The effect of sulphates on anaerobic digestion of municipal wastewaters by using UASB reactors at 20 °C

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KEYWORDS

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ABSTRACT

The aim of the work on sulphates was to investigate their impact on UASB performance, including the response to step changes in influent concentration. It has been shown that UASB reactors treating municipal-type wastewaters at 20 °C can remove sulphate effectively even at relatively low COD/SO4 ratios and/or high concentrations. In this experiment, therefore the UASB reactors were fed on influent with different sulphate concentrations to establish the effects on key performance parameters. It was used eight 4-litre continuously fed UASB reactors. The effect of sulphate addition on methane production was much greater than on COD removal, the specific methane production and the ratio of actual to theoretical methane produced per g of COD removed showed relatively little effect from influent sulphate concentrations below ~120 mg SO4/l (COD/SO4 ratio 5.8), although this may in part have reflected a period of acclimatisation while the population of sulphate-reducing bacteria (SRB) increased.

Introduction

The concept of high-rate low temperature digestion systems is particularly attractive for municipal wastewater treatment in areas where ambient and/or wastewater temperatures are normally above 15 °C, such as around the Mediterranean (Mahmoud et al., 2003). Sulphates are a common pollutant in this type wastewater: they are known to have inhibitory effects in anaerobic systems, and are associated with competition for substrate between methanogens and sulphate-reducing bacteria (SRB) (Colleran et al., 1995). The effect of sulphates on the performance of high rate anaerobic digestion at ambient temperatures is thus an important area for the future development and application of these systems in the full flow wastewater treatment.

The sulphate concentration in domestic sewage is typically in the range of 20 to 50 mg/l (Metcalf and Eddy, 2003); values reported for the Middle East include Egypt 35 mg/l and Palestine 138 mg/l (Pescod, 1992).

The presence of sulphate (SO4^2-) in wastewaters causes problems in anaerobic treatment processes. During the treatment process sulphates are reduced to sulphides, with potentially negative effects that include microbial toxicity (O’Flaherty and Colleran, 2000), corrosion (Vincke et al., 2001), unpleasant odours and toxicity to humans (Lens and Kuenen 2001), increases in effluent COD and a reduction in methane productivity (Lens et al., 1998).

Harada et al. (1994) reported effluent concentrations of 100-200 mg SO4/l over more than 100 days of operation, for an influent concentration of 600 mg SO4/l. Several authors have noted the presence of layered structures within sludge granules that may create zones of different redox potential, pH, and etc. (Santegoeds et al., 1999; Yamaguchi et al., 1999). Precipitation of sulphides may account for the removal of sulphate during the accumulation phase, but it is more difficult to explain why these should be re-released when the influent sulphate concentration falls, as the solubility of sulphides is typically very low. Sulphides may be oxidised to sulphur in micro-aerobic conditions.

Sulphates are known to be a problem in anaerobic digestion, but there has been relatively little work on the effect of changes in concentration at low operating temperatures. In this experiment, therefore the UASB reactors were fed on influent with different sulphate concentrations to establish the effects on key performance parameters. Gas volume production and composition, COD removal...
efficiency, total suspended solid removal and operational aspects

Research Methods
This experiment used eight 4-litre continuously fed UASB reactors (Reactors R1-4 worked at 20 °C while the temperature of reactors R5-8 was raised from 15 to 20 °C in a single step on day 0, then all eight reactors were run for 36 days to confirm that performance in the two sets was similar and to provide a check on baseline operation. The target influent COD concentration was 750 mg COD/l with a target HRT of 7.2 hours, giving an OLR of ~2.5 g COD/l/day. The influent sulphate concentration was adjusted by the addition of sodium sulphate (Na2SO4).

Results and Discussion
Reactor performance
The main performance parameters are summarised in Tables 1 and 2.

Treatment performance. Effluent COD concentrations and removal rates showed a short-term reaction to changes in the influent sulphate concentration. In R1-4 effluent COD rose slightly as the influent sulphate was increased to 60 mg SO4/l then to 120 mg SO4/l; then recovered to varying degrees when the sulphate addition ceased. When the influent concentration was subsequently increased to 160 mg SO4/l there was an initial fall in COD removal, but by the last 12 days of the period this recovered to the typical baseline value of around 81%. Similar behaviour was observed in R5-8, although when the influent sulphate concentration increased to 160 then 170 mg SO4/l, R5 and R8 were less seriously affected than R6 and R7. On cessation of sulphate addition COD removal rates in R5-8 all recovered strongly to around 81%. When the influent concentration was subsequently increased to 240 mg SO4/l there was again a fall in COD removal efficiency: although the period of application was too short to see any signs of recovery in this case, removal again improved once the sulphate loading was reduced, indicating that no permanent damage had occurred.

