Waste Management and Byproducts Recovery for the Blue Crab (*Callinectes sapidus*) Industry

Part V: UASB and Air Stripping Treatment Technologies

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CHAPTER I. INTRODUCTION

The Chesapeake Bay, the nation's largest estuary, supports over 290 fish species and 2,700 plant species. Thirteen million people reside in the bay's 64,000 square mile watershed area (Hudson, 1995).

Concerns regarding the bay's declining water quality have prompted the increased regulation of regional wastewater discharges. Pollutants of concern have included: nutrients, such as nitrogen and phosphorus; organic compounds, as measured by the 5-day biochemical oxygen demand test (BOD_5); and total suspended solids (TSS). For industries that have historically discharged processing effluents directly into the bay without treatment, installing a wastewater treatment plant or paying a publicly owned treatment works (POTW) to accept wastewater can impose a large financial burden.

The Virginia blue crab (*Callinectes sapidus*) processing industry is comprised of approximately 60 small processing plants. The Environmental Protection Agency (EPA) has established effluent quality guidelines for the industry; however, the Virginia Department of Environmental Quality (DEQ), which regulates wastewater discharge, is empowered to set more stringent limits. Table 1 contains the EPA's best conventional pollutant control technology currently available (BCT) federal effluent guidelines for the crab processing industry.

The Virginia DEQ is formulating a new general permit for the seafood industry. Although specific contaminant limits have not been set, the BOD_5 and TSS limits under consideration for the blue crab processing industry are similar to the BCT limits. While ammonia limits of 1 and 2 mg/L have been considered, the general permit may not regulate ammonia.

The severity of the new general permit will determine the blue crab processing industry's treatment needs. For new sources of wastewater discharge, wastewater discharge into the bay without prior treatment would not be a wastewater disposal option. If ammonia limits are imposed, new and existing sources of wastewater discharge would require an alternative means of wastewater disposal.

Table 1. Federal Effluent Guidelines. Conventional and Mechanized Blue Crab Processing Category. Average of Daily Values for 30 Consecutive Days[*]. (Adapted from 40 CFR 408 - Subparts B & C)

	Conventional[†]		Mechanized[‡]	
Parameter[**]	Existing Source	New Source	Existing Source	New Source
BOD_5	no limit	0.15	no limit	2.5
TSS	0.74	0.45	12.0	6.3
Oil & Grease	0.20	0.065	4.2	1.3
pH	6.0 - 9.0	6.0 - 9.0	6.0 - 9.0	6.0 - 9.0

(*) Federal effluent guidelines also limit one day maximum values

(†) Applies to existing facilities manually processing more than 3,000 lbs of raw seafood on any day during the calendar year

(‡) Applies to all facilities in which mechanical picking or separation of crab meat from shell is utilized

(**) All units, except pH, lb/1,000 lb raw seafood processed

Blue crab processing plants that require an alternative means of wastewater disposal would have several options: on-site treatment and direct discharge, on-site treatment and discharge to a POTW, discharge to a POTW without treatment, or treatment of wastewaters combined from several facilities at one site. Processing plants that discharge to a POTW would incur surcharges based on total Kjeldahl nitrogen (TKN), BOD_5, and TSS. Some processing plants would not have access to sewer lines.

The ideal on-site wastewater treatment technology for the crab processing industry would have the following characteristics: low capital and operating costs, flexibility in adapting to seasonal fluctuations and interruptions in wastewater flow, and limited supervision requirements. Two potential treatment technologies are anaerobic biological wastewater treatment and air stripping.

Anaerobic biological wastewater treatment would reduce wastewater BOD_5 and TSS levels prior to discharge to a POTW. By treating wastewater anaerobically, the high cost of supplying oxygen to aerobic treatment units would be eliminated. Anaerobic treatment requires temperatures of about 30 to 35° C; however, the high retort effluent temperatures would lessen required heating costs. The utilization of methane generated during anaerobic treatment would further offset operating costs.

Several high rate anaerobic treatment systems are available that allow large volumes of wastewater to be treated with relatively small reactor volumes. Upflow Anaerobic Sludge Blanket (UASB) technology has effectively treated a number of high strength wastewaters. The UASB adapts well to seasonal changes and interruptions in wastewater flow, especially when compared to aerobic treatment systems (Souza, 1986).

Air stripping is a potential treatment technology for the removal of ammonia from crab processing effluents. Air stripping offers several advantages over other ammonia removal treatment processes, including simplicity of operation and accommodation of different wastewater flows.

The research goals of this investigation were as follows:

- Evaluate UASB treatment of blue crab processing wastewater with lab-scale reactors.
- Compare UASB treatment, in terms of BOD_5 and TSS reduction, with the performance of other systems used to treat crab processing wastewaters.
- Demonstrate UASB treatment of blue crab processing wastewater on a pilot-scale.
- Research operational alternatives to improve UASB treatment of blue crab processing wastewater.
- Supplement previous studies on air stripping of blue crab processing wastewater. Determine if operational or structural modifications to the air stripping tower would improve tower performance.

CHAPTER II. LITERATURE REVIEW

BLUE CRAB PROCESSING AND WASTE STREAM IDENTIFICATION

In this section, blue crab processing operations and liquid waste generation are described briefly as outlined by Boardman *et al.* (1993) and Harrison (1993). Figure 1 illustrates mechanized and conventional blue crab processing.

Blue crabs are delivered to processing facilities by truck or boat. During the dredging season, crabs are washed to remove sand and grit. The crabs are then cooked in retorts at high temperature and pressure. The cooking process generates a concentrated wastewater referred to as 'retort effluent' or 'crab cooker wastewater'.

Crabs are removed from the retort and allowed to cool. The meat is then separated from the crab. In conventional processing plants, a single 'picker' removes all the crab meat by hand. Mechanized plants may use a Harris Claw machine, a Quik Pik machine, or both machines to supplement the hand picking. After the meat picking is completed, remaining shell pieces are removed from the product by hand.

The Quik Pik machine separates body meat from the crab by vibration. The process may include a bobber which "mechanically cuts off the legs, removes the carapace, and then removes the viscera from the remaining core using spray jets and brushes" (Harrison, 1993). The bobber creates a concentrated waste stream referred to as the 'Quik-Pik bobber effluent'.

The Harris Claw machine uses a brine bath to separate crab meat from the crab claws. Claws are pulverized and directed into the bath where crab meat floats while shell fragments sink. The process generates several waste streams. The initial washing of the claws generates the 'claw wash reel effluent'. Crab claw shell pieces are withdrawn from the bath along with a

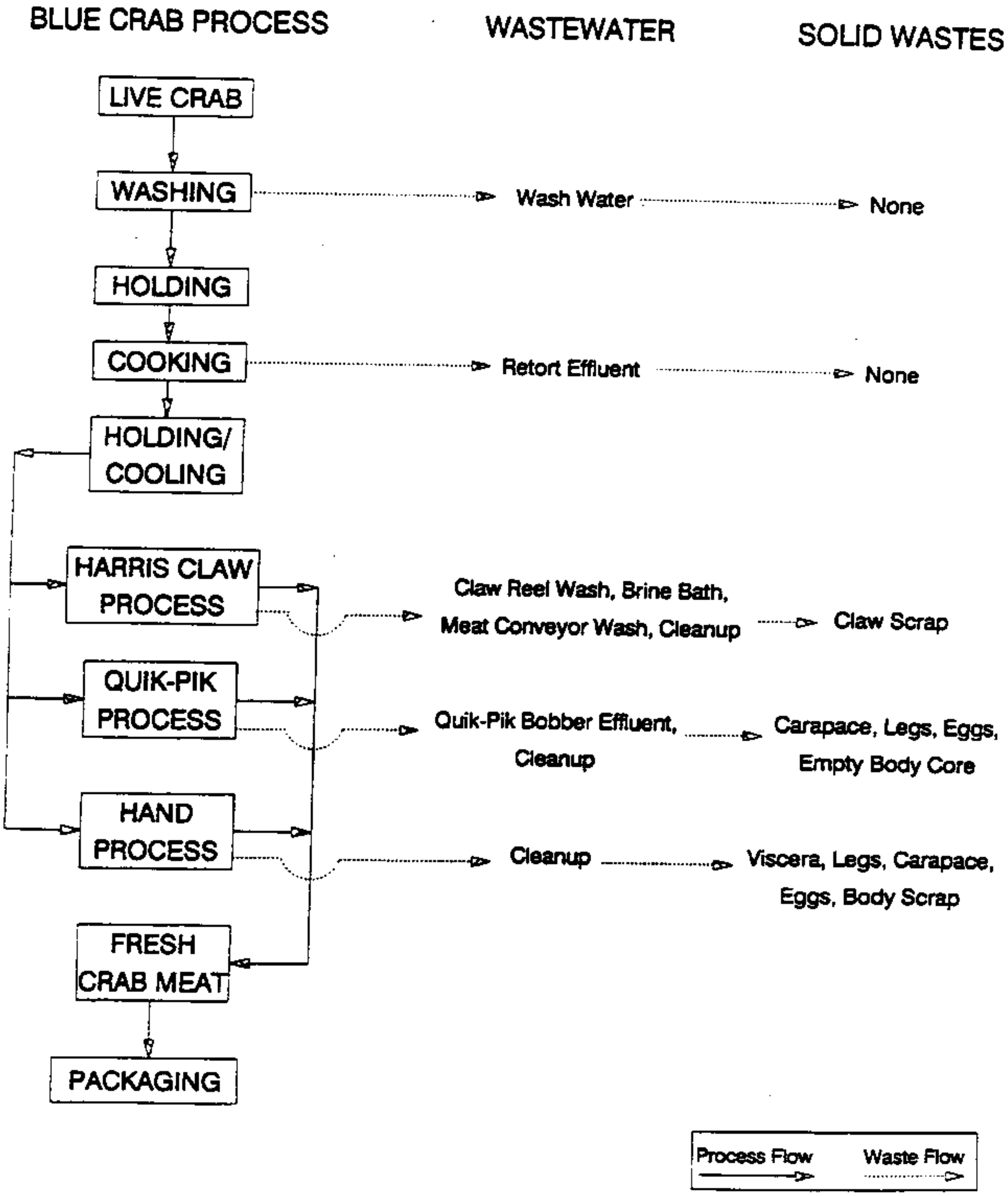


Figure 1. The Mechanized and Conventional Processing of Blue Crabs. Product and Waste Flows. (After Boardman *et al*., 1993 and Harrison, 1993)

large quantity of brine bath liquid producing the 'shell waste effluent'. Meat is withdrawn from the bath on a conveyor and washed producing the 'claw meat conveyor wash' waste stream. The brine bath is filled one or two times daily. The dumping of this bath produces the 'Harris Claw brine bath' waste stream.

Clean-up operations generate the final two waste streams: the 'claw room clean-up' effluent and the 'hand pick/pack room cleanup' effluent.

BLUE CRAB PROCESSING WASTEWATER CHARACTERISTICS

Harrison *et al.* (1991) surveyed three blue crab processing plants in Virginia and characterized processing effluents with respect to chemical oxygen demand (COD), BOD_5, TSS, TKN, and various other parameters. Table 2 shows selected typical daily waste stream characteristics from one of the three blue crab processing plants surveyed.

Table 2. Blue Crab Processing Waste Stream Characterizations. Average Daily Values Determined Over One, Two, or Three Days at a Virginia Crab Processing Plant. (Adapted from Harrison *et al.*, 1991, plant #2)

Process	Wastewater Volume (L)	COD (mg/L)	BOD_5 (mg/L)	TSS (mg/L)	TKN (mg/L)[*]
Harris Claw Reel Wash[†]	2,000	9,200	8,700	5,400	1,400
Shell Waste Effluent	1,600	23,000	15,000	24,000	2,800
Harris Claw Brine Bath	830	17,000	11,000	14,000	2,100
Claw Meat Conveyor Wash	8,600	2,300	1,600	900	380
Claw Room Cleanup	910	550	420	590	160
Quik-Pik Bobber Effluent	2,300	19,000	12,000	7,500	1,500
Retort Effluent[‡]	190	25,000	23,000	1,200	2,200
Hand Pick/Pack Room Cleanup	950	3,680	2,480	1,200	25

(*) Milligrams/liter (mg/L) as nitrogen (N)

(†) BOD_5 value calculated from COD/BOD_5 ratio and average COD value

(‡) Wastewater volume = volume per cook

ANAEROBIC MICROBIOLOGY, CHEMISTRY, AND KINETICS

The following sections describe the microbiology, chemistry, and kinetics of anaerobic wastewater treatment. The first section contains an overview of the anaerobic digestion process. Anaerobic microbiology, chemistry, and kinetics are discussed in the following sections.

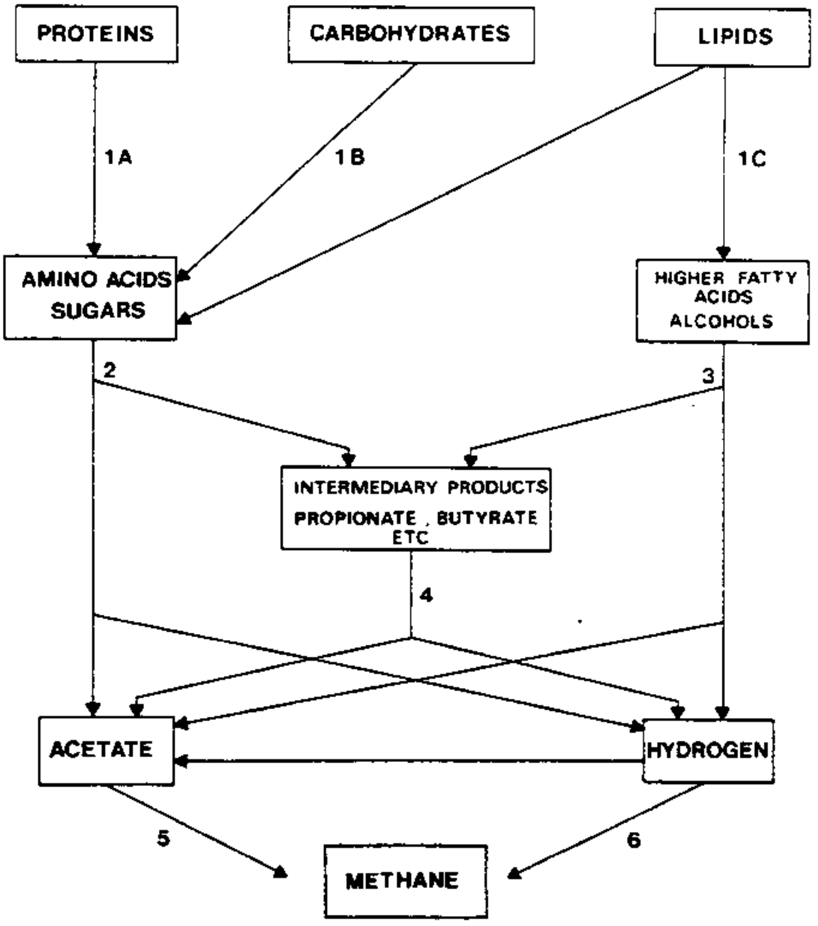
Overview of Anaerobic Digestion

Anaerobic digestion refers to the biological conversion of organic compounds into methane, carbon dioxide, and other end products under conditions that exclude oxygen. The first application of anaerobic treatment was the treatment of solids removed from municipal wastewater in 1881 (McCarty, 1982).

Anaerobic digestion proceeds in stages. Each stage is mediated by different microorganisms. Henze and Harremoës (1983) described the process in three stages as follows:

Stage 1.	Hydrolysis of complex organic compounds to small soluble organic molecules.
Stage 2.	Conversion of small soluble organic molecules to intermediates, including volatile fatty acids. Conversion of intermediates to acetic acid, hydrogen, and carbon dioxide.
Stage 3.	Conversion of acetic acid, carbon dioxide, and hydrogen to methane.

Each of the stages is comprised of several pathways. Figure 2 illustrates the pathways of anaerobic digestion (Stronach *et al.*, 1986).



1. **Hydrolysis**
2. **Fermentation**
3. **Anaerobic (β) Oxidation**
4. **Anaerobic Oxidation**
5. **Decarboxylation of Acetate** $CH_3COO^- + H_2O \longrightarrow CH_4 + HCO_3^-$
6. **Hydrogen Oxidation** $CO_2 + 4H^+ \longrightarrow CH_4 + 2H_2O$

Figure 2. Pathways of Anaerobic Digestion. (After Stronach *et al.*, 1986)

Anaerobic Microbiology

In the first stage of anaerobic digestion, insoluble polymers such as lipids, proteins, and carbohydrates are converted to soluble organic compounds. The conversion is performed by hydrolytic extracellular enzymes such as lipases, proteases, and cellulases (Stronach *et al.*, 1986). The products of hydrolysis include sugars, amino acids, higher fatty acids, and alcohols. The relative quantities of the hydrolysis products vary with waste composition.

In the second stage of anaerobic digestion, the products of the first stage undergo further transformation. Acid forming bacteria (acidogens) convert amino acids, sugars, higher fatty acids, and alcohols into intermediate products, such as propionic acid and butyric acid, by fermentation or anaerobic oxidation (Gujer and Zehnder, 1983). The intermediate products are converted to acetic acid by the acetic acid forming bacteria (acetogens).

Methane is produced in anaerobic systems from a limited number of substrates. While most methanogenic species can produce methane from hydrogen and carbon dioxide, very few species utilize acetic acid (Archer and Kirsop, 1990). The acetic acid (or acetate) utilizing species are critical to the anaerobic treatment process since about 70 percent of the methane produced from the anaerobic digestion of complex wastes is produced from acetic acid (McCarty, 1964a).

The morphology of methanogens is usually described as: rods, sarcinae, or cocci (Pine, 1971). Two methanogenic species that utilize acetate are: *Methanosarcina* and *Methanothrix*. *Methanothrix* are "sheathed rods, sometimes growing as long filaments" while *Methanosarcina* are "coccoid bacteria that grow together in discrete clumps" (McCarty, 1991).

Anaerobic Chemistry

The maintenance of a near neutral pH during anaerobic treatment is of critical importance. The optimum pH range for methanogenic growth is 7.0 to 7.2; however, the microorganisms operate satisfactorily in the range from pH 6.6 to 7.6. As the pH decreases below 6.2, methanogenic activity decreases significantly (McCarty, 1964b).

Volatile fatty acid accumulation within an anaerobic reactor decreases the pH. The negative log of the dissociation constant (pK_a) for acetic acid is 4.7 (Snoeyink and Jenkins, 1980), and the pK_a values for the other volatile fatty acids are similar (McCarty, 1991). Since the volatile fatty acids are completely dissociated at near neutral pH, the preservation of a neutral pH requires the balance of volatile fatty acid production and utilization.

The acidogenic and acetogenic bacteria are not as sensitive to low pH conditions as the methanogens. Therefore, when the pH decreases, methanogenic activity can decrease rapidly while volatile fatty acids continue to accumulate. When enough volatile fatty acids accumulate, the pH decreases sufficiently to almost completely stop methanogenic activity. This condition is referred to as a 'stuck' or 'upset' digester. The very low pH conditions of an 'upset' digester are toxic to the methanogens. Because of the slow growth rate of methanogens, the rejuvenation of a 'upset' system can require weeks (Kugelman and Chin, 1971).

At pH levels common to anaerobic treatment, anaerobic reactors are buffered by the bicarbonate buffering system (McCarty, 1991). Equation 1 shows the dissociation of aqueous carbon dioxide (H_2CO_3) to bicarbonate (HCO_3^-).

$$\{H^+\} = K_a\{H_2CO_3\}/\{HCO_3^-\} \qquad (1)$$

where:

pK_a = 6.3 at 25° C (Snoeyink and Jenkins, 1980)

In a poorly buffered anaerobic system, even a small accumulation of volatile fatty acids may cause process upset. Conversely, a well buffered reactor may withstand very high levels of volatile fatty acids.

The best strategy to prevent a reactor from becoming 'upset' is early detection of unbalanced conditions. Indicators of reactor unbalance include (McCarty, 1964b).

- Increase in volatile fatty acid concentrations
- Increase in the carbon dioxide (CO_2) fraction of the biogas
- Decrease in pH
- Decrease in total biogas production
- Decrease in treatment performance.

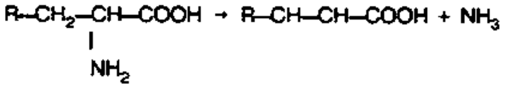
Equation 2 illustrates methane production from acetate. Equation 3 illustrates methane production from hydrogen and carbon dioxide.

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{2}$$

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O \tag{3}$$

From equation 2, one mole of methane and one mole of carbon dioxide are produced for every mole (64 g COD, see Appendix A) of acetic acid utilized. The corresponding volume of methane at 37° C can be calculated from the universal gas law as 400 milliliters (mL) per gram of COD.

Other reactions are important within the anaerobic environment. The release of ammonia during the degradation of amino acids is called deamination. Equation 4 illustrates a reductive deamination (Stronach *et al.*, 1986).



$$R{-}CH_2{-}\underset{NH_2}{\underset{|}{CH}}{-}COOH \rightarrow R{-}CH{-}CH{-}COOH + NH_3 \qquad (4)$$

The released ammonia is distributed between the ionized (NH_4^+) and unionized (NH_3) forms according to equation 5.

$$\{H^+\} = K_a\{NH_4^+\}/\{NH_3\} \qquad (5)$$

where:

$pK_a = 9.3$ at 25° C (Snoeyink and Jenkins, 1980)

Anaerobic Kinetics

The overall rate of anaerobic degradation is determined by the slowest stage. First order kinetics are usually used to describe the hydrolysis stage while monod kinetics are used to describe the other stages (McCarty, 1991). Equation 6 shows substrate utilization according to monod kinetics.

$$\frac{dS}{dt} = \frac{-k \cdot X \cdot S}{(K_s + S)} \qquad (6)$$

where:

S = substrate concentration at time (t)
k = maximum specific rate of substrate utilization (mass/volume/time)
dS/dt = rate of substrate utilization ($time^{-1}$)
X = concentration of microorganisms (mass/volume)
K_s = half-velocity constant, substrate concentration where the growth rate is one-half the maximum rate (mass/volume)

Methanogens grow slowly, especially when compared to aerobic organisms (McCarty, 1964b). For soluble wastes, methanogenesis is usually the rate limiting step. Lawrence and McCarty (1969) investigated the kinetics of acetic acid, propionic acid, and butyric acid utilization. Acetic acid utilization was slower than propionic acid and butyric acid utilization at temperatures between 25 and 35° C.

The analysis of anaerobic kinetics is complicated by differences between methanogenic species. Figure 3 shows the variation of *Methanothrix* and *Methanosarcina* growth rates with acetate concentration (Gujer and Zehnder, 1983). Figure 3 shows that *Methanothrix* will predominate in an environment with low acetate concentrations while *Methanosarcina* will predominate in an environment with high acetate concentrations.

Reaction rates generally increase with temperature; however, two optimum temperature ranges exist: mesophilic and thermophilic. The mesophilic range includes temperatures from 29 to 38° C (85 to 100° F) . The thermophilic range includes temperatures from 49 to 57° C (120 to 135° F) (McCarty, 1964b). Figure 4 shows the variation of methanogenic activity with temperature for several methanogenic species (Zehnder *et al.*, 1982). Generally, the cost of heating waste produced at mesophilic temperatures to thermophilic temperatures outweighs the benefit of higher reaction rates (Souza, 1986).

Nutrient Requirements

Anaerobic bacteria's nitrogen and phosphorus requirements are lower than aerobic bacteria's requirements because of the anaerobic bacteria's lower relative growth yields. In addition to nitrogen and phosphorus, several micronutrients have been found to affect the growth of methanogens.

