Treatment of textile dyes in two-phase and single-phase anaerobic bio-treatment systems

D. Bhattacharyya and K. S. Singh

ABSTRACT

This research integrates two different concepts of anaerobic biotechnology- two-phase anaerobic treatment and anaerobic granular sludge bed technology, in treatment of colored wastewaters from textile industries. Four anaerobic reactors based on upflow anaerobic sludge blanket (UASB) technology were used as acid reactors and an expanded granular sludge bed (EGSB) reactor was used as a methane reactor. A conventional single-phase anaerobic reactor, working on EGSB technology was run in parallel to compare the performances of the two systems. Reactors were operated at different hydraulic retention times. The results from the study, which span over a period of 400 days, indicated that the two-phase system produces a higher quality of effluent in terms of color, COD and suspended solids than single-phase anaerobic treatment when operated under similar conditions. Alkalinity requirement of two-phase system was also observed to be lower than that of single-phase system which is important regarding design consideration.

Key words | anaerobic, color, dye, textile, two-phase

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INTRODUCTION

This research integrates two different concepts of anaerobic biotechnology, namely, two-phase anaerobic treatment and anaerobic granular sludge bed technology, in treatment of colored wastewaters from textile industries. Conventional aerobic biological processes are not very successful in removing dye from wastewater streams. The reason is that dyes are designed to be bio-resistant (Bahorsky 1998). The main mechanism of color removal in aerobic processes is through adsorption by biomass. Suitability of anaerobic bio-treatment technology in color removal has been an area under intensive study in recent years. It has been reported that the primary degradation and decolorization of dyes can be achieved through reductive cleavage of $-N{=}N-$ or azo bonds (Delée *et al.* 1998). The amines produced by the reduction of azo bonds cannot be degraded further under anaerobic environment but can be mineralized under aerobic conditions. Researchers have advocated merits of two-phase anaerobic system in treating simple and complex wastewaters (Fox & Pohland 1994). Treatment through phase separation enhances the potential of anaerobic treatment in treating a wide variety of toxic and recalcitrant compounds. Anaerobic high-rate reactors are fast replacing aerobic and conventional treatment units all over the world with the development and successful implementation of anaerobic granular sludge bed technology (Lettinga *et al.* 1980). By immobilizing anaerobic bacteria through a process of self-granulation, solid retention times can be separated from the hydraulic retention times in anaerobic granular sludge bed reactors. This makes reactors "high-rate" as they can withstand higher organic and hydraulic loads or they can treat a given waste in a much shorter time period. These two popular concepts (two-phase anaerobic treatment and anaerobic sludge bed technology) have been combined in this study in treating a synthetic dye wastewater.

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METHODS

Synthetic feed. A mixture of equal proportions (by weight) of three Procion reactive dyes – Red MX-8B, Red MX-5B and Orange MX-2R, was used in this study. A synthetic feed of total chemical oxygen demand, COD = 3,000 mg/L was prepared. Soluble COD = 2,500 mg/L was made up with sucrose, which acts as a co-substrate, and different doses of dyes. Particulate COD (= 500 mg/L) was added in the form of cellulose (Table 1), and kept in suspension in feed tanks with the help of mechanical stirrers. Sodium bicarbonate (buffer) was added to the synthetic wastewater to give an influent $NaHCO_3$ concentration of 1,000 mg/L in the acid reactor. Additional bicarbonate was added to the effluent prior to pumping into the methane reactor so as to achieve a total sodium bicarbonate concentration of 2,000 mg/L in the two-phase system. Single-phase system was started up with a sodium bicarbonate dose of 2,000 mg/L but had to be increased stepwise to 6,000 mg/L with decrease in HRTs. Nutrient and mineral composition of the feed was (mg/L): NH_4Cl–300, $MgCl_2.6H_2O$–300, $K_2HPO_4.3H_2O$–300, $CaCl_2.2H_2O$–50, $FeCl_3.6H_2O$–10, $ZnCl_2$–0.5, $CuCl_2.2H_2O$–0.5, $CoCl_2.6H_2O$ –0.5, $MnSO_4.7H_2O$–0.5, $NiCl_2.6H_2O$–0.5, $NaWO_4.2H_2O$ –0.5, $(NH_4)_6Mo_7O_{24}.4H_2O$–0.5, NH_4VO_3–0.5, KI–0.5, H_3BO_3–0.5

