

## **BIOLOGICAL TREATMENT OF WASTES USING FLUIDIZED BED TECHNOLOGY**

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### **ABSTRACT**

This study investigated the feasibility of employing biological fluidized bed reactors for effective wastewater treatment. The reactors were operated under aerobic, anoxic, and anaerobic conditions treating phenol, monoethylamine, di-isopropylamine, and glucose. Amines are widely used in refinery operations to remove hydrogen sulfide from flue gas; phenol is often present in refinery wastestreams; and glucose decomposition to methane and carbon dioxide is a multistep process that uses various bacterial species, representing typical anaerobic complex-waste treatment.

The performance of fluidized bed reactors in treating these compounds under aerobic, anoxic, and anaerobic conditions was examined. Treatment pathways that were promoted in the reactors were simultaneous carbon oxidation and nitrification under aerobic conditions, simultaneous carbon removal and denitrification under anoxic conditions, and volatile organic acid formation followed by methanogenesis under anaerobic conditions. For the treatment of phenol and the amines, several quasi-steady-state experiments were conducted in continuous-flow, aerobic, and anoxic reactors with the feed loading rate as the experimental variable. Complete carbonaceous oxidation was achieved with a 50% nitrification rate. Carbon removal under anoxic conditions was closer to completion at carbon loading rates less than 0.05 mg TOC/mg biomass-day and decreased to 75-89% at higher loading rates. Nevertheless, over the range of loading rates tested, the average ratio of mg TOC removed to mg NO<sub>3</sub>-N utilized was observed to be 1.48.

Anaerobic treatment of glucose was investigated under continuous and batch operating conditions with feed loading rate and bulk-liquid substrate concentration, respectively, as the experimental variables. Quasi-steady-state, as well as transient leading response, was investigated. The reactors were able to successfully handle organic loading rates of up to 12,000 mg TOC/L-day. Substrate removal efficiencies above 98% were consistently observed. Specific biogas production rates of 1.4 - 1.7 l CH<sub>4</sub>/g TOC removed were attained.

The feasibility of utilizing amines and phenol as the organic carbon source for denitrification, as well as high glucose loading-rates under anaerobic conditions, was successfully demonstrated. Moreover, the results from this research demonstrate that the amines and phenol can be used as the sole organic carbon source, significantly reducing chemical costs.

## INTRODUCTION

Industrial wastewaters often contain a significant amount of nitrogenous organic compounds. The nitrogen in these compounds can be converted to ammonia during conventional wastewater treatment through abiotic and biotic mechanisms. Deleterious effects of high concentrations of ammonia in water and wastewater range from biostimulation of surface waters, aquatic toxicity, and assault on public health, to corrosion of industrial structures, which use reclaimed wastewater (US EPA, 1975). Because ammonia is a regulated wastewater parameter and nitrogenous organic compounds themselves can have major negative effects on the environment and public health, the removal of these compounds has become an essential component in industrial wastewater treatment. Although many physico-chemical processes can be employed to remove nitrogen from wastewaters (US EPA, 1975),

biological nitrogen removal is one of the most cost-effective treatment processes for both industrial and domestic wastewaters (Winkler, 1984).

In this work the feasibility of biological treatment of di-isopropylamine ( $C_6H_{15}N$ ), monoethylamine ( $C_2H_7N$ ) and phenol ( $C_6H_5OH$ ) was investigated. These compounds are commonly found in wastewater from petroleum refining operations. The target amines are widely used in refinery operations for removing hydrogen sulfide from flue gas by absorption (Norman, 1985). The hydrogen sulfide is subsequently released from the amines and then processed into sulfuric acid or elemental sulfur, while the amines are recycled for further use. However, when the amines absorb the hydrogen sulfide, they also absorb impurities from the flue gas and are susceptible to foaming. As a result, the foam concentrated with amines overflow and frequent spills occur (Shieh, 1993). The spills can severely disrupt the normal operation of conventional wastewater treatment commonly employed in refineries, since the amines used are highly concentrated and caustic (Norman, 1985). Phenol, a carbonaceous organic compound, is also targeted for simultaneous biodegradation in this investigation, since it is often present in the refinery wastewater stream along with the amines.

The biological degradation of phenols in wastewater treatment processes is well documented (Becarri *et al.*, 1984; Donaldson *et al.*, 1984; Luthy, 1981; Neufeld and Valiknac, 1979; Livingston and Chase, 1989; Richards and Shieh, 1989). However, little has been reported about the biological degradability of di-isopropylamine (DIPA) and monoethylamine (MEA). Moreover, phenol has been shown to be an effective primary internal organic carbon source in an anoxic/oxic activated sludge system treating coke plant wastewater (Shieh and Richards, 1988); however, very little has been reported about the utilization of DIPA and monoethylamine MEA as organic carbon sources for denitrification.

Anaerobic reactors have been studied extensively over the past three decades. Successful operation in bench- and pilot- scale studies has improved process reputation for stability and reliability. Anaerobic digestion is steadily becoming an integral part of available wastewater treatment technologies.

