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The role of sulphidogenesis in anaerobic treatment phase of tannery wastewater treatment in advanced integrated wastewater pond system

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Abstract

An outdoor experiment was conducted to study the competition between Sulphate Reducing Bacteria (SRB) and Methanogenic Archaea (MA) in anaerobic treatment phase of tannery wastewater treatment in pilot-scale Advanced Facultative Pond (AFP). The relative electron flow towards sulphate reduction was higher (59–83%) than towards methanogenesis (17–41%), although the COD recovery within the reactor varied between 15 and 90%. The results also demonstrated that the flow of electrons towards SRB increased with increase of the sulphate concentration and decrease of the COD : $SO_4^=$ ratio.

Introduction

Anaerobic treatment of tannery wastewater has been demonstrated in different bench-and pilot-scale reactors with satisfactory results of high organics removal (Abdel-Shafy et al. 1995; Bailey et al. 1984; Tunick et al. 1981). The presence of high concentration of proteinaceous matter necessitates the retention of tannery wastewater in anaerobic reactors for no less than 2 days (Schenk et al. 1999). Such high strength wastewaters require anaerobic digestion prior to aerobic treatment. The rate-limiting step in anaerobic treatment of tannery wastewater is the hydrolysis of the proteinaceous matter into smaller peptides and amino acids (Bailey et al. 1984). The major drawback of conventional low-rate, isolated anaerobic units used for sludge digestion is their high unit volume cost which is in the order of 100 times higher than the submerged fermenters of the Advanced Facultative Ponds (AFP) and the operational complexity associated with internal heating, recirculation and mixing (Oswald et al. 1994). AFP with internal fermentation pit usually performs better than its closely related conventional open anaerobic ponds, with many process and economic advantages. Firstly, the fermentation pit located in the bottom of AFP is protected against the intrusion of dissolved oxygen from the overlying water column during high wind mixing (Green et al. 1995; Oswald et al. 1994). During intense wind mixing of cold spells, the top wind-oxygenated water surface of open anaerobic ponds may sink into the lower anaerobic zone thereby causing process upset and the release of malodorous gases such as H_2S.

Secondly, submerged fermentation pit equipped with well-engineered submerged gas canopy and surface gas collector allows the efficient collection of methane-rich biogas, which is usually lost to the atmosphere from open anaerobic ponds. Sufficient water column provided over the gas canopy of the fermentation pit filters out unwanted constituents of the biogas, namely CO_2 and N_2 thereby increasing the methane's composition by over 50% (Green et al. 1995). A scrubbing efficiency of 50% was achieved for N_2 in the overlying water column and most of the carbon dioxide was utilized by microalgae inhabiting the top water layer (Green et al. 1996). The third important advantage of the AFP is its odour free operation. Hydrogen sulphide produced from anaerobic process is effect-

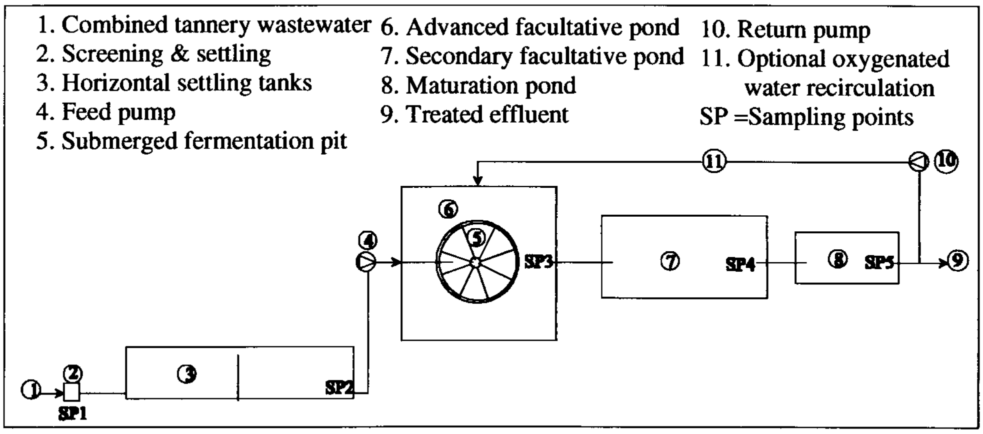

Figure 1. Schematic flow diagram of pilot-scale AIWPS (Tadesse et al. 2003).