Experimental Setup. Schematic of the experimental setup is shown in the Figure 1. Two-phase setup consisted of four poly acrylic upflow anaerobic acid reactors (volume = 3.35 L; internal diameter = 7.3 cm; height = 80 cm) and one EGSB reactor (volume = 17.43 L; internal diameter = 10.2 cm; height = 2.13 m), which was used as methane reactor. Four acid reactors (U1, U2, U3 and U4) were dosed with 0, 25, 50 and 100 mg/L of dyes respectively to study the effect of dyes on acidification. Doses of co-substrate (sucrose) were adjusted so as to ensure same organic loading in all the reactors at all hydraulic loading rates. Reactor U1 with no dye in the feed acted as a control for comparing the performances of other acid reactors. Acidified effluent from reactors U2, U3 and U4, after pH adjustment with sodium bicarbonate, was pumped into the EGSB reactor (E1) which served as methane reactor. For the single-phase system, only one EGSB reactor (E2) was used whose dimensions are same as that of E1. Concen tration of dye in the feed for single phase system was kept at 60 mg/L to ensure same dye loading rate in both the systems. The reactors were operated at different hydraulic retention times (HRTs).The mode of operation is shown in Figure 2. All the reactors were kept in an environmental chamber (Coldstream, Winnipeg, Canada) at 35°C.

Analytical procedure. Influent and effluent samples were tested for total and volatile suspended solids, and COD (titrimetric and colorimetric), following *Standard Methods* (1998). Volatile fatty acids (VFA) were analyzed by titration (DiLallo & Albertson 1961) as well as by chromatography using flame ionization detector (FID) in Varian CP 3,800 gas chromatograph, equipped with fused silica capillary column and helium as carrier gas. Color in the filtered samples was analyzed in Genesis 6 scanning spectrophotometer (Thermo Electron Corporation). Gas samples are analyzed using thermal conductivity detector (TCD) in Varian CP 3,800 GC, equipped with packed (Hayesep Q) column and helium as carrier gas.

RESULTS AND DISCUSSION

Acid reactors U1, U2, U3, and U4 were dosed with different concentrations of dyes, as mentioned earlier, to see the effect of dye on the production of volatile fatty acids. Figure 3 compares the VFA production at four different hydraulic

Table 1 | Major components of the synthetic wastewater (mg/L)

	Two-phase system				Single-phase system
	U1	U2	U3	U4	E2
Soluble COD (sucrose + dye)	2,500	2,500	2,500	2,500	2,500
Particulate COD	500	500	500	500	500
Dyes	0	25	50	100	60
$NaHCO_3$	1,000	1,000	1,000	1,000	2,000–6,000