The results reported in available related literature (Lawrence and McCarty, 1969; Parkin and

Owen, 1986; Worthy, 1991; Ryhiner *et al.*, 1993; Thiele, 1991; Jeris and McCarty, 1965; Jeris and Kugelman, 1985; Ozturk *et al.*, 1989), agree that anaerobic fermentation is a complex, multistep biological process. This process converts the biodegradable portion of the wastewater into bacterial cells, carbon dioxide, and methane gas, and is often described as having the following three basic stages:

- Hydrolysis, liquefaction, and fermentation
- Hydrogen and acetic acid formation
- Methane formation

Hydrolysis and liquefaction are necessary to convert complex organics that may be insoluble to a size and form that is readily usable by the bacteria as energy or nutrient sources. Hydrogen can be produced by fermentative and acetogenic bacteria. Acetic acid is also produced by these groups, as well as by hydrogen-consuming acetogenic bacteria. Hydrogen has been shown to play a key role in the production of methane gas. Final waste stabilization (COD or TOC removal) occurs when acid-utilizing and CO<sub>2</sub>-reducing methanogens produce methane and carbon dioxide. The decomposition of glucose, as well as other complex carbohydrate wastes, to methane and carbon dioxide is a complex process that uses up to five different groups of bacterial species, each interdependent on the other's function and performance. The overall process kinetics may be better characterized by considering the integrated process functioning as a whole rather than by studying the kinetics of utilization of specific intermediates (i.e., acetate, propionate, butyrate, and others).

Proper design and selection of reactor configuration for specific wastewater streams play an important role in the success of the treatment process. Research results for various reactor configurations have been difficult to compare due to inconsistencies in study conditions. A comprehensive investigation of various reactor configurations under uniform study conditions is needed to provide a better understanding of design merits.

This study recognizes the importance of anaerobic wastewater treatment technology and attempts to examine the response of such reactors employing various configurations under pseudo-steady-state operating conditions. Three reactor configurations were concurrently investigated, allowing for direct comparison of reactor performance and minimizing the effects of non-uniform study conditions.

This study was divided into three separate investigations:

- The oxic investigation involved removal of the amines and phenol by promoting carbon removal and nitrification in a biological fluidized bed (BFB) reactor.
- The anoxic investigation involved the use of the amines and phenol as internal organic carbon sources for denitrification in a BFB reactor. When the amines and phenol are used as the sole organic carbon source for denitrification, economic costs involved in the use of an external carbon source can be minimized. Moreover, the carbon removal efficiency of the BFB reactor can be maximized, since after passing through both anoxic and oxic stages, the carbonaceous removal should be nearly complete.
- The anaerobic investigation involved the use of glucose as the sole carbon source to promote methanogenesis through an intermediate acidogenesis step.

## MATERIALS AND METHODS

### Materials

Identical reactors were employed for both oxic and anoxic investigations. Three BFB reactors were operated concurrently. Each reactor comprises a glass tube with a bottom cone and several sampling ports. Diatomaceous earth—Celite R-633—beads (Manville, Colorado, USA) were used as the growth support media. The bacterial culture was obtained from the activated sludge process at the Southwest Philadelphia Water Pollution Control Plant. Detailed descriptions of reactor design, growth support media, synthetic feed, and bacterial consortium are published elsewhere (Nguyen and Shieh, 1995a).

The fluidized bed reactors (R1 and R2) were fabricated and operated under similar conditions (with the exception of the immobilization media). Two identical reactors were used, each consisting of a glass column 76 cm long with an inner diameter (ID) of 5.1 cm. The column was fused to another column with wider cross-sectional area for enhanced solid-liquid-gas separation. The upper section consisted of a glass column 25.4 cm long with a 7.6 cm ID. The reactor body was sealed using a glass cap with three outlet ports. The cap was fixed in place with a rubber ring (to prevent gases from escaping) and a horseshoe-shaped clamp. The reactors had a conic section at the bottom with an inlet for recycled flow. A flow distribution zone was constructed of large uniform glass beads with annular cavities. The packed-bed reactor (R3) consisted of a cylindrical glass container with an ID of 14.3 cm and a height of 30 cm (total reactor volume of 4,850 mL). The suspended growth reactor (R4) consisted of a prefabricated fermenter system. The reactor chamber consisted of a cylindrical glass container with an ID of 11.6 cm and a height of 22.9 cm (total reactor volume of 2,400 mL).

The bacterial inoculum was obtained from anaerobic sludge collected from the Southwest Philadelphia Water Pollution Control Plant, and was first passed through a fine sieve to remove particulates then thickened prior to use. The inoculum culture had a measured volatile solids (VS) concentration of 500-3,000 mg/L, and was used for the reactor start-up and reseeded during the start-up stage. Detailed descriptions of reactor design, growth support media, synthetic feed, and bacterial consortia are published elsewhere (El-Farhan and Shieh, 1996).

### Experiment Design

#### *Oxic and Anoxic Investigation*

The following experimental conditions were maintained in the BFB reactors: expanded bed volume 0.46-0.55 L; reactor pH,  $7.5 \pm 0.1$ ; reactor temperature,  $25^{\circ}\text{C} \pm 0.1$ ; reactor DO  $> 4.0$  mg/L (oxic) and  $< 1.0$  mg/L (anoxic).

*Reactor start-up.* BFB reactors were started-up as oxic reactors prepared for nitrification. The reactors were batch fed with the feed solution with a TOC concentration of 177 mg/L until effective TOC removal was attained within one cycle and good attachment of bacterial cells was evident. When these conditions were met, the reactors were switched to continuous-flow conditions.