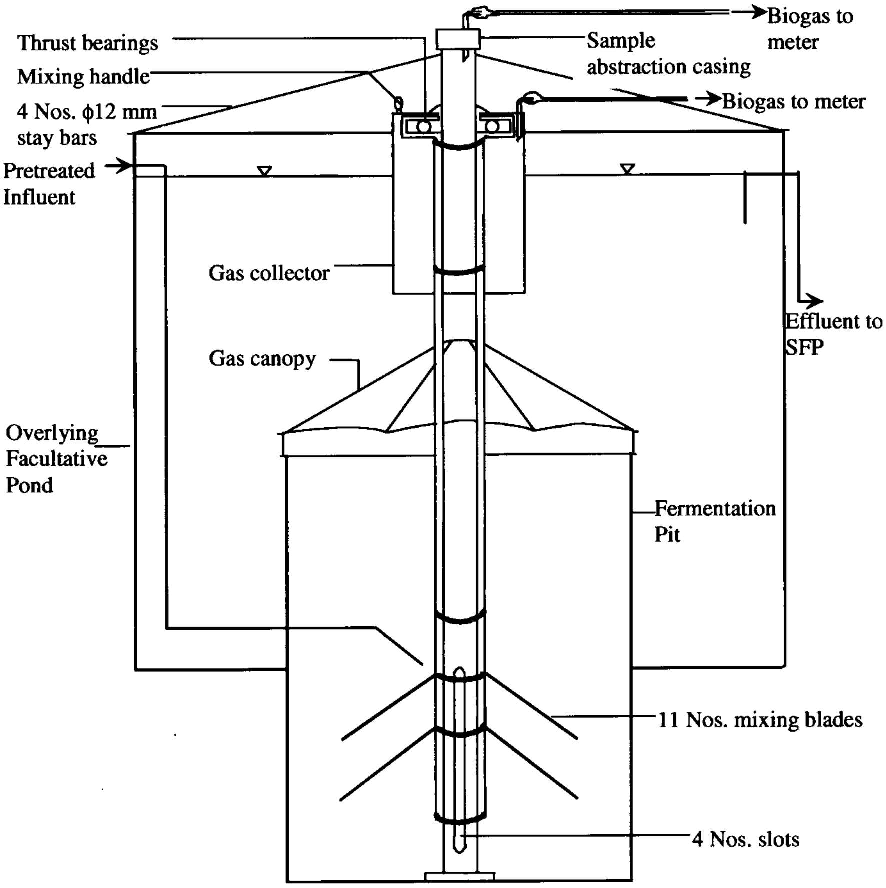

Figure 2. Sectional details of the pilot-scale AFP.

ively oxidized to recoverable elemental sulphur in the upper solar irradiated water layers of the AFP by anoxygenic photosynthetic sulphur bacteria (Tadesse et al. 2003). Fourthly, because of its high volume to area ratio and integration of anaerobic fermenter within an overlying facultative pond, AFP has a lower land area requirement than conventional open anaerobic ponds. This feature could make AFP more competitive than open anaerobic ponds, especially, in built-up areas and places where land is at high premium.

Tannery wastewaters are characterised by high concentrations of sulphate and sulphide in addition to high amounts of organics, chromium (III), solids and inorganic salts such as sodium chloride (Jochimsen et al. 1997; Szpyrkowicz et al. 1991). Many studies have been conducted (Lovley & Klung 1983; Schonheit et al. 1982; Winfrey & Zeikus 1977; Yoda et al. 1987) to elucidate the competition between sulphate reducing bacteria (SRB) and methanogenic archaea (MA) for electron donor during anaerobic degradation of sulphate-rich wastewaters. Factors affecting the competition between SRB and MA vary greatly. Some reported that the competition between SRB and MA was mainly dependent upon the ratio of COD and sulphate in the wastewater (Li et al. 1996; Mizuno et al. 1994; Uberoi & Bhattacharya 1995); others attributed to factors such as substrate concentration (Isa et al. 1986a), organic loading rate (Yoda et al. 1987) and even reactor design (Isa et al. 1986a). Yet, some believed that SRB have a higher affinity to substrate than MA (Kristjansson et al. 1982; Widdel 1988) and thus would out-compete the latter for substrate, such as hydrogen, formate and acetate. Studies by Harada et al. (1994), Lens et al. (1998) and Zhou & Fag (1998) also demonstrated that sulphidogenesis gains prominence, as a COD removal pathway, as the $SO_4^{=}$—S concentration in the feed wastewater increases. Organics removal by sulphate reduction also offers a more robust treatment process less affected by high H_2 partial pressure in the reactor (Lens et al. 2000) or high sulphide concentration (Visser 1995 cited in O'Flaherty & Colerain 2000).