Soluble CO. No obvious trends were seen, with average values between 0.34-0.43 of unfiltered COD. It should be noted that the reported effluent COD concentrations are as-measured values and have not been adjusted to take into account any potential oxygen demand from sulphide produced in the UASB by SRB. If this exists, it would lead to an increase in the measured effluent COD, an apparent reduction in the COD removal rate, an increase in the SMP per g COD destroyed, and a reduction in the ratio of actual to theoretical CH4 production.

Effluent TSS concentrations and removal rates generally showed similar trends to COD, with distinct falls in TSS removal associated with an increase in influent sulphate concentration followed by gradual recovery when the concentrations applied were sustained for longer periods. Although the sulphate loadings were low, particularly in the early stages of the trial, these results suggest that some acclimatisation was required.

Biogas production. Gas production in R5-8, appeared to have stabilised at values similar to those in R1-4, and it was therefore considered that all of the reactors were now acclimated to running at 20 °C.

In R1-4 there were slight reductions in volumetric and specific gas production when the influent sulphate concentration was increased to 60 and then to 120 mg SO4/l, but after signs of stabilisation were seen. Gas production, then showed some recovery after sulphate addition ceased, although values were still slightly below those before any sulphate addition had occurred (Table 1). R5-8 showed a similar trend as sulphate concentrations increased to 90 and then 160 mg SO4/l, but with more variation between the replicate reactors. On day 106 the influent sulphate concentration to R5-8 was raised from 150 to 160 mg SO4/l. This small change produced quite a sharp decline in specific gas production in R5, R6 and R8: the effect was less marked in R7 where the gas production was already slightly lower. To determine whether this increase of 10 mg SO4/l was solely responsible for the change, on day 119 the influent sulphate concentration to R5-8 was reduced to 150 mg SO4/l, but without producing a marked recovery; at the same time the influent concentration to R1-4 was raised from 30 to 160 mg SO4/l and gas production fell to values similar to those seen in R5-8. It was concluded that 160 mg SO4/l was not a critical threshold, and that the changes observed so far reflected ongoing acclimatisation to the increases in sulphate content, with the intervals between them (of strength and of time) too small to provide a reliable guide to the kinetics of sulphate removal in the system.

Reactors R1-4 were therefore maintained at 160 mg SO4/l for a longer period to allow gas production to stabilise, which it did from day ~165 onwards at around 0.15 [0.19] l CH4/g COD added [removed]. On day 178 sulphate addition to R1-4
ceased to see if the gas production recovered: this occurred over the following ~10 days with specific methane production reaching a value of around 0.23 [0.30] l CH₄/g COD added [removed] by day 190.