Goodwin *et al.* (1990) investigated the effects of nutrient addition on Upflow Anaerobic Sludge Blanket (UASB) performance. The authors found that supplementation of phosphate, magnesium, calcium, and one of nine trace metals was necessary to maintain satisfactory

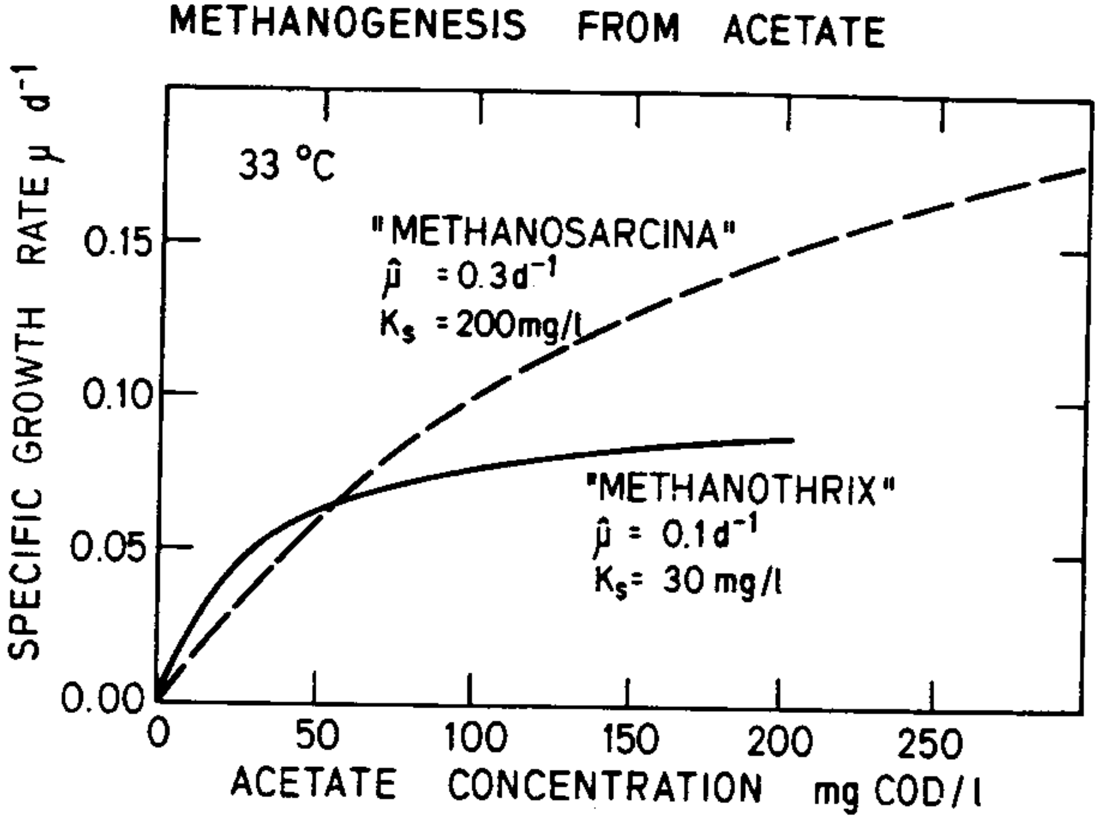


Figure 3. Variation of Growth Rate with Acetate Concentration for Acetate Utilizing Methanogens. (After Gujer and Zehnder, 1983)

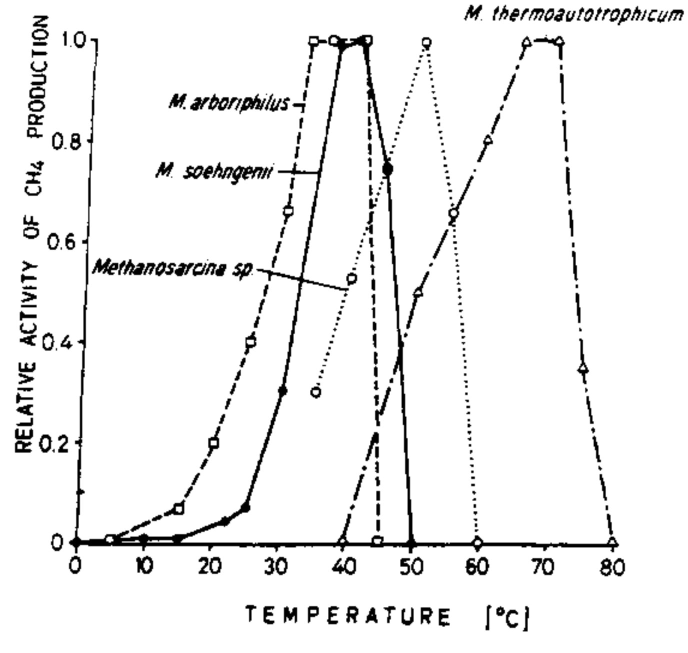


Figure 4. Variation of Relative Methane Production with Temperature for Several Species of Methanogens. (After Zehnder, 1982; Compiled from Several Sources)

granulation and overall reactor performance. The effect of individual trace metals was not determined.

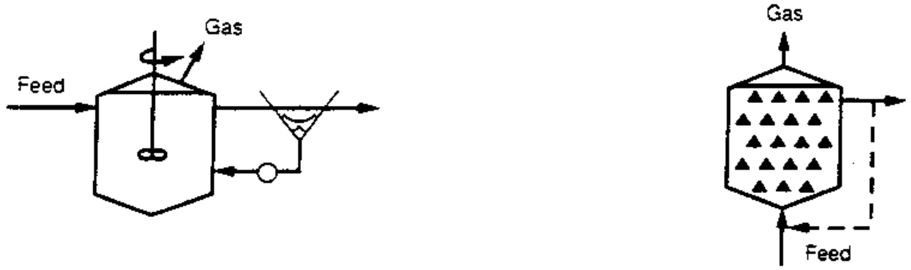
Murray and van den Berg (1981) investigated the effect of trace metals addition on methanogens with 1.4 and 35 L fixed-film reactors. The reactors treated food processing wastewater. The addition of 50 nanomoles/L (nm/L) of nickel, cobalt, and molybdenum stimulated biogas production. The additional of all three metals increased biogas production 42 percent. Nickel and cobalt had the greatest effect on biogas production. The addition of molybdenum to a reactor already receiving nickel and cobalt increased biogas production only slightly.

Bryant *et al.* (1971) studied the nitrogen requirements of hydrogen utilizing methanogens. The authors determined that the methanogens could utilize ammonia but not other organic nitrogen sources.

ANAEROBIC TREATMENT PROCESS CONFIGURATIONS

Anaerobic treatment processes are classified as either high or low-rate systems. The most common low-rate system is the anaerobic lagoon which is usually an unmixed, unheated pond. Anaerobic lagoons have been used successfully to treat high strength wastewaters with high concentrations of suspended solids and have been constructed up to 30 feet in depth (Tchobanoglous and Burton, 1991).

By maintaining large biomass populations, high-rate treatment systems can treat large quantities of wastewater with small reactor volumes. Figure 5 shows several high-rate treatment processes (Tchobanoglous and Burton, 1991). Iza *et al.* (1991) reported that all high-rate anaerobic treatment systems currently have full-scale applications. The following sections briefly describe and compare the high-rate anaerobic treatment processes.



Anaerobic Contact Process

Anaerobic Filter (AF)

Upflow Anaerobic Sludge Blanket (UASB)

Fluidized Bed Reactor

Figure 5. Anaerobic Treatment Process Configurations. (Adapted From Tchobanoglous and Burton, 1991)

Anaerobic Contact Process

The anaerobic contact process consists of a completely mixed reactor and a separate clarifier. The retention of biomass within the system relies on the effectiveness of the solid/liquid separation within the settler. This solid/liquid separation is the critical link in treatment performance.

Anaerobic Filter (AF) / Hybrid Designs

The anaerobic filter, described by Young and McCarty (1969), utilizes packing within the reactor body to retain biomass. The disadvantages of the system include higher investment costs for the packing and poor mixing within the reactor. The anaerobic filter has several advantages including the excellent removal of suspended solids (Lettinga *et al.*, 1983).

Several variations of the anaerobic filter have been proposed. The Upflow Bed Filter (UBF), which was proposed as a compromise between the UASB and AF, contains packing only in the upper part of the reactor. The reactor may contain granular or flocculent sludge. A similar hybrid style reactor was used by Öztürk *et al.* (1993) to successfully treat dairy wastes.

Upflow Anaerobic Sludge Blanket (UASB)

The Upflow Anaerobic Sludge Blanket (UASB) reactor, described by Lettinga *et al.* (1980), utilizes a gas-liquid-solid separator to retain granular sludge at high concentrations within the reactor. Granular sludge has excellent settling properties which allow very high solids retention times at low hydraulic retention times. The gas-liquid-solid separator keeps granules containing entrapped biogas from floating out with the effluent.

Fluidized Bed (FB) Reactor

The fluidized bed reactor is similar to the UASB except that sufficient effluent is recycled to suspend the granular biomass. The main disadvantage of the fluidized bed reactor is the power required for the effluent recycle. According to Iza *et al.* (1991), the fluidized bed reactor can treat wastewaters with very high suspended solids concentrations, especially when compared to other anaerobic treatment systems; however, even biodegradable solids pass through the reactor untreated.

Guiot *et al.* (1992) evaluated the effect of suspension on methanogenic activity. Several different upflow velocities were used to suspend the biomass. The methanogenic activity of the granules increased with increasing upflow velocity.

Comparison of High-Rate Anaerobic Treatment Systems

Table 3 compares three high rate treatment systems with respect to various operational considerations (Weiland and Rozzi, 1991).

Table 3. Comparison of High-Rate Anaerobic Treatment Processes. (Adapted from Weiland and Rozzi, 1991)

Operation	UASB	AF	FB
Reactor Start-Up	-	-	-
Biomass Accumulation	+ +	+	+ +
Liquid-Phase Mixing	-	+	+ +
Response to Organic Shock Loading	+	+	+
Handling of Wastes With High Suspended Solids Concentrations	-	+	+ +
Resistance to Clogging	+ +	-	+ +
Demand for Reactor Control	+	+	-

(-) unfavorable
(+) favorable
(+ +) very favorable

Lettinga *et al.* (1983) compared the treatment performance of a lab-scale anaerobic filter to the performance of a lab-scale UASB reactor. The reactors had identical volumes and were operated under the same conditions. Although the anaerobic filter responded faster to the initial start-up, the UASB eventually treated a higher volume of waste with greater efficiency. The relatively poor performance of the anaerobic filter was attributed to channeling, which decreased contact between the biomass and the wastewater.

Kennedy and Guiot (1986) compared a lab-scale UASB to a lab-scale Upflow Bed Filter (UBF). The reactors were operated over three phases under identical operating conditions. The soluble COD removal of the UBF was superior to the UASB during two of the three phases. The authors attributed the superior performance of the UBF to better biomass retention. The wastewater feed used in the study was a completely soluble sucrose containing wastewater.

UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) TECHNOLOGY

As of September 1991, more than 200 full-scale UASB reactors had been constructed world-wide (240 to 60,600 m^3 reactor volumes) treating wastewaters produced by at least 28 different industrial sources (Lettinga and Hulshoff Pol, 1991). The following sections describe various aspects of UASB operation.

Granulation in UASB Reactors

The success of UASB treatment relies on the formation and maintenance of granular sludge. When granular sludge is not available from another UASB reactor, digested sewage sludge is used as inoculum. The granulation of digested sewage sludge occurs under conditions that are optimal for biological growth and favor sludge with superior settling characteristics (Hulshoff Pol *et al.*, 1982).

The granulation process has been shown to be dependent on wastewater composition. Hulshoff Pol *et al.* (1983) studied the effect of ammonia on sludge granulation. Granulation of digested sewage sludge was possible with ammonia concentrations from 40 to 400 mg/L (as N). Granulation did not occur at ammonia concentrations of 1,000 mg/L (as N).

Alibhai and Forster (1986) studied granulation using diluted fermentation liquor as wastewater feed. A control reactor was fed unamended wastewater. Another reactor was fed wastewater supplemented with 80 mg/L of phosphate and 192 mg/L of calcium. Another reactor was seeded with a small quantity of crushed granular sludge and was fed unamended wastewater. The reactors supplemented with granular sludge or calcium and phosphate formed granular sludge after about 47 days while the control did not form granules after 75 days. Additional experiments showed that phosphorus addition was more important than calcium addition for granulation.

Sam Soon *et al.* (1990) studied the effect of nitrogen limitation on granulation. The authors determined that a nitrogen source in excess of the theoretical growth requirements of the anaerobic bacteria was necessary to induce granulation. According to the authors, a high partial pressure of hydrogen and a near neutral pH were also prerequisites for granulation.

Lettinga *et al.* (1984) outlined UASB start-up using digested sewage as follows:

- Inoculum Quantity (g VSS/L Reactor Volume): 10 - 15
- Initial Organic Loading Rate (g COD/g VSS/day): 0.05 - 0.1
- Allow poor settling sludge to wash out of reactor.

Gas-Solid-Liquid Separator (GSL)

The GSL functions to retain granular sludge within the reactor. Methane and carbon dioxide often become entrapped within a granule. The gas entrapment causes the granules to float. The GSL prevents buoyed sludge from floating out of the reactor and creates a quiescent zone (gas free zone) for sludge settling.

The design of a gas-solid-liquid settler has been outlined by Lettinga *et al.* (1980).

- Settler wall's angle of incline: 50°, to facilitate the return of sludge from the settler to the reactor
- Upflow velocity within the settler: Less than 0.7 m/hour, to prevent accidental sludge washout.

Start-up of UASB Reactors

Reactor inoculation with biomass is the first step in the UASB start-up process. Reactor start-up using digested sewage sludge has been described previously. Souza (1986) described the proper start-up of a UASB reactor using granular sludge as follows:

- Granular sludge volume: 10 to 15 percent of the reactor volume
- Start-up loading: 0.5 g COD/L/day, or 0.05 to 0.1 g COD/g VSS/day
- Increase COD loading: when gas production stabilizes and volatile fatty acid concentrations decrease below 500 mg/L as acetic acid.

Superficial Upflow Velocity and Effluent Recycle

The superficial upflow velocity is calculated from the reactor cross-sectional area and the influent wastewater flow rate. For dilute wastewaters, high organic loadings cause high reactor upflow velocities and sludge washout.

Recommended maximum design values for the superficial upflow velocity are 1.2 to 1.5 m/hour for peak daily wastewater flow (Souza, 1986). For a given reactor volume and wastewater flow rate, the upflow velocity increases with the design reactor height. For stronger wastes, the upflow velocity is small and large reactor heights are possible; however, the recommended maximum height is 6 meters (Souza, 1986).

The recycle of effluent dilutes the influent wastewater and increase the superficial upflow velocity. Sik Shin and Cheon Paik (1990) studied the effect of recycle with 2.5 L lab-scale UASB reactors and diluted milk wastewater feed (10,000 mg/L COD). The authors found that effluent recycle increased COD removal efficiency, sludge retention, and methane content of the biogas. The effluent recycle increased the upflow velocity to about 0.2 m/hour.

Sam-Soon *et al.* (1991) studied the effect of effluent recycle on reactor alkalinity. The authors concluded that high recycle rates could compensate for small deficiencies in wastewater feed alkalinity.

Wastewater Composition

Wastewater composition has been shown to effect UASB performance. The presence of lipids and proteins can cause excessive foaming and scum accumulation. High concentrations of lipids and proteins may require operation at lower loading rates, the installation of spray nozzles, or the installation of a skimmer (Lettinga and Hulshoff Pol, 1991).

The UASB can treat wastewaters with high concentrations of suspended solids; however, the UASB can treat soluble wastes at higher relative organic loading rates. (Lettinga *et al.*, 1984).

Excess Sludge Production

Granular sludge is "relatively stable and has superior dewatering characteristics" (Souza, 1986). Henze and Harremoēs (1983) reported yield coefficients from a number of anaerobic studies. The authors reported an average maximum yield of 0.18 g VSS/g COD utilized. The authors noted a relationship between observed yield and food to microorganism (F/M) ratio. Reported observed yields generally increased as the F/M ratio increased.

TOXICITY IN ANAEROBIC TREATMENT SYSTEMS

The following sections discuss toxicity in anaerobic treatment systems. The first section presents an overview of anaerobic toxicity, including generalizations regarding toxicant's behavior and targets. The remaining sections summarize studies of individual toxicants.

Overview of Anaerobic Toxicity

Inhibitory compounds can limit anaerobic treatment system performance. Because of the relative importance of methanogens to the anaerobic treatment process and the relative sensitivity of methanogens to environmental conditions, toxicity studies usually focus on these species of anaerobic microorganisms. Furthermore, since most methane is produced from acetic acid, many toxicity studied focus specifically on the acetate utilizing methanogens.

Toxicity resulting from the presence of inorganic salts is usually attributed to the cation rather than the anion (McCarty, 1964c). Cation toxicity testing is complicated by stimulatory, antagonistic, and synergistic effects. A number of compounds, when present in low concentrations, are stimulatory to anaerobic microorganisms. Compounds, such as heavy metals, have been reported to stimulate methanogens at very low concentrations (less than 1 mg/L) while other compounds, such as sodium, have been reported to stimulate methanogens at higher levels (over 100 mg/L) (McCarty, 1964b).

Kugelman and McCarty (1965) studied antagonism and synergism in multi-cation systems. Figure 6 illustrates the relationship between antagonism and synergism in a two compound system (Kugelman and McCarty, 1965). As shown in figure 6, a compound cannot be both synergistic and antagonistic to the toxicity resulting from another compound.

The authors noted that the range of peak antagonism for a compound decreased as toxicant concentration increased. The authors also noted that synergistic effects began at lower concentrations as a toxicants concentration increased. Several antagonists added together produced greater overall antagonism.

Toxicity testing is further complicated by microbial adaption. Parkin *et al.* (1983) studied a number of industrial toxicants. The authors noted that while a toxicant often produced an initial interruption of methane production, biogas production often resumed after several days.

Parkin and Speece (1983) compared a plug-flow attached growth anaerobic reactor to a completely mixed suspended growth reactor. The authors noted less interruption and faster recovery of methane production in the attached growth reactor. The results were attributed to the longer solids retention time and plug flow hydraulic regime of the attached growth reactor.

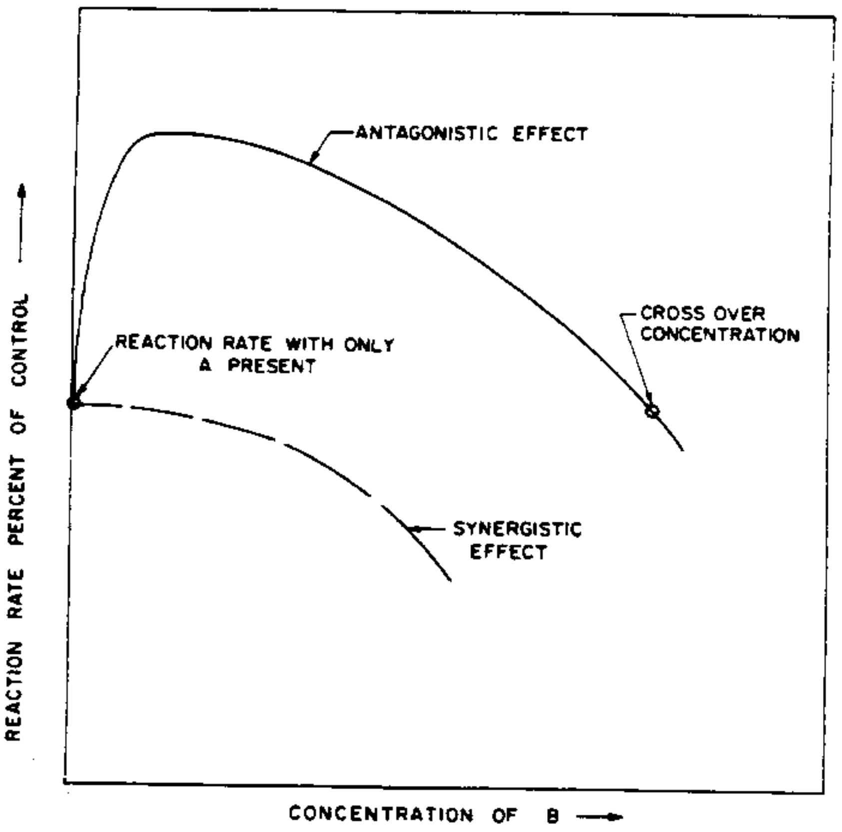


Figure 6. Antagonism and Synergism of Toxicity. Toxic Compound = A; Synergistic or Antagonistic Compound = B. (After Kugelman and McCarty, 1965)

Sodium Inhibition

Kugelman and McCarty (1965) studied sodium toxicity with continuously fed reactors at 35°C. An acetic acid containing solution was used as wastewater feed. The reported sodium concentration leading to 50 percent inhibition was 7,400 mg/L. Table 4 summarizes the antagonistic effect of potassium on sodium toxicity.

Table 4. Antagonistic Effect of Potassium on Sodium Toxicity in Continuously Fed Digesters at pH 7.0 and 35° C. (Adapted from Kugelman and McCarty, 1965)

Sodium Concentration (mg/L)	Antagonistic Cation	Range of Peak Antagonism (mg/L)
6,900	Potassium	78 - 2,300
9,200	Potassium	200 - 1,200

Kugelman and McCarty (1965) found calcium, magnesium, and ammonia to be synergistic to sodium toxicity as shown in table 5.

Table 5. Synergistic Effects of Various Cations on Sodium Toxicity in Continuously Fed Digesters at pH 7.0 and 35° C. (Adapted from Kugelman and McCarty, 1965)

Sodium Concentration (mg/L)	Synergistic Cation	Concentration of Synergist Where Synergism Begins (mg/L)
6,900	Ammonium	350*
9,200	Ammonium	140*
6,900	Calcium	400
9,200	Calcium	200
6,900	Magnesium	240
9,200	Magnesium	1,200

(*) mg/L as nitrogen

Rinzema *et al.* (1987) reviewed batch and continuous flow studies of sodium toxicity. The sodium concentration leading to 10 percent inhibition generally varied between 3,000 and 7,000 mg/L; however, several very high tolerances were noted (up to 26,000 mg/L) in continuous flow assays. The authors attributed the inconsistency in reported values to "antagonistic and synergistic effects, differences in sensitivity between microorganisms, and - quite important - differences in the test method."

Rinzema *et al.* (1987) also conducted short term batch activity tests (acetate feed, 30° C) which investigated sodium inhibition of granular sludge at various pH levels. Sodium was reported more inhibitory at pH 8 than at lower pH levels (6.5 to 7.2). Sodium concentrations of 5, 10, and 14 g/L caused 10, 50, and 100% inhibition, respectively, at near neutral pH. No adaptation of bacteria to sodium could be observed after 12 weeks. *Methanothrix* was assumed to be the predominant acetate utilizing methanogen in the study.

Boardman *et al.* (1995) investigated sodium toxicity using a clam processing wastewater as the assay medium. Sodium concentrations of 5.3, 6.3, 8.4, and 12.6 g/L reduced the specific methanogenic activity of granular sludge 40, 55, 85, and 90 percent, respectively. The sodium concentration in the control was 4,200 mg/L.

Soto *et al.* (1993) treated mussel processing wastewater with an anaerobic filter at a pH of 6.9 and a temperature of 37° C. The anaerobic filters were operated at high effluent volatile fatty acid concentrations to avoid substrate diffusion limitations. Sodium concentrations of 5 to 12 g/L did not affect methane production significantly. Batch activity tests confirmed the high resistance to sodium toxicity which was attributed to antagonism and microbial adaption.

Ammonia/Ammonium

Kugelman and McCarty (1965) investigated ammonium toxicity at pH 7.0 with acetate fed reactors maintained at 35° C. An ammonia concentration of 3,500 mg/L (as N) caused 50 percent inhibition. Table 6 summarizes the antagonistic effect of sodium on ammonia toxicity. Table 7 shows the synergistic effects of various cations on ammonia toxicity.

Table 6. Antagonistic Effect of Sodium on Ammonia Toxicity in Continuously Fed Digesters at pH 7.0 and 35° C. (Adapted from Kugelman and McCarty, 1965)

Ammonia Concentration (mg/L)[*]	Antagonistic Cation	Range of Peak Antagonism (mg/L)
2,100[†]	Sodium	60 - 1,100
3,500[‡]	Sodium	110 - 570

(*) mg/L as nitrogen
(†) 5.2 mg/L unionized ammonia as nitrogen
(‡) 8.7 mg/L unionized ammonia as nitrogen

Table 7. Synergistic Effects of Various Cations on Ammonia Toxicity in Continuously Fed Digesters at pH 7.0 and 35° C. (Adapted from Kugelman and McCarty, 1965)

Ammonia Concentration (mg/L)[*]	Synergistic Cation	Concentration of Synergist Where Synergism Begins (mg/L)
2,100[†]	Potassium	980
3,500[‡]	Potassium	980
2,100[†]	Calcium	800
3,500[‡]	Calcium	400
2,100[†]	Magnesium	240
3,500[‡]	Magnesium	120

(*) mg/L as nitrogen
(†) 5.2 mg/L unionized ammonia as nitrogen
(‡) 8.7 mg/L unionized ammonia as nitrogen

Koster and Lettinga (1984) studied ammonia toxicity with granular sludge in batch assays and continuous flow experiments at 30° C. A mixed volatile fatty acid (acetic, propionic, and butyric acids) feed was used in the batch studies while the continuous flow experiments used diluted potato juice. In the batch experiments, the maximum specific methane production rate decreased from 75 to 7.7 percent of the control (680 mg/L as N) as the ammonia concentration was increased from 759 to 2,600 mg/L (as N). The pH during the batch studies was reported as 7.6 to 8.0. In the continuous flow experiments, the authors used different dilutions of wastewater to achieve different ammonia concentrations. The authors noted an accumulation of propionic acid in the reactor when the ammonia concentration was about 1,500 mg/L (as N) at pH 7.5. The authors speculated that ammonia inhibited the hydrogen utilizing methanogens and that the accumulation of hydrogen subsequently inhibited propionic acid breakdown.

Wiegant and Zeeman (1986) studied ammonia inhibition of the thermophilic digestion of livestock wastes. The authors proposed a similar mechanism of ammonia inhibition as Lettinga and Koster (1984).

Soto *et al.* (1991) studied ammonia toxicity with acetate fed batch reactors at 37°C. Granular sludge that had been acclimated to about 1.1 g/L (as N) of ammonia was used in the studies. An ammonia concentration of 2.8 g/L (as N) inhibited methane production by 50 percent at pH 7.4. An ammonia concentration of 4.4 g/L (as N) inhibited methane production 80 percent at pH 7.4.

Potassium, Calcium, and Magnesium

Kugelman and McCarty (1965) studied potassium, calcium, and magnesium toxicity under conditions similar to the sodium and ammonia studies. Table 8 summarizes the cation concentrations causing 50 percent inhibition of methane production.

Table 8. Cation Concentrations Causing 50 Percent Inhibition of Acetate Utilizing Methanogens in Continuously Fed Digesters at pH 7.0 and 35° C. (Adapted from Kugelman and McCarty, 1965)

Cation	Concentration Causing 50 Percent Inhibition (mg/L)
Potassium	5,900
Calcium	4,400
Magnesium	1,900

Sulfide Inhibition

Sulfate is reduced within anaerobic treatment systems to sulfide by sulfate reducing microorganisms. The wastewater sulfate concentration is not a complete indicator of sulfide potential since some organic compounds, such as amino acids, release additional sulfate when they are degraded. At pH levels common to anaerobic treatment, sulfide is present as unionized hydrogen sulfide (H_2S) or bisulfide (HS^-). The pK_a for the dissociation of H_2S to HS^- is 7.1 at 25° C (Snoeyink and Jenkins, 1980).