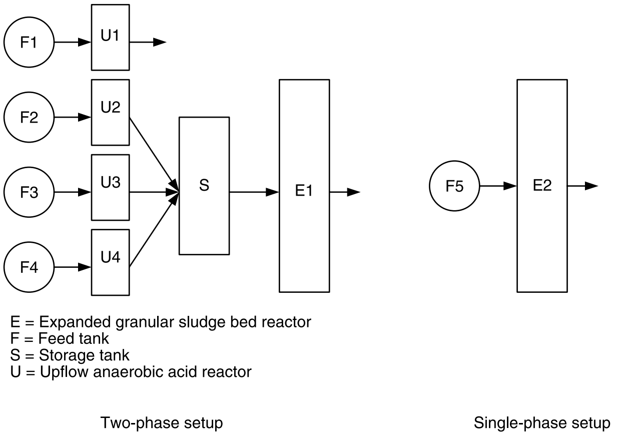


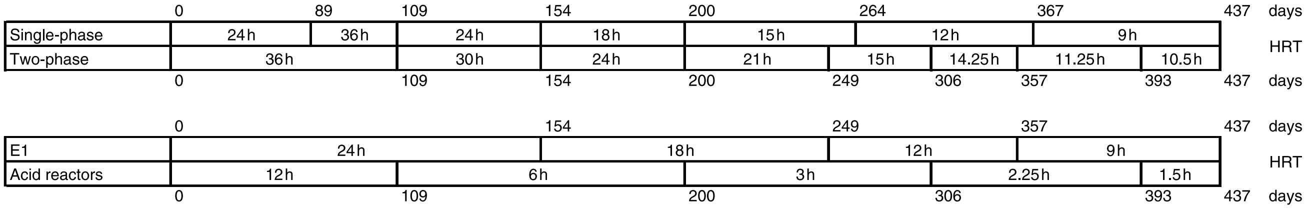
Figure 1 | Schematic of the experimental setup.

retention times – 12 h, 6 h, 3 h, and 2.25 h. At higher 12 h and 6 h HRTs, volatile fatty acid production was found to be higher in control reactor (U1) than the other reactors which were fed with dyes. However, at lower HRTs, that trend was not clear. A distinct inhibition-effect of concentrations of dyes on VFA production was not observed in the concentration range at which study was performed. It was seen that at 12 h HRT volatile acid concentration in the effluent of the acid reactors tend to decrease with time with a gradual increase in pH. The effluent COD also showed a decreasing trend with a gradual increase in biogas production. 12 h HRT samples did not show good acid production as the reactors tend to be methanogenic. Periodic removal of sludge seems to help increase in VFA production. At low HRTs higher sludge production was noticed due to deposition of cellulose in the bed and removal of sludge became more essential to maintain a constant sludge bed height. A rapid increase in sludge bed at 3 h HRT indicated a poor hydrolysis of cellulose at lower hydraulic retention times. A pH range between 5 and 6 was found to be adequate for acidification. On an average, 15% of influent COD was obtained as VFA in the effluent of acid reactors.

Volatile fatty acid was found to be low in the effluent of the methane reactor of the two-phase system. Figure 4 compares the effluent VFA of two-phase and single-phase system over the period of the study. It was seen that the effluent VFA was about 50–60 mg/L for two-phase system over the most part of the study. Effluent VFA was found to increase when HRT of acid reactors were decreased to 2.25 h from 3 h while HRT of methane reactor was maintained at 9 h. On the other hand, VFA in the effluent of single-phase system was found to greatly increase when HRT was reduced from 15 h to 12 h.

Concentrations of original dyes and in the influent and effluent filtered samples were analyzed by spectrophotometry. Standards were scanned using Genesis 6 UV/Vis spectrophotometer and maximum absorbance in the visible region of the spectrum was observed to be at 514 nm. Concentrations of dye in the effluent samples were determined using a calibration curve, prepared at 514 nm wavelength, using standard dye solutions. Figure 5 compares the efficiencies of two-phase and single-phase system in removing original dyes from the wastewater. Both systems displayed a decrease in the efficiency of removal of dye with decreasing HRTs. However, the reduction in efficiency for two-phase system was gradual. Even at a low HRT of 10.5 hours removal efficiency was still approximately 85%. For single-phase system, the decline was found to be much steeper. Efficiency fell sharply from 80% to about 63% when HRT was reduced from 18 hours to 15 hours.

Gregor (1994) suggested a different method of measuring color. Influent and effluent samples were scanned over the entire range of the visible spectrum (400 nm to 800 nm) and the area under the curve was calculated and expressed in space unit. Removal efficiency of color was assessed by comparing the space units of the influent and effluent samples. The reason for such an approach of calculation of color removal is due to a possible shift in the peak from its



HRT (days)	0	89	109	154	200	249	264	306	357	367	393	437
Single-phase	24 h	36 h	24 h	18 h	15 h		12 h			9 h		
Two-phase	36 h		30 h	24 h	21 h	15 h		14.25 h	11.25 h		10.5 h	

HRT (days)	0	109	154	200	249	306	357	393	437
E1	24 h		18 h		12 h		9 h		
Acid reactors	12 h	6 h		3 h		2.25 h		1.5 h	

Figure 2 | Operation of the reactors.