Isa et al. (1986a) introduced the concept of "electron flow" to quantify the extent of competition between SRB and MA in a bench-scale upflow anaerobic filter. As the electron flow designates the ratio of COD scavenged by the SRB and MA (Harada et al. 1994) it can be used to express the relative significance or competition between SRB and MA in anaerobic mineralization of the organic wastes.

Therefore, this study was conducted to quantify the competition between SRB and MA, in terms of % electron flow diverted to each group, in anaerobic degradation of tannery wastewater in a pilot-scale AFP.

Materials and methods

Study site

The pilot-scale Advanced Facultative Pond (AFP) as an integral part of the Advanced Integrated Wastewater Pond System (AIWPS) (Figure 1) was installed at Modjo tannery 75 km south of the capital city, Addis Ababa, Ethiopia on a major highway connecting the capital to the Red Sea port of Djibouti. Modjo town is located 8°35′ North and 39°10′ East at an altitude of 1,825 m above mean sea level (EMA 1988). The climatic conditions are tropical with the mean annual rainfall varying between 680 to 2,000 mm. The mean daily air temperature recorded at the site during the conduct of the experiment varied between 15 °C and 30 °C.

Pilot-scale reactor

The outdoor pilot-scale AFP (No. 6, Figure 1 and Figure 2), which was the focus of this study served as primary anaerobic pond in three-pond AIWPS (Figure 1). The raw combined tannery wastewater was pre-treated by passing it first through successive bar screens and then detaining it for one day in a two-chamber horizontal settling tank (No. 3, Figure 1).

The AFP was comprised of two parts. It contained a square tank serving as an Overlying Facultative Pond (OFP) (Figure 2), which had at its base a cylindrical Fermentation Pit (FP) (No. 5, Figure 1 & Figure 2). The overlying tank was resting on level masonry foundation while half the height of the FP was buried below ground. The AFP was open at its top and had a liquid volume of 23 m^3. Physical dimensions of the components of the AFP are given in Table 1.

Mode of operation

The pre-treated tannery wastewater was fed directly into the fermentation pit, FP, by feed peristaltic pump (No. 4, Figure 1). The wastewater having been digested in the FP for the specified detention times, overflowed into the overlying facultative pond (Figure 2).

Table 1. Physical dimensions of the AFP components

Reactor	Reactor geometry	Areal dimensions (m) × (m)	Reactor depth (m)	Water depth (m)	Mid-depth area (m^2)	Liquid volume (m^3)
Fermentation pit	Cylindrical	ϕ 1.6	2	2	2	4
Overlying facultative pond	Square	3 × 3	3.5	2.3	9	19

The biogas from the FP was focused through the opening between the casing and top open end of the gas canopy and was collected at the surface gas collector (Figure 2). The gas canopy was provided to protect the fermentation pit from any conceivable intrusion of dissolved oxygen from overlying water column while at the same time converging the emerging biogas into the surface gas collector.