*Steady-state experiments.* At the completion of the start-up phase, steady-state experiments were conducted with three oxic reactors, with the TOC loading rate as the experimental parameter. The feed to the oxic reactors contained phenol, DIPA, and MEA in a mineral solution. The average loading rate covered a range of 0.076 to 0.207 mg TOC/mg biomass-day for the oxic series of experiments. After the oxic steady-state experiments were completed, the reactors were placed under anoxic conditions—by discontinuing the air supply to the reactors. The feed to the anoxic reactors consisted of phenol, DIPA, MEA, and sodium nitrate in a mineral solution. Anoxic steady-state experiments were conducted again with the TOC loading rate as the experimental parameter. The average loading rate covered a range of 0.015 to 0.100 mg TOC/mg biomass-day for the anoxic series of experiments. The TOC/NO<sub>3</sub><sup>-</sup>-N ratio was maintained at a ratio of approximately 0.7, in order to provide a sufficient amount of NO<sub>3</sub><sup>-</sup>-N to prevent nitrate-limited conditions. At each new loading rate, each reactor was operated under the prescribed conditions continuously for at least two times the mean cell residence time (MCRT) to ensure that steady-state had been reached. At steady-state, daily grab samples were collected from each reactor and from the feed solution for at least 14 days. The samples were analyzed for the following parameters: TOC, TKN, NH<sub>4</sub><sup>+</sup>-N, NO<sub>2</sub><sup>-</sup>-N, NO<sub>3</sub><sup>-</sup>-N, and VSS concentrations. Periodic analyses of the attached volatile solids concentration (AVS) were also performed.

### ***Anaerobic Investigation***

Four reactors were constructed and operated continuously under anaerobic conditions. The reactors were fed a nutrient-supplemented wastestream with glucose as the main carbon source. Reactor one (R1) was an anaerobic fluidized bed reactor (AFBR) with diatomaceous earth (Manville R-633 beads) as the immobilization medium. Reactor two (R2) was an AFBR with granular activated carbon (Calgon GAC type OL) as the immobilization medium. Reactor three (R3) was an upflow packed-bed reactor with a bed consisting of a Celite biocatalyst carrier (Manville R-635 beads). Reactor four (R4) was a suspended-growth reactor (continuous flow stirred tank reactor, CFSTR).

The start-up strategy employed was based on maximum substrate utilization while maintaining an optimal operational environment. A glucose-enriched bacterial culture was used to seed the reactors to facilitate start-up and to provide a homogeneous environment which would allow for better isolation of the control parameters: immobilization media and reactor configuration. This circumvents complications and otherwise improper interpretation of data.

### **Analytical Techniques**

The analytical techniques employed are fully described in Nguyen and Shieh (1995a), and El-Farhan and Shieh (1996).

## RESULTS AND DISCUSSION

### Oxic Investigation

During the oxic investigation, the carbon oxidation/nitrification BFB reactors were operated at steady-state under seven different total organic carbon loading rates: 0.057, 0.076, 0.096, 0.103, 0.123, 0.189, and 0.207 mg TOC/mg biomass-day. Based on TOC measurements and gas chromatographs, it was observed that DIPA and MEA were in fact biodegradable under oxic conditions. As shown in Figure 1, close to complete TOC removal (> 99%) was achieved under all of the loading rates less than 0.15 mg/mg-day. TOC removal dropped to 90% as the loading was increased to 0.207 mg/mg-day. Since samples were taken daily for at least 14 days at each loading rate, the removal rate is calculated as an average of the rates measured throughout the duration of the experiment at a specified TOC loading rate. As shown in Figure 2, the corresponding nitrification rate achieved under these conditions was approximately 50%.

The nitrification rate was calculated based on the proportion of feed TKN that was converted to  $\text{NO}_3^-$ -N. In addition, there was no evidence of  $\text{NO}_2^-$ -N and a minimal concentration (< 0.1 mg/L) of  $\text{NH}_4^+$ -N in the effluent. Nevertheless, the rest of the feed TKN could be accounted for in biomass cell growth (Nguyen and Shieh, 1995a).

### Anoxic Investigation

The anoxic steady-state experiments covered a range of six TOC loadings: 0.012, 0.017, 0.023, 0.045, 0.072, and 0.098 mg TOC/mg biomass-day. DIPA and MEA were found to be also biodegradable under anoxic conditions, although the degradation was weaker than that in the oxic experiments. In Figure 3 it is seen that the TOC removal at loadings less than 0.05 mg/mg-day was > 85%, while at higher loadings the TOC removal decreased to 60%. As shown in Figure 4, the average ratio of mg TOC removed to mg  $\text{NO}_3^-$ -N utilized was observed to be 1.26 over the range of loading rates tested in the steady-state experiments. This ratio is higher than a stoichiometric ratio of 0.83 —calculated based on theoretical denitrification reactions in which a combination of DIPA, MEA, and phenol is used as the carbon source. In denitrification, since the carbonaceous nutrients are required as the carbon source for biomass synthesis as well as an energy source, the amount of carbon required for dissimilation of a given amount of nitrate is in practice larger than the stoichiometrically calculated quantity (Winkler, 1984). The TOC utilization rate observed in this study is comparable to those reported elsewhere —e.g., methanol: 1.17 mg TOC/mg  $\text{NO}_3^-$ -N, acetic acid: 1.71 mg TOC/mg  $\text{NO}_3^-$ -N, formaldehyde: 1.38 mg TOC/mg  $\text{NO}_3^-$ -N, and isopropanol: 1.82 mg TOC/mg  $\text{NO}_3^-$ -N (Monteith *et al.*, 1980).