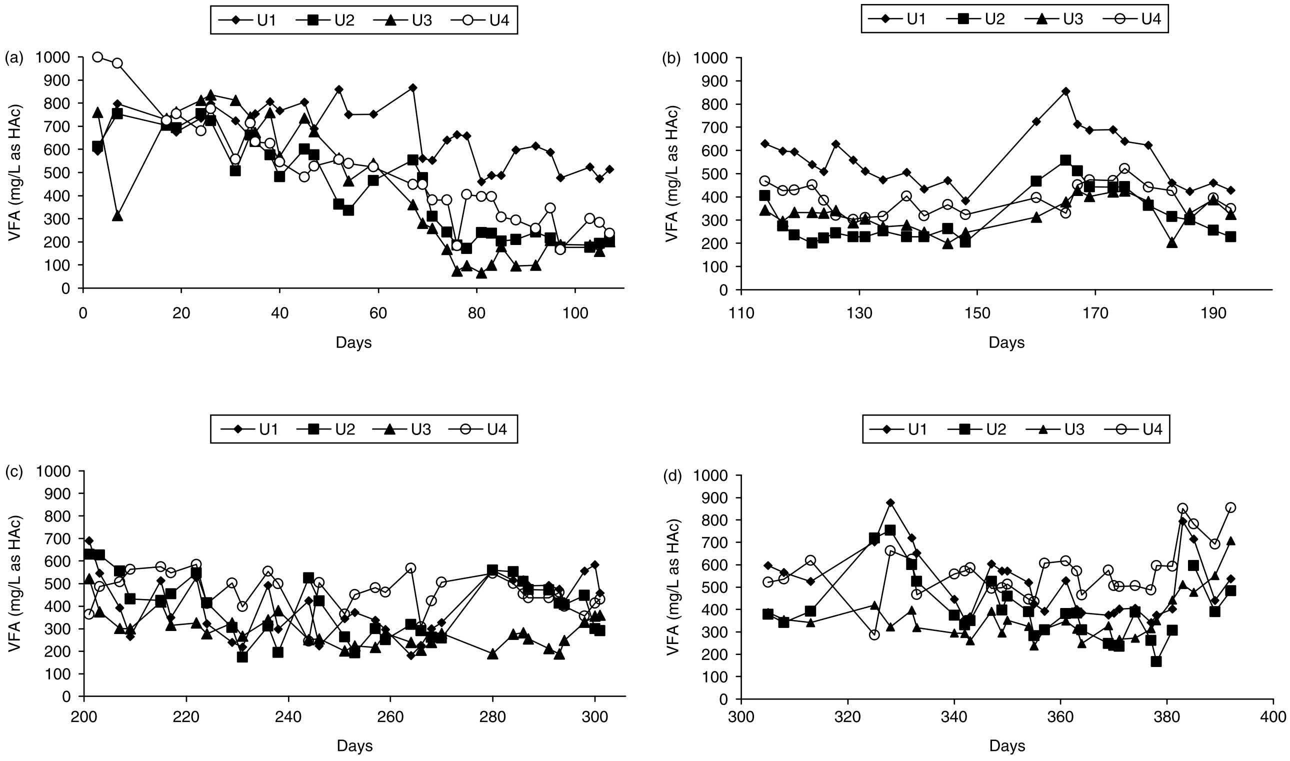


Figure 3 | Volatile fatty acids production in acid reactors at different HRTs – (a) 12 h, (b) 6 h, (c) 3 h, and (d) 2.25 h.

original position in course of the treatment. This peak shift can happen when the degraded intermediates are themselves colored compounds. In that case, measurement of absorbance at any fixed wavelength will produce an erroneous assessment. However, the approach of measuring absorbance at the characteristics wavelength is still required to find out the extent of biotransformation of the original compound. Figure 5(b) shows the color removal efficiencies of two-phase and single phase systems based on the space units. The figure shows similar pattern as that of Figure 5(a).