Anderson *et al.* (1982) suggested that sulfide is the most important toxicant to anaerobic treatment technology since sulfide toxicity prevents several large potential commercial applications. The authors noted that sulfide toxicity studies fall into two categories: the competition of sulfate reducers with methanogens for substrate, and toxicity due to the sulfide concentration.

Koster *et al.* (1986) investigated sulfide toxicity at different pH levels using short term batch activity tests. The batch tests utilized granular sludge and an acetate feed. The observed inhibition of specific methanogenic activity correlated well with unionized hydrogen sulfide (H_2S) concentration between pH 6.4 and 7.2. The H_2S concentration causing 50 percent inhibition of methane production was 250 mg/L (as sulfide). In the pH range of 7.8 to 8.0, the H_2S concentration causing 50 percent inhibition was 90 mg/L (as sulfide).

Choi and Rim (1991) investigated the competition between sulfate reducers and methane producers with acetate fed lab-scale anaerobic contact units maintained at 35° C and pH 7.0. The units were seeded with polluted marine sediment. As the wastewater feed COD/SO_4 ratio was increased from 2.7 to 15, relative methane production (L CH_4/g COD) increased and sulfate reduction efficiency decreased. The authors concluded that methane producers outcompeted sulfate reducers at COD/SO_4 ratios greater than 2.7. As the COD/SO_4 ratio was increased from 0.4 to 1.7, COD removal efficiency was fairly constant while sulfate reduction efficiency increased. The authors concluded that sulfate reducers outcompeted methane producers when the wastewater feed COD/SO_4 ratio was less than 1.7. The actual COD and SO_4 reduction efficiencies were influenced significantly by the applied hydraulic retention time (HRT).

Heavy Metals

Heavy metals when present in solution are toxic to anaerobic bacteria. Lawrence and McCarty (1965) studied toxicity due to zinc, copper, and nickel. The authors found that the tolerable quantity of these heavy metals depended directly on the amount of sulfide present for precipitation. The authors also studied toxicity from iron. An iron concentration of 700 mg/L was tolerable even in the absence of sulfide for precipitation.

Kugelman and Chin (1971) reviewed toxicity due to copper, nickel, zinc, and chromium. Table 9 shows the range of toxic concentrations reported by the authors. The high values and wide ranges were attributed to sulfide and other "complex-type" reactions.

Table 9. Heavy Metal Concentrations Reported Toxic in Anaerobic Wastewater Treatment (Compiled from several sources by Kugelman and Chin, 1971)

Metal	Reported Toxic Concentrations (mg/L)
Copper	150 - 250, 500, 1000
Nickel	200, 1000
Zinc	1000, 350
Chromium	2000, 200

Volatile Fatty Acids

The accumulation of volatile fatty acids is caused by a decrease in methanogenic activity. The simultaneous observation of high volatile fatty acid levels and decreased methanogenic activity has caused some reports of volatile fatty acid toxicity. However, cation toxicity resulting from the addition of salts, such as sodium hydroxide, intended to neutralize the volatile fatty acids is a more accepted explanation for these observations (Anderson *et al.*, 1982; Kugelman and Chin, 1971). The addition of salts is necessary because the accumulation of volatile fatty acids decreases the reactor pH.

According to McCarty and McKinney (1961), volatile acid concentrations of 10,000 mg/L (as acetic acid) can be neutralized with lime without significant toxic effects. Because of the relatively strong inhibitory nature of sodium, this observation suggests the use of lime for pH stabilization instead of sodium hydroxide.

Oxygen

Kato *et al.* (1993) studied the tolerance of five different granular sludges to oxygen in batch activity tests using a methanol substrate. Oxygen was added to the flasks' headspace, and the flasks were shaken for three days. The specific methanogenic activity of the sludges was then measured. The authors reported that the oxygen headspace concentrations causing 50 percent inhibition ranged from 7 to 41 percent. The authors attributed the relatively high oxygen tolerance of the granular sludges to oxygen uptake by facultative microorganisms outlying the methanogenic species. Presumably, facultative microorganisms located near the granule surface utilized enough oxygen to deplete dissolved oxygen concentrations within the granules.

AIR STRIPPING THEORY AND DESIGN CONSIDERATIONS

Air stripping is a proven technology for the removal of volatile contaminants from liquids. The following sections describe air stripping tower configurations, mass-transfer theory, air stripping design equations, and other design considerations.

Air Stripping Tower Configurations

Air stripping towers can be considered of two types: countercurrent and crosscurrent. Both configurations rely on packing to provide surface area for air-liquid contact. Liquid flows downward through the packing in both configurations. Air flows vertically up through the packing in countercurrent towers. Air flows horizontally across the packing in crossflow towers.

Mass-Transfer Theory

In dilute solutions, the equilibrium distribution of a compound between the gas and liquid phases is governed by Henry's Law as shown in equation 7. The Henry's constant increases with increasing temperature, but the degree of temperature dependency is compound specific. Equation 8 expresses the temperature dependency of the Henry's Law constant (Selleck *et al.*, 1988).

$$y = m \cdot c \tag{7}$$

$$m = (1/T)10^{-(J/T)} \tag{8}$$

where:

y = molar gas phase concentration

m = dimensionless Henry's constant

c = molar concentration of contaminant in the liquid phase

J = temperature correction coefficient (°K)

T = liquid temperature (°K)

Table 10 contains Henry's constant values and temperature dependencies for several compounds of environmental interest (Selleck *et al.*, 1988).

Table 10. Dimensionless Henry's Constants and Temperature Dependencies for Several Compounds. (Adapted From Selleck *et al.*, 1988)

Compound	Henry's Constant, m*	Temp. Correction Coefficient, J† (°K)
1,1,1-Trichloroethane	0.57	1,770
Trichloroethylene	0.32	1,960
Chloroform	0.12	1,930
Bromoform	0.017	2,170
Ammonia	0.00055	1,890

(*) Dimensionless
(†) $m \propto (1/T)10^{-(J/T)}$, T = Temperature, °K

The direction of mass-transfer between the gas and liquid phases proceeds toward equilibrium according to Henry's constant. The rate of mass-transfer (or flux) of a compound from the liquid to the gas phase depends on the difference between the actual and equilibrium concentrations in the liquid phase and the overall mass-transfer coefficient as shown in equation 9 (Treybal, 1980).

$$J = K_L \cdot a(c^* - c) \qquad (9)$$

where:

J = rate of mass-transfer (mole/L/min)
K_L = overall mass-transfer coefficient (m/min^{-1})
a = specific interfacial area (m^2/m^3)
c^* = compound equilibrium liquid phase concentration given by Henry's constant (mole/L)

According to the two phase resistance theory, the total resistance to mass-transfer is equal to the sum of the gas and liquid phase resistances. The overall mass-transfer coefficient is inversely proportional to the total resistance. Similarly, the local gas and liquid phase mass-transfer coefficients, which are directly proportional to the rate of mass-transfer through each phase, are inversely proportional to the gas and liquid phase resistances, respectively. Equation 10 shows the overall mass-transfer coefficient for the transfer of a compound from the liquid to the air (Treybal, 1980).

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_G m} \qquad (10)$$

where:

k_L = local liquid phase mass-transfer coefficient (m/min^{-1})

k_G = local gas phase mass-transfer coefficients (m/min^{-1})

Equation 10 indicates that the Henry's constant determines whether gas or liquid phase resistance controls the rate of mass transfer. If the Henry's constant is very large, the gas phase resistance, expressed in equation 10 as $1/(k_G \cdot m)$, will be relatively small and liquid phase resistance will control the overall mass-transfer coefficient. Similarly, if the Henry's constant is small, the gas phase resistance will be relatively large and will exert more influence on the overall mass-transfer coefficient.

When liquid phase resistance controls mass-transfer, the overall mass-transfer coefficient is not affected by changes in the air flowrate which increase or decrease air turbulence, and therefore k_G. Under these conditions, the overall mass-transfer coefficient can be increased by increasing the liquid loading rate. When gas phase resistance controls mass-transfer, the overall mass-transfer coefficient increases with increasing air flowrate (Kavanaugh and Trussell, 1980). According to equation 9, the mass-transfer rates per unit packing volume can always be increased by selecting a packing that permits a greater specific interfacial area.

Liquid phase resistance, or a combination of liquid phase and gas phase resistance, controls most compounds of concern in water treatment (AWWA, 1990).

Air Stripping Design Equations

The required tower height for an air stripping tower depends on the required number of transfer units (NTU) and the height of a transfer unit (HTU) as shown in equation 11. The NTU depends on the applied stripping factor and required degree of removal. Equation 12 defines the NTU, but is only valid if the stripping gas does not contain the target compound. Equation 13 defines the stripping factor which depends on the compounds Henry's constant and the applied liquid and gas loading rates. The HTU depends on the overall mass-transfer coefficient, the applied liquid loading rate, and the specific interfacial area according to equation 14.

$$Z = NTU \cdot HTU \tag{11}$$

$$NTU = \frac{R}{(R-1)} \cdot \ln\left(\frac{c_{in}/c_{out}(R-1)+1}{R}\right) \tag{12}$$

$$R = H \cdot G / L \tag{13}$$

$$HTU = L / K_L \cdot a \tag{14}$$

where:

Z = total tower height (m)

NTU = number of transfer units

HTU = height of a transfer unit (m)

c = influent contaminant concentration in liquid phase (mg/L)

c_{out} = effluent contaminant concentration in liquid phase (mg/L)

R = stripping factor

L = liquid loading rate ($m^3/m^2 \cdot min$)

G = gas flow rate ($m^3/m^2 \cdot min$)

By manipulation of equations 11, 12, and 14, the product of the mass-transfer coefficient and the specific interfacial area may be calculated from experimental data. Empirical models are available in the literature for the prediction of mass-transfer coefficients. The Onda model (Onda, *et al.*, 1968), for example, takes into account resistance to mass-transfer in both phases.

Other Design Considerations

The pressure drop across the air stripping tower packing is an important design consideration. Treybal (1980) made the following observations regarding pressure drop and packing size.

- Air stripping towers are typically designed with pressure drops from 0.25 to 0.5 inches of water column pressure drop per foot of packing height
- The ratio of packing size to the tower diameter should be at least 1:8 and preferably 1:15
- For a given packing volume, smaller packings provide more surface area for air/liquid contact, but also create more resistance to air flow. Larger packings are recommended for applications requiring high gas flow rates.

TREATMENT OF BLUE CRAB PROCESSING WASTEWATERS

In the next few sections, the treatment of blue crab processing wastewaters with the following technologies is reviewed: anaerobic biological treatment in completely mixed stirred tank reactors, anaerobic biological treatment in Upflow Bed Filters (UBF) and Upflow Packed Bed Filters (UPF), aerobic biological treatment, coagulation by pH adjustment, and air stripping.

Anaerobic Biological Treatment in Completely Mixed Stirred Tank Reactors

Harrison *et al.* (1992) operated two completely mixed stirred tank reactors (2 L volume) at 35° C. Reactor A treated retort effluent while Reactor C treated a theoretical combined wastewater. The composition of the combined wastewater was 1:1:1:3 of retort effluent, Harris Claw reel wash water, Harris Claw brine bath, and Harris Claw meat conveyor wash water. The study period lasted 55 days.

Reactor A was operated at a food to microorganism ratio (F/M) of 0.25 day^{-1} from day 31 to day 55. During this period, Reactor A's effluent soluble COD (SCOD) varied from 620 to 805 mg/L. The TKN of the reactors' effluent increased from 800 mg/L on day 21 to 1,200 mg/L on day 55. Reactor B was operated at a F/M ratio of 0.05 day^{-1} from day 11 to day 55. From day 11 to day 55, Reactor B's effluent SCOD varied from 360 to 895 mg/L. Harrison *et al.* (1992) simultaneously operated two additional Reactors B and D that treated retort effluent and combined effluent, respectively. The wastewaters were treated by pH adjustment, flocculation, and settling prior to use as feed. Reactors A and C performed slightly better than Reactors B and D over the study period.

The operation of the reactors was continued by another investigator (Boardman *et al.*, 1993; Wolfe, 1993). Reactors A and B treated retort effluent at F/M ratios of 0.35 and 0.25 day^{-1}, respectively. Over a 131 day period, Reactor A removed 87 percent of the wastewater COD. Over a 41 day period, Reactor B removed 91 percent of the wastewater COD. The reactors were eventually shut down after showing signs of failure. The environmental conditions of the reactors when treatment efficiency decreased was summarized as follows:

- Ammonia concentrations peaked at 1750 mg/L and 1,500 mg/L (as N) in Reactors A and B, respectively
- Sodium concentrations were about 4,000 mg/L in both reactors
- Reactor A pH was 7.5; Reactor B pH was about 7.7.

Reactors C and D treated unamended combined effluent wastewater at F/M ratios of 0.1 and 0.07 day^{-1}, respectively. BOD$_5$ removals in Reactors C and D were 79 percent and 83 percent, respectively over an extended period; however, both reactors eventually exhibited signs of failure. The conditions when treatment efficiency began to decrease were summarized as follows:

- Ammonia concentrations peaked for Reactors C and D near 1,000 mg/L and 800 mg/L (as N), respectively
- Sodium concentrations were between 24,000 and 27,000 mg/L in both reactors
- Both reactors' pH were about 7.6.

Upflow Anaerobic Bed Filter and Upflow Anaerobic Packed Filter

Diz and Boardman (1994) treated retort effluent using anaerobic treatment followed by aerobic treatment. System A included a 4 L Upflow Anaerobic Bed Filter (UBF), a 4 L anaerobic clarifier, and an 8 L activated sludge tank. System B included an 4 L Upflow Anaerobic Packed Filter (UPF), a 4 L anaerobic clarifier, and an 8 L activated sludge tank. The study included four phases at different organic loading rates.

Table 11 summarizes the treatment performance of the UBF and UPF during the study period. Table 12 summarizes average values obtained for effluent BOD$_5$ and COD over a 21 day period during phase 4 for System B.

Table 11. Treatment Performance of UBF (System A) and UPF (System B) Reactors at Different Organic Loading Rates. (Adapted from Diz and Boardman, 1994)

Phase	UBF (System A) F/M (day^{-1})	Effluent COD (mg/L)*	UPF (System B) F/M (day^{-1})	Effluent COD (mg/L)*
1. 33 Days	1.0	3,100	0.4	2,400
2. 30 Days	1.1	11,400	0.5	9,200
3. 47 Days	0.4	6,500	0.2	6,000
4. 34 Days	0.5	8,500	0.2	7,200

(*) Soluble COD

Table 12. Wastewater Feed and Soluble Effluent BOD$_5$ and COD Values for System B. Samples From a 21 Day Period During Phase 4. (Adapted from Diz and Boardman, 1994)

Parameter	Wastewater Feed	UPF*	Anaerobic Clarifier	Activated Sludge Tank
COD (mg/L)†	19,600	7,300	7,600	2,400
BOD$_5$ (mg/L)†	14,000	4,100	3,900	110
COD/BOD$_5$ Ratio	1.4	1.8	2.0	20

(*) Upflow Packed Filter
(†) Unfiltered Wastewater Feed Value, Soluble Effluent Value

In an anaerobic semi-continuous batch study conducted by Diz (1994), micronutrient supplementation did not appear to improve anaerobic treatment. Micro-nutrients were added to the feed wastewater (crab cooker wastewater) in the following concentrations: 10 mg/L iron, 1 μM (micro-molar) cobalt, 1 μM molybedenum, and 1 μM nickel.

Aerobic Treatment

Wheaton *et al.* (1984) operated a waste treatment system for one year at a blue crab processing facility. An aerated biological treatment tank was fed periodically from a sump which served as a holding tank for wastewater produced at the processing plant. The average retention time in the aerobic biological treatment tank was 2 days. The performance of the treatment tank was not sufficient to meet EPA Best Available Technology Economically Achievable (BAT) limits for TSS and BOD_5. The plant wastewaters treated included retort, washdown, and hand picking effluents.

Coagulation by pH Adjustment

Boardman *et al.* (1993) and Harrison (1993) reported the efficacy of pH adjustment for wastewater coagulation and subsequent suspended solids removal. Jar tests were performed on several crab processing effluents after the wastewaters were adjusted to pH 6, 5, 4, 3, or 2. Table 13 summarizes the removal of suspended solids from the retort effluent.

Table 13. Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) Removal Through Coagulation by pH Adjustment With Concentrated Sulfuric Acid. Retort Effluent. (Adapted from Harrison, 1993)

pH	TSS (mg/L)	VSS (mg/L)
8.2 (Control)	1,120	974
6.0	1,040	926
5.0	241	212
4.0	266	235
3.0	1,560	1,440
2.0	338	295

The authors reported similar results with the other processing effluents. COD and BOD_5 reductions, for all effluents, ranged from 12 to 37 percent and 6 to 30 percent, respectively.

Air Stripping

Wolfe (Wolfe, 1993; Boardman *et al.*, 1993) investigated air stripping for ammonia removal from retort effluent. A 46 centimeter (cm) diameter tower was filled with 5.8 cm LanPac packing. The useful tower height (packing depth) was 1.8 m. The author reported an ammonia reduction of 71 percent using an air to water ratio of 6,200 (L/L), a pH of 12.2, and a wastewater temperature of 58° C. The author reported an ammonia reduction of 67 percent using an air to water ratio of 3,100 (L/L), a pH of 11.0, and a wastewater temperature of 65° C. Liquid flowrates of 2.3 and 4.5 L/min were utilized in the study.

The author also investigated air stripping for ammonia removal from retort effluent at ambient temperatures. An ammonia reduction of 32 percent was reported using an air to water ratio of 6,200 (L/L), a pH of 11.0, and a wastewater temperature of 20 °C. An ammonia reduction of 50 percent was reported using an air to water ratio of 3,100 (L/L), a pH of 12.2, and a wastewater temperature of 20° C.

The temperature of the wastewater leaving the tower was between 13 and 20 °C for all air stripping trials.

AIR STRIPPING LITERATURE REVIEW

The following sections review applications of air stripping technology. Ammonia stripping experiences are summarized. Air stripping studies where gas side resistance has been discussed are noted in a separate section.

Ammonia Removal By Air Stripping

Trulsson (1979) investigated ammonia stripping with a 2.4 meter high, 0.3 m inside diameter tower. The tower feed was tap water spiked with ammonia, adjusted to pH 11.2, and heated to 35° C. The author reported an ammonia reduction of 95 percent using a gas loading rate of 35 kg/m^2/sec and a liquid loading rate of 1.5 kg/m^2/sec. The author reported an ammonia reduction of 50 percent using a gas loading rate of 35 kg/m^3/sec and a liquid loading rate of 5 kg/m^2/sec. The authors advised the use of very low liquid loading rates for ammonia stripping, and advocated the use of liquid loading rates below the minimum wetting rate. The authors also studied ammonia recovery in phosphoric acid. Conditions favoring ammonia recovery were high ionic strength and low pH.

O'Farrell *et al.* (1972) utilized five crossflow towers in series for ammonia stripping. Each tower was 3 m high, 1.5 m long, 1.2 m wide, and packed with polypropylene grids. The liquid loading rate was varied between 40.7 and 100 L/m^2/min while the air to water ratio varied from 750 to 5600 L/L. The authors reported increasing stripping performance with increasing pH to pH 10.5. The additional increase of the pH to 11.7 only increased stripping performance 6 percent. When the air and influent water temperatures were about 27° C, ammonia reductions of up to 90 percent were achieved. When the air temp dropped to 5.5° C, ammonia reductions decreased 30 percent. Scale accumulation was also studied. Over a 75 day period, ammonia reductions decreased from 80 to 55 percent because of scale accumulation that reduced air flow.

Minocha and Prabhakar Rao (1988) used a 1.4 m high tower containing rashig rings to study ammonia stripping. The tower feed was tap water spiked with ammonia. Studies were conducted at air temperatures of about 26° C. Liquid flowrates between 0.2 and 0.8 m^3/m^2/hour were examined. The author reported ammonia reductions of 81, 91, and 99 percent using air flow rates of 180, 300 and 420 m^3/m^2/hour, respectively. The authors also investigated ammonia recovery. By assuming a 90 percent ammonia removal efficiency, the authors calculated that one liter of commercial grade phosphoric acid could absorb the ammonia stripped from more than 275 liters of wastewater having an influent ammonia concentration of 2,000 mg/L.

Experiences With Gas Phase Resistance in Air Stripping Studies

Roberts *et al.* (1985) evaluated several mass-transfer models and found the Onda model to best predict mass-transfer coefficients. The author investigated the removal of several volatile organic compounds and oxygen with a 0.22 m inside diameter tower using nitrogen as the stripping gas. Several liquid flowrates were examined at a constant nitrogen flowrate. For the very volatile compounds, the overall mass-transfer coefficient increased with increasing liquid flowrate. For the less volatile compounds, liquid flowrate had no effect or a perceived negative effect on the overall mass-transfer coefficient. The observations regarding the less volatile compounds were attributed to operation at low stripping factors. The authors illustrated the sensitivity of observed mass-transfer coefficients to errors in the stripping factor graphically. The sensitivity was much larger at low stripping factors.

Roberts *et al.* (1985) also performed experiments with different nitrogen flowrates at constant liquid flowrates. For the very volatile substances, the overall mass-transfer coefficient was independent of gas flowrate. For the less volatile substances, the overall mass-transfer coefficient increased with nitrogen flowrate. The results reported with the less volatile compounds were attributed to gas phase resistance. The least volatile substance in the study was chloroform. The overall mass-transfer coefficient for chloroform increased 79 percent as the result of a 300 percent increase in air flowrate.

Ball *et al.* (1984) investigated mass-transfer relationships with a pilot-scale tower that treated 20 to 380 m^3/day of tidal estuary water combined with secondary wastewater effluent. The combined tower feed was spiked with several volatile organic compounds. Mass-transfer coefficients increased as the liquid loading was increased for all compounds except Bromoform which had the smallest Henry's constant. The authors attributed the Bromoform results to either gas phase resistance or inaccurate data which could have resulted from the low stripping factors utilized in the study.

CHAPTER III. MATERIALS AND METHODS

The following chapter describes experimental apparatus, experimental procedures, and analytical techniques used during the course of this investigation. Apparatus and methods are described separately for the following studies: lab-scale Upflow Anaerobic Sludge Blanket (UASB) reactors, pilot-scale Upflow Anaerobic Sludge Blanket (UASB) reactor, pilot-scale Upflow Anaerobic Bed Filter (UBF), batch anaerobic toxicity assays, and pilot-scale air stripping column.

LAB-SCALE UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTORS

Two identical lab-scale reactors were used to assess the anaerobic treatability of blue crab (*Callinectes sapidus*) cooker wastewater with UASB technology. The reactors were located at the Virginia Polytechnic Institute and State University (VPI & SU) Price's Fork Research Center in Blacksburg, Virginia.

Wastewater Feed & Granular Sludge Inoculum

Wastewater feed was collected in 20 L carboys from the crab cooker at Graham & Rollins, Inc. in Hampton, Virginia. The wastewater was transported to the VPI & SU environmental engineering laboratory in Blacksburg, Virginia where it was refrigerated at 4° C. Granular sludge inoculum was obtained from the full-scale UASB located at Fleischmann's Yeast Inc. in Gastonia, North Carolina. The granular sludge was obtained July 20, 1994 and stored at 4° C prior to use.

Lab-Scale UASB Reactor Design

Figure 7 illustrates the lab-scale UASB design. The design was adapted from the lab-scale UASB design used by Tisinger (1991). Each reactor consisted of a reactor vessel and a gas-liquid-solid separator (GLS). The reactor vessel was a plexiglas cylinder with an inside diameter of 7.0 centimeters (cm) and a height of 0.6 meters (m). At reactor base, the reactor vessel's inside diameter tapered from 7.0 cm to 1.3 cm. The reactor vessel was capped with a silicone stopper. The liquid and headspace volumes were 2 L and 200 mL, respectively.

The 0.5 L GLS was a polyethylene funnel. A piece of plastic covered the funnel to keep out air. A ¾ inch polyvinyl chloride (PVC) pipe connected the GLS with the reactor vessel. The PVC pipe penetrated the silicone stopper and was capped 3 centimeters below the reactor's liquid surface. Liquid entered the pipe through several 0.7 cm horizontal holes.

A peristaltic pump delivered wastewater from a refrigerator (4° C) into the reactor base. The direction of flow was up through the reactor vessel and into the GLS. Effluent flowed by gravity from the GLS to a collection vessel. The liquid volume in the collection vessel was recorded daily and used to monitor the wastewater feed flow rate. A peristaltic pump recycled flow from the GLS to the reactor base. An effluent recycle of 20 mL/min was maintained throughout the lab-scale UASB experiments. This flow rate created a superficial upflow velocity of 0.3 m/hour within the reactor.

Biogas flowed from the reactor headspace through ¾ inch tubing into a gas collection bag. Ten and 40 L volume bags were utilized. Biogas production was quantified by disconnecting the collection bag from the reactor and measuring the collected volume. The collected volume was measured by liquid displacement using a graduated plexiglas cylinder (60 L volume). The gas collection bag was equipped with a 12 mm septum.