Table 1. UASB performance in R1-4

| Reactor | Influent Sulphate mg/l | Effluent Sulphate mg/l | Sulphate removal %| Average inf. COD | COD/ SO₄ | HRT hour | Average OLR g COD/ l/day | COD removal % |
|---------|------------------------|------------------------|-------------------|------------------|----------|---------|------------------------|--------------|
| S = 40 mg/l, day 22-36 (last 15 days) | | | | | | | | |
| R1 | 42 | 18 | 0.58 | 733 | 17.3 | 7.51 | 2.35 | 0.83 |
| R2 | 42 | 18 | 0.57 | 733 | 17.3 | 7.09 | 2.49 | 0.8 |
| R3 | 42 | 19 | 0.55 | 733 | 17.3 | 7.15 | 2.47 | 0.81 |
| R4 | 42 | 20 | 0.53 | 733 | 17.3 | 7.33 | 2.40 | 0.81 |
| Ave R1-4 | 42 | 19 | 0.56 | 733 | 17.3 | 7.27 | 2.43 | 0.82 |
| S = 60 mg/l, day 38-52 (15 days) | | | | | | | | |
| R1 | 61 | 12 | 0.80 | 729 | 12 | 7.66 | 2.29 | 0.8 |
| R2 | 61 | 10 | 0.84 | 729 | 12 | 7.20 | 2.44 | 0.81 |
| R3 | 61 | 10 | 0.83 | 729 | 12 | 7.28 | 2.41 | 0.8 |
| R4 | 61 | 11 | 0.82 | 729 | 12 | 7.51 | 2.34 | 0.81 |
| Ave R1-4 | 61 | 11 | 0.82 | 729 | 12 | 7.41 | 2.37 | 0.8 |
| S = 120 mg/l, day 91-105 (last 15 days) | | | | | | | | |
| R1 | 126 | 27 | 0.78 | 728 | 5.8 | 7.97 | 2.19 | 0.78 |
| R2 | 126 | 27 | 0.79 | 728 | 5.8 | 7.61 | 2.30 | 0.79 |
| R3 | 126 | 26 | 0.79 | 728 | 5.8 | 8.14 | 2.15 | 0.78 |
| R4 | 126 | 27 | 0.79 | 728 | 5.8 | 7.75 | 2.26 | 0.78 |
| Ave R1-4 | 126 | 27 | 0.79 | 728 | 5.8 | 7.87 | 2.23 | 0.78 |
| S = 45 mg/l, day 107-118 (12 days) | | | | | | | | |
| R1 | 44 | 18 | 0.60 | 730 | 16.4 | 7.63 | 2.30 | 0.81 |
| R2 | 44 | 22 | 0.52 | 730 | 16.4 | 7.31 | 2.40 | 0.82 |
| R3 | 44 | 18 | 0.59 | 730 | 16.4 | 8.40 | 2.10 | 0.78 |
| R4 | 44 | 20 | 0.56 | 730 | 16.4 | 7.58 | 2.32 | 0.82 |
| Ave R1-4 | 44 | 20 | 0.56 | 730 | 16.4 | 7.73 | 2.28 | 0.81 |
| S = 160 mg/l, day 166-177 (last 12 days) | | | | | | | | |
| R1 | 166 | 27 | 0.84 | 746 | 4.5 | 7.47 | 2.40 | 0.78 |
| R2 | 166 | 29 | 0.83 | 746 | 4.5 | 7.29 | 2.46 | 0.78 |
| R3 | 166 | 28 | 0.83 | 746 | 4.5 | 7.24 | 2.48 | 0.78 |
| R4 | 166 | 30 | 0.82 | 746 | 4.5 | 7.25 | 2.47 | 0.78 |
| Ave R1-4 | 166 | 30 | 0.82 | 746 | 4.5 | 7.31 | 2.45 | 0.78 |
Table continued UASB performance in R1-4

