Treatment of exhausted reactive dyebath effluent using anaerobic digestion: Laboratory and full-scale trials

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Abstract

Reactive dyes are difficult to remove from textile waste water due to their solubility and they pass through conventional aerobic biological sewage treatment systems and enter the receiving water body. Investigations into the use of anaerobic digestion to decolourise reactive azo dyes have been successful on a laboratory scale and the investigation was extended to full-scale trials. Exhausted reactive dyebath effluent (3 kℓ/d) was discharged into a primary digester (1.34 Mℓ) on weekdays for a 151-d period. On average, 48 kℓ/d of sludge was fed to the experimental and control digesters. The overflow was monitored for colour, sodium and sulphide concentrations. A laboratory digester was also set up to simulate the full-scale conditions but was operated at twice the exhausted dyebath loading recipe. No visual difference in colour was noted between the overflow of the primary or laboratory digester and the control digester, but elevated levels of sodium and sulphide were obtained due to the high concentration of sodium sulphate used in the reactive dyeing process. The laboratory digester became unstable at sulphide concentrations of 400 mg/ℓ. However, the sulphide concentrations in the primary digester never increased such that it threatened digester stability.

Introduction

Waste water from textile finishing industries is complex and highly coloured. Colouration of the liquid effluent results from wastage and washing during dyeing and printing processes, with the degree of colouration being dependent on the colour/shade dyed and the type of dye used. Water insoluble dyes (e.g. disperse and vat dyes) generally exhibit good exhaustion properties (i.e. most of the dye bonds to the fibre) and can be removed from the effluent by physical means such as flocculation. When this effluent is discharged to a conventional sewage treatment works most of the colour is removed by adsorption to the biomass (Shaul et al., 1986; 1988). However, since the introduction of water soluble dyes, e.g. reactive dyes, conventional biological treatment processes are no longer able to achieve adequate colour removal.

Reactive dyes are coloured molecules capable of forming a covalent bond between the dye molecule and the fibre, and they are used to dye cellulosic fibres. The reactive systems of these dyes react with ionised hydroxyl groups on the cellulose substrate. However, hydroxyl ions present in the dyebath due to the alkaline dyeing conditions compete with the cellulose substrate, resulting in a percentage of hydrolysed dyes which can no longer react with the fibre. Thus between 10 and 50% of the initial dye load will be present in the dyebath effluent (ENDS Report, 1993), giving rise to highly coloured effluent which is difficult to treat due to the water-soluble nature of the hydrolysed dyes.

Unless additional treatment steps are implemented, water-soluble dyes pass through a sewage treatment works and give rise to colouration of the receiving water body. Although anaerobic treatment has traditionally only been used to treat the solids fraction of the waste at a sewage treatment works, recent studies have resulted in this process being adapted to the successful high-rate treatment of liquid industrial wastes. Moreover, the literature indicates the potential of anaerobic systems for the non-specific decolourisation of water soluble azo dyes (Brown and Laboureur, 1983). Since azo dyes account for over 50% of all textile dyestuffs produced and are the most common chromophore of reactive textile dyes (Waring and Hallas, 1990), an anaerobic treatment system was proposed as a viable option for the decolourisation of textile effluents from reactive dyeing. Initial laboratory investigations were undertaken using a target reactive dye (C.I. Reactive Red 141), the results of which are documented in Carliell et al. (1995).

The target compound in the treatment system (azo dye) is not biodegraded by the micro-organisms, instead the dye acts as an oxidising agent for the reduced flavin nucleotides of the microbial electron transport chain and is reduced and decolourised concurrently with re-oxidation of the reduced flavin nucleotides (Gingell and Walker, 1971). Therefore, a source of reduction equivalents, resulting from the degradation of a suitable carbon source, is essential to ensure decolourisation and maintain the anaerobic population in the treatment system. In other words, a labile carbon source (other than the dyes) is required for decolourisation to take place. The carbon source requirement was fulfilled by glucose in the laboratory systems (Carliell et al., 1995); however, this is clearly not suitable for large-scale applications. It was decided to investigate the possibility of combining textile effluent decolourisation with the chemical oxygen demand (COD) removal operation of an existing anaerobic digester. This is shown in Fig. 1. The primary and secondary sludge are the carbon sources for anaerobic digestion. The carbon is converted to methane and carbon dioxide, during which process electrons are released. These electrons cascade down the electron transport chain (as indicated in the box in Fig. 1) to a final electron acceptor such as nitrate, sulphate or an azo reactive dye. The electrons react with the dye by reducing the azo bonds and thus causing decolourisaton.

The results reported in this paper are from a 5-month trial in which concentrated reactive dyebath effluent was added daily (weekdays only) to an operating anaerobic sewage sludge digester at the Umbilo Sewage Purification Works (USPW) in Pinetown (KwaZulu-Natal). The objectives of the trial were to ensure that the addition of the textile effluent did not increase the colouration of the digester effluent and did not adversely affect the daily operation of the digester.