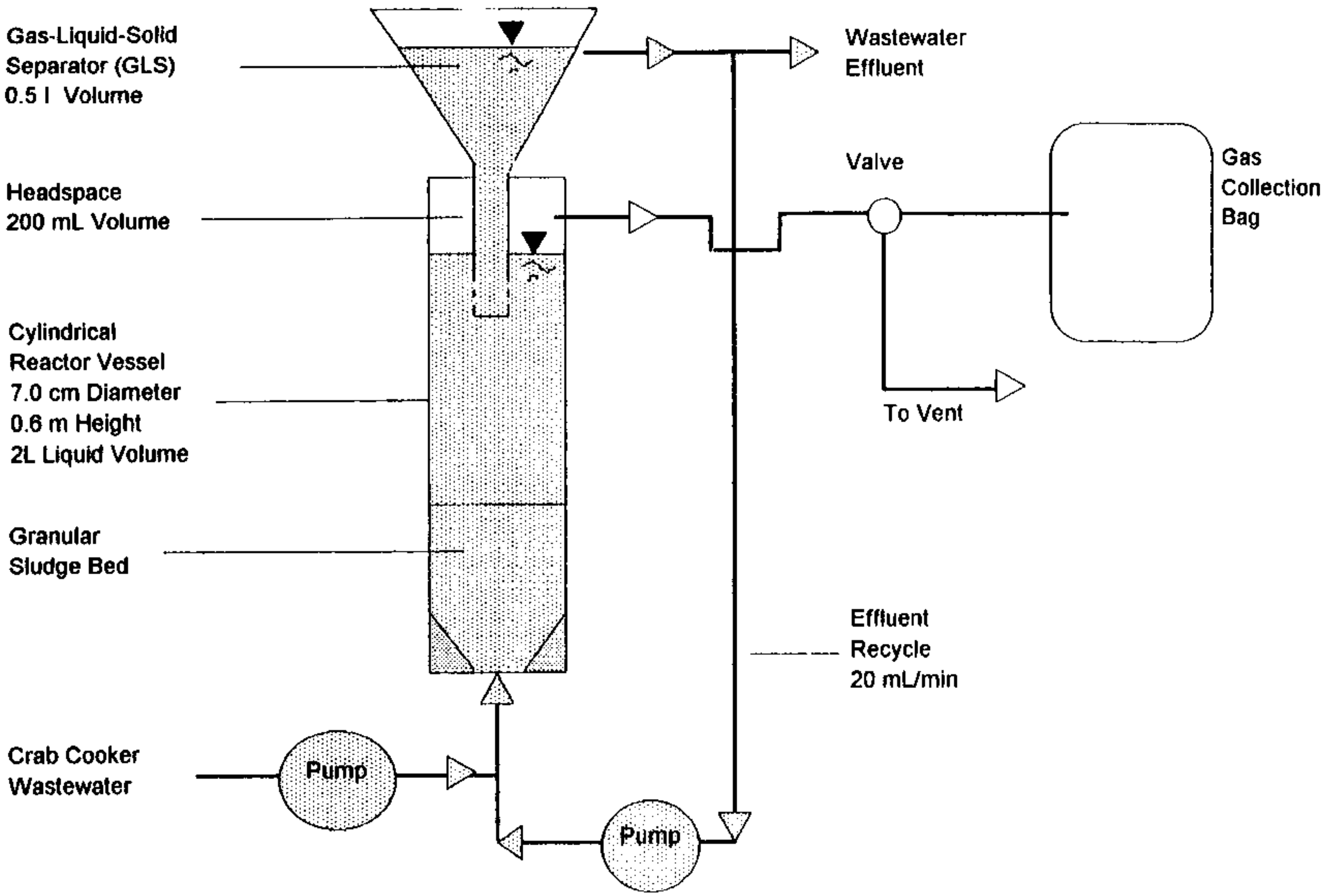


Figure 7. Lab-Scale Upflow Anaerobic Sludge Blanket (UASB) Reactor

Temperature Control

Each reactor was maintained at 37° C (± 2°C). A peristaltic pump circulated hot water through approximately 2.5 meters of ⅜ inch vinyl tubing which was wrapped around each reactor. A point-of-use hot water heater (15 L capacity) heated the circulated water. Each reactor was surrounded by a Styrofoam® housing. The housing and vinyl tubing surrounded only the body of the plexiglas cylinder and not the GLS.

Sampling

Effluent samples were withdrawn from the GLS. Granular sludge samples were withdrawn from a sample port located 8 cm above the reactor base.

First Study Period

During the first study period, the lab-scale UASB reactors treated unamended crab processing wastewater. Reactor A was inoculated with 24 g of Volatile Suspended Solids (VSS). Reactor B was inoculated with 17 g of VSS. The reactors were operated for 75 days. Wastewater feed was diluted 1:5 with tap water until day 30. Table 14 shows the organic loading rates (OLR, g COD/L reactor volume/day) placed on the reactors.

Table 14. Organic Loading Rates (OLR) for Lab-Scale UASB Reactors During First Study Period.

	OLR (g COD/L/day)		
Time (days)	Reactor A	Reactor B	Comment
1 - 30	0.5	0.5	Feed wastewater diluted 5:1
30 - 44	1.0	1.0	Full-strength wastewater
44 - 55	3.0	3.5	Day 55: reactor B feed rate increased
55 - 75	3.0	5.7	Day 75: end study period

Second Study Period

The effect of pH adjustment on reactor performance was evaluated during the second study period. Two reactor start-up alternatives were compared. Reactor's A treatment performance and methane production had declined severely in the 21 days previous to the second study period. The reactor's failure was attributed to an excessive organic loading rate. On day 1 of the second study period, reactor A contained 24 g of VSS. Reactor B was inoculated with granular sludge that had been stored at 4° C for four months. The reactor contained 17 g of Volatile Suspended Solids (VSS) after inoculation.

Hydrochloric acid (6N HCl) was added to the feed wastewater to decrease the reactors' pH. The target reactor pH was 7.0 until day 97 when the target reactor pH was changed to 7.3. The reactors were operated for 151 days. Wastewater feed was diluted 1:5 with tap water until day 30. Table 15 shows the OLRs placed on the reactors.

Table 15. Organic Loading Rates (OLR) for Lab-Scale UASB Reactors During Second Study Period.

Time*	OLR (g COD/L/day)		
(days)	Reactor A	Reactor B	Comment
1 - 11	0.5	0.5	Feed wastewater diluted 1:5
11 - 20	0.5	1.0	-
20 - 30	0.8	1.6	-
30 - 45	1.6	1.3	Full-strength wastewater
50 - 63	7.6	5.3	-
63 - 97	5.7	2.5	-
97 - 151	6.4	2.8	Reactor pH increased to 7.3

(*) Reactors inoculated on day 1

PILOT-SCALE UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTOR

The pilot-scale UASB reactor was assembled at the Virginia Tech Seafood Research and Extension Center in Hampton, Virginia.

Wastewater Feed & Granular Sludge Inoculum

Blue crab cooker wastewater was pumped approximately 100 m from the crab cooker at Graham & Rollins, Inc., in Hampton, Virginia to a 65 L holding tank located at the Hampton research center. The pumping facility and holding tank have been described previously by Diz (1994). Granular sludge was obtained from Fleischmann's Yeast in Gastonia, North Carolina on November 2, 1994. The sludge was stored at ambient temperatures for several days prior to use.

Reactor Design

Figure 8 shows the pilot-scale UASB design. The reactor vessel was a Solar Components (Manchester, New Hampshire) reinforced fiberglass cylindrical tank (46 cm diameter, 1.5 m height) with a conical cover and base. An additional conical cover was used as a gas-liquid-solid separator (GLS). The angle of incline of the GLS's sloped surface was 50 degrees; the GLS's diameter expanded to 36 cm at the open face. A ½ inch cpvc pipe suspended the GLS from the reactor cover. A plexiglas baffle directed biogas into the GLS and created a quiescent zone above the GLS's outer surface.

A peristaltic pump delivered wastewater from the holding tank into the bottom of the UASB. The direction of flow was up through the reactor vessel and into the quiescent zone.

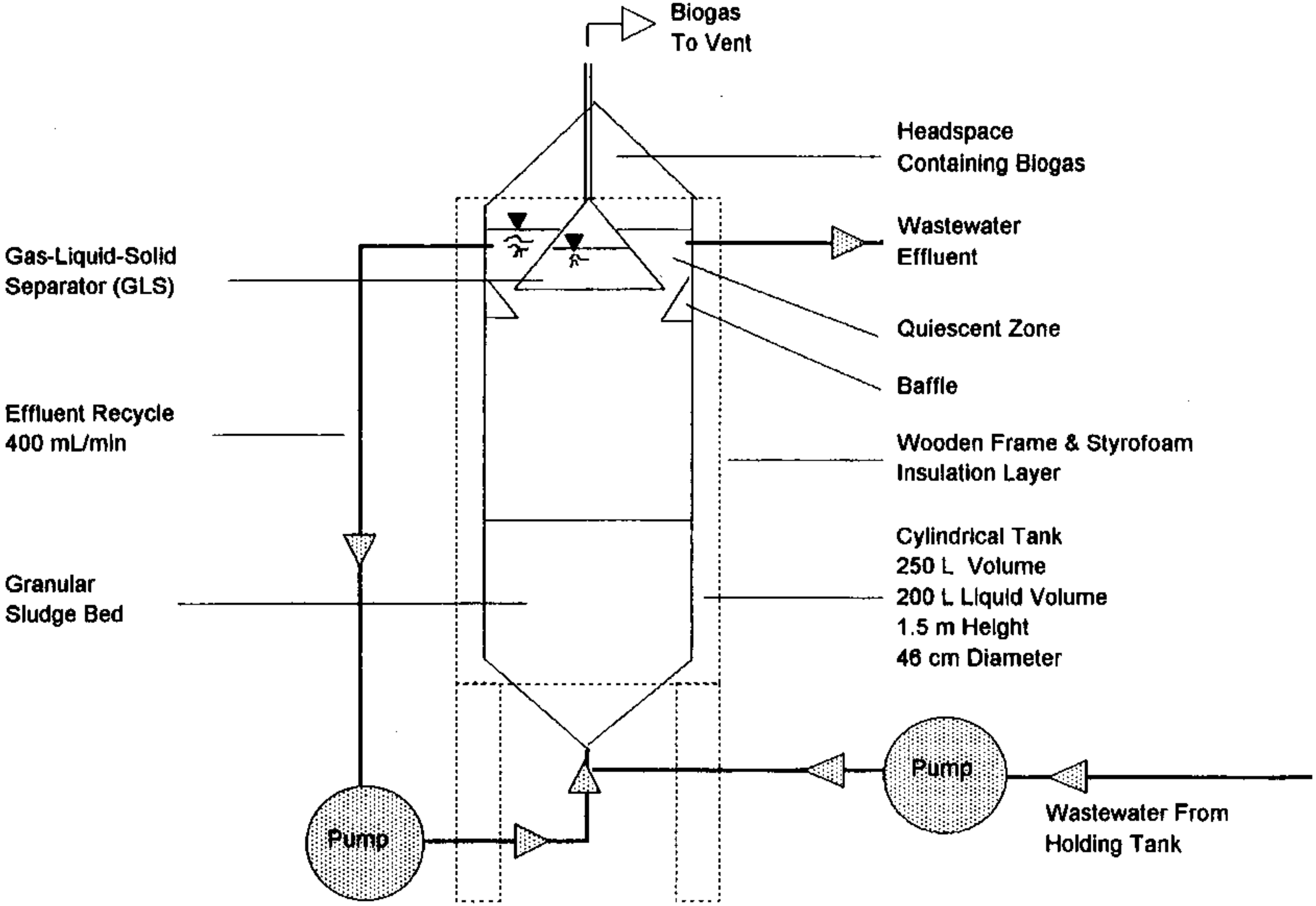


Figure 8. Pilot-Scale Upflow Anaerobic Sludge Blanket (UASB) Reactor

Effluent flowed by gravity from the quiescent zone into a ¾ inch PVC pipe that emptied into the Hampton River. A peristaltic pump withdrew recycle from the quiescent zone. The recycle flow was pumped through a ¾ inch chlorinated polyvinyl chloride (CPVC) pipe and into the reactor base. An effluent recycle of 300 mL/min was maintained throughout the study. This flow rate created a superficial upflow velocity of 0.1 m/hour within the reactor.

The CPVC pipe that supported the GLS also carried biogas out of the reactor. The CPVC pipe connected to a ½ inch PVC pipe which led to a vent above the building. Several 0.5 cm holes, that were drilled in the cpvc pipe above the reactor's liquid level, allowed biogas to flow freely in the reactor's headspace.

The reactor was supported by a wooden frame. Styrofoam® sheets were placed between the wooden beams of the frame.

Temperature Control

The UASB was maintained at 35° C (± 2° C). Hot water was circulated through 20 meters of 3/8 inch vinyl tubing that was wrapped around the reactor. The water was heated by a 15 L capacity point-of-use hot water heater. A layer of fiberglass insulation was wrapped over the tubing. The fiberglass insulation and the Styrofoam®/wood encasing insulated the tank.

Sampling

Effluent samples were taken from the quiescent zone of the GLS. Sludge samples were taken from a ¾ inch drain valve located 8 cm above the conical bottom.

Reactor Operation

The pilot-scale UASB reactor was inoculated with 4.7 kg of VSS on November 5, 1994 (day 1 of the study). The feed flowrate was maintained at 7.5 L/day from November 5 until February 11, 1995. This period served to acclimate the granular sludge inoculum to the crab processing wastewater. The acclimation period was prolonged due to mechanical difficulties with the reactor.

Wastewater feed was not available from February 11, 1995 to April 1, 1995. From April 1, 1995 to May 25, 1995 the feed flow rate was 24 L/day. Table 16 shows OLRs and F/M ratios for the reactor.

Table 16. Organic Loading Rates (OLR) and Food to Microorganism (F/M) Ratios for the Pilot-Scale UASB Reactor.

Date[*]	OLR (g COD/L/day)[†]	F/M Ratio (1/days)[‡]	Comment
1 - 95	0.7	0.03	Start-up prolonged due to mechanical difficulties
95 - 142	-	-	Feed interrupted due to wastewater shortage
142 - 199	2.7	0.12	Constant feed rate maintained

(*) Reactor inoculated on Day 1 (November 5, 1994)
(†) Based on 200 L reactor volume
(‡) Based on 4.7 kg of VSS

PILOT-SCALE UPFLOW ANAEROBIC BED FILTER (UBF)

The UBF pilot-plant was designed, assembled, inoculated, and operated (until 6/94) by Diz (1994). The UBF reactor was part of an anaerobic/aerobic treatment facility which included: the UBF reactor, an anaerobic clarifier, an aerated drum, and an activated sludge tank. Tank sizes and configurations have been described by Diz (1994).

The treatment facility was located at the Virginia Tech Seafood Research and Extension Center in Hampton, Virginia. The facility treated blue crab cooker wastewater produced at

Graham and Rollins, Inc., in Hampton Virginia. The reactor was fed wastewater from the same holding tank that was used to feed the pilot-scale UASB. During the course of this study, Rodenhizer (1995) maintained the treatment system and operated a biogas collection/utilization facility with biogas from the UBF.

The feed flow rate was 40 L/day from July 9, 1994 to July 29, 1994. The flow rate was increased to 110 L/day on July 29 and maintained until November 23, 1994. The flow rate was 40 L/day from November 23 and February 11, 1995 due to wastewater shortages. Wastewater was not available from February 11 to April 1, 1995. The flow rate was 60 L/day from April 1, 1995 to May 25, 1995. Table 17 shows the organic loading rates placed on the reactor.

Table 17. Organic Loading Rates (OLR) for Pilot-Scale UBF Reactor

Time (Days)*	OLR (g COD/L/day)†	Comment
1 - 20	1.4	Start-up loading
20 - 119	3.5	Constant feed rate maintained
119 - 200	1.2	Feed rate reduced due to wastewater shortage
200 - 247	No feed	Feed interrupted due to wastewater shortage
247 - 304	2.3	Constant feed rate maintained

(*) Study period began on July 29, 1994 (day 1)
(†) Based on 600 L reactor volume

BATCH ANAEROBIC TOXICITY ASSAYS

Inhibition of acetate utilizing methanogens by ammonia and sodium was investigated with batch anaerobic toxicity assays. The specific methanogenic activity of granular sludge exposed to different ammonia and sodium concentrations under non-substrate limiting conditions (very high acetate concentrations) was measured and used to evaluate inhibition.

Apparatus Design

Figure 9 illustrates the experimental apparatus. In the batch assays, 370 mL serum bottles with plastic screw caps and 23 mm teflon septa were utilized. A hypodermic syringe was inserted through the serum bottle septum and connected to a graduated gas measurement cylinder with plastic tubing. The graduated gas measurement cylinder quantified gas production by displacement of a colored salt saturated solution of 5% sulfuric acid (H_2SO_4).

The serum bottles were submerged in a 35° C (± 0.2° C) water bath. A Lauda K-2/RD constant temperature circulator maintained the water bath temperature. The serum bottles contained magnetic stirring bars. Magnetic stirrers, located beneath the water bath, mixed the bottles.

Granular Sludge Source and Handling

Granular sludge inoculum was withdrawn from lab-scale UASB Reactor A. Table 18 summarizes the steady-state conditions of the UASB when the sludge was withdrawn. Withdrawn sludge was elutriated for one-half hour to remove fines and placed in one of two batch reactors (1 L volume, 35° C). The batch reactors were maintained at pH 7.4 and pH 7.8. The granular sludge was fed acetate and maintained in the macro/micro nutrient solution described in the next section.

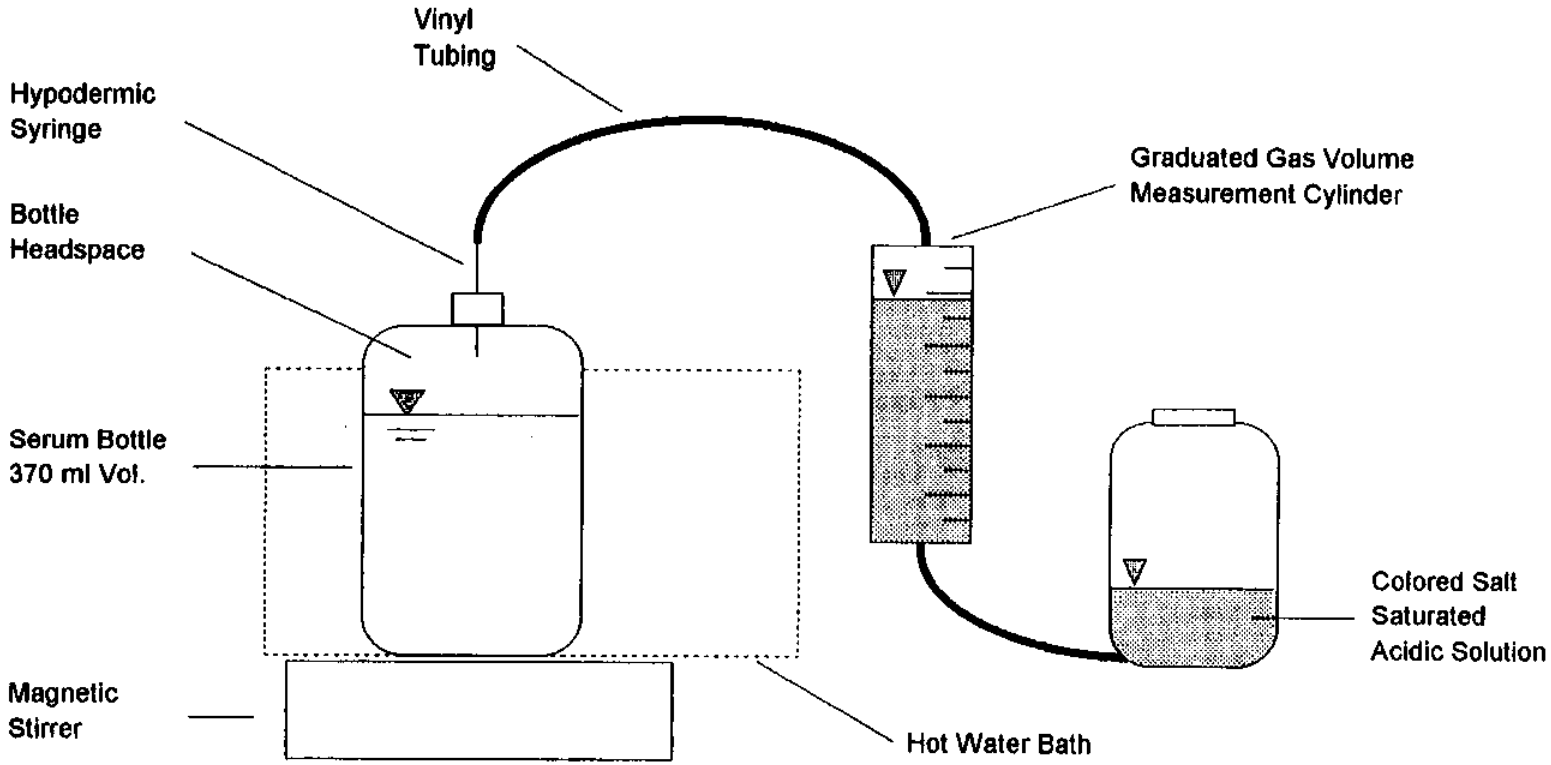


Figure 9. Anaerobic Batch Toxicity Assay Apparatus

Table 18. Operating Conditions of Lab-Scale UASB Reactor A When Inoculum Sludge was Withdrawn For Toxicity Assays.

Parameter	Value
F/M Ratio	0.3 mg COD/mg VSS/day
Soluble COD Reduction	95 percent
Ammonia Concentration	2,480 mg/L NH_3-N
Sodium Concentration	4,370 mg/L
pH	7.3
Temperature	37° C
Days at Steady-State	40

Macro and Micro Nutrient Solutions

Table 19 summarizes the macro-nutrient buffer solution composition. The table also shows the cation concentration contributed by each compound. The solution composition was chosen to reflect the calcium, potassium, and magnesium concentrations typical of the crab cooker wastewater. One mL of a concentrated micro-nutrient solution was added per liter of buffer solution used in the toxicity assay. Table 20 summarizes the concentrated micro-nutrient solution composition.

Table 19. Macro-Nutrient Buffer Solution Composition.

Compound	Concentration (mg/L)	Cation Concentration (mg/L)
$NaHCO_3$	4,000	1,100
NH_4Cl	500	130*
K_2HPO_4	250	110
$MgCl_2 \cdot 6H_2O$	1,100	130
$MgSO_4 \cdot 7H_2O$	100	10
$CaCl_2 \cdot 2H_2O$	1,400	380
KCl	1,150	600

(*) mg/L NH_3-N

Table 20. Concentrated Micro Nutrient Solution Composition.

Compound	Concentration (mg/L)
$FeSO_4 \cdot 7H_2O$	2,800
H_3BO_3	50
$ZnCl_2$	50
$CuCl_2 \cdot 2H_2O$	30
$MnCl_2 \cdot 4H_2O$	500
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	50
$AlCl_3 \cdot 6H_2O$	90
$CoCl_2 \cdot 6H_2O$	200
$NiCl_2 \cdot 6H_2O$	50
HCl, 36%	1 mL/L

Experimental Procedure

Experiments were conducted simultaneously in eight serum bottles. Each bottle was handled as described below.

The following additions were made to a bottle: 330 mL of macro-nutrient buffer solution, 0.33 mL of concentrated micro-nutrient solution, 1.0 mL of glacial acetic acid, quantities of NaCl and NH_4Cl depending on the desired sodium and ammonia concentrations, and 3 mL of 6N NaOH. The bottle's liquid phase was flushed with nitrogen gas for 4 minutes to remove any oxygen from the assay medium. After the bottle was capped, the gas phase was flushed for one minute with nitrogen gas. The bottle was then allowed to come up to temperature in the water bath.

Once the bottle temperature was 35° C, the bottle was inoculated with sludge from one of the batch reactors. More sludge was added to bottles where greater inhibition was anticipated. Between 134 and 377 mg of VSS was added per bottle. The pH was then adjusted with concentrated hydrochloric acid (HCl), and the bottle's gas phase was flushed with nitrogen gas for one minute. The inoculated bottle was connected to the gas measurement cylinder and stirred intermittently. The specific methanogenic activity was measured on the next day.

After 24 hours, the bottle pH was readjusted with concentrated HCl, if necessary. The bottle was capped and the bottle headspace was flushed with nitrogen gas for one minute. The bottle was reconnected to the gas measurement cylinder, and the specific methanogenic activity measurement was initiated.

Gas composition was sampled hourly from the bottle headspace. Carbon dioxide (CO_2) and methane (CH_4) were both quantified. Gas volume was measured hourly from the change in the level of the colored acidic solution. The activity determination lasted 8 hours.

After 8 hours, pH was measured immediately. Samples for acetic acid and ammonia determination were withdrawn. The gas headspace volume was measured by filling the bottle with distilled water. The Volatile Suspended Solids (VSS) concentration of the full bottle was determined.

Calculation of Specific Methanogenic Activity

Hourly methane production was calculated from methane accumulated within and expelled from the headspace (see Appendix B). The average methane production rate was calculated between hours 2 and 8. The maximum specific methanogenic activity was calculated from the VSS measurement and the average methane production rate.

Experimental Variables

A total of sixteen specific methanogenic activity measurements were made. Table 21 shows the pH, sodium concentrations, and ammonia concentrations considered.

Table 21. Description of Batch Toxicity Assay Experiments.

Trial	pH	Sodium Conc. (mg/L)	Ammonia Conc. (mg/L NH_3-N)
1	7.4	2,500	130
2	7.4	2,500	1,600
3	7.4	2,500	2,400
4	7.4	2,500	3,200
5	7.4	2,500	130
6	7.4	2,500	1,600
7	7.4	2,500	2,400
8	7.4	2,500	3,200
9	7.8	5,000	130
10	7.8	5,000	800
11	7.8	5,000	1,600
12	7.8	5,000	2,400
13	7.8	5,000	130
14	7.8	5,000	800
15	7.8	5,000	1,600
16	7.8	5,000	2,400

PILOT-SCALE AIR STRIPPING COLUMN

Ammonia removal by air stripping was investigated with a pilot-scale air stripping tower. The stripping tower was originally designed, constructed, and operated by Wolfe (1993). During the course of this study, the tower was operated at the Virginia Tech Seafood Research and Extension Center in Hampton, Virginia.

Stripping Tower Liquid Feed

The original experimental plan was to operate the stripping tower with effluent from the UBF pilot-plant; however, lack of wastewater production by Graham & Rollins, Inc. (the wastewater source of the UBF pilot-plant), necessitated a change in the experiment. For this study, pilot-plant effluent was diluted 15:1. One trial that was originally performed with diluted pilot-plant effluent was repeated with undiluted pilot-plant effluent to assess the effect of dilution on air stripping performance.