### Anaerobic Investigation

Upon completion of start-up experimentation, the reactors were operated for up to an additional 250 days at different loading rates. The OLRs were maintained relatively constant over extended periods to allow the reactors to stabilize at each operational load. Steady-state experimental runs lasted for 45-150 days (16-54 HRTs) to ensure that reactor performance was

representative. R1 was operated at an OLR of approximately 6,000 mg/L-day from days 55-205. The OLR was then gradually increased to 12,000 mg/L-day and was maintained at this level from days 230-305. The OLR was then reduced to 6,000 mg/L-day from days 306-450. R2 was operated at an OLR of approximately 6,000 mg/L-day from days 95-217. An attempt was made to operate R2 at an OLR of 12,000 mg/L-day, but due to high effluent TOC and VSS measurements, an OLR of 7,500 mg/L-day was applied instead from days 230-275. An OLR of approximately 6,000 mg/L-day was applied from days 276-395. R3 and R4 were subjected to an OLR of about 6,000 mg/L-day from days 80-140, and from days 45-115, respectively. Figures 5 through 8 show the response and performance of R1 through R4, respectively.

### ***Total Organic Carbon Removal***

The importance of TOC removal is due to government regulations that stipulate that industry may not discharge wastewater containing organic materials above certain levels. TOC removal is also indicative of digestion efficiency, and consequently, high TOC removal is necessary for efficient methane production and destruction of organic matter.

Figures 5 through 8 show TOC removal efficiencies for R1 through R4, respectively. R1 showed consistent TOC removal efficiencies above 97% for the periods from days 55-205, and from days 306-450. Removal efficiency was slightly lower at 95% for the period from days 230-305 for the 12,000 mg/L-day OLR. R2 showed removal efficiencies above 95% in general. Lower removal efficiency (91%) was observed from days 217-230 due to increased OLR. R3 showed removal efficiencies of 83-99 % from days 75-135. Finally, R4 showed removal efficiencies ranging from 87-98% for pseudo-steady-state operation (days 45-112).

### ***Biogas Production***

Because methane is a valuable byproduct of anaerobic digestion, biogas is an important monitoring variable. In addition, biogas production can be an effective and economical indicator of severe stress or failure. About 72% of the substrate for methanogenesis is supplied by acetate, 13% by propionate and 15% by other intermediates (McCarty, 1965). From this, we can expect about 1 L/CH<sub>4</sub>/g TOC<sub>r</sub> depending on bacterial populations and digestion pathways.

Figures 5 through 8 show biogas production rates for R1 through R4, respectively. As expected, a close correlation exists between the biogas production rate and the applied OLR. A biogas production rate of about 13 L biogas/L expanded bed volume-day (15.6 L biogas/day) was attained by R1 at the 6,000 mg/L-day OLR. This rate was doubled to about 26 L/L-day (31.2 L/day) when the applied OLR was increased to 12,000 mg/L-day. The biogas production rate returned to previous levels upon reduction of the OLR to the 6,000 mg/L-day OLR level. R2 behaved similarly with lower biogas production rates than R1. A biogas production rate of about 12.5 L/L-day (10.4 L/day) at an OLR of 6,000 mg/L-day increased proportionately to a biogas production rate of approximately 16 L/L-day (13.3 L/day) at an OLR of 7,500 mg/L-day. R3 produced about 7 L biogas/L packed bed volume-day (18.2 L biogas/day) for pseudo-steady-state operation at an OLR of 6,000 mg/L-day. Finally, R4 produced about 0.6 L biogas/L reactor volume-day (1.4 L biogas/day) for pseudo-steady-state operation at an OLR of 6,000 mg/L-day.

Gas chromatography analysis showed that CO<sub>2</sub> and CH<sub>4</sub> were sole constituents of the produced biogas (> 99.99%). Sample purity was temporarily compromised when reactors were opened for periodic maintenance. Average CH<sub>4</sub> contents of 55.9, 55.8, 52.5, and 55.0% were observed for R1-R4, respectively. Since carbon dioxide is highly soluble in water relative to methane, low HRTs greatly affect biogas composition. Assuming saturation concentrations of CO<sub>2</sub> are achievable, the effluent stream acts as a CO<sub>2</sub> removal mechanism. This lowers the relative CO<sub>2</sub> content in the biogas. Digestion pathways established in each reactor also affect biogas composition. Efficient digestion with low VOA accumulation will have higher methane content in the produced biogas.

The methane content seems to stabilize within a narrow range soon after reactor start-up, suggesting that biogas composition is not a good parameter for monitoring reactor performance or for indicating stress onset. The observed biogas yield rate (based on substrate utilization) ranged from 0.89-0.94, 0.8-0.9, 0.6-0.8, and 0.5-0.72 L CH<sub>4</sub>/g TOC<sub>r</sub> for R1 through R4, respectively. This translates into approximate reactor efficiencies of 87-92%, 79-88%, 59-78%, and 49-69% for R1-R4, respectively. This theoretical yield estimation clearly affirms AFBR superiority (and in general ICRs) over conventional high-rate suspended growth digesters.

## ***Biomass Inventory and Characteristics***

### *Immobilized Biomass Population*

The primary advantage of ICRs over suspended growth reactors is that they offer much higher bacterial population densities. The biomass accumulation accompanying the OLR for R1 and R2 is presented in Figures 5 and 6, respectively. The values shown are AVS concentrations per liter of expanded bed volume. The biomass exhibits a linear correlation with time and increased OLR for R1, while remaining relatively steady for R2. AVS values of 17-25 g/L for R1 and 60-80 g/L for R2 were measured after achieving the design loading rate.

The high biomass concentrations obtained for R2 may include some carbon weight loss due to mass volatilized while exposing the sample to high temperatures (550°C) to determine the AVS. A study performed on virgin media indicated that R-633 loses less than 0.1% of its weight due to volatilization, while GAC loses on average about 20.3% of the sample weight. The AVS values shown for R2 were thus calculated based on this loss coefficient. The attained AVS values compare favorably with those reported elsewhere (Aivasidis *et al.*, 1988; Heijnen *et al.*, 1989; Pascik, 1989; Yee *et al.*, 1990; Hsu and Shieh, 1993).