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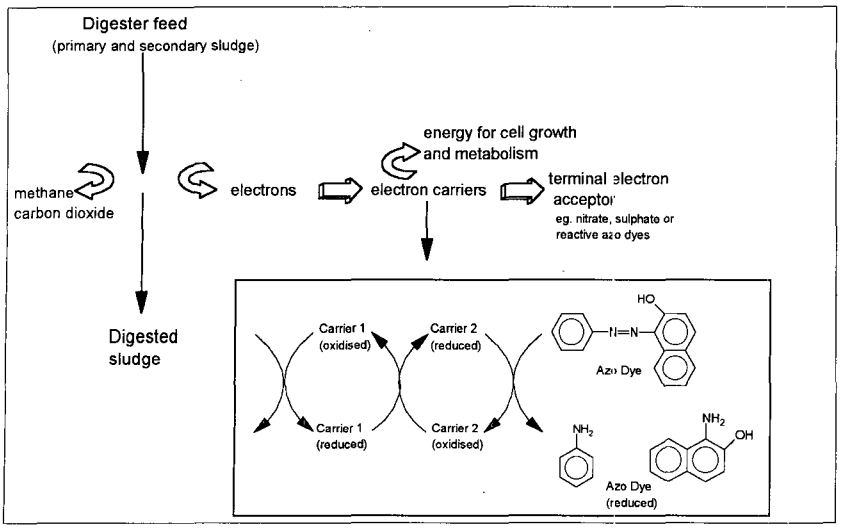

Figure 1
Mechanism for azo reduction under anaerobic conditions

Materials and methods

The USPW has 4 heated digesters, one of which was made available for this trial. Concentrated reactive dye effluent was obtained from the yarn dyehouse of Ninian and Lester (Pty) Ltd., a local textile company. An effluent segregation system at the mill allowed the discharge of the exhausted dyebaths to a holding tank (6 kℓ) to prevent dilution of the effluent with the subsequent washes. The effluent was collected daily (Monday to Friday) from the storage tank by a municipal tanker (5 kℓ) and transported to USPW where it was discharged into the empty primary pump-station sump. The experimental sludge digester was isolated and the textile effluent pumped into the digester. An adjacent digester was used as the control for this trial. In addition a laboratory-scale investigation was run concurrently with the full-scale trial. The laboratory digester (20 ℓ) was constructed to simulate the operation of the full-scale digester and to investigate the effect of increased loading of the dye effluent on digester operation. Samples of the dye effluent were taken from the storage tank prior to collection each day and analysed for colour, pH and sodium and sulphate concentrations.

Concentrated dyebath effluent

The effluent was highly coloured due to the presence of hydrolysed reactive dyes, with American Dye Manufacturers Institute (ADMI) colour values ranging from 3 110 to 36 600. The pH ranged from 11.7 to 12.4. The CODs of the samples were not measured. The use of sodium sulphate during reactive dyeing resulted in high concentrations of sodium (9.5 to 20 g/ℓ) and sulphate (20 to 42 g/ℓ) in the effluent. Other auxiliary products used during the yarn dyeing were also present in the effluent (i.e. surfactants, wetting agents, sequesterants and an alkaline liquid buffer). Table 1 lists some of the dyes present in the dyebath effluent during the trial and Table 2 lists the auxiliaries and typical concentrations used during the trial.

Full-scale investigation

The USPW is situated in Pinetown on the banks of the Umbilo River. It is divided into two sections; the old plant which uses biofilters for primary treatment, and the new activated sludge plant (commissioned in 1992). The works treats approximately 18 Mℓ per day, of which 10 Mℓ is treated in the new plant (full capacity) and the balance in the old plant.

TABLE 1
REACTIVE DYES PRESENT IN THE DYEBATH EFFLUENT

Dye range	Commercial name	CI name
Remafix	Yellow HE 4R	Reactive Yellow 84
	Red HE 7B	Reactive Red 141
	Navy HER	Reactive Blue 171
	Blue HERD	Reactive Blue 160
	Blue HEGN	Reactive Blue 198
	Red HE 3B	Reactive Red 120
Remazol	Yellow 3RS	Reactive Yellow 176
	Yellow 4GL	
	Orange 3R	
	Red 3B	Reactive Red 23
	Red 3BS	
	Blue BB	
	Dark Blue HR	Reactive Blue 89
	Green 6B	
	Black B	Reactive Black 5
	Turquoise Blue G	Reactive Blue 21
	Blue R Spec	
Drimarene	Yellow XRN	Reactive Yellow 165
	Blue X 3LR	Reactive Blue 52
	Turquoise XB	Reactive Blue 41
	Navy XGN	Reactive Blue 214

Old plant

The raw sewage and waste water flows into one of 6 primary settling tanks. The primary sludge that collects at the bottom of the settling tanks is removed every morning and anaerobically digested. The supernatant liquor is treated in biofilters. The effluent then passes into one of 6 secondary clarifiers, the sludge is returned to

TABLE 2
LIST OF AUXILIARIES PRESENT IN THE DYEBATH EFFLUENT

Auxilliary	Description	Typical concentration (g/ℓ)
Avcolit LSPN-L	Blend of surfactants and de-aerating agents; low foaming wetting agent.	0.2
Meropan VD-L	Protective colloid; sequesterant.	1
Avcontrol	Alkaline liquid buffer for the fixation of reactive dyes. Improves reproducibility.	5
Sodium sulphate	Exhaustion.	80

the primary settling tanks, and the supernatant flows onto rapid sand filter beds. The filtrate is chlorinated and discharged to the Umbilo River.

New plant

The raw sewage and industrial waste water flows into one of 2 primary sedimentation tanks. The settled sludge is pumped to the old plant where it is sent for anaerobic digestion. The supernatant is aerobically treated in an activated sludge reactor. Wasted mixed liquor is concentrated by dissolved air flotation (DAF); the float (sludge) is pumped to the anaerobic digesters and the underflow returned to the activated sludge reactor. The mixed liquor from the activated sludge reactor is then sent to 2 clarifiers, the sludge returned to the reactor and the clarified effluent chlorinated and discharged to the Umbilo River.

Anaerobic digestion

There are 4 primary anaerobic digesters and 4 secondary digesters, each having a volume of approximately 1.34 Mℓ. The primary digesters are heated to about 37°C and have a sludge residence time of between 25 to 30 d. The secondary digesters are not heated and have a much longer residence time (approximately 100 d).