| Reactor | Influent Sulphate | VBP * | Specific biogas | Methane | VMP b | SMP added c | SMP removed d | Actual/ Th CH4 e |
|---------|------------------|-------|-----------------|---------|-------|-------------|---------------|-----------------|
|         | mg/l | l/l/day | l/g COD | % | l/l/day | 1 CH4/g COD added | 1 CH4/g COD removed |                 |
| R1      | 42   | 0.75   | 0.32   | 0.87 | 0.65  | 0.28        | 0.33          | 0.95            |
| R2      | 42   | 0.74   | 0.30   | 0.88 | 0.65  | 0.26        | 0.33          | 0.93            |
| R3      | 42   | 0.74   | 0.30   | 0.87 | 0.64  | 0.26        | 0.32          | 0.92            |
| R4      | 42   | 0.71   | 0.29   | 0.87 | 0.62  | 0.26        | 0.32          | 0.91            |
| Ave R1-4| 0.73 | 0.30   | 0.87   | 0.64 | 0.26  | 0.32        | 0.93          |                 |
| S = 40 mg/l, day 22-36 (last 15 days) |
| R1      | 61   | 0.66   | 0.29   | 0.87 | 0.58  | 0.25        | 0.32          | 0.9             |
| R2      | 61   | 0.72   | 0.29   | 0.87 | 0.62  | 0.26        | 0.32          | 0.91            |
| R3      | 61   | 0.63   | 0.26   | 0.87 | 0.55  | 0.23        | 0.29          | 0.82            |
| R4      | 61   | 0.64   | 0.27   | 0.86 | 0.55  | 0.24        | 0.29          | 0.84            |
| Ave R1-4| 0.66 | 0.28   | 0.87   | 0.58 | 0.24  | 0.30        | 0.87          |                 |
| S = 60 mg/l, day 38-52 (15 days) |
| R1      | 126  | 0.63   | 0.28   | 0.87 | 0.55  | 0.25        | 0.32          | 0.91            |
| R2      | 126  | 0.57   | 0.25   | 0.88 | 0.50  | 0.22        | 0.27          | 0.78            |
| R3      | 126  | 0.54   | 0.25   | 0.88 | 0.48  | 0.22        | 0.28          | 0.81            |
| R4      | 126  | 0.56   | 0.25   | 0.88 | 0.49  | 0.22        | 0.28          | 0.80            |
| Ave R1-4| 0.57 | 0.26   | 0.88   | 0.50 | 0.23  | 0.29        | 0.83          |                 |
| S = 120 mg/l, day 91-105 (last 15 days) |
| R1      | 44   | 0.69   | 0.30   | 0.86 | 0.59  | 0.26        | 0.32          | 0.90            |
| R2      | 44   | 0.72   | 0.30   | 0.86 | 0.62  | 0.26        | 0.32          | 0.90            |
| R3      | 44   | 0.61   | 0.29   | 0.86 | 0.52  | 0.25        | 0.32          | 0.90            |
| R4      | 44   | 0.65   | 0.28   | 0.87 | 0.56  | 0.24        | 0.30          | 0.85            |
| Ave R1-4| 0.66 | 0.29   | 0.86   | 0.57 | 0.25  | 0.31        | 0.89          |                 |
| S = 45 mg/l, day 107 - 118 (12 days) |
| R1      | 166  | 0.40   | 0.17   | 0.86 | 0.35  | 0.14        | 0.19          | 0.53            |
| R2      | 166  | 0.42   | 0.17   | 0.87 | 0.36  | 0.15        | 0.19          | 0.54            |
| R3      | 166  | 0.43   | 0.17   | 0.87 | 0.37  | 0.15        | 0.19          | 0.55            |
| R4      | 166  | 0.43   | 0.17   | 0.87 | 0.37  | 0.15        | 0.19          | 0.55            |
| Ave R1-4| 0.42 | 0.17   | 0.87   | 0.36 | 0.15  | 0.19        | 0.54          |                 |

a Volumetric biogas production  
b Volumetric methane production  
c Specific methane potential (SMP) per g COD added  
d Specific methane potential (SMP) per g COD removed  
e ratio of actual SMP per g COD removed to the theoretical value of 0.35 l/g COD
Table 2. USAB performance in R5-8