Because the packed-bed reactor was sealed to achieve an anaerobic environment, attached solids sampling for R3 was not possible during experimentation, and only at the conclusion of experimentation was an estimate of attached/entrapped biomass for R3 obtained. This estimated AVS value was assumed to be indicative of pseudo-steady-state experimentation only. Upon opening the reactor, three phases of biomass were observed: suspension in bulk liquid, attachment on and entrapment between bed particles, and attachment on reactor wall. The attached/entrapped biomass was measured to be 21 g VS/L for 2.7 L of bed. The low design



upflow velocity and resulting shear forces allowed for the development of a thick biofilm on the top 10 cm of the reactor walls above the bed. This biofilm had a thickness of 0-4.1.0 mm, a measured VS of 50.3 g/L and a total volume 90.8 mL (5.7% of total estimated reactor biomass). Similarly, upon opening the suspended growth reactor (R4), a thin biofilm was detected covering the inside walls of the reactor. The biofilm was approximately 40  $\mu\text{m}$  thick with a measured VS of 49.8 g/L and a total volume of 16.6 mL (8.5-25.6% of total reactor biomass). The observed biofilms on reactor walls for R3 and R4 were assumed to be active and were included in reactor performance modeling.

### *Mean Cell Residence Time*

The mean cell residence time (MCRT) is defined as follows:

$$\text{MCRT} = \frac{X_t V_r}{Q_{\text{eff}} X_e} \text{ (days)}$$

$$\text{and } X_t = \frac{X_{\text{AVS}} V_{\text{bed}} + X_e V_1}{V_r}$$

where  $X_t$  = average bacterial cell concentration (g VS/L total reactor volume)  
 $V_r$  = total reactor volume (L)  
 $Q_{\text{eff}}$  = effluent flow rate (L/day)  
 $X_e$  = effluent biomass concentration (g VS/L)  
 $X_{\text{AVS}}$  = immobilized biomass concentration (g AVS/L)  
 $V_{\text{bed}}$  = expanded bed volume (L)  
 $V_1$  = bulk liquid volume (L)

The MCRT can be used to further assess the ability of the immobilization media to retain biomass. Figures 5 through 8 show MCRTs for R1 through R4, respectively. The observed MCRTs were extremely long for the FBRs. R1 exhibited MCRT values of about 100-160 days, while R2 values were in the range of 25-days. These high MCRT values may reflect non-viable biomass, especially in the case of R1. High VSS losses caused MCRT values for R2 to be considerably lower than those for R1. Nevertheless, R2 still had high MCRT values compared with typical high rate digesters. It is probably well advised to use these MCRT values as a parameter to describe the ability of the immobilization media to hold biomass rather than an actual control parameter for process design. For the latter case, the active/inactive biomass fractions may need to be accounted for in the mathematical modeling for substrate utilization and biomass accumulation.

The viable or active biomass fraction can be obtained experimentally by measuring DNA/RNA levels in biomass samples, since active cells have been shown to have considerably higher DNA levels than inactive organic matter. This ratio may also be estimated, with less accuracy, using reactor performance history data. Figure 5 shows that close to day 60, R1 had stabilized with a TOC removal efficiency greater than 97% and an AVS of about 25 g/L. Around day 300, it had an AVS of about 85 g/L with the same removal efficiency. This suggests that roughly 30% of the existing biomass is active (since the feed is entirely soluble and no VS can be attributed to inert feed particles). Similarly, Figure 6 shows that R2 had a stable TOC removal efficiency of greater than 90% by day 70 with an AVS of about 80 g/L, while around day 250, similar TOC

removal efficiencies was sustained with AVS concentrations as low as 40 g/L. This indicates that up to 50% of the biomass in R2 was nonviable. The higher viable biomass population of R2 could be due to the high VSS wastage rate carrying out dead cell mass and stimulating fresh, “active” sites for cell regeneration.

The MCRT values for R1 and R2 confirm the ability of R-633 and GAC to effectively retain high biomass concentrations. It seems that after start-up has been completed, at true steady-state conditions, R-633 offers better protection for biomass colony structure than does GAC in AFBRs.

Since the performance of R1 and R2 were comparable, it can be concluded that R-633 is favorable for steady-state operational requirements from the standpoint of sludge production. R1 produced about four times less biomass waste (0.05-0.15 g VSS/day) than R2 (0.5-0.40 g VSS/day).

It is important to note here that the AVS data for R2 has a degree of uncertainty due to GAC weight loss under 550°C temperatures. As previously mentioned, a preliminary study on fresh media particles showed that an average of 20.3% of the sample weight was lost due to volatilization of GAC, while less than 0.1% of the R-633 was lost. This result was used in calculating the AVS values for R2. Figure 6 includes this uncertainty.

R3 and R4 had MCRTs of 13-25 and 10-12 days, respectively, for pseudo-steady-state operation. It is evident that for immobilized cell reactors, it is much more important to design for an optimal MCRT in order to take full advantage of biomass attachment.

## CONCLUSIONS

Although di-isopropylamine and monoethylamine are significantly inhibitive compounds (Nguyen and Shieh, 1995b), their degradation was observed to be feasible under both oxic and anoxic conditions in a BFB treatment process. Nevertheless, it was apparent that microbial activity under anoxic conditions was diminished compared with that under oxic conditions. Carbon removal under oxic conditions was nearly complete, with nitrate production levels observed at 50%. Under anoxic conditions, carbon removal levels at lower loadings were close to complete, yet at higher loadings, decreased to a range of 60%. The average ratio of mg TOC removed to mg  $\text{NO}_3^-$ -N utilized was observed to be 1.26, over the range of loading rates tested in the steady-state experiments. Although DIPA and MEA were found to be effective as organic carbon sources, more research is required to determine the full extent of their usefulness.