Sludge handling

The raw sludge from the primary settling tanks in the old and new plants, and the waste activated sludge from the DAF unit are distributed equally to the anaerobic digesters on a regular basis (approximately 4 times per day; twice in the morning, once in the afternoon and once at night). The raw sludge is pumped from the raw sewage sump to a division box where it is evenly split into 4 streams which flow into each of the digesters. The digested sludge is displaced from the primary digesters for between 2 and 3 h. There are two overflow points; one at the bottom of the digester and the other just below the half-way mark. Sludge is discharged from both points. The bottom draw-off lines are prone to blockages and are unblocked every morning. The displaced sludge from the primary digesters is fed to the secondary digesters.

Approximately 3 kℓ/d (Monday to Friday) of reactive dyebath effluent was added to the experimental digester. The average daily flow of raw sludge to the digester was 48 kℓ/d (taken as an average of the four daily feeds). Standard laboratory analyses were conducted daily by the USPW personnel on samples of digested sludge displaced after the morning feed. Analyses included pH, alkalinity, volatile acids, total solids and volatile solids. In addition, the sodium and sulphide concentrations of digested sludge from the experimental and control digesters were measured.

Laboratory investigation

The laboratory-scale digester was constructed from a 20ℓ aspirator bottle. Glass ports at the top and base of the vessel were used for feed addition and sludge overflow, respectively. An overhead stirrer (125 rpm) was used to mix the contents of the vessel. The digester was incubated in a water bath at 37°C. The gas evolved during digestion was collected in a 5 ℓ bottle containing acidified brine solution. Innoculum was obtained from the full-scale primary digester. The laboratory digester was filled with 20 ℓ of digested sludge and fed once daily (7 days per week) with raw sludge from the plant. The residence time was 30 d. After 10 d of operation, 155 mℓ of dye effluent (identical to that added to the primary digester) was added to the digester after the feed (week days only). This was equivalent to co-treating 10 kℓ/d in the 1.34 Mℓ digester. Similar chemical analyses were performed on this digester overflow as for the full-scale digester.

Analytical methods

American Dye Manufacturers Institute (ADMI) colour values

This method enables the measurement of sample colour independent of hue (Allen et al., 1972). Samples (20 mℓ) were mixed with diatomaceous earth filter aid and filtered through a 0.45 μm membrane to remove turbidity. The filtrate was analysed using a Hitachi U-2 000 spectrophotometer for transmission from 400 to 700 nm, at 10 nm intervals. Tristimulus values were obtained from this data and the corresponding ADMI values calculated (Allen et al., 1972).

Alkalinity

Digested sludge from the digester overflow was centrifuged at 4 000 rpm for 5 min. A 50 mℓ volume of the supernatant was transferred to a beaker and the pH determined using an Orion model 701/A pH meter. The sample was titrated to pH 4.0 with 0.05 M H_2SO_4. The treated sample was then used for volatile acid determination. The methods used to determine alkalinity and volatile acids used by the USPW laboratories are not according to *Standard Methods* (1989).

Volatile acids

Once the alkalinity of the digester supernatant had been determined the pH of the sample was reduced to 3.5 and boiled for 3 min. The sample was then cooled to room temperature and the

volatile acid concentration determined by titrating to pH 4.0 (a) and pH 7.0 (b) with 1 M NaOH. The volatile acids content was calculated from (b - a) x 120 and reported as mg/ℓ acetic acid.

Total and volatile solids

Total and volatile solids were measured according to *Standard Methods* (1989).

Sodium

The digester overflow sample was centrifuged at 4 000 r/min for 5 min and the sodium concentration of the supernatant determined using a GBS 906 atomic absorption spectrophotometer. Samples of the dyebath effluent were diluted 10 fold and the sodium concentration determined in the same manner.

Sulphates

The sulphate concentration in the dyebath effluent was calculated from the sodium concentrations assuming sodium sulphate was the only source of sodium and sulphate ions.

Sulphides (total)

The iodometric method (4 500-S^2E) for total sulphide determination (*Standard Methods*, 1989) was used to determine the sulphide concentration of the digester samples.

Digester gas analysis

A Varian Star 3 600 gas chromatograph with a molecular sieve column was used to determine the concentration of methane and carbon dioxide in the digester gas. The molecular sieve packed column (5A 60/80) (2 m x 3 mm) was used in conjunction with a thermal conductivity detector (TCD). Helium was the carrier gas. The detector temperature was set at 180°C and the injector temperature at 240°C. The column temperature was programmed to hold at 50°C for 3 min, after which time it was ramped to 240°C at a rate of 50°C/min and held at this temperature for 4 min.

Results

Full-scale trials

ADMI colour measurements of the digested sludge proved unsuccessful because of residual turbidity and therefore a visual comparison was made between the supernatant of the sludge from the experimental digester and that from the control digester. There was no noticeable difference in colour between the samples. Due to the high concentration of sodium sulphate used in the dyebath, elevated levels of sodium were detected in the experimental digester. This is shown in Fig. 2. Sulphate is reduced to sulphide under the anaerobic conditions, thus resulting in increased sulphide levels in the experimental digester as shown in Fig. 3. The rapid decrease in sulphide concentration from day 66 to 77 (experimental digester) shown in Fig. 3 corresponds to a period when no dye effluent was added to the experimental digester. Once addition of the effluent re-commenced on day 78 the sulphide concentration increased accordingly. The sulphide concentration in the experimental digester rarely exceeds 100 mg/ℓ, and that in the control digester has an upper limit of approximately 30 mg/ℓ. Figure 4 shows the mass of sulphate added to the experimental