Figure 6 shows an absorbance versus wavelength curve of a sample of wastewater before and after treatment. The figure shows a definite decrease in the area and the peak of the absorbance curve in the visible region of the spectrum. No shifting of peak from the original position was noticed which implies absence of colored intermediates of the dyes, under investigation. However, a peak in the ultraviolet region which showed slight or no decrease after the treatment indicates the possibility of the presence of intermediate products like amines which are colorless but

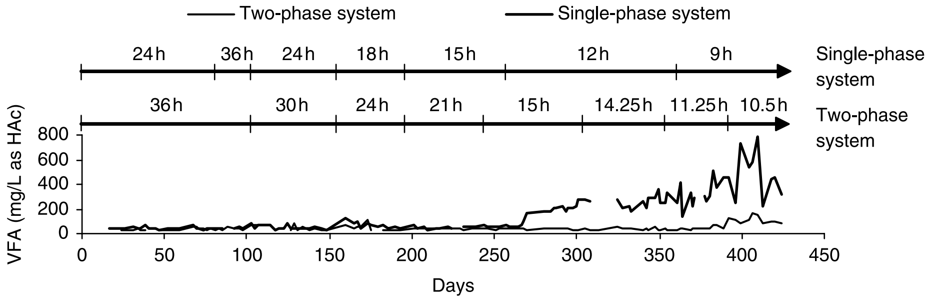


Figure 4 | Volatile fatty acids in the effluent of two-phase and single-phase systems.

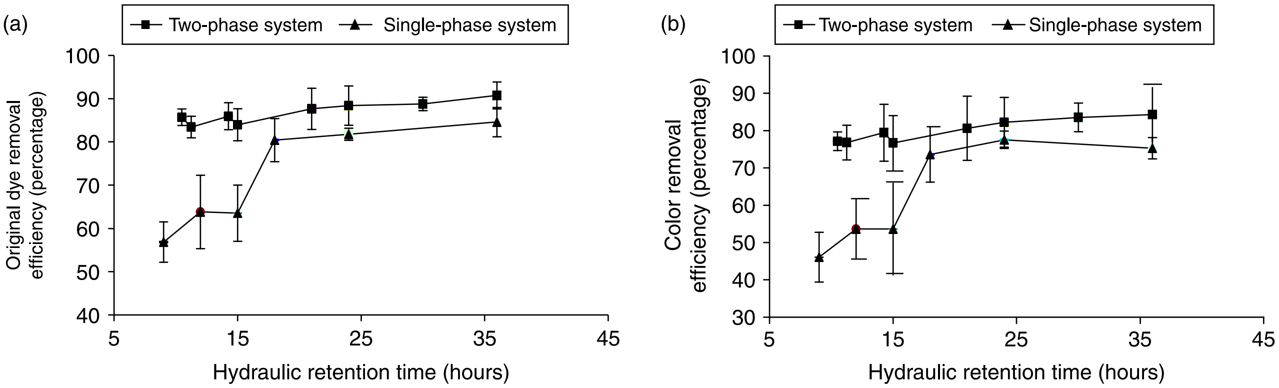


Figure 5 | Removal efficiencies of two-phase and single-phase systems at different HRTs (a) dye and (b) color.

can be detected in the UV region. A study to identify the possible intermediates products of anaerobic biotransformation of the dyes is currently in progress.

Treatment efficiencies of two-phase system and single phase system were compared in terms of total chemical oxygen demand (COD). Figure 7 shows that two-phase system consistently removed more than 90% of COD at all HRTs, whereas single-phase system registered a sharp drop in efficiency when HRT was reduced to below 15 hours.