The work discussed here involved investigations of biological degradation of DIPA, MEA, and phenol in separate single BFB reactors under oxic and anoxic conditions. An obvious recommendation as a result of this study is to conduct future investigations into the feasibility of a two-stage BFB reactor system achieving effective removal of the amines and phenol with the compounds themselves as internal organic carbon sources for the denitrification stage.

Anaerobic reactor performance data presented here shows that successful start-up and operation was achieved for anaerobic fluidized bed, packed-bed, and suspended growth reactors. The

immobilized-cell reactors were able to handle high loading rates under pseudo-steady state and transient state conditions. Anaerobic reactors achieved substrate removal and biogas production under stressful batch conditions. Successful treatment of initial TOC concentrations of 270-5,500 mg/L were attained.

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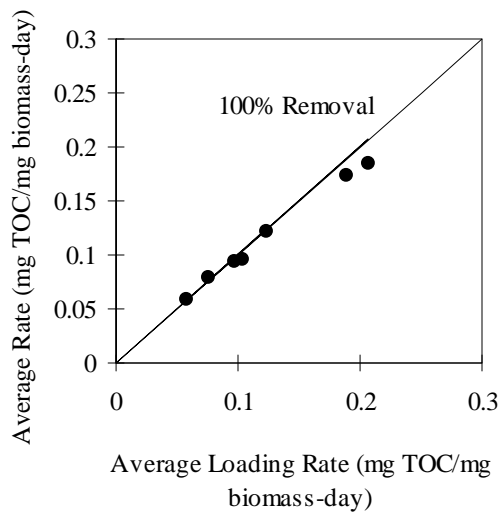