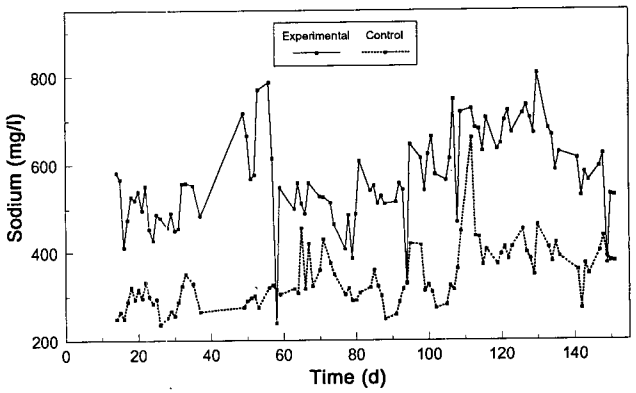

Figure 2
Sodium concentration measured in the supernatant from the experimental and control digesters over 151 d

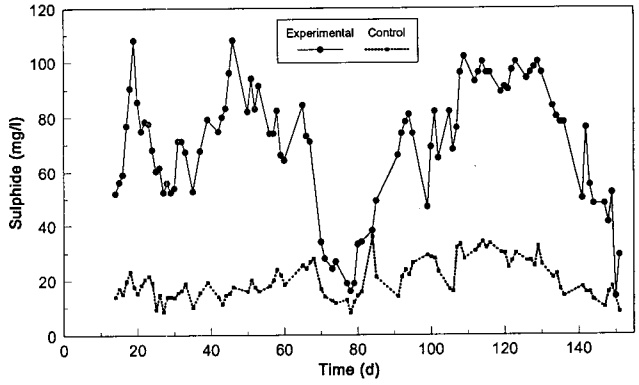

Figure 3
Sulphide concentration measured in the supernatant from the experimental and control digesters over 151 d

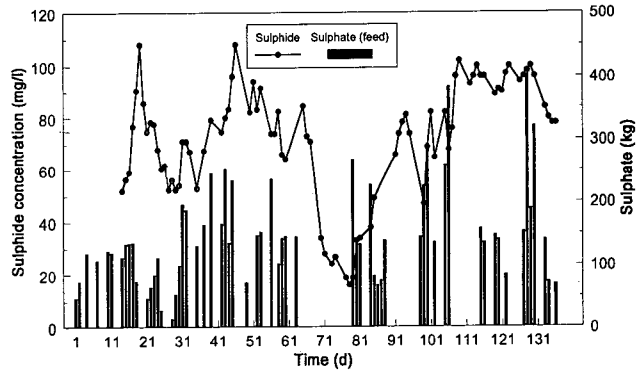

Figure 4
The relationship between the sulphide concentration measured in the experimental digester (day 0 to 151) and the mass of sulphate added to the experimental digester as a component of the reactive dye effluent

digester daily as a result of co-treatment of the reactive dyeing effluent and the resultant sulphide concentration.

Figure 5 shows that the pH values of both the experimental and control digesters remained fairly constant throughout the trial period, although it did exceed the acceptable range for an anaerobic treatment system, i.e. pH 6.8 to 7.2 (Ross et al., 1992). However,

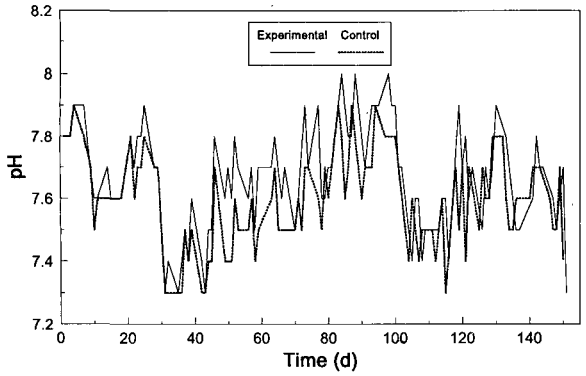

Figure 5
pH in the experimental and control digesters over 151 d

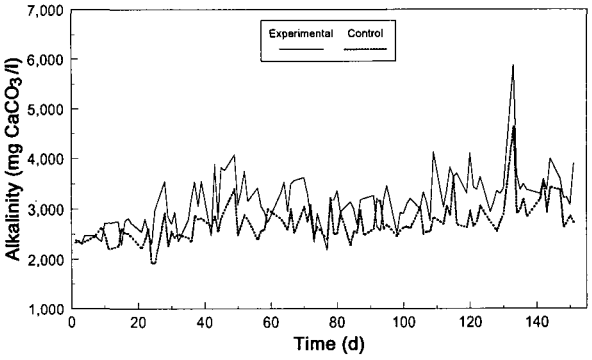

Figure 6
Alkalinity measured for the experimental and control digesters over 151 d

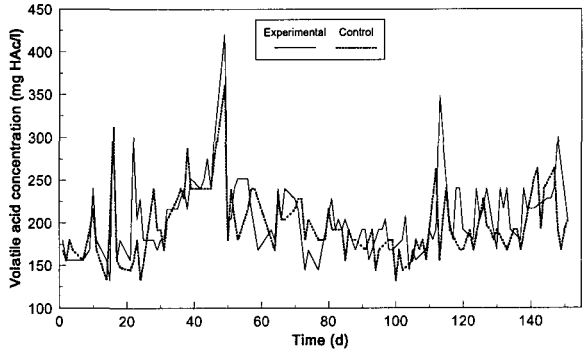

Figure 7
Volatile acid concentration for the experimental and control digesters over 151 d