An important observation during the study was a sludge flotation problem. This occurred in single-phase system at every hydraulic retention time below 18 hours, particularly at the time of change of HRT. It has been reported that granules cultivated under lower loading conditions have a tendency to float due to substrate depletion at the core, which leads to the lysis and decay of cell inside granule. Resulting hollow spaces trap biogas, thereby increasing the buoyancy of the granules (Yoda & Nishimura 1997). However, observations made in the present study seem to have contradicted the previous theory, as the phenomenon was noticed at higher loading rates. At every HRT below 18 h, sludge granules were found to float in lumps, clogging the three phase separator at the top, making it impossible to run the reactor. Mechanical breakdown of the lumps did not provide a solution as flotation could not be prevented and recurred. A decrease in pH (below 6.7) and an increase in percentage of carbon dioxide in biogas (above 45%) were noticed. There is a need to increase the alkalinity dosage under such conditions. Hulshoff-Pol (1989) reported that sludge settleability and granulation can be enhanced by addition of calcium hydroxide, which also increases the alkalinity. The reduction of sludge flotation was attributed to calcium ions which increase the binding capacity between different layers of bacteria in granules.

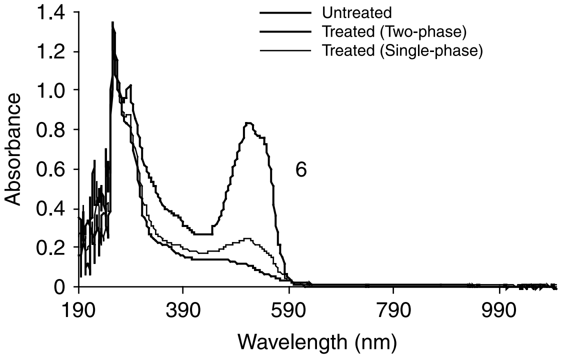


Figure 6 | Sample absorbance versus wavelength curves of the dye wastewater before and after treatment.

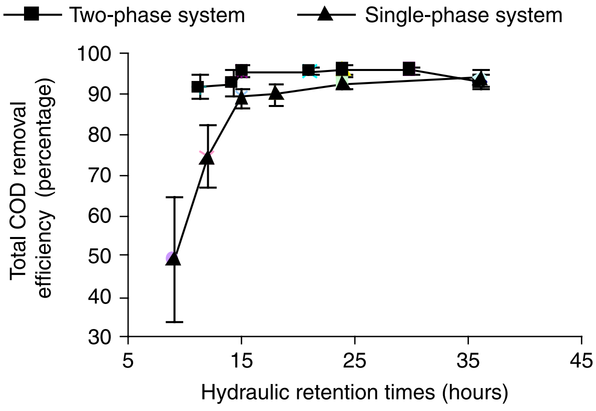


Figure 7 | Total COD removal efficiencies of two-phase and single-phase systems at different HRTs.

Sodium bicarbonate was increased stepwise in the following order: 2,000 mg/L (36 h HRT) → 3,000 mg/L (24 h HRT) → 5,000 mg/L (15 h HRT) → 6,000 mg/L (12 h HRT) in the present study. An increase in the dosage of sodium bicarbonate was found to decrease the percentage of carbon dioxide in the biogas, thereby restoring the effluent pH at neutral level. Moreover, the sludge flotation problem was also alleviated at the same time. The role of sodium ions or alkalinity in prevention of sludge flotation was not studied as it was not covered in the realm of the present study. Both systems were started up with an alkalinity dose of 1,200 mg/L as $CaCO_3$, which is well below the minimum alkalinity requirement of 1.2 g $CaCO_3$/g influent COD converted to VFA (Speece 1996). While the two-phase system could perform consistently well at all HRTs without any increase in alkalinity dosage, performance of single-phase system was reduced due to want of alkalinity. Acidification, accompanied by CO_2 escape, which was noticed in the acid reactors, reduced the alkalinity requirement of the two-phase system as also reported by Speece (1996).

CONCLUSION

The two-phase system produced a higher effluent quality than the single phase system in terms of all the tested parameters at all HRTs. Scanned data of the influent and effluent samples indicate a reduction of absorbance peak in the treated samples within the visible region of spectrum. However, no apparent reduction in the peak in the ultraviolet region of spectrum was noticed which indicates the possibility of the presence of intermediate products. No clear effect of dye dosage on acid production was noticed within the range of these experiments. The alkalinity requirement of the two-phase system was found to be much less than single-phase system which is important regarding design consideration.

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