The surface gas collector was an inverted PVC barrel fixed onto the upper plate of the thrust bearing assembly (Figure 2). The lower plate of the thrust bearing assembly was welded to the outer wall of 150 mm diameter galvanized steel casing. The casing, while supporting the surface gas collector and the thrust bearing assembly, was also used to abstract sludge and liquid samples from the fermentation pit. Dissolved oxygen, pH and temperature probes were also lowered through the casing for routine monitoring and profiling. The FP was regularly mixed and degassed by turning the surface gas collector. The rotational motion imparted on the gas collector was transferred to the lower mixing blades by four 12 mm diameter steel roads running along side the casing (Figure 2). Four slots were provided at lower end of the casing to allow the contents of the FP to enter the casing. Vents were provided one at the top of the casing cap and the other on the surface gas collector to permit separate collection and assessment of the biogas. The vent on the casing cap received biogas from the sludge layer through the casing water column, while the vent on surface gas collector captured it after the biogas ascended through the overlying water column. Biogas from the surface collector was used for quantification, as the biogas emerging through the casing was relatively small. All gas lines were disconnected and vents plugged while mixing was in progress. After sufficient mixing was done (usually ten rotations per operation), the annular space between the bearings collar and the casing was sealed with rubber rings and finally glued with a sealant and gas lines reconnected. The mixing operation was accomplished relatively quickly, usually less than half an hour, in order to minimize the entrainment of air in the casing. The effluent from the AFP was finally drawn from 40 cm below the water surface and fed by gravity into the bottom of the Secondary Facultative Pond, SFP (No. 7, Figure 1) for further aerobic/anaerobic treatment.

Start-up

The first attempt of starting up the AFP was not successful, mainly due to unfavourable temperature during the start up period and lack of acclimated sludge seed. In the second trial, the FP was filled with septage and acclimatized tannery sludge from nearby evaporation pond receiving tannery wastewater, in proportions of 80 and 20% of its volume, respectively. The overlying facultative pond was filled with seed material composed of sewage and acclimated river water from the tannery outfall into Modjo River in proportion of 60 and 40% of its volume, respectively. Within two months of the inoculation, gas bubbles began to emerge as sign of the early onset of methane fermentation. The FP was then started with continuous feed of a mixture of one third tannery wastewater and two thirds of sewage, which was terminated and continued with only the pre-treated tannery wastewater after one month of acclimation. At the beginning, biogas evolution was very low. Four months after seeding started, detectable amounts of biogas began to emerge.

Sampling and analytical methods

Sample collection was based on the techniques outlined by Pearson et al. (1987). COD, sulphate and sulphide were determined in accordance with the

Standard Methods (APHA et al. 1992). For sulphate determination, a Hach formulation reagent called Sulfa Ver 4 containing barium with a stabilizing agent was used in the preparation of the samples. The Sulfa Ver 4 reagent forms a milky precipitate of barium sulphate with sulphate. The turbidity formed, which is proportional to the sulphate concentration was then red from a Hach DR/4000 spectrophotometer at wavelength of 450 nm. Total dissolved sulphide was determined by methylene blue method of the Standard Methods (APHA et al. 1992). Two Hach formulation reagents containing ferric chloride and N,N-dimethyl-p-phenylenediamine oxalate were added in equal amount to a blank and sample to form the distinctive blue colour which is then read from Hach DR/4000 spectrophotometer at wave length of 665 nm to give the equivalent concentration of total sulphide in mg/l. Dissolved hydrogen sulphide was estimated from the plotted percentage distribution of dissolved sulphide between H_2S and HS^- given in the Standard Methods (APHA et al. 1992). The data required for such determination was the sample pH, temperature and electrical conductivity, which were all measured at the time of analysis. Dissolved oxygen was monitored using Hach model 16046 portable dissolved oxygen meter and pH using an Inventron pH/mV meter fitted with a combined pH electrode. Mid-depth temperatures were measured by a maximum and minimum thermometer suspended by polystyrene-float in the OFP, while electrical conductivity was measured by a WTW-8120 Weilheim conductivity meter. Biogas was recorded by water filled Ritter gas meter, and wastewater feed rates by Masterflex peristaltic pumps of Cole-Parmer Instrument Co., Chicago, Illinois, USA.

Tannery wastewater production and categorization

On average, Modjo tannery processed 25 tones of skins to wet-blue and crust leather and produced 250 m^3 effluent daily during the experimental period. All waste streams emerging from the different processes were diverted into underground channel from where all was conveyed in an open ditch to Modjo River. The tannery was close to EPA (1982) subcategory I in terms of its hair pulping and chrome tanning, retanning and wet-finishing processes. Unlike EPA's subcategory I, Modjo tannery was processing exclusively sheep and goatskins.