| Reactor | Influent Sulphate | Effluent Sulphate | Sulphate removal | Average infl. COD | COD/ SO₄ | HRT | Average OLR | COD removal |
|---------|------------------|------------------|------------------|------------------|---------|-----|------------|------------|
|         | mg/l             | mg/l             | %/100            | g COD/ l/day      | hour   | g COD/l/day | %          |
| S = 40 mg/l, day 22-36 (last 15 days) |
| R5      | 39               | 19               | 0.50             | 731              | 18.8   | 7.21  | 2.44       | 0.83       |
| R6      | 39               | 21               | 0.46             | 731              | 18.8   | 7.28  | 2.41       | 0.81       |
| R7      | 39               | 19               | 0.51             | 731              | 18.8   | 7.26  | 2.42       | 0.78       |
| R8      | 39               | 19               | 0.50             | 731              | 18.8   | 7.77  | 2.26       | 0.82       |
| Ave R5-8| 20               | 0.49             | 731              | 18.8             | 7.38   | 2.38  | 0.81       |
| S = 90 mg/l, day 38-52 (15 days) |
| R5      | 85               | 9                | 0.89             | 746              | 8.8    | 7.07  | 2.54       | 0.84       |
| R6      | 85               | 12               | 0.86             | 746              | 8.8    | 7.12  | 2.52       | 0.83       |
| R7      | 85               | 13               | 0.85             | 746              | 8.8    | 7.27  | 2.47       | 0.81       |
| R8      | 85               | 14               | 0.83             | 746              | 8.8    | 7.93  | 2.26       | 0.84       |
| Ave R5-8| 12               | 0.86             | 746              | 8.8              | 7.35   | 2.45  | 0.83       |
| S = 160 mg/l, day 91-105 (last 15 days) |
| R5      | 158              | 32               | 0.80             | 739              | 4.7    | 8.42  | 2.12       | 0.81       |
| R6      | 158              | 33               | 0.79             | 739              | 4.7    | 8.08  | 2.20       | 0.78       |
| R7      | 158              | 33               | 0.79             | 739              | 4.7    | 7.92  | 2.25       | 0.78       |
| R8      | 158              | 30               | 0.81             | 739              | 4.7    | 8.20  | 2.17       | 0.81       |
| Ave R5-8| 32               | 0.80             | 739              | 4.7              | 8.15   | 2.18  | 0.8        |
| S = 170 mg/l, day 107 - 118 (last 12 days) |
| R5      | 169              | 29               | 0.83             | 740              | 4.4    | 7.35  | 2.42       | 0.81       |
| R6      | 169              | 33               | 0.80             | 740              | 4.4    | 7.42  | 2.40       | 0.78       |
| R7      | 169              | 36               | 0.79             | 740              | 4.4    | 8.44  | 2.11       | 0.80       |
| R8      | 169              | 33               | 0.81             | 740              | 4.4    | 8.30  | 2.15       | 0.78       |
| Ave R5-8| 33               | 0.81             | 740              | 4.4              | 7.88   | 2.27  | 0.79       |
| S = 160 mg/l, day 120-133 (14 days) |
| R5      | 160              | 32               | 0.80             | 746              | 4.7    | 7.79  | 2.30       | 0.78       |
| R6      | 160              | 32               | 0.80             | 746              | 4.7    | 7.80  | 2.30       | 0.77       |
| R7      | 160              | 32               | 0.80             | 746              | 4.7    | 8.37  | 2.14       | 0.77       |
| R8      | 160              | 34               | 0.79             | 746              | 4.7    | 8.06  | 2.22       | 0.76       |
| Ave R5-8| 33               | 0.80             | 746              | 4.7              | 8.00   | 2.24  | 0.77       |
| S = 30 mg/l, day 144-163 (last 20 days) |
| R5      | 33               | 13               | 0.60             | 729              | 21.8   | 7.68  | 2.29       | 0.77       |
| R6      | 33               | 14               | 0.57             | 729              | 21.8   | 7.73  | 2.28       | 0.77       |
| R7      | 33               | 14               | 0.58             | 729              | 21.8   | 8.06  | 2.17       | 0.77       |
| R8      | 33               | 15               | 0.55             | 729              | 21.8   | 8.09  | 2.17       | 0.77       |
| Ave R5-8| 33               | 0.57             | 729              | 21.8             | 7.89   | 2.23  | 0.77       |
| S = 240 mg/l, day 166-177 (last 12 days) |
| R5      | 240              | 106              | 0.56             | 748              | 3.1    | 7.48  | 2.40       | 0.79       |
| R6      | 240              | 100              | 0.59             | 748              | 3.1    | 7.38  | 2.43       | 0.78       |
| R7      | 240              | 99               | 0.59             | 748              | 3.1    | 8.27  | 2.17       | 0.79       |
| R8      | 240              | 100              | 0.58             | 748              | 3.1    | 8.47  | 2.13       | 0.78       |
| Ave R5-8| 101              | 0.58             | 748              | 3.1              | 7.90   | 2.28  | 0.79       |
Table continued UASB performance in R5-8.