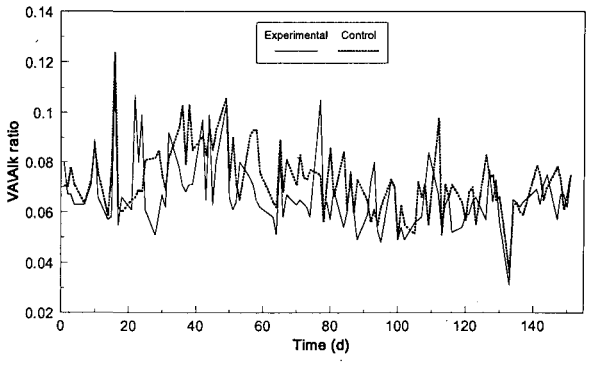

Figure 8
Volatile acid/alkalinity ratio for the experimental and control digesters over 151 d

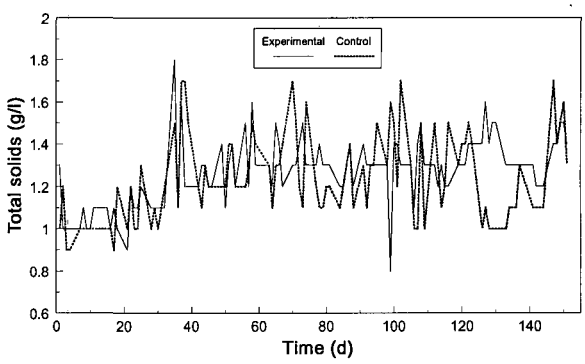

Figure 9
Total solids for the experimental and control digesters over 151 d

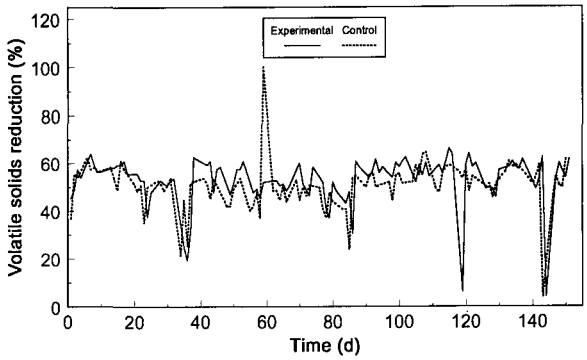

Figure 10
Percentage volatile solids reduction for the experimental and control digesters over 151 d

as the pH in the experimental and control digesters was similar, the higher pH values were attributed to the nature of the effluent entering USPW and not to the effect of the dye concentrates. Figure 6 depicts the total alkalinity measured for the experimental and control digesters during the trial period. The alkalinity follows a similar pattern in both of the digesters although that of the experimental digester is consistently higher than that of the control digester. This suggests that the co-treatment programme may have affected the total digester alkalinity. Figure 7 shows the volatile acid concentrations for the experimental and control digesters. No marked difference in volatile acid concentration can be seen for the experimental digester, indicating a stable system despite the addition of dye effluent. Figure 8 shows the volatile acid : alkalinity ratio for the experimental and control digesters, respectively. The ratio is fairly constant for both digesters and no operational imbalances are indicated. The total solids of the digesters are shown in Fig. 9. No marked difference in digester solids occurred as a result of the addition of dye effluent to the experimental

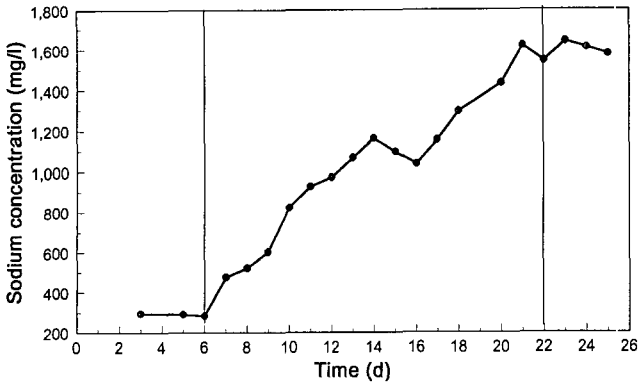

Figure 11
Sodium concentration measured in laboratory digester supernatant

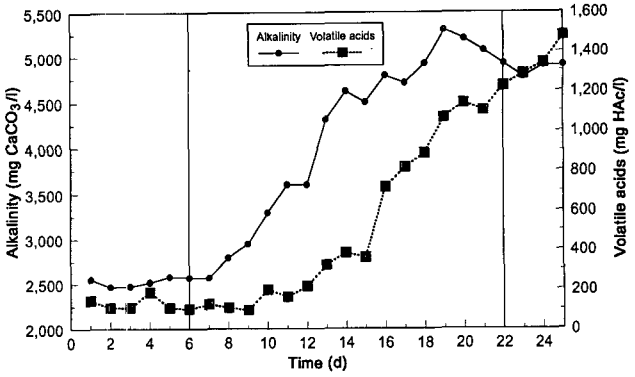

Figure 13
The alkalinity and volatile acid concentrations measured in the laboratory digester supernatant before, during and after addition of reactive dye effluent

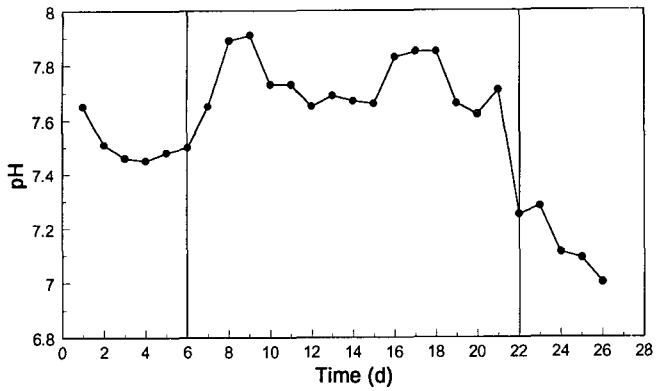

Figure 12
pH for the laboratory digester before, during and after co-treatment of the dye effluent