Results and discussion

Reactor performance

The AFP remained fully anaerobic throughout the experiment as witnessed by its low dissolved oxygen profile (0.1–0.2 mg O_2 l^{-1}), Figure 3. A mean loading rate of 0.560, 1.480 and 1.860 kg COD m^{-3} d^{-1} were applied during the first, second and third phases of the experiment, respectively (Figure 4a). The corresponding hydraulic retention times in the FP were about 8, 5 and 3 days. The COD removal efficiency steadily increased during phase 1 from an average of 70% to 94% and levelled off quickly at 80% and continued more or less unchanged until it reached end of phase 2 (Figure 4a). At the highest organic loading rate of 1.860 kg COD m^{-3} d^{-1}, during phase 3, the COD removal efficiency decreased from an average of 80% to 60%. This was the time when the AFP was overloaded and the biogas production stopped altogether (Figure 4c). The mid-depth temperatures varied within a narrow range of 19 to 20 °C throughout the experiment. The sulphate reduction, which continued to increase in a somewhat erratic manner during phase 1, remained above 90% during much of phase 2 and 3 (Figure 4b). Figure 4 also shows that the sulphate reduction and biogas production, during phase 1, was increasing along with the COD removal. This indicates that the loading during phase 1 was somewhat moderate to both SRB and MA and their population was on the increase. After phase 2, methanogenic activity was dropping progressively while sulphate reduction remained at high level. The high sulphidogenesis activity observed along with 80% COD removal was clear evidence that SRB out-competed MA. The suppression of methanogenesis in the AFP was not likely caused by H_2S toxicity, but the consequence of outcompeting SRB over MA. Figure 5 shows that the dissolved hydrogen sulphide level in the AFP was much smaller than the threshold toxicity level for anaerobic processes reported in literature (over 1000 mg l^{-1}, Isa et al. 1986b; 90-250 mg S l^{-1}, Koster et al. 1986; 50 mg l^{-1}, Kroiss & Plahl-Wabnegg 1983). Much of the sulphide was in the ionised forms and converted to elemental sulphur by pink photosynthetic sulphur bacteria that were in extreme abundance in the upper water layer of the AFP (Tadesse et al. 2003).

Competition between SRB and MA

To quantify the competition between SRB and MA, a COD mass balance was computed around AFP using

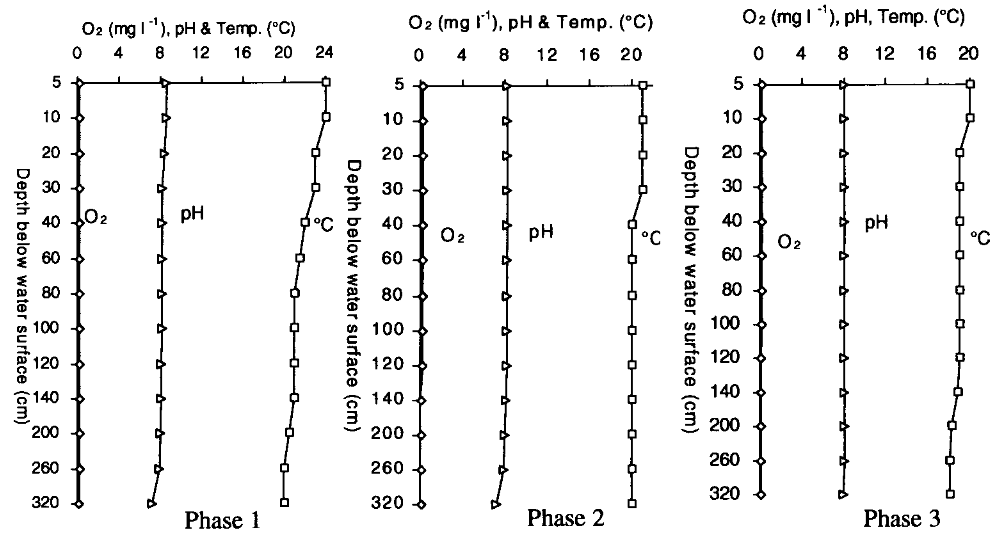

Figure 3. Vertical variations of dissolved oxygen, pH and temperature within the AFP.