Modified Tower Design

Before use in this study, the air stripping tower was modified as follows: a wooden support frame was constructed, a new air delivery system was installed, a new system for measuring air flow was assembled, a gravity-fed orifice-riser type liquid distributor was constructed, and a 2 inch diameter drain was installed in the tower base.

Figure 10 illustrates the modified stripping tower design. The main tower section was an 18 inch inside diameter PVC pipe that contained 1.8 meters of 5.8 cm (2.3 inch) LANPAC® packing. The original tower specifications are described in detail by Wolfe (1993).

A Dayton (Chicago, Illinois) backward incline blower (2 horsepower motor, 12½ inch wheel diameter) was connected to the stripping tower with galvanized steel duct (10 inch inside diameter). A t-section connected the blower to a 3 meter section of straight duct. The straight section was connected to the tower. A 90° elbow directed air upwards within the tower. Small holes that were drilled in the elbow base allowed liquid to escape the air delivery duct.

Different air flow rates were attainable by opening or covering the t-section's open end. An obstruction was placed within the t-section to achieve the lesser air flow rates (12 and 9 m^3/min). Air flow rates were quantified by determining the average air velocity within the delivery duct and then multiplying that velocity by the duct area.

A gravity-fed orifice-riser type liquid distribution plate was constructed from plexiglas and PVC pipe (see Appendix C). Liquid flowrate was monitored using a stand-pipe that was connected to the storage tank. The stand-pipe was graduated every 18.9 liters (five gallons).

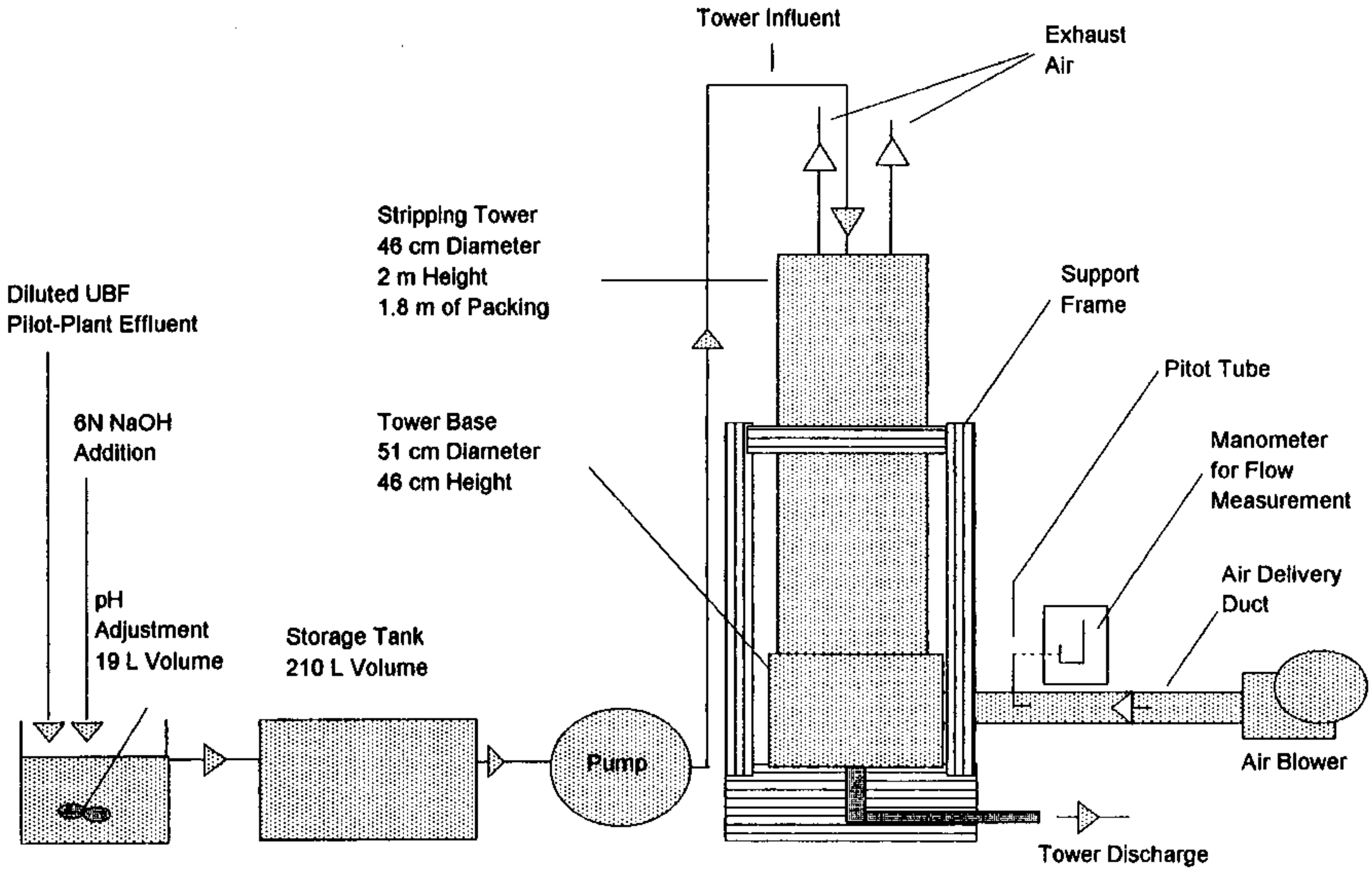


Figure 10. Pilot-Scale Air Stripping Tower

Air Flow Measurement

Air velocity was determined using a Dwyer (Michigan City, Indiana) pitot-tube (model 167-7, 6 inch insertion length, 1/8 inch diameter) and U-inclined manometer (Dwyer model 1227, dual-range flex-tube style). The manometer registered differences between the total and static head within the duct. The air velocity was calculated from the manometer reading and the local atmospheric conditions (see Appendix D).

Air velocity was measured in the straight duct section, one meter from the tower. Initially, the duct's average air velocity was determined by averaging measurements from sixteen points located across the duct cross-section. Each measuring point was located in one of sixteen equal area divisions of the cross-section (see Appendix E). By comparing the duct's average air velocity to the duct's centerline air velocity at several air flow rates, the author determined that the average air velocity was consistently 95% of the centerline velocity. Subsequently, the duct's average air velocity was calculated from the centerline measurement.

Pressure Drop Measurement

Static pressure was measured in the straight duct section, one meter from the tower. The pitot tube and manometer described previously also measured static pressure. The static pressure resulted from the pressure drop across the galvanized duct (downstream of the measuring point), the tower packing, and the liquid distribution plate. The pressure drop across the galvanized duct and liquid distributor were assumed negligible; the pressure drop across the packing was assumed to equal the measured static pressure.

Experimental Procedure

Effluent from the UBF pilot plant was collected, diluted, and pumped into the pH adjustment tank (19 L volume). A pH adjustment device maintained the tank's pH at 12 with 6N Sodium Hydroxide (NaOH). Effluent flowed by gravity from the pH adjustment tank to the 210 L storage tank. When the storage tank was filled to capacity, an air stripping experiment was initiated. A typical air stripping experiment lasted 25 minutes. After the air flowrate was adjusted to the desired rate, liquid was pumped from the storage tank into the liquid distribution plate, beginning the experiment. Effluent samples were typically taken at 7, 16, and 25 minutes. Influent samples were typically taken at 11 and 21 minutes. Several measurements of air velocity and static pressure were made over the experiment duration. The time elapsed in reaching each 18.9 L (5 gallon) graduation on the stand pipe was recorded.

Description of Experiments

Table 22 lists the nominal air and water flowrates investigated in this study.

Table 22. Nominal Liquid and Air Flowrates Utilized for Air Stripping Experiments.

	Air Flowrate (m^3/min)			
Liquid Flowrate (L/m^2/min)*	9	12	15	21
20	x	x	x	x
25	x	x	x	x
33		x	x	x
41			x	x

(*) liters per square meter of tower area
(x) experiment performed

SAMPLE HANDLING AND STORAGE

Samples from the pilot-scale treatment systems in Hampton, Virginia were preserved, if necessary, packed in ice, and transported to the Virginia Polytechnic Institute and State University (VPI & SU) environmental engineering laboratory in Blacksburg, Virginia. Samples from the lab-scale UASB reactors, located at the VPI & SU Price's Fork Research Center were preserved, if necessary, and transported to the VPI & SU environmental engineering laboratory.

LABORATORY METHODS

All analysis, except pH measurement, were performed at the VPI & SU environmental engineering laboratory. Measurements of pH were performed immediately after sampling to avoid errors due to cooling or the release of carbon dioxide (CO_2). When an analysis could not be performed immediately, samples were refrigerated in the environmental engineering laboratory at 4° C. Samples were diluted when necessary for an analysis.

All analysis were performed according to Standard Methods for the Analysis of Water and Wastewater (1992), if there was a method available.

Chemical Oxygen Demand (COD) was determined by Method 5220 C, the Closed Reflux Titrimetric Method. Samples were digested for two hours at 150° C and then titrated with 0.05 N ferrous ammonium sulfate. Soluble COD samples were filtered through Whatman 934-AH glass fiber filters. Samples were preserved by acidification to below pH 2 with concentrated sulfuric acid (H_2SO_4), when necessary.

Alkalinity was determined by Method 2320 B. The titration was performed to pH 4.5 with 0.1 N sulfuric acid (H_2SO_4). A Cole Parmer (Niles, Illinois) hand-held pH meter with a sealed electrode was used to measure pH.

Ammonia was determined by distillation into boric acid according to Method 4500-NH_3 B, followed by titration of the boric acid solution with 0.02 N H_2SO_4 according to Method 4500-NH_3 E. Samples were preserved by acidification to below pH 2 with concentrated H_2SO_4, when necessary.

Total Kjeldahl Nitrogen (TKN) was determined by Method 4500-N_{org} C, the Semi-Micro-Kjeldahl Method. The procedure included a 30 minute digestion followed by distillation into boric acid. The boric acid solution was titrated with 0.02 N H_2SO_4. Samples were not filtered. Samples were preserved by acidification to below pH 2 with concentrated H_2SO_4, when necessary.

Biochemical Oxygen Demand (BOD) was determined by Method 5210 B. HACH (Ames, Iowa) nitrification inhibitor, 2-chloro-6-(trichloromethyl)pyridine, was added to the dilution water. Soluble BOD samples were filtered through Whatman 934-AH filters. To determine BOD_u (ultimate BOD), the BOD was measured every fifth day over 25 days. If the resulting oxygen demand curve appeared to reach a plateau, the BOD_u was equal to the 25 day BOD. On one occasion, the BOD_u was determined by measuring BOD over 20 days instead of 25 days.

Total Suspended Solids (TSS) was determined by Method 2540 D using a 103° C oven temperature. Volatile Suspended Solids (VSS) was determined by Method 2540 E using a 550° C oven temperature.

Sodium, potassium, magnesium, and calcium were determined by Method 3111 B, the Direct Air-Acetylene Flame Method, with a Perkin-Elmer (Norwalk, Connecticut), Model 703, Atomic Absorption Spectrophotometer. An appropriate quantity of standard cesium chloride solution was added to sodium and potassium samples and standards. Standard lanthanum chloride solution was added to magnesium and calcium samples and standards.

Volatile Fatty Acids (VFA) were measured by gas chromatography using a Tracor (Austin, Texas), Model 560, gas chromatograph. A flame ionization detector was used at 200°

C with a helium flow rate of 30 mL/min and an air flow rate of 300 ml/min. A 30" x 4 mm ID glass column containing 60/80 Carbopack C/ 0.3% Carbowax 20M/ 0.1% H_3PO_4 was utilized with a nitrogen flow rate of 4 mL/min. The column and injector temperatures were 120° C and 200° C, respectively. Samples were acidified with either 1% or 2% formic acid prior to analysis. Sample injection volumes of 1 μL were utilized. Acetic acid, propionic acid, iso-butyric acid, and n-butyric acid were all quantified when present in concentrations exceeding 10 mg/L.

Total Organic Carbon (TOC) was determined by Method 5310 B using a Dohrmann (Santa Clara, California), Total Organic Carbon Analyzer. Prior to the analysis, samples were acidified to below pH 2 with 85% phosphoric acid (H_3PO_4) and purged of carbon dioxide with oxygen gas for 10 minutes. The results reported as TOC are therefore actually Non-Purgeable Organic Carbon (NPOC). Soluble TOC samples were filtered through Whatman 934-AH glass fiber filters.

The anions, chloride, nitrate, phosphate, and sulfate were determined by Method 4110 B, Ion Chromatography with chemical suppression of eluent conductivity, with a Dionex (Sunnyvale, California) Ion Chromatograph. The eluent composition was 1.8 millimole/L (mM) sodium carbonate and 1.7 mM sodium bicarbonate. An eluent flow rate of 2.0 mL/min was utilized.

Gas composition was measured using a Gow-Mac (Bridgewater, New Jersey), Series 550, gas chromatograph equipped with a thermal conductivity detector. A 80/100 Porapak Q column was used with 10 mL/min of the carrier gas, helium. The column and injection port were maintained at 35° C. The detector temperature was 60° C. Carbon dioxide and methane were both quantified.

CHAPTER IV. RESULTS

The following chapter contains results obtained during the course of this study. Raw data are presented and trends in the data are noted. A considerable quantity of data was obtained from anaerobic biological treatment systems. The goal of each biological study was to reach a period of constant performance or 'steady-state'; however, a steady-state was often not attainable. The non-steady-state data is included in this chapter because the data illustrates the anaerobic chemistry and toxicity involved in the anaerobic treatment of crab cooker wastewater.

LAB-SCALE UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTORS

Results from the lab-scale UASB study are divided into two sections: first study period, and second study period. The second study period section includes a comparison of start-up alternatives and a description of reactor operation following the start-up period.

First Study Period

During the first study period, the reactors treated unamended crab cooker wastewater. The reactors were acclimated for 30 days with wastewater diluted 1:5 with tap water. This section presents data acquired after the acclimation period.

Figure 11 shows the variation of effluent soluble COD and organic loading rate (OLR) for Reactor A during the first study period. The reactor was fed wastewater for 14 days at an OLR of 1 g COD/L/day. The reactor's OLR was then increased and maintained at 3 g COD/L/day for the next 31 days. After the OLR was increased, the effluent COD increased and fluctuated

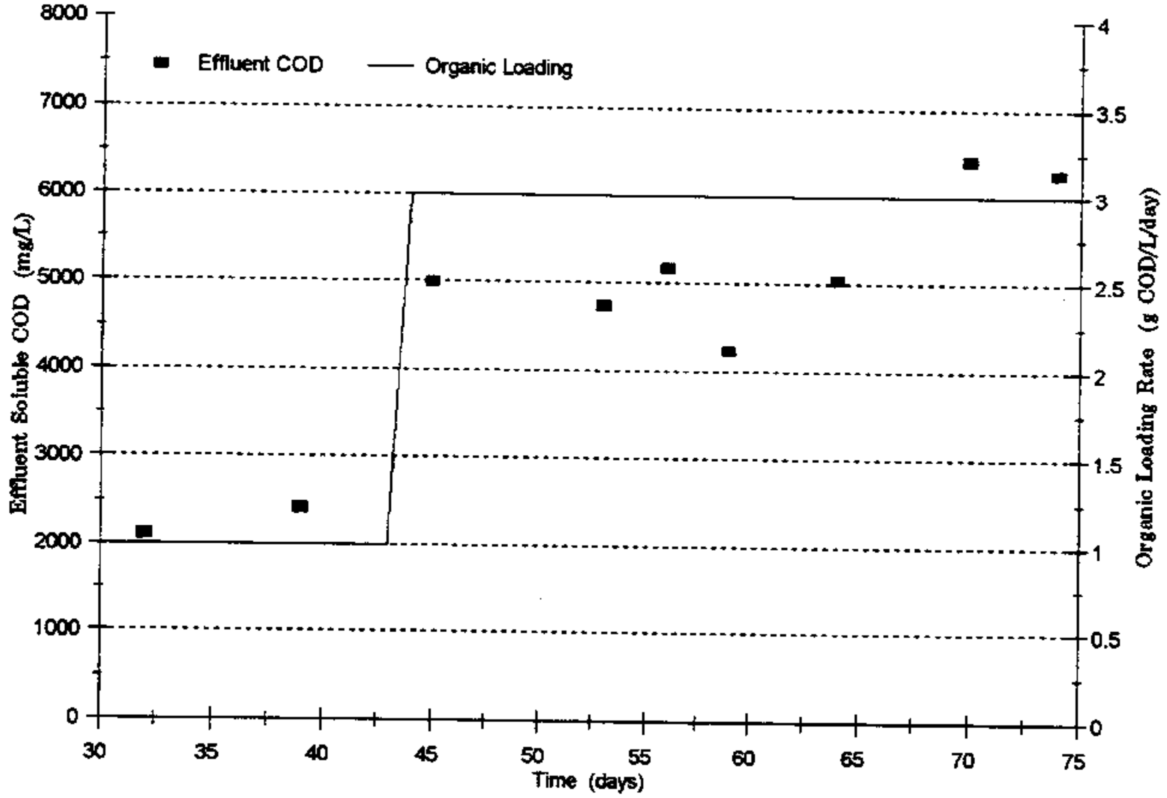


Figure 11. Variation of Effluent Soluble COD and Organic Loading Rate Over Time for Reactor A, First Study Period.

during the next 31 days. A period of steady-state operation was not attained. The study period was terminated when the effluent COD increased to greater than 6,000 mg/L.

Figure 12 displays the variation of effluent soluble COD and OLR for Reactor B during the first study period. The reactor was fed wastewater at an OLR of 1 g COD/L/day for 14 days. The loading rate was then increased and maintained at 3.5 g COD/L/day for 11 days. On day 55, the OLR was increased to 5.7 g COD/L/day. This OLR was maintained for 20 days. The effluent COD increased after the initial increase in organic loading. After the additional increase in organic loading, the effluent COD increased further (above 8,000 mg/L). The reactor's biogas production steadily declined after day 55 and the study period was terminated on day 72.

Second Study Period

During the second study period, hydrochloric acid (HCl, 6N) was added to the wastewater feed to maintain the reactor's pH near neutral. During the first 45 days, two reactor start-up alternatives were compared. After the start-up period, each reactor reached two steady-state periods of operation.

The first steady-state period (steady-state #1) was reached using wastewater with fairly low concentrations of TKN (993 mg/L as nitrogen), sodium (1,890 mg/L), and COD (8,320 mg/l, unfiltered). The second steady-state period (steady-state #2) was reached using wastewater with fairly high concentrations of TKN (2,760 mg/L as nitrogen), sodium (4,510 mg/L), and COD (24,100 mg/L, unfiltered). For clarity, data from the steady-state periods are presented separately. Average parameter values, which are presented for each steady-state period, were calculated from 3 to 5 measurements made during the steady-state period, unless otherwise noted.

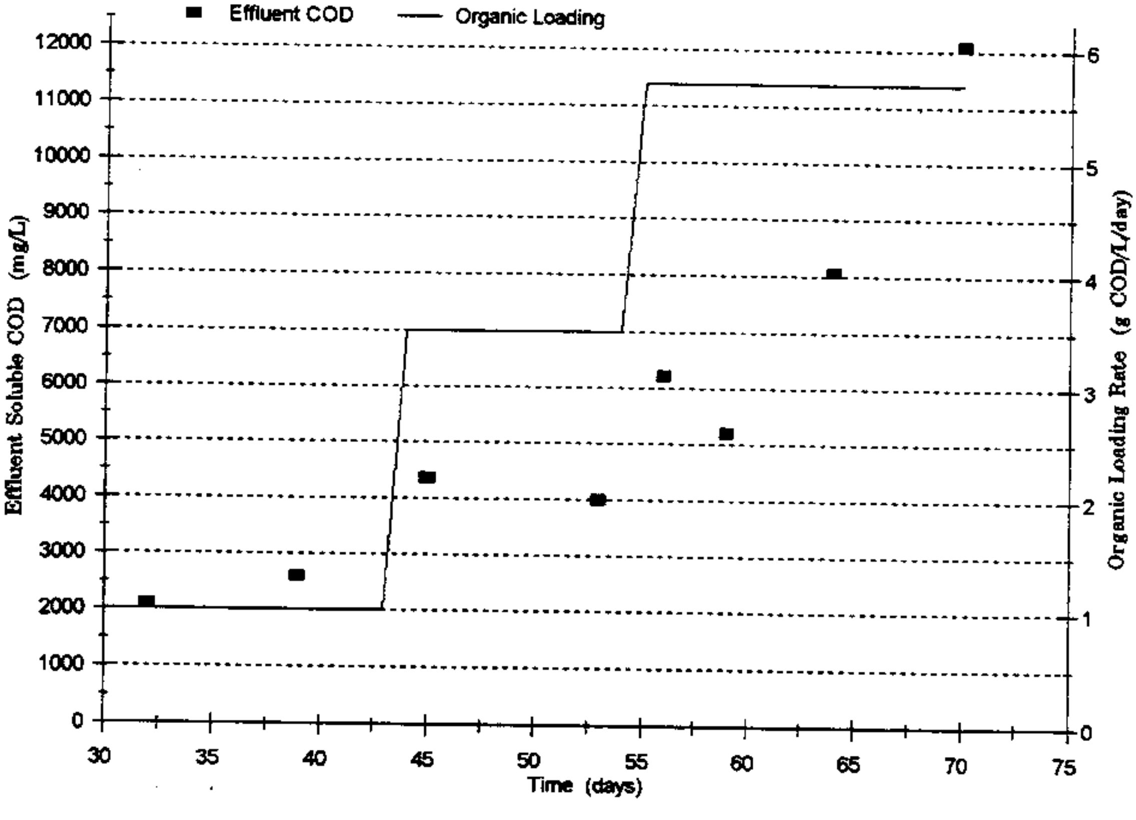


Figure 12. **Variation of Effluent Soluble COD and Organic Loading Rate Over Time for Reactor B, First Study Period.**

Additional granular sludge was added to Reactor A after the first study period; however, the reactor's performance declined instead of improving. The reactor's COD reduction decreased to less than 50 percent and the biogas production declined steadily over the next few weeks. Instead of reinoculating Reactor A, the rejuvenation of the 'failed' reactor was attempted and compared with the start-up of a reinoculated reactor (Reactor B). Initially, the reactors were fed diluted wastewater (1:5 dilution with tap water) at an OLR of 0.5 g COD/L/day.

Reactor B's OLR was increased to 1.0 g COD/L/day on day 11 and to 1.6 g COD/L/day on day 20. Reactor A's OLR was not increased during the first 30 days. After day 30, full-strength wastewater was fed to Reactors A and B at 1.6 and 1.3 g COD/L/day, respectively. Figure 13 shows the variation of the reactors' effluent soluble COD during the start-up period. Figure 14 shows the variation of the reactors' biogas production during the start-up period.

As shown in figure 13, Reactor A's effluent COD was higher than Reactor B's effluent COD until day 24. As shown in figure 14, Reactor A generated less biogas (per gram of COD in wastewater feed) than Reactor B until day 40. By the end of the 45 day start-up period, the reactors were producing biogas at similar relative rates and had comparable effluent COD concentrations. The reactors' relative biogas production and soluble effluent COD were about 500 mL/g COD and 1,000 mg/L, respectively.

Figure 15 displays the variation of Reactor A's effluent soluble COD and OLR from day 45 to day 151 (end of second study period). Figure 16 shows the variation of Reactor B's effluent soluble COD and OLR from day 45 to day 151. After the start-up period, Reactor A's OLR was increased to 7.6 g COD/L/day and Reactor B's OLR was increased to 5.3 g COD/L/day. The reactors' OLR was decreased on day 63 when both reactors' performance declined.

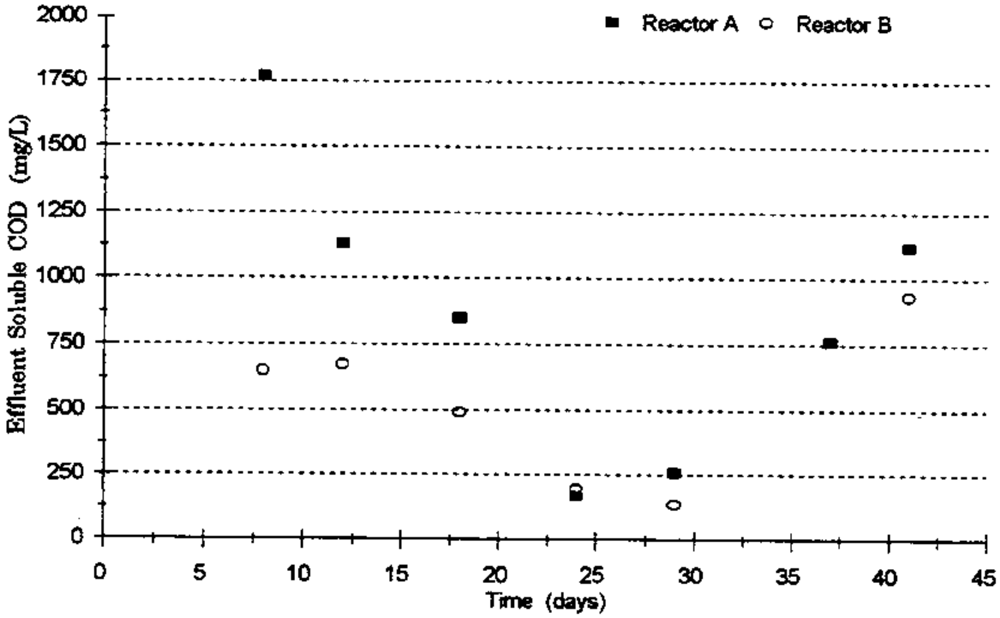


Figure 13. Variation of Effluent Soluble COD Over Time, During the Start-Up of Reactors A & B, Second Study Period.