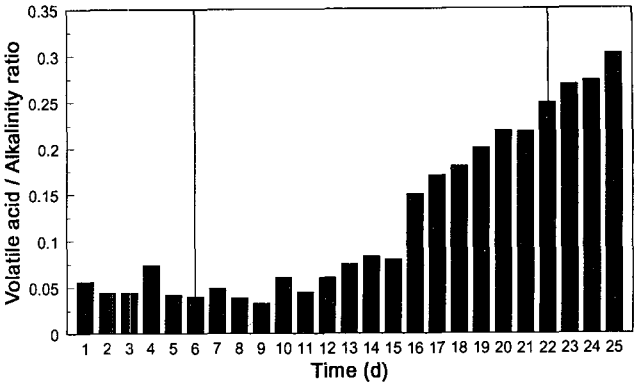

Figure 14
The VA/Alk ratio of the laboratory digester before, during and after addition of reactive dye effluent

digester. Figure 10 shows the volatile solids reduction for both the experimental and control digesters. The results show that the addition of dye effluent to the experimental digester did not adversely affect the performance of the system with respect to solids digestion.

Laboratory digester

The laboratory digester was monitored throughout the co-treatment programme in which reactive dye effluent was added to the laboratory digester. Following an initial stabilisation period, reactive dye effluent was added daily to the laboratory digester. The proportion of dye effluent added to the laboratory digester was 0.775% (v/v) in comparison to the full-scale digester which received on average 0.231% (v/v) of effluent. Routine analyses were carried out to determine whether addition of the dye effluent had any negative impact on the digester performance and the sodium and sulphide concentration in the digester supernatant was also monitored. The vertical lines on the figures denote the duration of the co-treatment phase in the laboratory digester.

Figure 11 shows the sodium concentration measured in the laboratory digester before, during and after the co-treatment phase. The sodium levels increased throughout the co-treatment phase due to the high concentration of sodium sulphate used in the dyeing

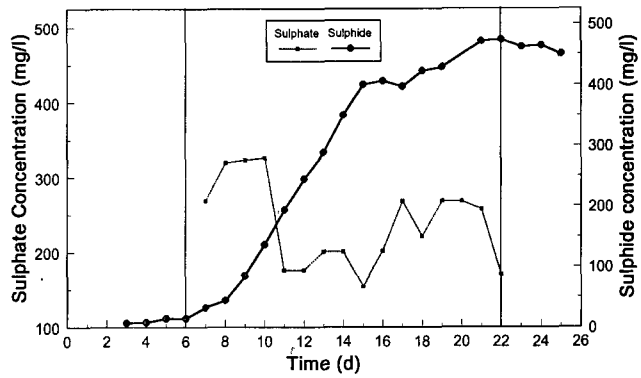

Figure 15
Sulphate concentration of the reactive dyeing effluent added to the digester, and sulphide concentration measured in the digester supernatant

process. Figure 12 shows the pH of the laboratory digester. This increased after the addition of dye effluent and decreased once the co-treatment phase had ended. However, this decrease is related to digester instability, which will be illustrated in the following figures.

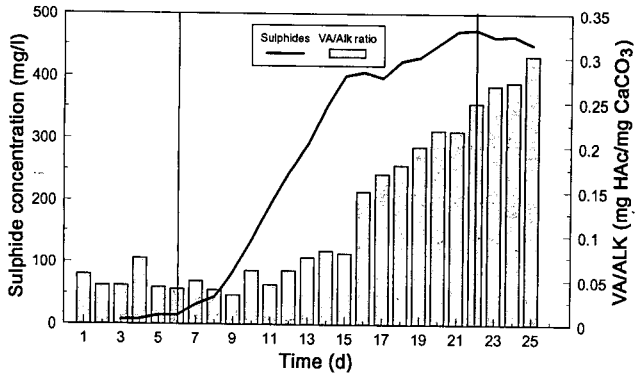

Figure 16
Sulphide concentration in the laboratory digester and the correlation with the VA/Alk ratio of the digester supernatant

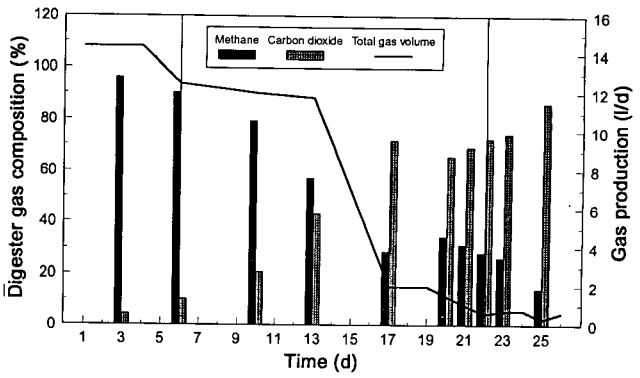

Figure 19
Digester gas composition in the laboratory digester showing a decrease in methane production and concomitant increase in carbon dioxide during co-treatment of reactive dye effluent. The total gas volume measured is shown to decrease over time

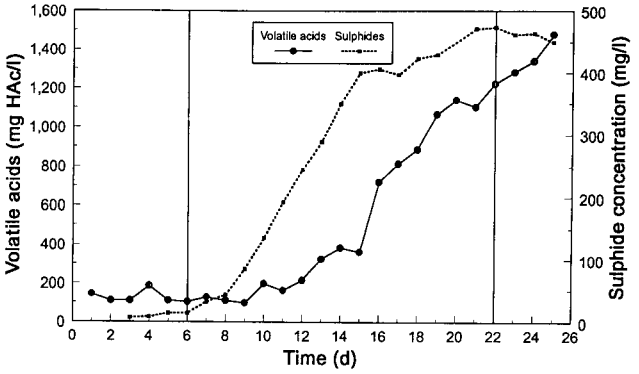

Figure 17
Volatile acid and sulphide concentrations for the laboratory digester before, during and after co-treatment of reactive dyeing effluent