the concept of "electron flow" introduced by Isa et al. (1986a) and presented in Table 2. According to Isa et al. (1986a), the competition between SRB and MA, in terms of % electron flow, is equal to the number of moles of sulphate reduced or methane produced divided by the total number of moles of sulphate reduced and methane produced (Columns 13 and 14, Table 2) and expressed as follows:

$$\%\ \text{electron flow to SRB} = [\Delta\text{SO}_4\text{-COD}/(\text{CH}_{4\,\text{gas}}\text{-COD} + \text{CH}_{4\,\text{aq.}}\text{-COD} + \Delta\text{SO}_4\text{-COD})]\ 100$$

$$\%\ \text{electron flow to MA} = [(\text{CH}_{4\,\text{gas}}\text{-COD} + \text{CH}_{4\,\text{aq.}}\text{-COD})/(\text{CH}_{4\,\text{gas}}\text{-COD} + \text{CH}_{4\,\text{aq.}}\text{-COD} + \Delta\text{SO}_4\text{-COD})]\ 100$$

It can be seen from Table 2 that mean % electron flows towards SRB, which are also, according to Isa et al. (1986a), related to % COD scavenged, were 59%, 70% and 83% during phase 1, 2 and 3, respectively. The corresponding mean % electron flows towards MA were 41%, 30% and 17%. This clearly demonstrates that sulphidogenesis had a more dominant role than methanogenesis. In sulphur rich wastes more electrons are directed towards the sulphate reduction than to the reduction of CO_2 to methane. Other works also underpinned this fact. Shin et al. (1997), treating tannery wastewater in UASB, reported an increase in the sulphidogenic fraction of COD from 13% to 67% with increase in the loading rate. Harada et al. (1994) reported a sulphidogenic COD degradation of 40–75% at feed S : COD ratio of 0.4. The overall material balance of the COD given in column 15 of Table 2 was, however, low with a recovery of 14–82%, 15–84% and 30–90% during phase 1, 2 and 3, respectively.

Other possible routes for the COD unaccounted would be denitrification, microaerobic oxidation and photosynthetic sulphide oxidation, especially, near the top water layers, bacterial cell synthesis and, of course, non-degradable COD retained in the reactor, all of which were not specifically investigated to give a full account of the COD in the reported mass balance. So, column 13 and 14 of Table 2 should be viewed, in light of this limitation, as the relative amounts of COD associated with SRB and MA.

Effects of sulphate concentration and COD : $SO_4^=$ ratio to sulphate reduction

Figure 6 illustrates that the flow of available electron towards sulphidogenesis increased with the increase of sulphate input and the decrease of COD : $SO_4^=$ ratio. It is also obvious from Figure 6a that the electron flow towards sulphidogenesis leveled off near the sulphate concentration of 1000 mg l^{-1} and a further increase in the sulphate concentration beyond that did not result in additional electron flow.