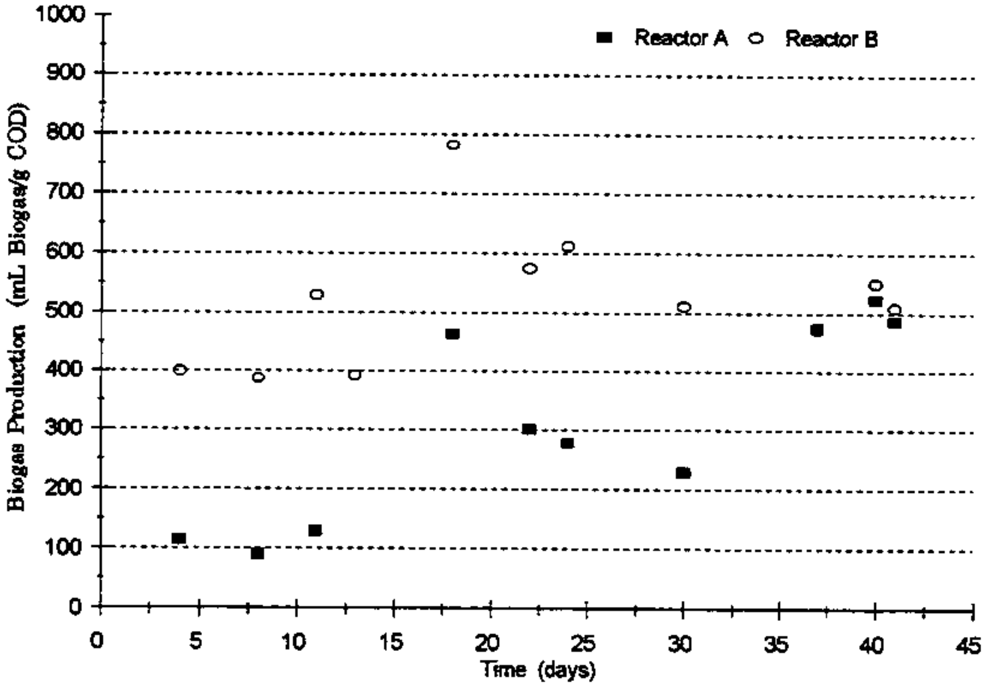


Figure 14. Variation of Biogas Production Over Time, During the Start-Up of Reactors A & B, Second Study Period.

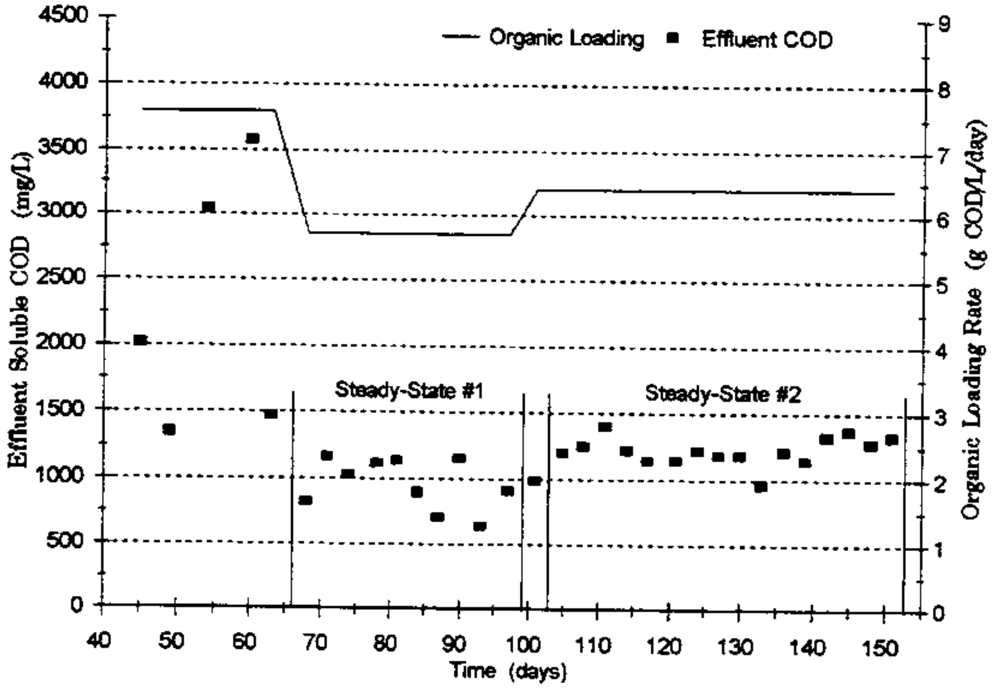


Figure 15. Variation of Effluent Soluble COD and Organic Loading Rate Over Time for Reactor A, Second Study Period: Days 45-151.

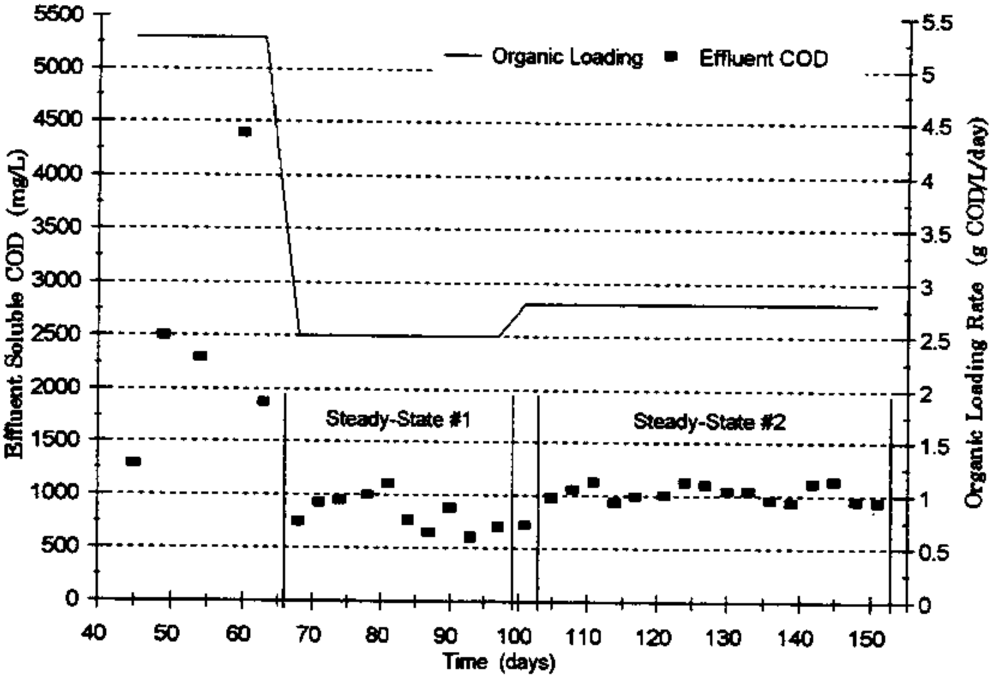


Figure 16. Variation of Effluent Soluble COD and Organic Loading Rate Over Time for Reactor B, Second Study Period: Days 45-151.

Each reactor treated wastewater of fairly constant composition at a constant OLR between days 63 and 97. From day 63 to 97, Reactor A's average OLR and hydraulic retention time (HRT) were 5.7 g COD/L/day and 1.5 days, respectively. Reactor B's average OLR and HRT were 2.5 g COD/L/day and 3.4 days, respectively.

Both reactors maintained a steady-state period of operation from day 68 to day 97. Table 23 shows wastewater and reactor effluent COD, BOD_5, and total organic carbon (TOC) concentrations during the first steady-state period. Average wastewater feed unfiltered COD, BOD_5, and TOC were 8,320, 6,070, and 3,120, respectively. Reactor A's effluent soluble COD, BOD_5, and TOC were 962, 203, and 287 mg/L, respectively. Reactor B's effluent soluble COD, BOD_5, and TOC were 830, 145, and 215 mg/L, respectively.

Table 23. Chemical Oxygen Demand (COD), 5-Day Biochemical Oxygen Demand (BOD_5), and Total Organic Carbon (TOC) Reductions for Reactors A & B During the Second Study Period, Steady-State Period #1. Average Values.

	Wastewater Feed	Reactor A		Reactor B	
Parameter	(mg/L)	(mg/L)	(% reduction)	(mg/L)	(% reduction)
Soluble COD	8,160	962	88.2	830	89.8
Total COD	8,320	1,140	86.3	1,040	87.5
BOD_5	6,070*	203†	96.7	145†	97.6
TOC	3,120*	287†	90.8	215†	93.1

(*) Total parameter value (not filtered)
(†) Soluble parameter value (filtered)

Biochemical Oxygen Demand (BOD) tests were performed for 5, 10, 15, 20, and 25 day durations to estimate the ultimate BOD (BOD_u) of the wastewater feed and reactor effluents. Figure 17 shows the exertion of BOD over time for samples taken on day 86 during the first steady-state period. As shown in figure 17, the ultimate soluble BOD was 348 and 245 mg/L for Reactor A and B effluents, respectively. The reactor effluents' soluble COD was also measured on day 86. The estimated non-degradable soluble COD, which was calculated from the

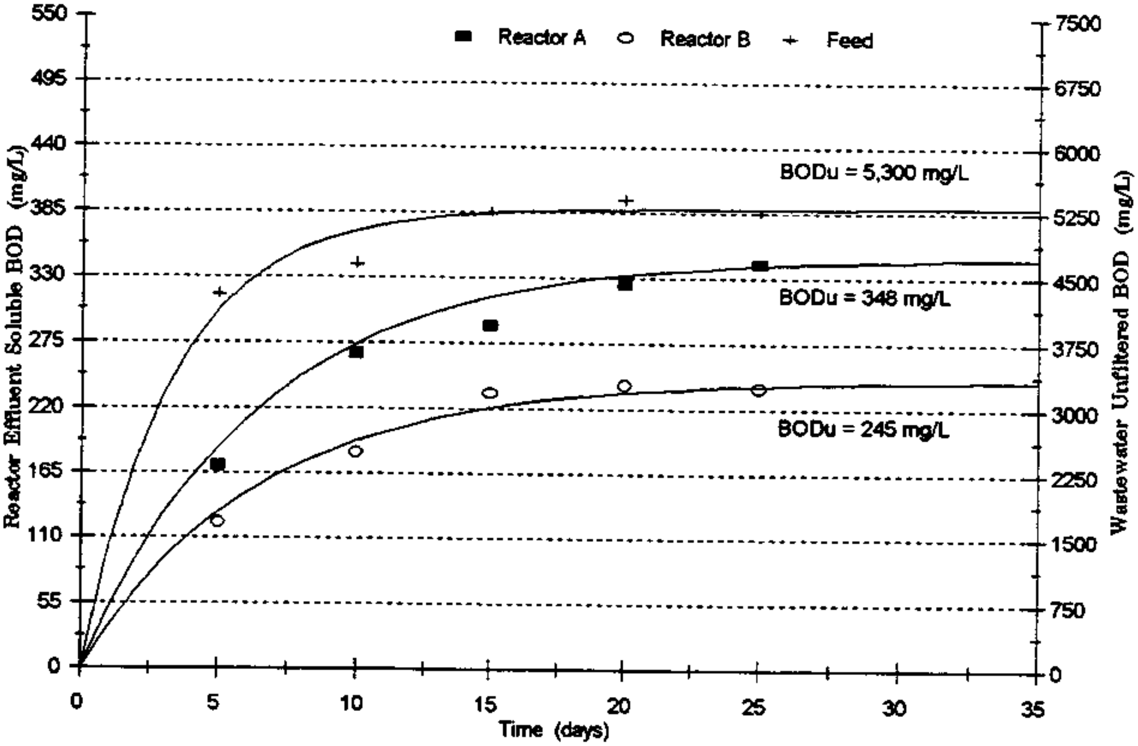


Figure 17. **Exertion of Biochemical Oxygen Demand (BOD) Over Time for Reactor Effluents and Wastewater Feed. Samples From Day 86, During Steady-State #1. BODu = Soluble BOD Ultimate.**

difference between the soluble COD and BOD_u, was 264 and 335 mg/L for Reactors A and B, respectively.

Table 24 displays wastewater feed and reactor effluent total suspended solids (TSS) and volatile suspended solids (VSS) concentrations during the first steady-state period. The wastewater feed contained 228 and 211 mg/L of TSS and VSS, respectively. The Reactor A effluent contained 107 and 70 mg/L of TSS and VSS, respectively. The Reactor B effluent contained 102 and 54 mg/L of TSS and VSS, respectively.

Table 24. Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) Reductions for Reactors A & B During the Second Study Period, Steady-State Period #1. Average Values.

Parameter	Wastewater Feed	Reactor A	Reactor B
TSS (mg/L)	228	107	102
TSS (% reduction)	n/a	53.1	55.3
VSS (mg/L)	211	70	54
VSS (% reduction)	n/a	66.8	74.4

(n/a) Not applicable

The wastewater feed TSS and VSS values were measured from samples withdrawn from the reactor feed lines. Thus, suspended solids that coagulated and settled after HCl was added to the feed are not included in the percent reductions. Wastewater feed TSS and VSS were not measured prior to the acidification step.

Table 25 contains average wastewater feed and reactor effluent ammonia, TKN, anion, and cation concentrations during the first steady-state period. The ammonia concentration increased from 102 mg/L (as N) in the wastewater feed to 843 and 962 mg/L (as N) in the Reactor A and B effluents, respectively. The wastewater feed, Reactor A effluent, and Reactor B effluent TKN concentrations were 993, 920, and 1,020 mg/L (as N), respectively.

The sulfate concentration decreased from 250 mg/L in the wastewater feed to 43 and 39 mg/L in the Reactor A and B effluents, respectively. The phosphate concentration increased from 85 mg/L in the wastewater feed to 136 and 154 mg/L in the Reactor A and B effluents, respectively. The wastewater feed and reactor effluents contained similar concentrations of sodium, potassium, calcium, magnesium, and chloride. The wastewater feed contained 1,890, 131, 168, and 84 mg/L of sodium, potassium, calcium, and magnesium, respectively. The wastewater feed contained 1,890 mg/L of chloride.

Table 25. Wastewater Feed and Reactor Effluent Ammonia, Total Kjeldahl Nitrogen (TKN), Anion, and Cation Concentrations During the Second Study Period, Steady-State Period #1. Average Values.

	Concentration (mg/L)		
Parameter	Wastewater Feed	Reactor A	Reactor B
Ammonia (NH_3-N)*	102	843	962
TKN*	993	920	1,020
Sodium (Na^+)	1,890	2,310	2,180
Potassium (K^+)	131	286	172
Calcium (Ca^{+2})	168	209	171
Magnesium (Mg^{+2})	84	116	112
Chloride (Cl^-)	3,960	3,500	3,570
Phosphate (PO_4^{-3})	85	136	154
Sulfate (SO_4^{-2})	250	43	39

(*) mg/L as nitrogen

Table 26 summarizes the reactors' biogas production and biogas composition during the first steady-state period. Reactor A's relative methane production was 280 mL/g COD (mL CH_4/g wastewater feed COD) while Reactor B's relative methane production was 300 mL/g COD.

Table 26. Biogas Production and Composition for Reactors A and B During the Second Study Period, Steady-State Period #1. Average Values.

Parameter	Reactor A	Reactor B
Biogas Production (L/day)	5.1	2.2
Biogas Production (mL/g COD)	450	440
Percent Methane*	63	67
Methane Production (mL/g COD)	280	300

(*) One measurement on day 75.

The average pH in both reactors during the first steady-state period was 7.0. Reactors A and B contained 2,970 and 3,170 mg/L (as calcium carbonate, $CaCO_3$) of alkalinity, respectively. Average effluent volatile fatty acid concentrations were 33 and 20 mg/L (as acetic acid) for Reactors A and B, respectively. The average VSS concentrations in Reactors A and B was 14,800 and 10,300 mg/L, respectively. The calculation of average reactor VSS concentration is described in Appendix F.

Each reactor treated a wastewater of fairly constant composition at a constant OLR between days 97 and 151. From day 63 to 97, Reactor A's average OLR and HRT were 6.4 g COD/L/day and 3.8 days, respectively. Reactor B's average OLR and HRT were 2.8 g COD/L/day and 8.7 days, respectively.

Each reactor maintained a steady-state period of operation (steady-state #2) from day 105 to day 151. Table 27 displays the average wastewater and reactor effluent COD, BOD_5, and TOC concentrations during the second steady-state period. The wastewater feed's unfiltered COD, BOD_5, and TOC were 24,100, 16,700, and 10,600 mg/L, respectively. Reactor A's effluent soluble COD, BOD_5, and TOC were 1,220, 298, and 324 mg/L, respectively. Reactor B's effluent soluble COD, BOD_5, and TOC were 1,040, 165, and 245 mg/L, respectively.

Table 27. Chemical Oxygen Demand (COD), 5-Day Biochemical Oxygen Demand (BOD_5), and Total Organic Carbon (TOC) Reduction for Lab-Scale Reactors A & B During the Second Study Period, Steady-State Period #2. Average Values.

Parameter	Wastewater Feed (mg/L)	Reactor A (mg/L)	Reactor A (% reduction)	Reactor B (mg/L)	Reactor B (% reduction)
Soluble COD	22,900	1,220	94.7	1,040	95.5
Total COD	24,100	1,790	92.6	1,440	94.0
BOD_5	16,700*	298†	98.2	165†	99.0
TOC	10,600*	324†	96.9	245†	97.7

(*) Total parameter value (not filtered)
(†) Soluble parameter value (filtered)

A BOD_u test was performed during the second steady state period. Figure 18 shows the exertion of BOD over time for a Reactor B effluent sample withdrawn on day 136. As shown in figure 18, the BOD_u of the Reactor B effluent sample was 353 mg/L. The estimated non-degradable COD in the reactor effluent was 887 mg/L.

Table 28 shows average wastewater feed and reactor effluent TSS and VSS concentrations during the second steady-state period. Wastewater feed TSS and VSS concentrations were 217 and 191 mg/L, respectively. Reactor A's effluent TSS and VSS concentrations were 249 and 150 mg/L, respectively. Reactor B's effluent TSS and VSS were 172 and 75 mg/L, respectively.

Table 28. Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) Reductions for Reactors A & B During the Second Study Period, Steady-State Period #2. Average Values.

Parameter	Wastewater Feed	Reactor A	Reactor B
TSS (mg/L)	217	249	172
TSS (% reduction)	n/a	-14.7*	20.7
VSS (mg/L)	191	150	75
VSS (% reduction)	n/a	21.4	60.7

(*) TSS increased
(n/a) Not applicable

The wastewater feed TSS and VSS values were measured from samples withdrawn from the reactor feed lines. The TSS and VSS concentrations in the feed, prior to acidification, were 910 and 819 mg/L, respectively. Thus, the total TSS reduction for Reactors A and B can be considered 73 and 81 percent, respectively. The total VSS reduction for Reactors A and B can be considered 82 and 91 percent, respectively.

Table 29 shows average wastewater feed and reactor effluent ammonia, TKN, anion, and cation concentrations during the second steady-state period. The ammonia concentration increased from 512 mg/L (as N) in the wastewater feed to 2,480 and 2,300 mg/L (as N) in the Reactor A and B effluents, respectively. The wastewater feed, Reactor A effluent, and Reactor B

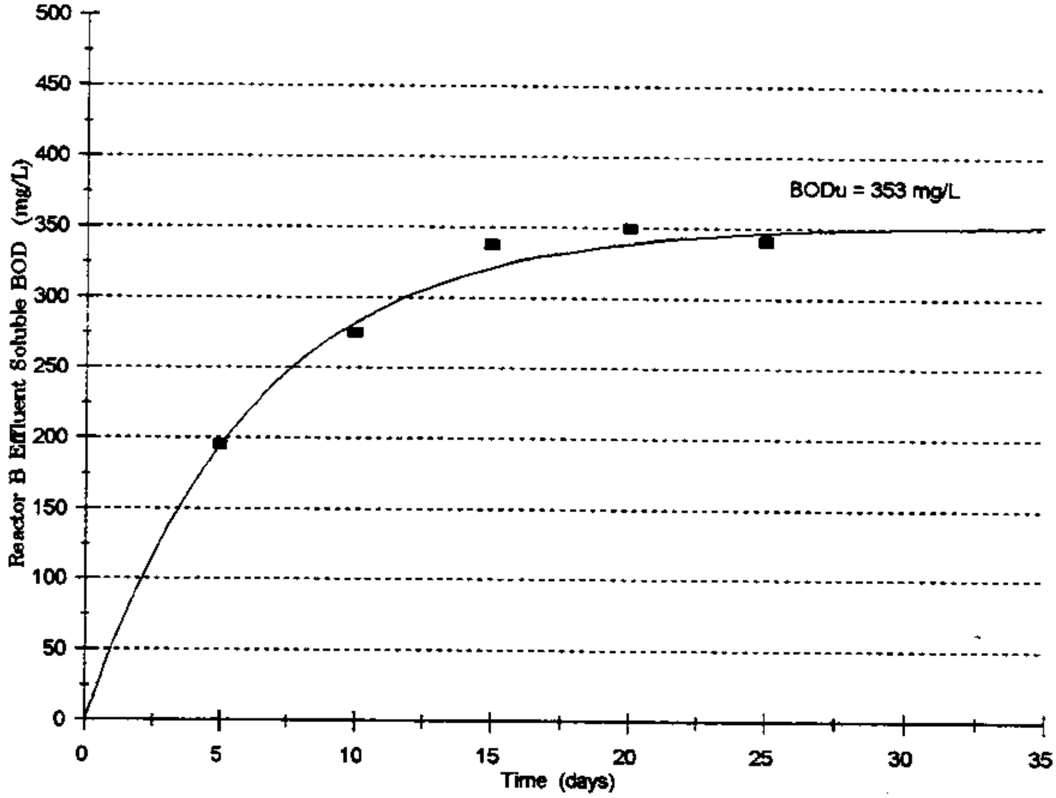


Figure 18. Exertion of Effluent Biochemical Oxygen Demand (BOD) Over Time. Reactor B Sample From Day 136, During Steady-State #2. BODu = Soluble BOD Ultimate.

effluent TKN concentrations were 2,760, 2,620, and 2,400 mg/L (as N), respectively.

The sulfate concentration decreased from 537 mg/L in the wastewater feed to 127 and 174 mg/L in the Reactor A and B effluents, respectively. The phosphate concentration increased from 137 mg/L in the wastewater feed to 111 and 110 mg/L in the Reactor A and B effluents, respectively. The wastewater feed and reactor effluents contained similar concentrations of sodium, potassium, calcium, magnesium, and chloride. The wastewater feed contained 4,510, 793, 403, and 184 mg/L of sodium, potassium, calcium, and magnesium, respectively. The wastewater feed contained 9,530 mg/L of chloride.

Table 29. Wastewater Feed and Reactor Effluent Ammonia, Total Kjeldahl Nitrogen (TKN), Anion, and Cation Concentrations During the Second Study Period, Steady-State Period #2. Average Values.

	Parameter Concentration (mg/L)		
Parameter	Wastewater Feed	Reactor A	Reactor B
Ammonia (NH_3-N)*	512	2,480	2,300
TKN*	2,760	2,620	2,400
Sodium (Na^+)	4,510	4,370	4,010
Potassium (K^+)	793	674	614
Calcium (Ca^{+2})	403	395	397
Magnesium (Mg^{+2})	184	144	136
Chloride (Cl^-)	9,530	10,300	9,810
Phosphate (PO_4^{-3})	137	111	110
Sulfate (SO_4^{-2})	537	127	174

(*) mg/L as nitrogen

Table 30 summarizes the average biogas production and biogas composition for the reactors during the second steady-state period. Reactor A's relative methane production was 340 mL/g COD while Reactor B's relative methane production was 370 mL/g COD.

The average pH in both reactors during the second steady-state period was 7.3. Reactors A and B contained 6,510 and 6,020 mg/L (as $CaCO_3$) of alkalinity, respectively. Average effluent volatile fatty acid concentrations were 25 and 18 mg/L (as acetic acid) for

Reactors A and B, respectively. The average VSS concentrations in Reactors A and B were 18,900 and 13,400 mg/L, respectively.

Table 30. Biogas Production and Composition for Reactors A and B, During the Second Study Period, Steady-State Period #2. Average Values.

Parameter	Reactor A	Reactor B
Biogas Production (L/day)	7.5	3.4
Biogas Production (mL/g COD)	590	610
Percent Methane*	57	60
Methane Production (mL/g COD)	340	370

PILOT-SCALE UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTOR

Figure 19 displays variations in the reactor's effluent COD and organic loading over the study period. Figure 20 shows variations in the reactor's pH and effluent volatile fatty acids concentration (expressed as a COD equivalent, VFA-COD). The calculation of the VFA-COD is discussed in Appendix A. Note from figures 19 and 20 the concurrence of high reactor pH with low effluent COD and VFA concentrations, and the concurrence of low reactor pH with high effluent COD and VFA concentrations.

The average unfiltered wastewater feed COD was 19,600 mg/L during the study period. From day 140 to day 199, the average OLR and effluent soluble COD were 2.7 g COD/L/day, and 4,200 mg/L, respectively. The volatile fatty acids contributed about 50 percent of the soluble effluent COD.

The reactor contained 4.7 kg of VSS on day 1. Table 31 contains reactor effluent ammonia and sodium concentrations measured during the study period. The average ammonia and sodium concentrations were 2,110 mg/L (as N) and 3,790 mg/L, respectively.