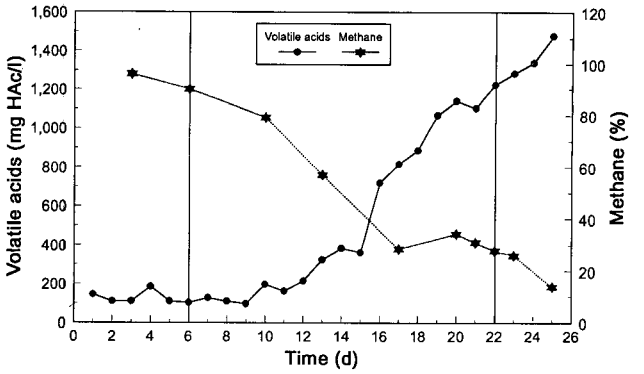

Figure 20
Methane production relative to volatile acid concentration of the laboratory digester supernatant during the course of the co-treatment programme

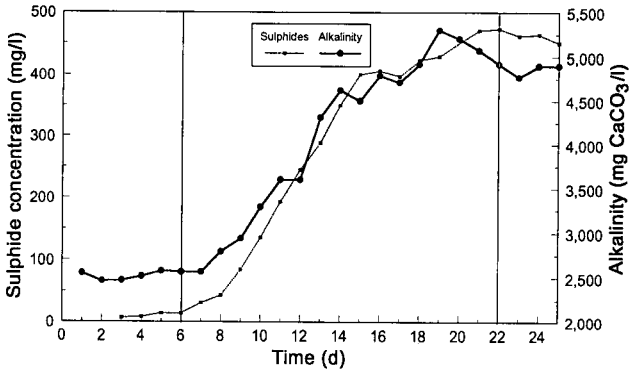

Figure 18
Sulphide and alkalinity concentrations for the laboratory digester before, during and after co-treatment of reactive dyeing effluent

Figure 13 shows the alkalinity and volatile acid concentrations in the laboratory digester. It can be seen that before the co-treatment phase both the alkalinity and volatile acid concentrations were stable and low, but on addition of the dye effluent to the digester the concentrations increased rapidly. Although the concentrations of volatile acids recorded should have indicated digester instability and sour conditions, the rapidly increasing alkalinity enabled the digester to maintain a near neutral pH. Figure 14 shows that the volatile acid to alkalinity ratio (VA/Alk, a good measure of digester performance and stability) remained steady until 15 d after which time a large increase in the VA/Alk ratio was recorded. This was followed by a steady increase in this ratio indicating increasing digester instability.

Figure 15 shows that the sulphide concentration in the laboratory digester was negligible prior to addition of the dyeing effluent; however, once the co-treatment phase commenced and sulphate was introduced into the laboratory digester the sulphide concentration increased to approximately 450 mg/*ℓ*. Figure 16 shows that when the sulphide concentration reached approximately 400 mg/*ℓ* the VA/Alk ratio increased considerably and continued to increase, indicating the higher sulphide concentrations contributed to digester instability.

Figures 17 and 18 show that both the volatile acid and alkalinity concentrations of the digester increased in relation to the increasing sulphide concentration. Figure 19 shows the composition and volume of the laboratory digester gas during the trial. Initially, a high production rate of gas was measured with a higher proportion of methane to carbon dioxide. However, as the trial continued, the rate of gas production dropped and the ratio of methane to carbon

dioxide was reversed. Figure 20 shows the relationship between the increasing volatile acid concentration in the laboratory digester and the decreasing proportion of methane being produced, indicating inhibition of the methanogenic digester population.

Discussion

The elevated sodium concentrations recorded for both the full-scale and laboratory experimental digesters indicated that addition of the dye effluent was directly responsible for the increased sodium concentrations. Sodium has been reported to be inhibitory to methanogenesis and, when compared to other cations has been proven to be the strongest inhibitor on a molar basis (Kugelman and McCarty, 1965; cited by De Baere, 1984). Moderate inhibition of methanogenesis has been reported at between 3.5 and 5.5 g/ℓ of sodium, with strong inhibition occurring at 8 g/ℓ (Kugelman and McCarty, 1965; cited by De Baere, 1984)). As the concentrations reported as inhibitory in the literature are significantly higher than the maximum of 786 mg/ℓ recorded for the full-scale experimental digester, and 1 500 mg/ℓ for the laboratory digester, sodium is not thought to have had an inhibitory effect on the methanogenic populations in the experimental systems. However, further increases in the volume of dye effluent to be co-treated increase the sodium concentration in the anaerobic system, and cation toxicity could become a limiting factor.

The second factor of interest is the elevated sulphide levels recorded for both experimental systems receiving reactive dye effluent. The sulphide is produced through the reduction of the sulphate in the dye effluent as a result of the action of sulphate-reducing bacteria (SRB) present in the anaerobic digester environment. The literature indicates that increased concentrations of sulphides in an anaerobic digester can be inhibitory to the methane-producing bacteria (MPB), resulting in digester instability and even failure if toxic levels of sulphide are reached (Karhadkar et al., 1987; Parkin et al., 1990). The dissolved sulphide levels reported as toxic to methanogenesis vary from 100 to 800 mg/ℓ (Parkin et al., 1990). With specific reference to anaerobic sewage sludge digestion, sulphides have been found to be toxic to the MPB's at concentrations in excess of 200 mg/ℓ at a pH near neutral, but sulphide concentrations between 50 and 100 mg/ℓ can be tolerated by the MPB with little acclimation (Malina and Pohland, 1992).