Figure 1: Carbon Removal Under Oxidic Conditions

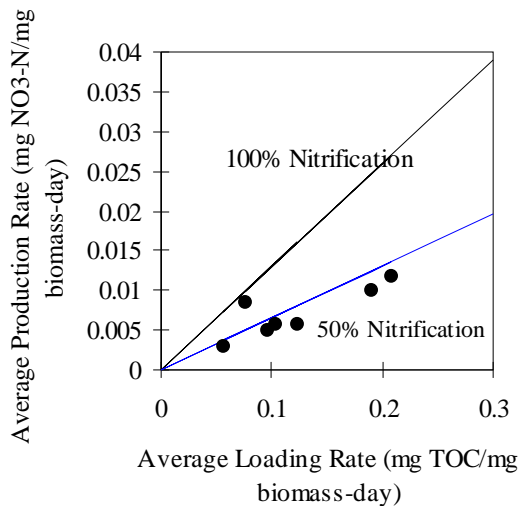


Figure 2: Nitrification Performance

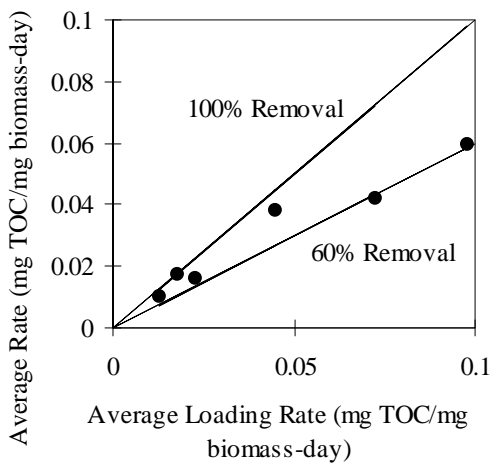


Figure 3: Carbon Removal Under Anoxic Conditions

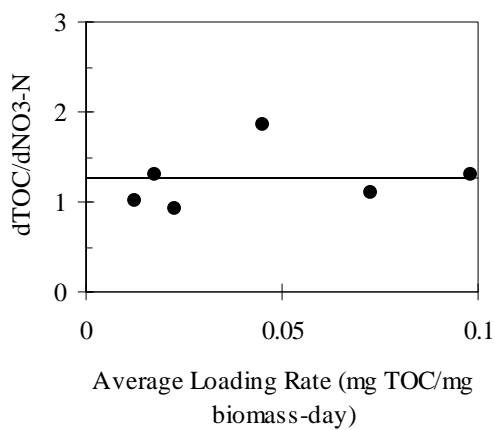
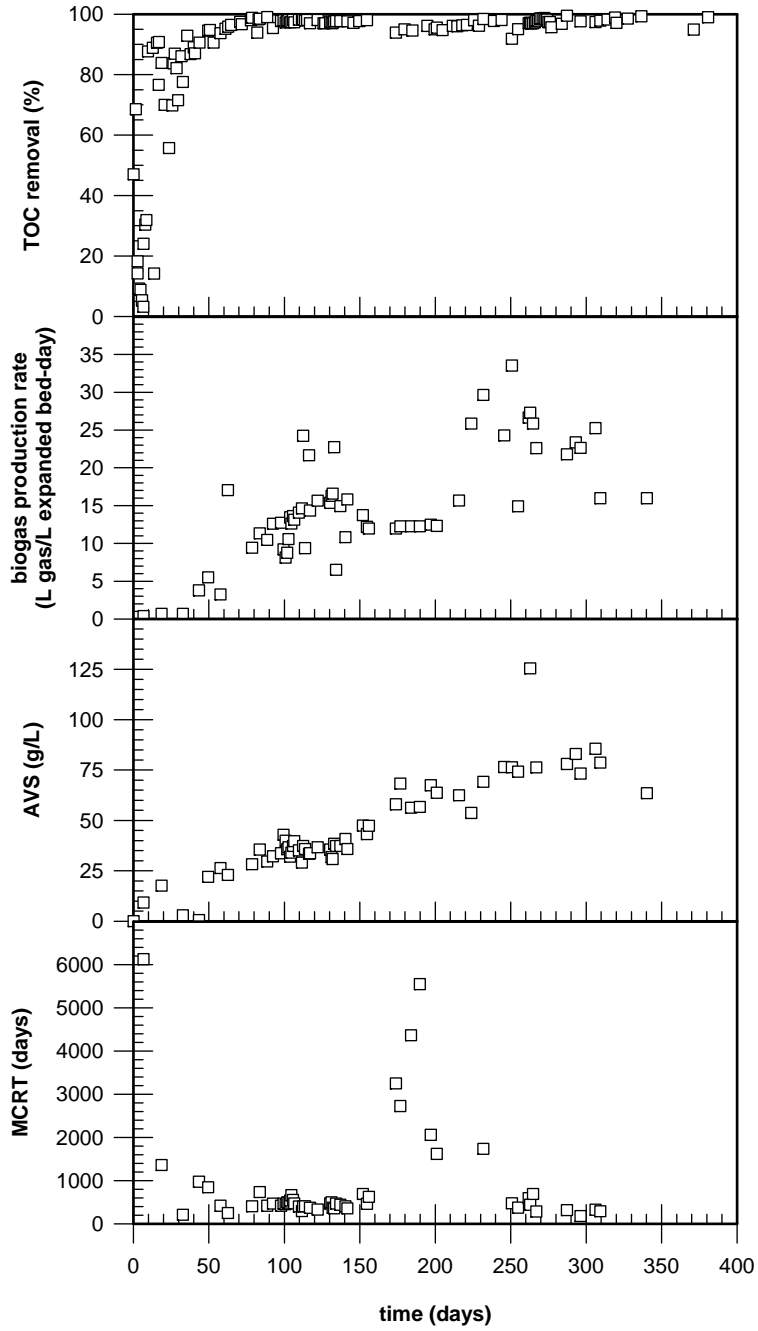
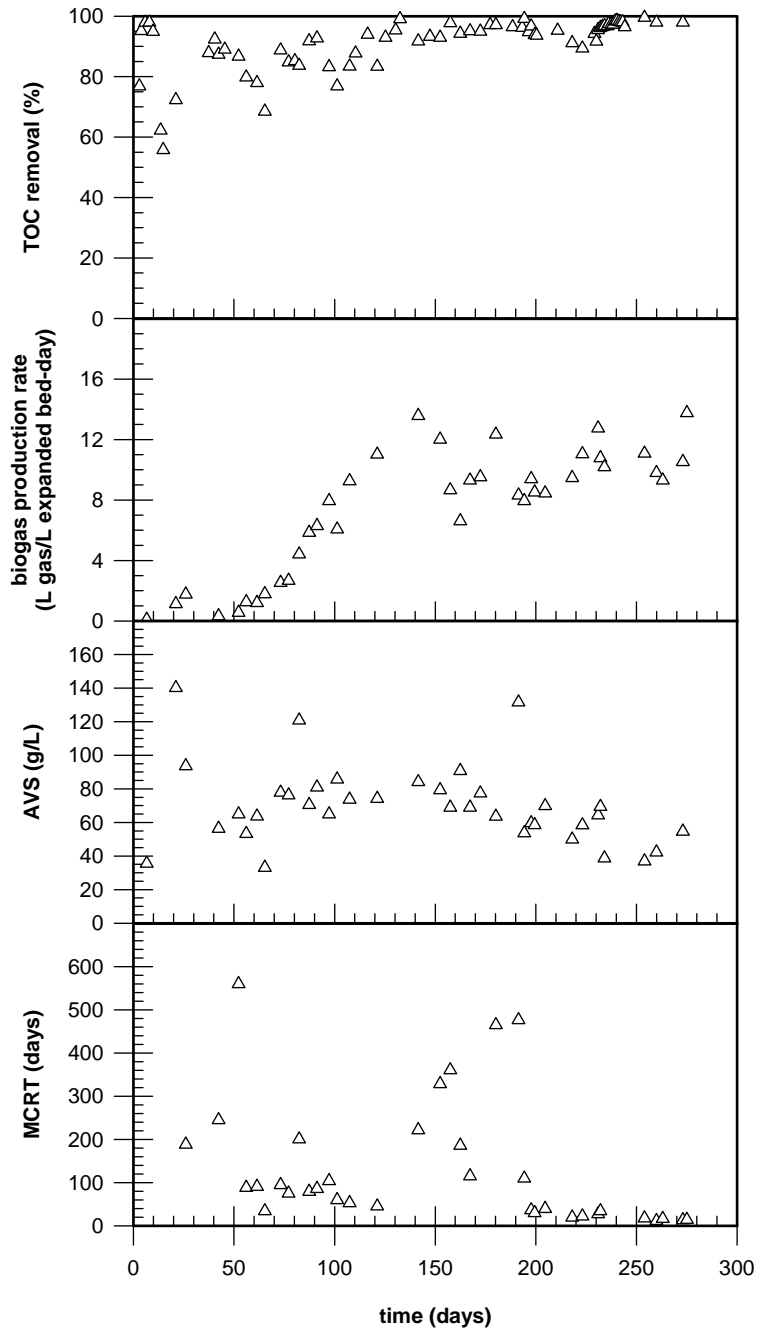