| Reactor | Influent Sulphate | VBP a | Specific biogas | Methane | VMP b | SMP added c | SMP removed d | Actual/ Th CH₄ e |
|---------|------------------|-------|-----------------|---------|--------|-------------|-------------|----------------|
|         | mg/l             | l/l/day | l/g COD | % | l/l/day | 1 CH₄ g⁻¹ COD added | 1 CH₄/g COD removed |
| S = 40 mg/l, day 22-36 (last 15 days) | | | | | | | |
| R5 | 39 | 0.8 | 0.33 | 0.87 | 0.70 | 0.29 | 0.35 | 0.99 |
| R6 | 39 | 0.73 | 0.3 | 0.88 | 0.64 | 0.26 | 0.33 | 0.93 |
| R7 | 39 | 0.68 | 0.28 | 0.87 | 0.6 | 0.25 | 0.31 | 0.9 |
| R8 | 39 | 0.75 | 0.33 | 0.87 | 0.66 | 0.29 | 0.35 | 1.01 |
| Ave R5-8 | 0.74 | 0.31 | 0.87 | 0.65 | 0.27 | 0.33 | 0.96 |
| S = 90 mg/l, day 38-52 (15 days) | | | | | | | |
| R5 | 85 | 0.75 | 0.3 | 0.87 | 0.65 | 0.26 | 0.31 | 0.88 |
| R6 | 85 | 0.69 | 0.27 | 0.87 | 0.6 | 0.24 | 0.29 | 0.83 |
| R7 | 85 | 0.61 | 0.25 | 0.88 | 0.53 | 0.22 | 0.27 | 0.76 |
| R8 | 85 | 0.71 | 0.32 | 0.88 | 0.62 | 0.28 | 0.33 | 0.94 |
| Ave R5-8 | 0.69 | 0.28 | 0.87 | 0.6 | 0.25 | 0.3 | 0.85 |
| S = 160 mg/l, day 91-105 (last 15 days) | | | | | | | |
| R5 | 158 | 0.61 | 0.29 | 0.87 | 0.53 | 0.26 | 0.32 | 0.9 |
| R6 | 158 | 0.56 | 0.26 | 0.88 | 0.5 | 0.23 | 0.29 | 0.82 |
| R7 | 158 | 0.56 | 0.25 | 0.88 | 0.5 | 0.22 | 0.28 | 0.81 |
| R8 | 158 | 0.64 | 0.3 | 0.88 | 0.57 | 0.26 | 0.32 | 0.92 |
| Ave R5-8 | 0.66 | 0.28 | 0.88 | 0.52 | 0.24 | 0.3 | 0.86 |
| S = 170 mg/l, day 107 - 118 (last 12 days) | | | | | | | |
| R5 | 169 | 0.47 | 0.19 | 0.86 | 0.41 | 0.17 | 0.21 | 0.59 |
| R6 | 169 | 0.46 | 0.19 | 0.87 | 0.4 | 0.17 | 0.21 | 0.61 |
| R7 | 169 | 0.49 | 0.23 | 0.87 | 0.43 | 0.2 | 0.25 | 0.73 |
| R8 | 169 | 0.46 | 0.22 | 0.87 | 0.4 | 0.19 | 0.24 | 0.69 |
| Ave R5-8 | 0.47 | 0.21 | 0.87 | 0.41 | 0.18 | 0.23 | 0.65 |
| S = 160 mg/l, day 120-133 (14 days) | | | | | | | |
| R5 | 160 | 0.42 | 0.18 | 0.86 | 0.36 | 0.16 | 0.2 | 0.58 |
| R6 | 160 | 0.41 | 0.18 | 0.87 | 0.35 | 0.15 | 0.2 | 0.57 |
| R7 | 160 | 0.45 | 0.21 | 0.87 | 0.39 | 0.18 | 0.24 | 0.68 |
| R8 | 160 | 0.43 | 0.19 | 0.87 | 0.37 | 0.17 | 0.22 | 0.63 |
| Ave R5-8 | 0.43 | 0.19 | 0.87 | 0.37 | 0.17 | 0.21 | 0.61 |
| S = 30 mg/l, day 144-163 (last 20 days) | | | | | | | |
| R5 | 33 | 0.59 | 0.26 | 0.87 | 0.52 | 0.23 | 0.29 | 0.84 |
| R6 | 33 | 0.6 | 0.27 | 0.87 | 0.53 | 0.23 | 0.3 | 0.86 |
| R7 | 33 | 0.59 | 0.27 | 0.87 | 0.52 | 0.24 | 0.31 | 0.88 |
| R8 | 33 | 0.59 | 0.27 | 0.87 | 0.51 | 0.24 | 0.31 | 0.88 |
| Ave R5-8 | 0.59 | 0.27 | 0.87 | 0.52 | 0.23 | 0.3 | 0.86 |
In R5-8 no extra sulphate was added to the influent from day 134 to allow observation of the recovery from a loading of 160 mg SO₄⁻/l: in this case also it took around 10 days for gas production to recover to 0.23 [0.30] l CH₄/g COD added [removed] (Table 3). From day 164 the influent sulphate concentration to R5-8 was increased to 240 mg SO₄⁻/l. Specific and volumetric gas production dropped rapidly, and specific methane production stabilised at 0.12 [0.16] l CH₄/g COD added [removed] (Table 2). Finally, in the last few days of the experiment, sulphate addition to R5-8 stopped and the gas production was observed to recover at a similar rate as in the previous unloading.