The above figures could explain why the full-scale experimental digester did not suffer a decrease in performance when fed with reactive dye effluent whereas the laboratory digester indicated severe inhibition of methanogenesis. Sulphide concentrations in the full-scale experimental digester did not exceed 100 mg/ℓ, which, according to Malina and Pohland (1992) complies with acceptable operating conditions for a sewage sludge anaerobic digester. However, sulphide concentrations in the laboratory digester increased rapidly throughout the co-treatment phase to peak at approximately 450 mg/ℓ, at which stage methane production had almost ceased and advanced digester failure was noted.

Digester failure occurs as a result of inhibition of the methanogenic bacteria. When this occurs the volatile organic acids (formed in the first stage of the digestion process) are not converted to biogas (methane and carbon dioxide) and instead accumulate in the digester. In a healthy anaerobic digester the volatile acid concentration of the digesting sludge is usually in the range of 50 to 300 mg/ℓ (Ross et al., 1992). These acid concentrations are balanced by alkalinity concentrations in the range of 2 000 to 3 000 mg/ℓ as $CaCO_3$, to give a volatile acid : alkalinity ratio of less than 0.3 (Ross et al., 1992). Thus, the VA:Alk ratio of the digester is a good indication of digester instability; if this rises above 0.3 the process is considered to be unstable.

The volatile acid and alkalinity concentrations in the laboratory digester were stable prior to addition of the reactive dyeing effluent; however, once the co-treatment phase was initiated both the acid and alkalinity concentration of the digester increased rapidly. The increase in volatile acids immediately indicated that methanogenesis had been inhibited. However, the concomitant increase in alkalinity meant that the VA:Alk ratio did not indicate digester failure even when methane production had all but ceased. It is not certain what caused the alkalinity of the digester to increase, although it is known that the reduction of sulphate to sulphide generates alkalinity in an anaerobic digester (McCartney and Oleszkiewicz, 1991). With respect to the full-scale trial, the alkalinity of the experimental digester is shown to be consistently higher than that of the control digester, suggesting a similar effect to that in the laboratory digester. However, no marked differences in volatile acid concentration could be seen between the experimental and control digester indicating that the experimental digester was not experiencing methanogenic inhibition. The VA:Alk ratios for the experimental and control digesters are stable in comparison to that of the laboratory digester which continued to increase throughout the trial.

Thus, it can be said that the high sulphide concentrations measured in the laboratory digester inhibited the methanogenic bacteria and resulted in digester failure. It must be noted that the VA:Alk ratio is not a suitable analytical tool for detecting digester instability during co-treatment of reactive dyeing effluent due to the increased alkalinity of the digester sludge and it is important that the volatile acid and sulphide concentrations in the digester are monitored closely. The full-scale experimental digester followed similar patterns to the laboratory digester; however, the lower volumes of dye effluent added resulted in lower levels of sulphides being produced which were able to be tolerated by the methanogenic bacteria.

There are a number of solutions to the problems experienced with sulphate reduction during the anaerobic co-treatment of reactive dye effluent. Firstly, methanogenic populations can be acclimated to tolerate higher levels of sulphides, and secondly, increasing the labile carbon to sulphate ratio in an anaerobic digester (i.e. decreasing the competition for available substrate between the SRBs and MPBs) also decreases the inhibitory effect of sulphide reduction. However, sulphides are still undesirable in the anaerobic digestion process due to odour and corrosion problems. A number of solutions are available to this problem, one being to add a suitable source of heavy metals (such as electroplating effluent) to complex with the sulphides. This approach should be carefully monitored to ensure that the addition is well balanced, as heavy metals are themselves inhibitory to methanogens. In addition, a low concentration of sulphide (1 to 25 mg/ℓ) is required for metabolism of the methanogens. Another option, as sulphate is not thought to be inhibitory to anaerobic digestion, is to control the sulphate reduction process by the addition of molybdate which blocks an initial step in sulphate reduction (Tanaka and Jayadevan, 1994).

A third option would be to change the reactive dyeing recipes to use sodium chloride or sodium carbonate instead of sodium sulphate and recycling the salt using nanofiltration (Erswell et al., 1988), thus removing the problem at source. As a result, the volume of dye concentrate to be transported would be reduced and the salt content of the dyeing effluent would also be substantially decreased, thus decreasing the sodium concentration in the digester. Sodium

nitrate could not be used as a replacement as nitrate is reduced preferentially to azo compounds under anaerobic conditions and decolourisation of the dyebath effluent would only occur once all the nitrate had been reduced to nitrite (Carliell et al., 1995).

Conclusions

Co-treatment of exhausted reactive dyebath effluent in an existing full-scale digester (at a ratio of 3:48 kℓ/d effluent to sludge) exhibited promising results. Although operational differences were recorded between the experimental and control digesters, at no time did these differences indicate a decrease in operational performance for the experimental digester. Results obtained with the more intense co-treatment programme for the laboratory digester showed that increasing the loading of reactive dyebath effluent can result in deterioration of the digester performance. However, it must be remembered that the laboratory digester was shock-loaded with a high concentration of dye effluent and not given a period to acclimate to the effluent.

Future work

Based on the results from this trial, a number of recommendations can be made as to future research into the treatment of textile concentrates by anaerobic digestion. Firstly, investigations should be carried out to determine the effect of replacing sodium sulphate by sodium chloride or sodium carbonate on both the dyeing efficiency and the performance of an anaerobic sludge digester. Secondly, the maximum ratio of concentrated dye effluent to sewage sludge that can be effectively treated should be determined, and finally, the addition of a supplemental carbon source to improve the performance of the sludge digester treating textile effluent and the effect it has on the above ratio should be investigated.

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