considering the use of acid-rich effluent, from fermented sludge, in the biological reactors (Pitman et al., 1991). This, however, needs to be measured in terms of load and process performance of the biological reactors. Fermented sludge liquors may require segregation and pre-treatment before being fed to the BNR plant (Jardin and Pöpel, 1995; Banister and Pretorius, 1998).

Lime dosing of fermented primary sludge

Lime was dosed at 0 to 5 g/l. Calcium precipitation of soluble P in fermented sludge liquor occurred at 2 to 5 g unslaked lime/l sludge (Table 2). Therefore, between 100 and 500 gCaO/kg sludge, was needed to increase the pH level above 9, and reduce the phosphate in the supernatant liquor to below 5 mg P/l. The lime dosages are relatively high since P removal requires high pH levels and due to the alkalinity of the digested sludges (approximately 500 to 1000 mg CaCO₃/l) the buffering capacity is high (Pitman, 1995; Jardin and Pöpel, 1996). Other metal salts, e.g. iron or aluminium, would be more cost-effective, but lime is an attractive chemical as it also assists sludge dewatering and cake quality (Pitman et al., 1991).

Stability of phosphate precipitate in fermented sludge after lime dosing

In Batch test 5, no re-release of phosphate to the liquid phase in the fermented sludge, was found after lime dosing (Table 3). This is important when considering storage of chemically treated digested sludge prior to handling and disposal, as may be the case at the Johannesburg works.

Sludge type	Total solids % (m/v)	σ -PO ₄ / COD(initial) mg P / mg COD	σ -PO ₄ / VFA(6d) mg P / mg VFA as acetic	NH ₃ -N / COD(initial) mg N / mg COD	NH ₃ -N / VFA(6d) mg N / mg VFA as acetic
NRAW1*	0.72	0.004	0.03	0.011	0.09
ORAW1	5.4	0.004	0.04	0.011	0.11
GRAW1	1.1	0.002	0.05	0.005	0.18
BRAW1	0.47	0.008	0.06	0.018	0.13
NRAW2*	1.7	0.003	0.03	0.008	0.08
ORAW2	5.5	0.001	0.01	0.009	0.13
GRAW2	0.72	0.003	0.03	0.010	0.10
BRAW2	0.49	0.003	0.03	0.011	0.09
NRAW3*	1.17	0.002	0.02	0.004	0.04
ORAW3	3.80	0.002	0.03	0.005	0.06
NRAW4*	0.98	0.004	0.04	0.008	0.08

*1-4 are separate batch experiments
(Daily maximum temperature:18 to 28°C)

Sludge type	TS % (m/v)	σ -PO ₄ mg P/l	Lime dose g CaO/kg sludge	pH after dosing	σ -PO ₄ mg P/l
NRAW	0.55	24	365	10	2
GRAW	0.88	11	228	12	3
BRAW	0.44	56	460	12	5
ORAW	4.15	150	121	12	4

(Daily maximum temperature 18 to 28°C)

Effect of the addition of settled sewage elutriant on lime dosage

The results obtained from Batch test 6, and summarised in Table 4, show that while the actual lime dose requirement to raise the pH to 9.5 has decreased from 2.9 to 1.0 g CaO/l in the diluted mixture, i.e. NRAW:NTE 1:2, it indicates only a slight drop in alkalinity and therefore the buffering capacity of the diluted digested sludge. In terms of solid content, the lime dosage required is approximately 60 g CaO/kg sludge for both the diluted and undiluted (NRAW) mixtures.

While recovery of VFA generated during acid fermentation of primary sludge, using elutriation with settled sewage (Pitman et al., 1991), is presently used at some of the Johannesburg wastewater treatment works, it can be problematic in terms of solid carryover to the biological reactors. This increases the potential P release (Pitman et al., 1992) and cost of chemical removal as seen above. In separate laboratory experiments, Banister and Pretorius (1997), reported that dewatering of fermented sludge with a cationic polyelectrolyte (Zetag 57, Chemserve colloids), can be used as an alternative, since it allowed for good recovery of VFAs (at least 84%) generated to the liquid phase as well as

TABLE 3 STABILITY OF PHOSPHATE PRECIPITATE AFTER LIME DOSING, AT 124 g CaO/kg SLUDGE, OF 6-D-OLD ACID FERMENTED PRIMARY SLUDGE					
Sludge type	pH	o-PO ₄ mg P/l	NH ₃ -N mg N/l	Alkalinity mg CaCO ₃ /l	Total VFA mg acetic acid/l
NRAW before dosing	4.5	138	156	860	4 341
NRAW dosed Morning 1	9.5	1.5	120	1 820	4 321
NRAW dosed Afternoon 1	9.5	2.5	128	2 130	4 372
NRAW dosed Morning 2	9.5	2.3	124	2 140	4 243
NRAW dosed Afternoon 2	9.5	1.7	128	2 250	4 559

(NRAW: 1.6% TS. Daily maximum temperature: 22 to 28°C)

TABLE 4 LIME DOSAGE REQUIREMENTS FOR P REMOVAL IN DILUTED AND UNDILUTED 6-D-OLD FERMENTED SLUDGE						
Sample	pH	Lime dose g CaO/l sludge	Lime dose g CaO/kg sludge	o-PO ₄ mg P/l	NH ₃ -N mg N/l	Total VFA mg acetic acid/l
Before dosing NRAW	5.4	–	–	62	250	1 915
NRAW: STE 1:2	6.3	–	–	15	87	617
After dosing and mixing NRAW	9.6	2.9	63	6.5	240	1 906
NRAW:STE 1:2	9.5	1.0	58	2.6	79	605

(NRAW: 0.8% TS. Daily maximum temperature: 19 to 22°C)

increased solids capture. New primary sludge fermentation design considerations may therefore include dewatering and liquor treatment for more efficient VFA recovery, P removal and BNR performance.

Conclusions and recommendations

The degree of phosphate and ammonia release from primary sludge is dependent on waste-water solid composition and retention time. It may also be affected by temperature and mixing effects, as reported by Jardin and Pöpel (1996). They found that while the transfer of released P from digested sludge into the supernatant was low in gravity thickeners, vertical mixing can result in an increase of soluble P in the supernatant. Operational parameters of fermenter systems and sludge composition therefore could have a significant impact on the extent of P release and emphasises the need to run preliminary evaluation studies for each sludge type and system approach.

Lime addition is an effective and stable means of removing phosphate from the liquid phase of acid-rich primary sludges. Lime addition also minimises P release from fermented sludge during storage periods of up to two days.

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