Table 2. Distribution of electron between SRB and MA

Exp. phase	Time (days)	COD removed (mg COD l^{-1})	SO_4^{-2} removed (mg SO_4^{-2} l^{-1})	Biogas (l biogas d^{-1})	CH_4 (m^3 CH_4 d^{-1})	Applied SO_4^{-2} loading rate (kg SO_4^{-2}-S m^{-3} d^{-1})	Applied COD loading rate (kg COD m^{-3} d^{-1})	Eff. COD (%)	$CH_{4\,gas}$-COD (%)	$CH_{4\,aq.}$-COD (%)	ΔSO_4^{-2}-COD (%)	% electron flow		COD recovery (%)
												SRB	MA	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
I	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	17	723	596	11	0.008	0.028	0.132	31.339	6.086	12.747	54.956	74.478	25.522	82.003
	25	1681	815	16	0.011	0.040	0.254	17.396	3.807	5.482	32.322	77.675	22.325	51.769
	93	4727	848	16	0.011	0.040	0.675	12.463	1.354	1.950	11.953	78.346	21.654	25.818
	100	4827	50	16	0.011	0.006	0.679	11.105	1.326	1.909	0.684	17.446	82.554	14.589
	148	4608	262	50	0.035	0.016	0.718	19.805	4.340	2.000	3.791	37.416	62.584	27.929
	161	3913	895	74	0.052	0.041	0.571	14.376	7.563	2.355	15.248	60.586	39.414	35.926
	180	4057	993	74	0.052	0.042	0.608	16.540	7.296	2.272	16.317	63.038	36.962	38.144
	217	3058	763	56	0.039	0.032	0.448	14.748	7.325	3.014	16.630	61.663	38.337	37.739
II	392	5581	2652	142	0.099	0.182	1.359	17.890	6.361	1.651	31.679	79.814	20.186	50.481
	399	7388	227	54	0.038	0.024	1.711	13.631	1.827	1.247	2.048	39.983	60.017	18.056
	420	6155	398	54	0.038	0.028	1.466	16.007	2.193	1.497	4.311	53.876	46.124	22.728
	434	8617	477	54	0.038	0.033	1.920	10.240	1.567	1.070	3.690	58.331	41.669	15.918
	449	2050	591	18	0.013	0.045	1.900	78.421	2.195	4.496	19.220	74.177	25.823	84.012
	533	4253	808	10	0.007	0.059	1.093	22.149	0.588	2.167	12.666	82.136	17.864	34.154
	547	8217	855	10	0.007	0.058	1.901	13.542	0.304	1.122	6.937	82.950	17.050	20.772
	554	4531	993	10	0.007	0.067	1.257	27.885	0.552	2.034	14.610	84.963	15.037	40.286
III	568	2898	1002	10	0.007	0.111	1.591	41.947	0.541	3.180	23.050	86.100	13.900	57.489
	573	1188	1050	0.875	0.001	0.119	1.388	72.727	0.116	7.758	58.923	88.213	11.787	90.944
	582	3528	1299	0.875	0.001	0.140	1.874	40.000	0.039	2.612	24.546	90.252	9.748	56.319
	604	2494	910	0.063	0.000	0.108	2.268	64.942	0.004	3.695	24.325	86.800	13.200	74.767
	609	3845	385	0.063	0.000	0.048	1.677	26.929	0.003	2.397	6.675	73.559	26.441	33.560
	629	4493	490	0.063	0.000	0.054	2.079	29.411	0.002	2.051	7.277	77.991	22.009	35.997
	643	5184	603	0	0.000	0.068	2.203	25.000	0.000	1.778	7.748	81.338	18.662	32.144

In all cases influent flow rate = 0.5, 0.8 and 1.275 m^{-3} d^{-1} during phase 1, 2 & 3, respectively; reactor volume = 4 m^3; CH_4 = 70% biogas; CH_4 conversion rate = 0.350 m^3 CH_4 per kg COD removed; CH_4 solubility rate at 20 ° = 0.0322561 CH_4 per l; SO_4^{-2}-COD = 0.67 kg COD kg^{-1} SO_4^{-2} reduced.