**Sulphate removal and other parameters.** At influent sulphate concentrations below 120 mg SO₄⁻/l the effluent concentration was low, averaging 12 mg SO₄⁻/l in the period up to day 52. After sulphate addition ceased in R1-4 from day 107-118 and in R5-8 from day 134-164, effluent concentrations fell to pre-addition values.

A temporary increase in effluent sulphate was seen in R1-4 for a period of around 17 days after the influent concentration was raised from ~40 to ~170 mg SO₄⁻/l: the reason for this is unknown, although it could perhaps reflect a lag while the population of sulphate-reducing bacteria increased in response to the new conditions.

There was an unexpected small but sharp rise in effluent sulphate immediately after influent sulphate concentrations dropped in R1-4 from day 187 and R5-8 from days 134 and 187. Interferences that may give a false increase in measured SO₄²⁻ include SO₃²⁻ and suspended matter, but there were no corresponding changes in the TSS concentration.

Sulphate removal rates were typically above 80 %, except in periods immediately following a change in influent concentration. This is higher than the result of Rizvi et al. (2013) who reported sulphate removal efficiency in a UASB reactor at an operational temperature of 20 C⁰ as between 56.4-76.2% at HRT 3-12 hours. For the periods of 'steady' operating conditions shown in Table 3: the average removal rate was 87 % for influent concentrations ≤ 170 mg SO₄⁻/l, although there may be a change of slope e.g. after 120 mg SO₄⁻/l. At an influent concentration of 240 mg SO₄⁻/l, however, it is clear removal has decreased significantly.

Effluent pH was influenced by the influent pH. The pH value of the influent was high compared to that of effluent but mainly followed the influent sulphate concentration, with average values of around 6.9, 7.0 and 7.2 at influent concentrations of 30, 120 and 160 mg SO₄⁻/l respectively in R1-4 and 6.9, 7.1 and 7.2 at influent concentrations of 30, 160 and 240 mg SO₄⁻/l respectively in R5-8. This is explained by the fact that sulphide compounds, like carbonate compounds, create buffering in anaerobic reactors through the production and emission of H₂S: H₂O + CO₂ + HS⁻ ↔ H₂S + HCO₃⁻ (Meh dizadeh and Shayegan, 2002). Fig. 1 shows the Sulphate removed for steady condition.

![Figure 1](image)

**Figure 1.** Influent sulphate concentration and Sulphate removed for 'steady' operation periods.
Specific experimental findings
When fed on influent with a high sulphate concentration, the UASB reactors showed some ability to store sulphur, possibly in elemental form, and subsequently to release it when the influent sulphate concentration decreased. Once equilibrium was achieved, as indicated by the daily sulphur balance approaching zero, the influent sulphate concentration had an effect on specific methane production that was around 1.5 times greater than the value predicted by stoichiometric considerations. The reactors were very robust with respect to shock changes in influent sulphate concentration up to 160 mg SO\textsubscript{4}/l. A step change in influent concentration from 30 to 240 mg SO\textsubscript{4}/l at a COD/SO\textsubscript{4} ratio of 3.1:1 produced a more marked drop in sulphate removal and specific methane yield, but no apparent effect on COD removal.

Step changes in influent sulphate concentration had an effect on reactor performance in terms of COD and TSS removal even at very low concentrations (from 30 to 90 mg SO\textsubscript{4}/l). Acclimatisation to the presence of raised sulphate concentrations in the influent appeared to be required before a consistent response was achieved in terms of the effect on specific gas production. Once acclimatisation had occurred specific methane production showed a decline of 0.7 l CH\textsubscript{4}/g SO\textsubscript{4} added, around 1.5 times greater than the stoichiometric value. At influent sulphate concentrations above 160 mg/l biogas H\textsubscript{2}S concentrations reached 8000-10,000 ppm. A sulphur balance provided a useful tool for assessment of reactor behaviour.

Conflict of interest
The authors declare that there is no conflict of interest in this publication.

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