Figure 4: Nitrate Utilization in Denitrification

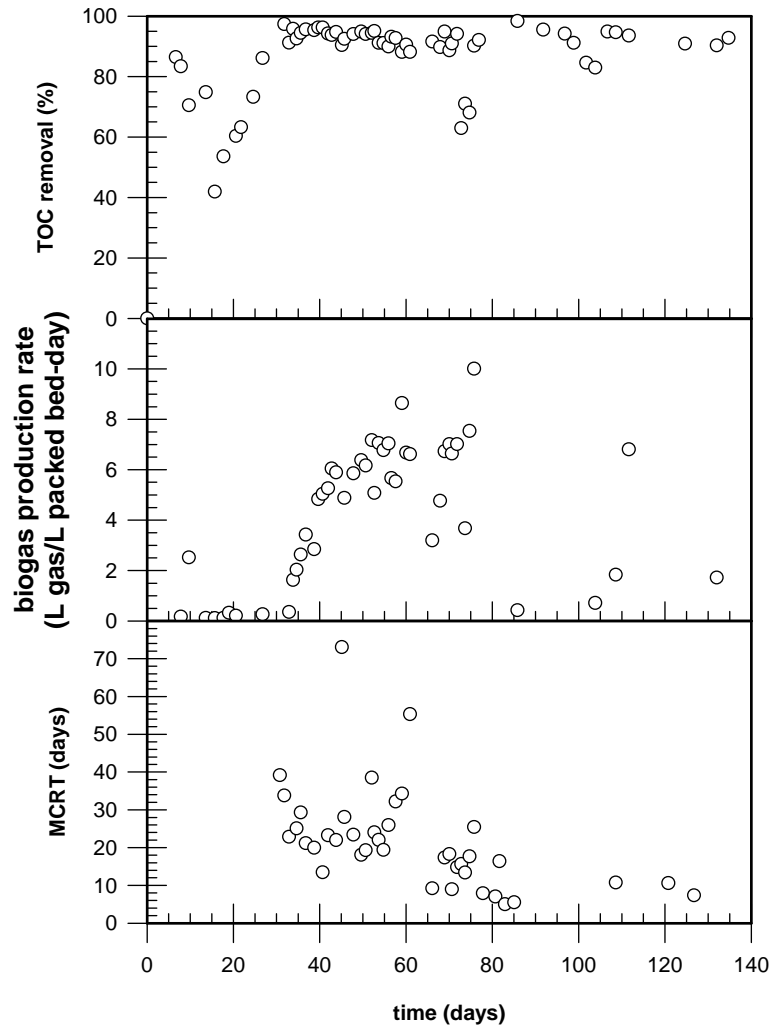


**Figure 5: Reactor 1 Performance Data**

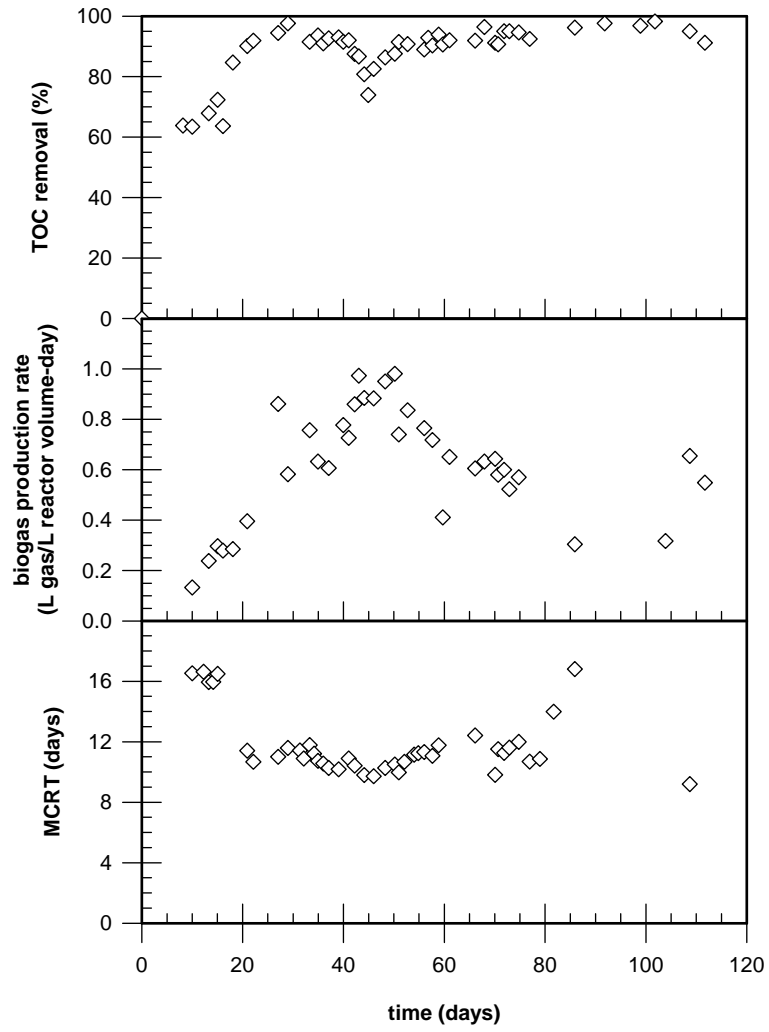




**Figure 6: Reactor 2 Performance Data**



**Figure 7: Reactor 3 Performance Data**



**Figure 8: Reactor 4 Performance Data**