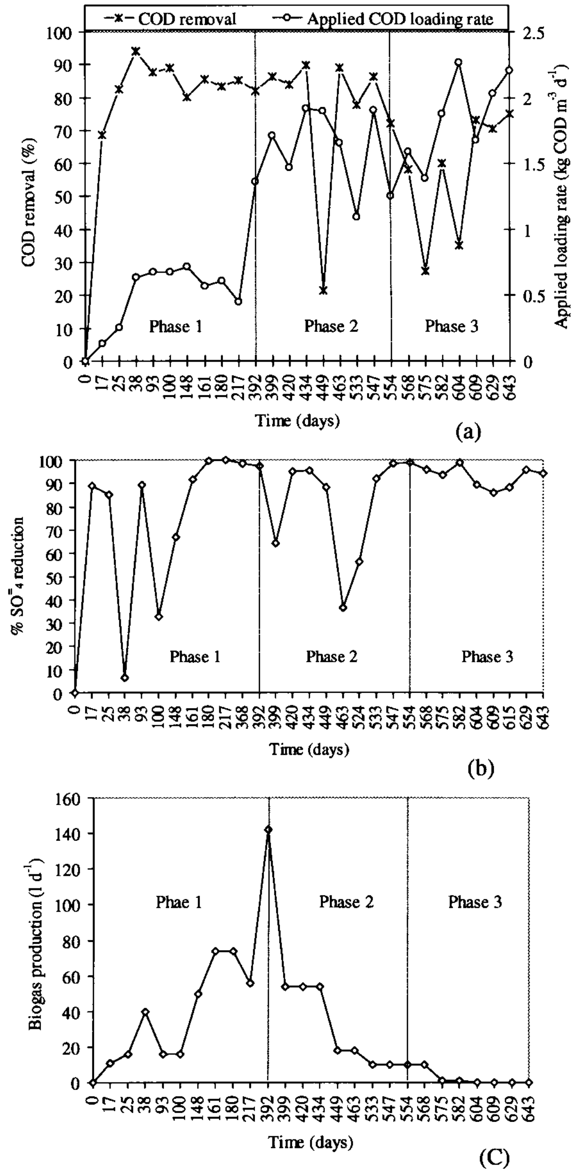

Figure 4. COD removal efficiencies (a); % sulphate reduction (b) and biogas production (c).

Conclusions

1. Although the overall % COD recovery within the AFP varied between 15–90%, the relative share of electron flow towards sulphidogenesis was higher (59–83%) than towards methanogenesis (17–41%).
2. Flow of available electrons towards sulphidogenesis increased with the increase of sulphate concentration and decrease of COD : SO ratio.

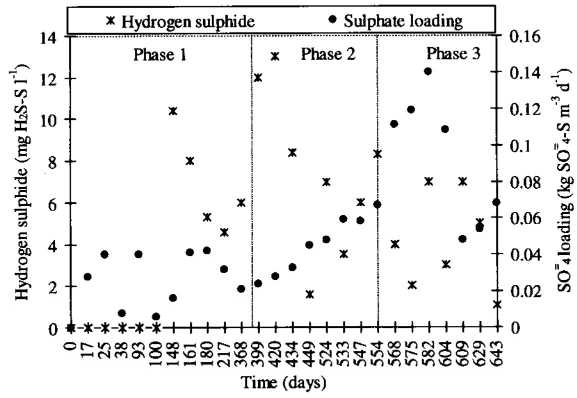

Figure 5. Dissolved H_2S concentrations and volumetric sulphate loading in the AFP.

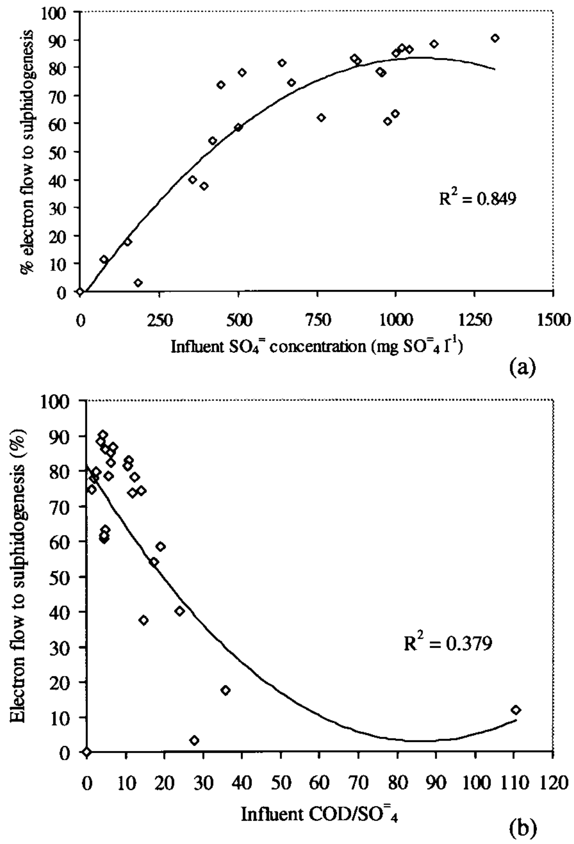

Figure 6. Percentage of electron flow for sulphidogenesis versus (a) sulphate concentrations, and (b) COD : $SO_4^=$ ratio.

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