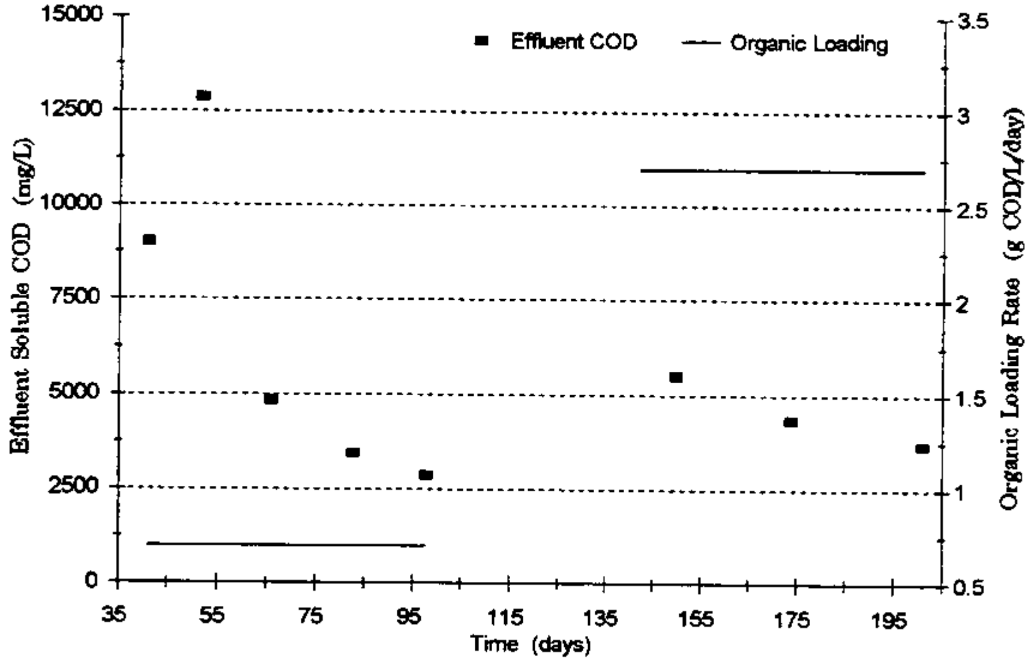


Figure 19. Variation of Effluent Soluble COD and Organic Loading Rate Over Time for the Pilot-Scale UASB Reactor. Wastewater Feed Interrupted From Day 98 to 142.

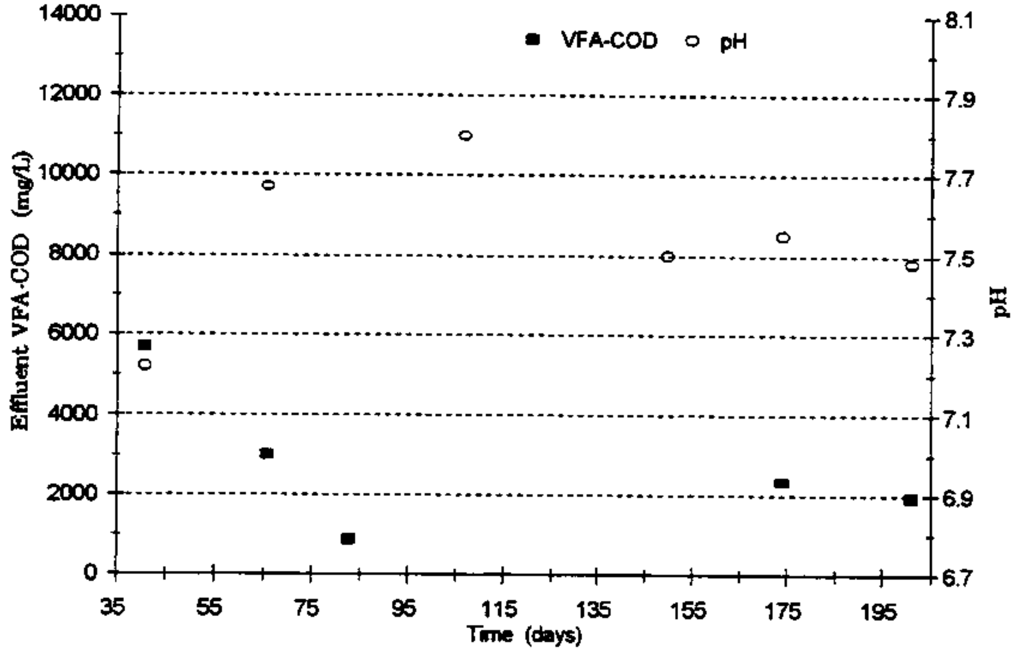


Figure 20. Variation of pH and Effluent Volatile Fatty Acid COD (VFA-COD) Over Time for the Pilot-Scale UASB Reactor.

Table 31. Pilot-Scale UASB Effluent Ammonia and Sodium Concentrations. Average Values.

Parameter	Concentration (mg/L)	Dates Measured (Day No.)
Sodium (Na^+)	3,790	98, 174, 201
Ammonia (NH_3-N)*	2,110	98, 174, 201

(*) mg/L as nitrogen

PILOT-SCALE UPFLOW ANAEROBIC BED FILTER (UBF)

Figure 21 displays variations in the reactor's OLR and effluent COD over the study period. Figure 22 shows variations in the reactor's pH and effluent VFA-COD concentration over the study period. Note from figures 21 and 22 the concurrence of low reactor pH with high effluent COD and VFA concentrations, and the concurrence of high pH with low effluent COD and VFA concentrations.

The average unfiltered wastewater feed COD was 20,200 mg/L during the study period. From day 20 to day 119, the OLR and effluent soluble COD were 3.5 g COD/L/day and 10,000 mg/L, respectively. From day 119 to day 200, the OLR and effluent soluble COD were 1.2 g COD/L/day and 7,500 mg/L, respectively. The wastewater feed was interrupted from day 200 to 247. From day 247 to day 304, the OLR and soluble effluent COD were 2.3 g COD/L/day and 6,000 mg/L, respectively. The volatile fatty acids contributed about 55 percent of the soluble effluent COD throughout the study period.

Table 32 contains average reactor effluent sodium, ammonia, TKN, chloride, TSS, and VSS concentrations during the study period. Wastewater feed TSS and VSS measurements were made simultaneously with reactor effluent measurements. The average wastewater TSS and VSS concentrations were 2,140 and 1,440 mg/L, respectively. The corresponding TSS and VSS reductions in the reactor were 35 and 31 percent, respectively. The average reactor ammonia and TKN concentrations were 1,940 and 2,040 mg/L (as N), respectively. The average reactor sodium and chloride concentrations were 3,790 and 6,290 mg/L, respectively.

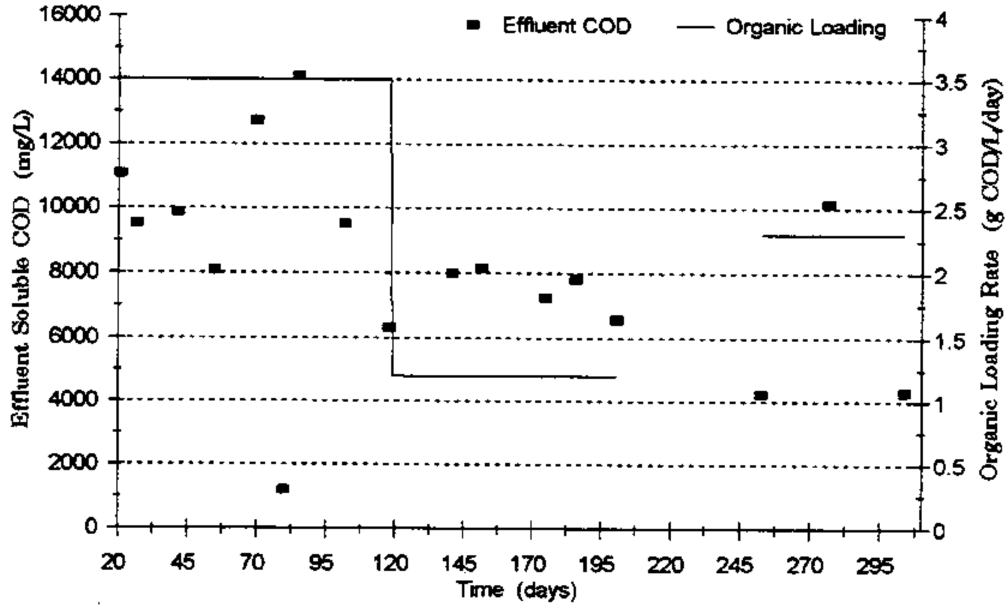


Figure 21. Variation of Effluent Soluble COD and Organic Loading Rate Over Time for Pilot-Scale UBF Reactor. Wastewater Feed Interrupted From Day 198 to 247.

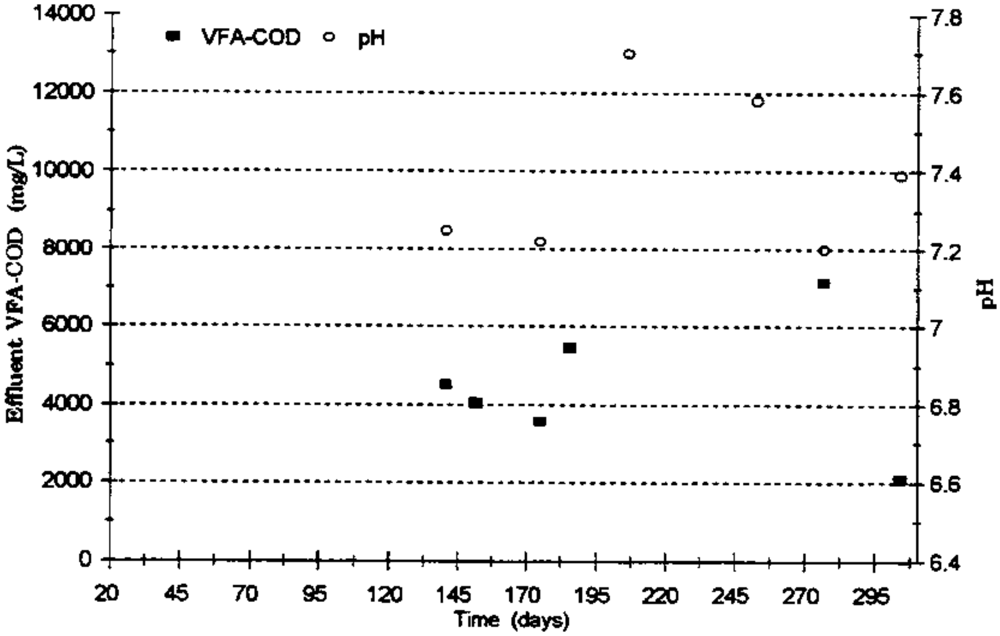


Figure 22. Variation of pH and Effluent Volatile Fatty Acid COD (VFA-COD) Over Time for Pilot-Scale UBF Reactor.

Table 32. Pilot-Scale UBF Reactor Average Effluent TSS, VSS, Sodium, Ammonia, TKN, and Chloride Concentrations With Measurement Dates.

Parameter	Concentration (mg/L)	Dates Measured (Day No.)
Sodium (Na^+)	3,790	55, 141, 175, 186, 277, 304
Ammonia (NH_3-N)*	1,940	55, 70, 85, 141, 201, 277, 304
TKN*	2,040	55, 70, 85, 141
Chloride (Cl^-)	6,290	3, 55, 141, 175, 186
TSS	1,400	9, 27, 55, 80, 85, 141
VSS	987	9, 27, 55, 80, 85, 141

(*) mg/L as Nitrogen

BATCH ANAEROBIC TOXICITY ASSAYS

Figure 23 displays the variation of specific methanogenic activity with total ammonia concentration at pH 7.4 at different (2,500 and 5,000 mg/L) sodium concentrations. Figure 24 shows the variation of specific methanogenic activity with total ammonia concentration at pH 7.8 at different sodium concentrations. Note from figures 23 and 24, the inverse relationship between specific methanogenic activity and total ammonia concentration.

When the sodium concentration was 2,500 mg/L at pH 7.4, the specific methanogenic activity decreased from 0.86 to 0.32 g COD/g VSS/day as the total ammonia concentration increased from 130 to 3,200 mg/L (as N). When the sodium concentration was 5,000 mg/L at pH 7.4, the specific methanogenic activity decreased from 0.78 to 0.32 g COD/g VSS/day as the total ammonia concentration increased from 130 to 3,200 mg/L (as N).

When the sodium concentration was 2,500 mg/L at pH 7.8, the specific methanogenic activity decreased from 0.78 to 0.2 g COD/g VSS/day as the total ammonia concentration increased from 130 to 2,400 mg/L (as N). When the sodium concentration was 5,000 mg/L at pH 7.8, the specific methanogenic activity decreased from 0.59 to 0.17 g COD/g VSS/day as the total ammonia concentration increased from 130 to 2,400 mg/L (as N).

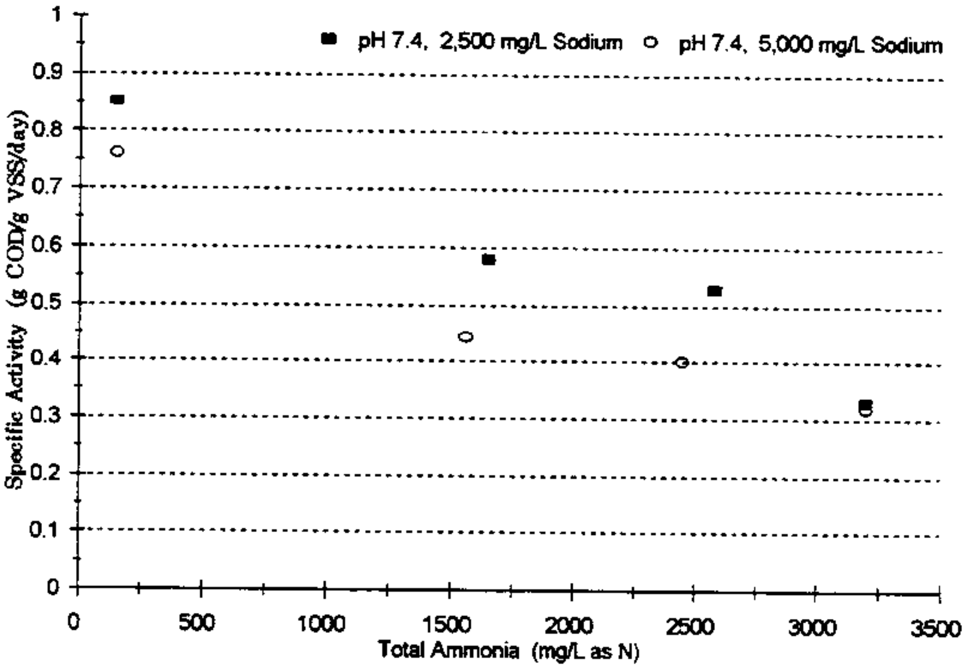


Figure 23. Anaeraobic Toxicity Assay Results: Variation of Specific Methanogenic Activity With Total Ammonia Concentration at pH 7.4.

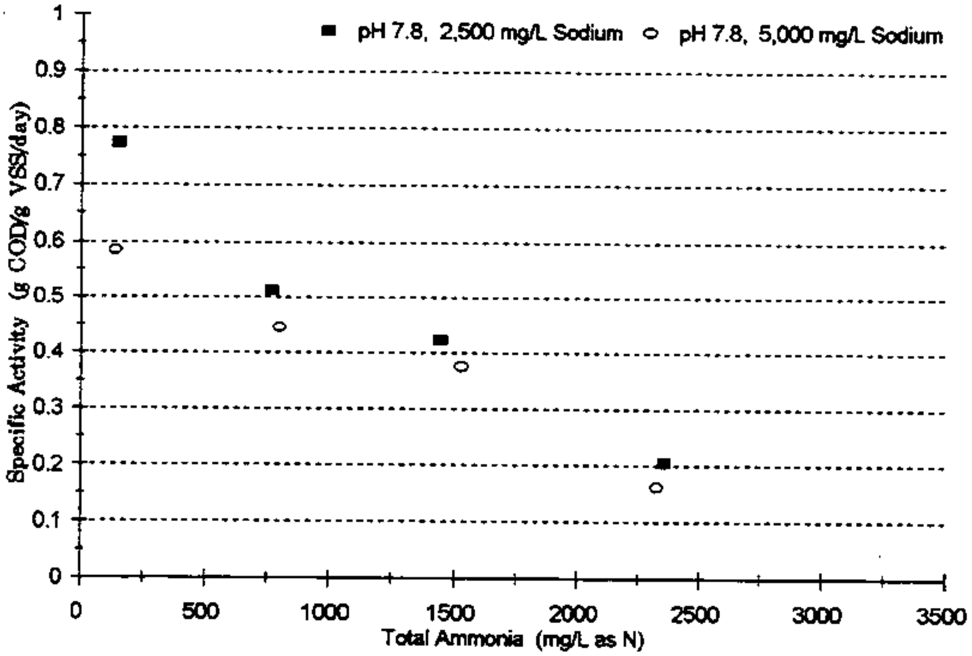


Figure 24. Anaerobic Toxicity Assay Results: Variation of Specific Methanogenic Activity With Total Ammonia Concentration at pH 7.8.

Figures 25 and 26 display the data from figures 23 and 24, as a function of unionized ammonia concentration. Figure 25 shows the variation of specific methanogenic activity with unionized ammonia concentration at a low sodium concentration (2,500 mg/L). Figure 26 shows the variation of specific methanogenic activity with unionized ammonia concentration at a high sodium concentration (5,000 mg/L).

When the sodium concentration was 2,500 mg/L at pH 7.4 or pH 7.8, the specific methanogenic activity decreased from 0.8 to 0.2 g COD/g VSS/day as the unionized ammonia concentration increased from 4 to 155 mg/L (as N). A linear regression of specific methanogenic activity versus unionized ammonia concentration yielded an r squared value of 0.92.

When the sodium sodium concentration was 5,000 mg/L at pH 7.4 or pH 7.8, the specific methanogenic activity decreased from 0.68 to 0.17 g COD/g VSS/day as the unionized ammonia concentration increased from 4 to 155 mg/L (as N). A linear regression of specific methanogenic activity versus unionized ammonia concentration yielded an r squared value of 0.87.

The combined data from figures 25 and 26 is plotted in figure 27. Note that the apparent influence of sodium on the specific methanogenic activity decreases as the unionized ammonia concentration increases.

PILOT-SCALE AIR STRIPPING COLUMN

Air stripping trials were performed on different days and thus at different air temperatures. The percent removals reported in this section have not been adjusted for temperature. A stripping factor was calculated for each trial based on the average liquid temperature (average of influent and effluent temperatures). The stripping factor was

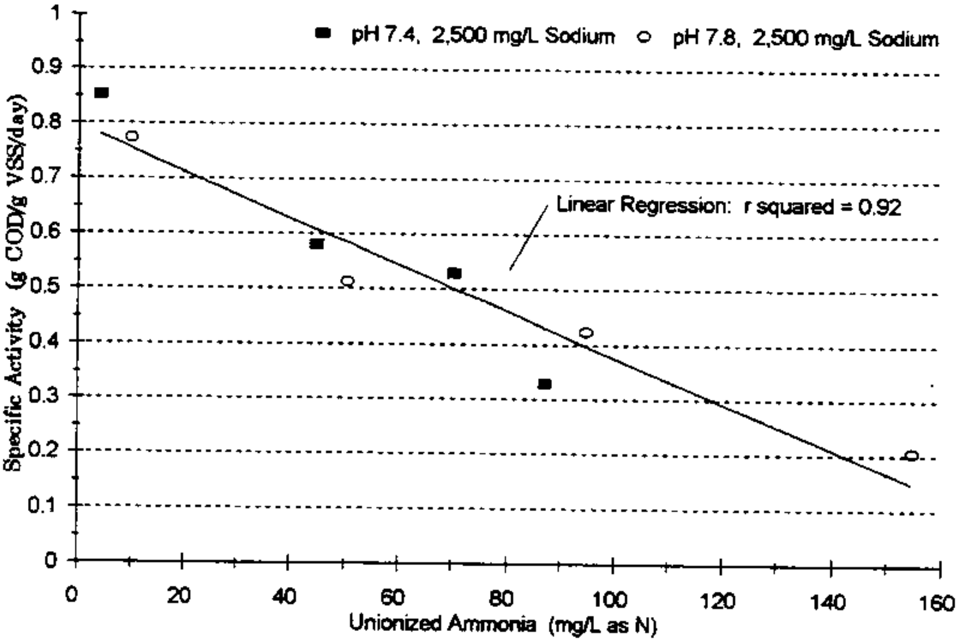


Figure 25. **Anaerobic Toxicity Assay Results: Variation of Specific Methanogenic Activity With Unionized Ammonia Concentration (2,500 mg/L Sodium Concentration).**

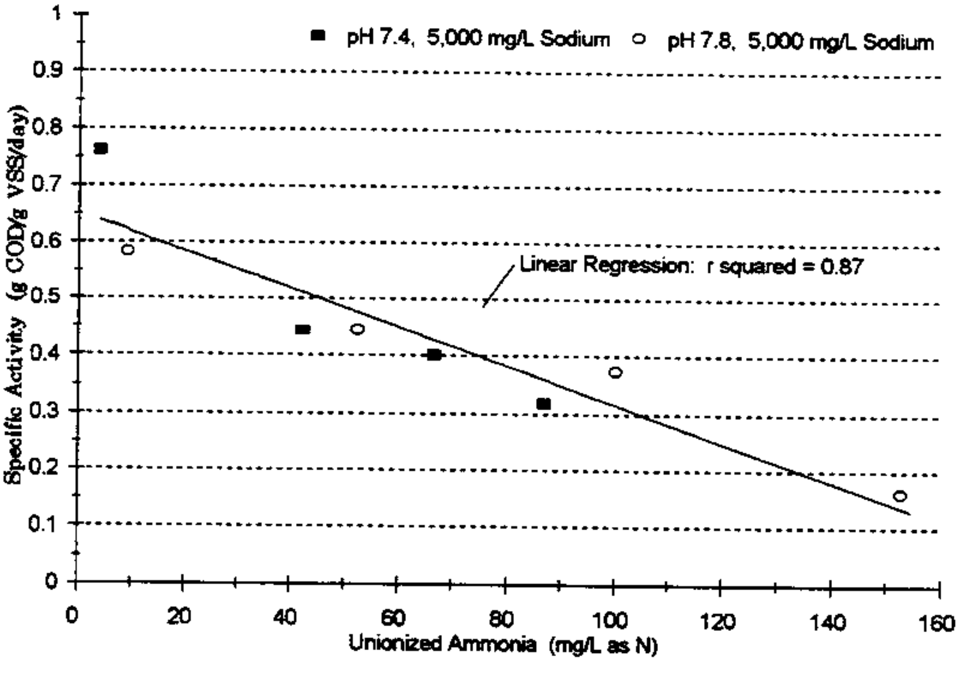


Figure 26. **Anaerobic Toxicity Assay Results: Variation of Specific Methanogenic Activity With Unionized Ammonia Concentration (5,000 mg/L Sodium Concentration).**

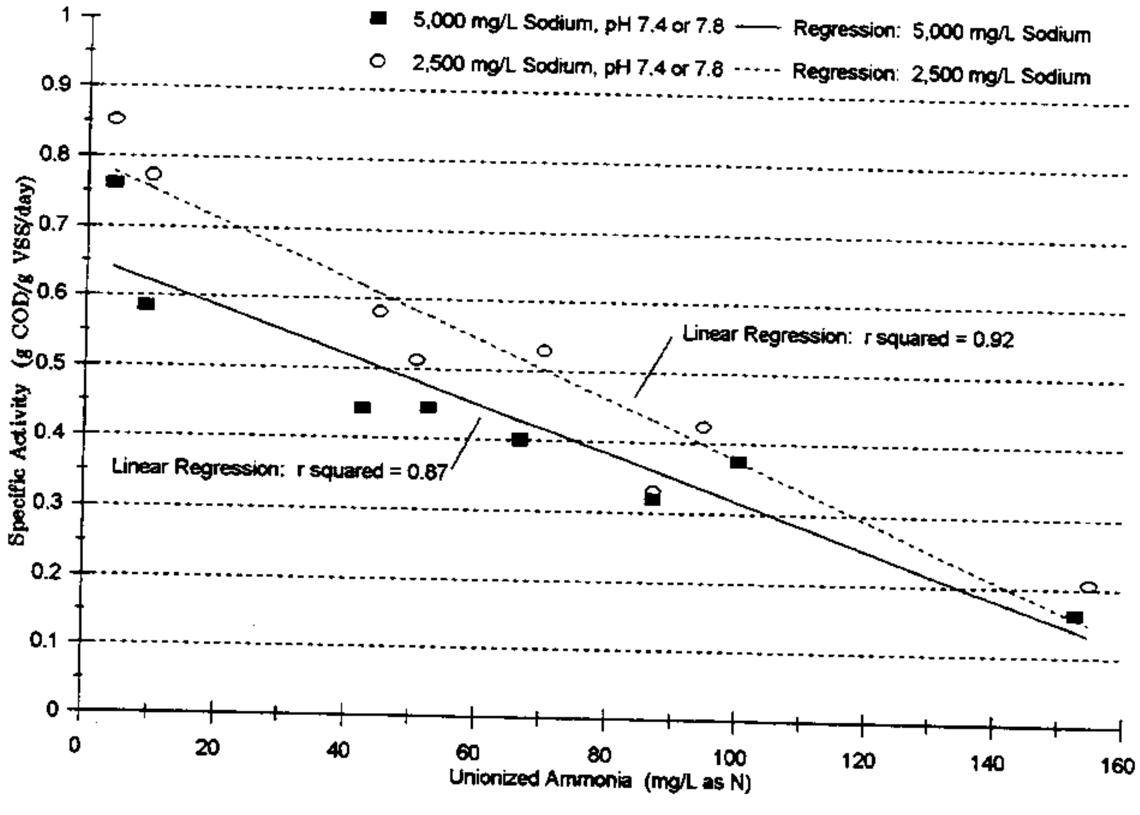


Figure 27. **Anaerobic Toxicity Assay Results: Effect of Sodium Concentration on Specific Methanogenic Activity at Various Unionized Ammonia Concentrations.**

subsequently used to calculate an overall mass transfer coefficient; however, no additional adjustment was made to the overall mass transfer coefficient for temperature. The data from each air stripping trial is included in Appendix L. Average liquid temperatures for all trials were between 9 and 19° C. The tower feed pH was 12.0 for all trials.

Table 33 shows a comparison of air stripping tower performance using undiluted and diluted UBF pilot-plant effluent. Both trials utilized liquid loading rates of 41 L/m^2/min and air flowrates of 21 m^3/min. At an average water temperature of 16.6° C, undiluted wastewater ammonia concentrations were reduced 57 percent. At an average water temperature of 11.8° C, diluted wastewater ammonia concentrations were reduced 53.3 percent.

Table 33. Comparison of Stripping Tower Performance Using Diluted and Undiluted UBF Pilot-Plant Effluent.

Parameter	Undiluted Feed	Diluted Feed (1:20 dilution)
Percent Ammonia Reduction	57.0	53.3
Water Flowrate (L/m^2/min)	41	41
Air Flowrate (m^3/min)	21	21
Average Temperature (° C)	16.6	11.8

Figure 28 shows the variation of percent ammonia removal with air flowrate for various liquid loading rates. Figure 29 displays the variation of percent ammonia removal with liquid loading rate at various air flowrates.

Percent removals increased with increasing air flowrate. At a liquid loading rate of 25 L/m^2/min, ammonia reductions increased from 50 to 72 percent as the air flowrate increased from 9 to 21 m^3/min. Percent removals decreased with decreasing liquid flowrate. At an air flowrate of 21 m^3/min, the ammonia reductions decreased from 77 to 52 percent as the liquid flowrate increased from 20 to 41 L/m^2/min.

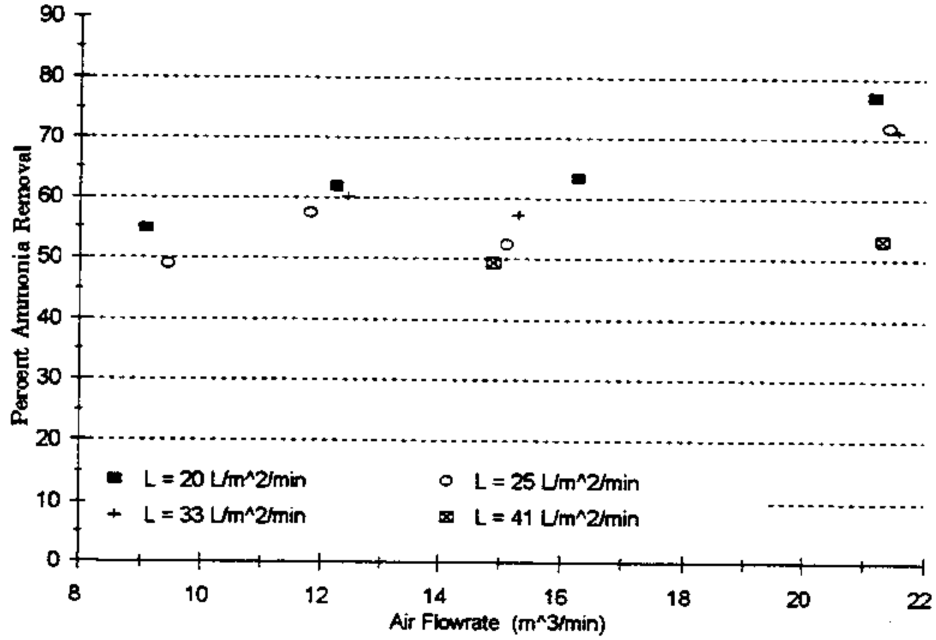


Figure 28. Variation of Air Stripping Tower Performance (Percent Ammonia Removal) With Air Flowrate at Various Liquid Loading Rates (L).

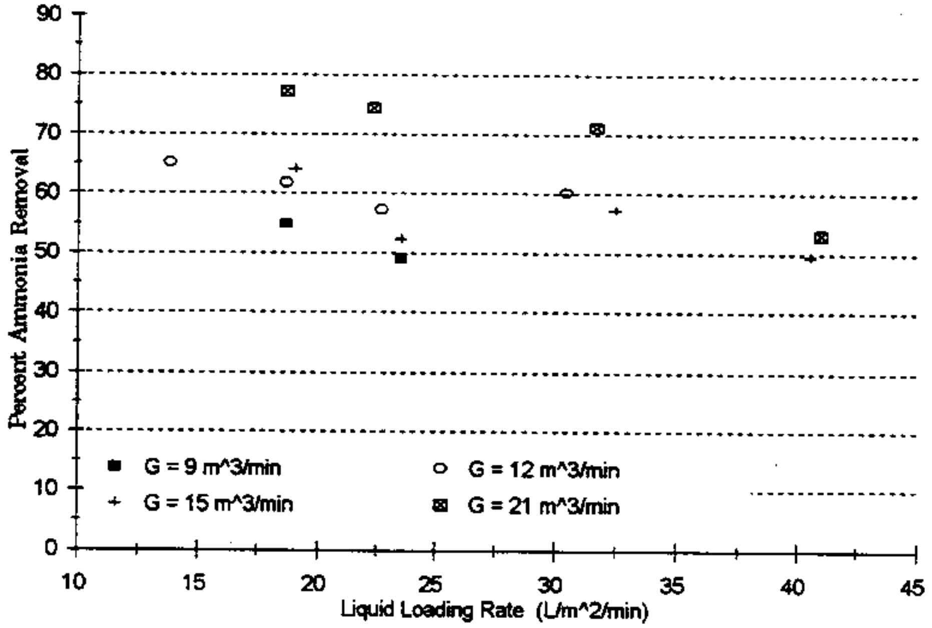


Figure 29. Variation of Air Stripping Tower Performance (Percent Ammonia Removal) With Liquid Loading Rate at Various Air Flowrates (G).

Figure 30 displays the variation of $K_L \cdot a$ (product of the overall mass transfer coefficient, K_L, and the specific interfacial area, a) with air flowrate at various liquid loading rates. Note from figure 30 that the overall mass transfer coefficient increased as the air flowrate increased at a constant liquid loading rate. At a liquid flowrate of 33 L/m^2/min, $K_L \cdot a$ increased from 1.1 to 1.6 min^{-1} as the air flowrate increased from 9 to 21 m^3/min.

Figure 31 shows the variation of $K_L \cdot a$ with liquid loading rate at various air flowrates. Note from figure 31 that $K_L \cdot a$ increased as the liquid loading rate increased at a constant air flowrate. At an air flowrate of 15 m^3/min, $K_L \cdot a$ increased from 0.8 to 1.5 min^{-1} as the liquid flowrate increased from 20 to 41 L/m^2/min.

Figure 32 shows the variation of pressure drop with air flowrate at various liquid loading rates. Note from figure 32 that the pressure drop increased as the air flowrate increased. Note also from figure 32 that the liquid loading rate has only a small effect on the pressure drop. At a liquid loading rate of 33 L/m^2/min, the pressure drop increased from 0.7 to 3.8 inches of water column (inches W.C.) as the air flowrate increased from 9 to 21 m^3/min.

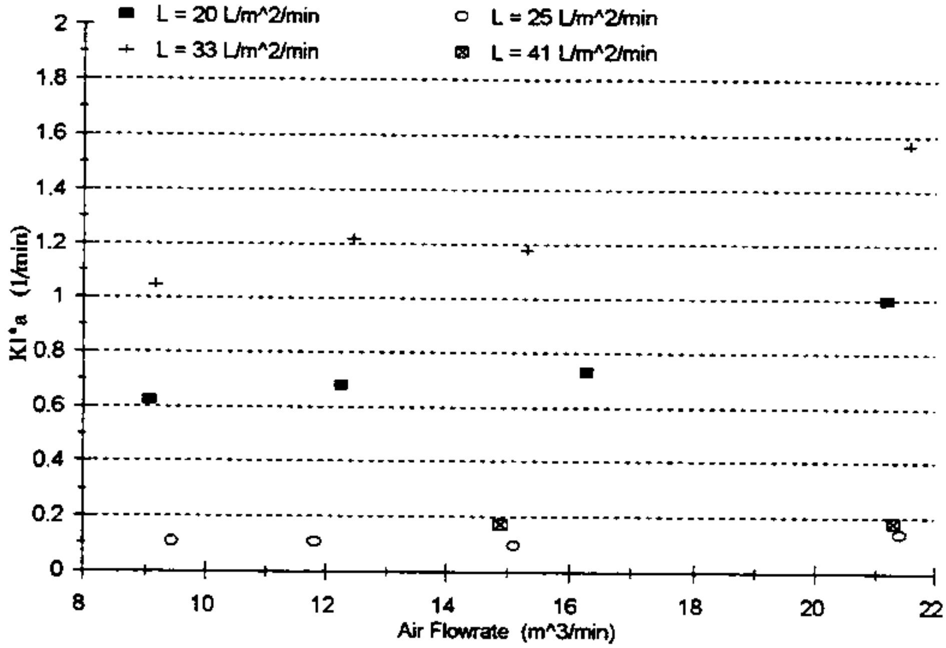


Figure 30. Variation of Kl*a (Overall Mass Transfer Coefficient * Specific Interfacial Area) With Air Flowrate at Various Liquid Loading Rates (L).

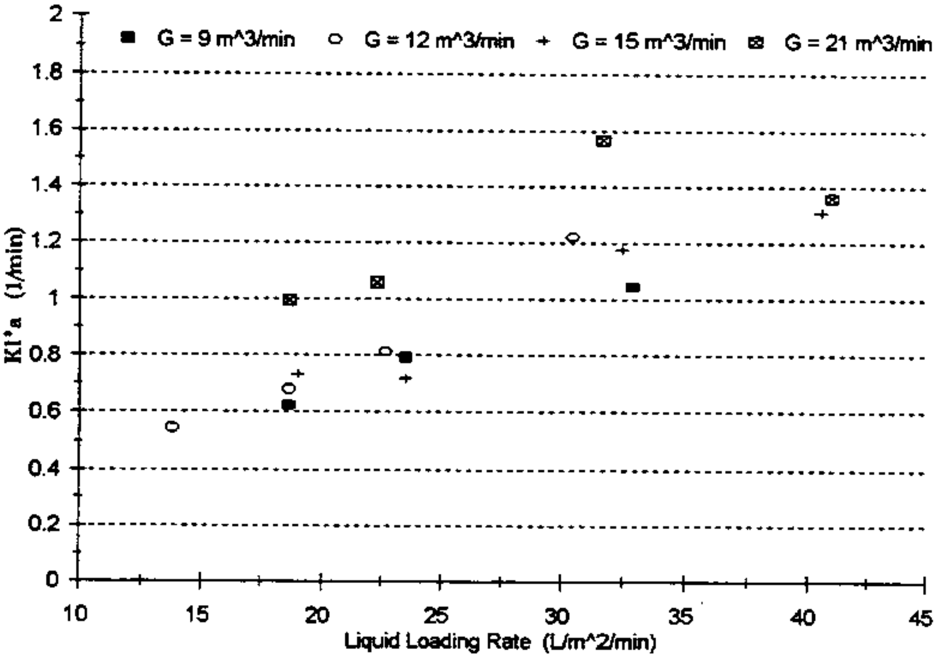


Figure 31. Variation of Kl*a (Overall Mass Transfer Coefficient * Specific Interfacial Area) With Liquid Loading Rate at Various Air Flowrates (G).

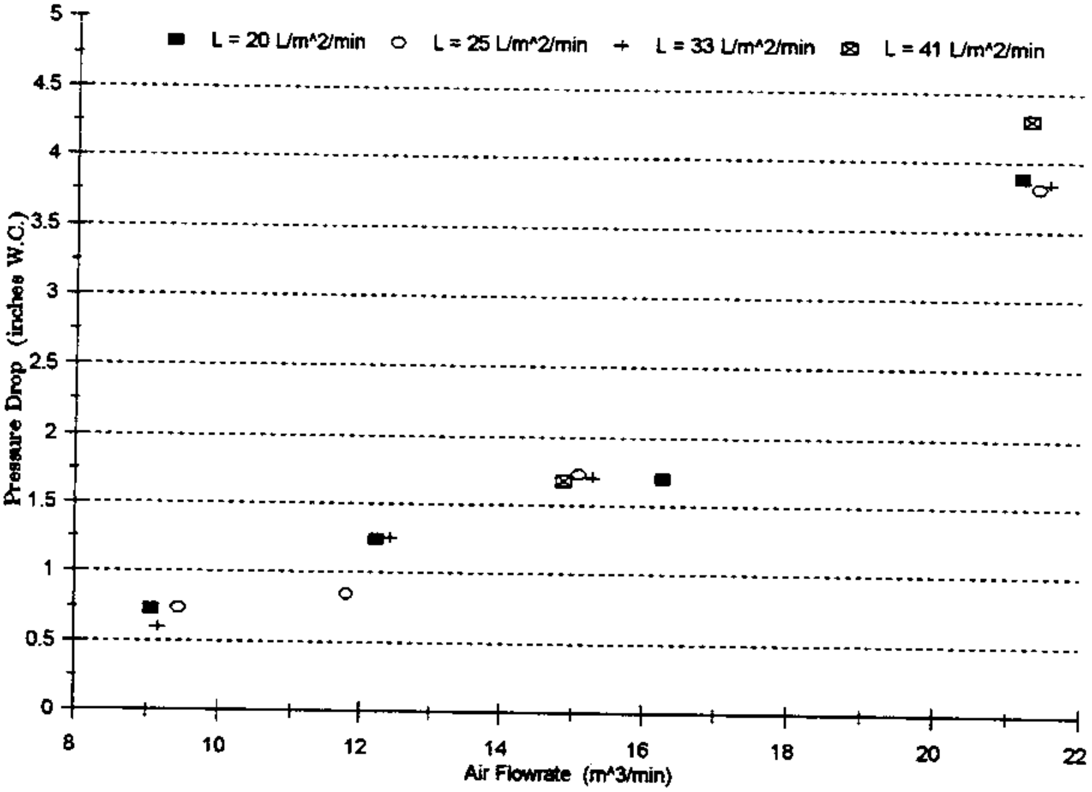


Figure 32. **Variation of Pressure Drop With Air Flowrate at Various Liquid Loading Rates (L).**

CHAPTER V. DISCUSSION

Anaerobic wastewater treatment and air stripping are discussed in separate divisions of this chapter. Estimations of full scale treatment unit sizes and costs are provided for a model blue crab processing plant.

ANAEROBIC WASTEWATER TREATMENT

The results from the lab-scale UASB reactors, pilot-scale treatment units, and anaerobic toxicity assays are discussed in separate sections. The final section contains a full-scale UASB reactor design for a model blue crab processing plant.

The F/M ratio receives considerable use in the following sections. When necessary, assumptions were made in the calculation of this parameter. The assumptions and calculations utilized are reported in Appendix G.

Lab-Scale UASB Reactors

The treatment performance of Reactor A during the first study period appeared similar to the results reported by Diz and Boardman (1994) with lab-scale UBF and UPF reactors. Diz and Boardman (1994) reported average soluble effluent COD levels of 6,500 mg/L at a F/M ratio of 0.4 day^{-1} for the UBF system, and average soluble effluent COD levels of 6,000 mg/L at a F/M ratio of 0.2 day^{-1} for the UPF system. Reactor A's effluent COD approached 6,000 mg/L at a F/M ratio of 0.25 day^{-1}.

Reactor B's F/M ratio of 0.65 day^{-1} exceeded the treatment capacity of the reactor. While this loading rate may be appropriate for other wastewaters, the treatment of unamended (not acidified) crab cooker wastewater requires low F/M ratios due to ammonia inhibition of methanogenic activity.

During the second study period, HCl was added to the feed wastewater. The intended effect of the wastewater acidification was to reduce the reactors' unionized ammonia concentration by decreasing the reactor pH. The wastewater acidification had the added effect of reducing the wastewater feed's suspended solids concentration. Previously, when the feed wastewater was unamended, the agitation provided by a peristaltic pump, which continuously circulated wastewater within the feed carboy, maintained most wastewater solids in suspension. When the wastewater feed pH was decreased below pH 5, a rapid coagulation occurred and approximately 76 percent of the TSS settled to the bottom of the feed carboy. Harrison (1993) suggested coagulation by pH adjustment for the pretreatment of crab cooker wastewater and reported comparable results. The results were reviewed in the literature review chapter.

The start-up of the reinoculated reactor during the second study period occurred faster than the rejuvenation of the 'failed' reactor. The rejuvenation of the failed reactor required several weeks while the reinoculated reactor responded satisfactorily after only several days. The comparison of the two start-up alternatives demonstrates the advantage of storing granular sludge for reinoculation. Reinoculation of a 'failed' reactor would clearly be preferable to rejuvenation; however, the cost of transporting new granular sludge to the 'failed' reactor site would determine the best financial solution.

Days 45 to 60 during the second study period served to assess the UASB reactors' treatment capacity. The preliminary OLRs were 7.6 g COD/L/day and 5.3 g COD/L/day for Reactors A and B, respectively. The increase in effluent COD in both reactors from day 50 to 60 indicated the reactors' treatment capacity had been surpassed. The remainder of the study period was conducted with lower OLRs.

Each reactor attained two steady-state periods of operation. The wastewater feed characteristics during the reactors' second steady-state period (24,100 mg/L unfiltered COD; 1,940 mg/L TKN-N) were closer to typical crab cooker wastewater than the feed characteristics during the first steady-state period (8,320 mg/L unfiltered COD; 993 mg/L TKN-N). For example, the pilot-plant wastewater feed averaged 20,000 mg/L unfiltered COD and 2,000 mg/L TKN-N from July 1994 to May 1995. Thus, data obtained during the second steady-state period is preferable for comparison with previous crab cooker wastewater treatment efforts.

Table 34 compares UASB treatment of crab cooker wastewater with results reported by other investigators. The UASB reactors' effluents contained, on average, 4,000 mg/L less soluble BOD_5 than UBF and UPF reactor effluents (Diz and Boardman, 1994) and 750 mg/L less soluble BOD_5 than CSTR effluents (Wolfe, 1993; Boardman *et al.*, 1993). The lower effluent BOD_5 levels were maintainable even though the UASB reactors' total ammonia concentration was 92 percent larger than the UBF and UPF reactors' ammonia concentrations and 48 percent larger than CSTR reactors' ammonia concentrations.

Table 34. Comparison of Lab-Scale UASB Reactors With Other Lab-Scale Anaerobic Treatment Systems. UASB Data From Second Study Period, Steady-State #2.

Anaerobic Reactor	F/M Ratio (day^{-1})	Effluent Soluble BOD_5 (mg/L)	Ammonia (mg/L as N)	pH
UBF (Diz and Boardman, 1994)*	0.2	4,100	1,100	7.9
UPF (Diz and Boardman, 1994)*	0.5	4,300	1,400	7.9
CSTR (Wolfe, 1993)	0.25	560	1,500†	7.7
CSTR (Wolfe, 1993)	0.35	1,400	1,750†	7.5
UASB, Reactor A‡	0.3	300	2,500	7.3
UASB, Reactor B‡	0.2	170	2,300	7.3

(*) Phase 4 of four phase study.
(†) Value approached before reactors failed.
(‡) Wastewater feed suspended solids reduced by acidification and subsequent coagulation and settling.

The UASB reactors' reduced unionized ammonia concentration enabled superior treatment performance. The UBF and UPF reactors' pH values averaged about 7.9 (Diz and

Boardman, 1994) while the CSTR reactors' pH averaged 7.6 (Wolfe, 1993). Comparatively, the UASB reactors' pH averaged 7.3. Thus, while the UASB reactors' unionized ammonia concentration was 61 mg/L, the unionized ammonia concentration was about 100 mg/L (as N) in the UBF and UPF reactors and 69 mg/L (as N) in the CSTR reactors. The CSTR reactors contained 3,200 mg/L less effluent soluble BOD_5, on average, than the UPF and UBF reactors. The comparisons illustrate the impact of unionized ammonia on anaerobic treatment of crab cooker wastewater.

The treatment performance of Reactor A during the second study period appeared similar to results reported with a lab-scale UASB treating clam processing wastewater (Boardman *et al.*, 1995; Tisinger, 1991). Tisinger (1991) reported an average reactor pH of 7.1, an average reactor temperature of 32° C, and a maximum total ammonia concentration of 275 mg/L (as N) during the study. The corresponding maximum unionized ammonia concentration was 3 mg/L (as N). At an OLR of 13.8 g COD/L/day, the UASB produced average effluent TSS and soluble BOD_5 levels of 90 and 200 mg/L, respectively. Comparatively, Reactor A produced an effluent soluble BOD_5 of 300 mg/L and an effluent TSS of 249 mg/L at an OLR of 6.4 g COD/L/day during the second steady-state period.

Reactor A's average unionized ammonia concentration during the second steady-state period was 61 mg/L (as N). The anaerobic toxicity assays showed that 61 mg/L (as N) of unionized ammonia caused about 40 percent inhibition of methanogenic activity. Thus, the reason that the UASB supported higher OLRs treating clam processing wastewater was probably that ammonia inhibited methanogenic activity during crab cooker wastewater treatment. The results of the anaerobic batch activity assays, which are discussed in detail in a later section, indicated that if the UASB reactors' pH had been decreased further, larger OLRs and F/M ratios could have been applied during the study.

Harrison (1993) reported that wastewater feed acidification and subsequent suspended solids removal did not improve anaerobic treatment performance with CSTR reactors. The removal of wastewater feed suspended solids was probably not responsible for improved organic reductions in this study either; however, the reduction of wastewater feed suspended solids did appear to influence the UASB reactors' effluent TSS and VSS levels. Table 35 compares the TSS and VSS reductions of the lab-scale UASB reactors with reductions reported by Diz (1994) with UBF and UPF reactors.

Table 35. Comparison of Lab-Scale UASB Reactors With Lab-Scale UBF and UPF Treatment Systems. UASB Data From Second Study Period, Steady-State #2.

Anaerobic Reactor	Effluent TSS (mg/L)	TSS Removal (percent)	Effluent VSS (mg/L)	VSS Removal (percent)
UBF (Diz, 1994)[*]	870	37	460	53
UPF (Diz, 1994)[*]	1,510	10	953	3
UASB, Reactor A[†]	249	-15[‡]	150	21
UASB, Reactor B[†]	172	21	75	61

(*) Phase 4 of four phase study.
(†) Wastewater feed suspended solids reduced by acidification and subsequent coagulation and settling.
(‡) TSS increased.

Percent TSS reductions of 37 and 10 percent were achieved in the UBF and UPF reactors, respectively, while percent reductions of -15 and 21 percent were achieved in Reactors A and B, respectively. Similar percent VSS reductions were observed. Overall, the differences in percent suspended solids reductions in the UASB, UBF, and UPF systems were not as significant as the differences in the effluent TSS and VSS concentrations. The UASB reactors' average effluent TSS concentrations were 82 percent less than the average UPF and UBF effluent TSS concentrations. Similarly, the UASB reactors' average effluent VSS concentrations were 84 percent less than the UPF and UBF effluent VSS concentrations. The lower effluent TSS and VSS concentrations in the UASB reactors probably resulted from the reduced feed suspended solids concentrations.

The F/M ratio appeared to effect suspended solids reductions in the UASB reactors. Reactor B reduced 39 and 35 percent more of the wastewater TSS and VSS, respectively, than Reactor A during the second steady-state period. During the first steady-state period, Reactor B reduced 2 and 8 percent more of the wastewater feed TSS and VSS, respectively, than Reactor A. Reactor B's F/M ratio was 50 percent lower than Reactor A's F/M ratio and this probably allowed more solids degradation.

The volatile fraction (VSS/TSS) of suspended solids in the UASB effluents was 50 percent during the second steady-state period. The volatile fraction of the wastewater feed was 90 percent. The relatively low volatile fraction in the reactor effluents probably resulted from the accumulation of non-degradable solids within the reactors. The non-degradable suspended solids were probably either by-products of anaerobic biodegradation or inorganic precipitates, such as sulfide precipitates.

An observed growth yield was calculated for each reactor over the second study period. Reactor A had an observed yield of 0.03 g VSS/g COD while Reactor B had an observed yield of 0.04 g VSS/g COD. As noted in the literature review chapter, Henze and Harremoës (1983) reported an average maximum growth yield of 0.18 mg VSS/mg COD for anaerobic reactors treating complex wastewaters. The UASB reactors' relatively low observed yields compared with the reported average maximum growth yield probably resulted from the low F/M ratios utilized in this study. Henze and Harremoës (1983) noted in their literature survey that reported observed yields were generally lower when the F/M ratio was lower. Presumably, when anaerobic bacteria are fed slowly or starved, more of the energy derived from biological conversions is used for maintenance functions. The reactors relative observed growth yields did not follow this trend. Reactor A's observed yield was 25 percent lower than Reactor B's yield while Reactor B's F/M ratio was about 50 percent lower than Reactor A's F/M ratio over the study period.

Although the wastewater feed pH was decreased below 4, the UASB reactors' alkalinity averaged 6,000 mg/L as $CaCO_3$ during the second steady-state period. The increase in reactor pH and alkalinity was the direct result of amino acid deamination. As was shown in the literature review chapter, deamination releases unionized ammonia. Released unionized ammonia combines with H^+ to form ammonium. The uptake of H^+ is balanced by the conversion of CO_2 to HCO_3^-. Thus, the magnitude of deamination determines the bicarbonate alkalinity. The relatively high alkalinity resulted from a very high wastewater feed TKN concentration (2,700 mg/L as N) during the second steady-state period.

Proteins and amino acids were not measured directly during this study; however, the wastewater feed TKN determination is a fair indicator of deamination potential. The TKN measurement predicts two important quantities: the reactor ammonia concentration, and the potential for deamination within the reactor.

When the wastewater feed TKN concentration is large, ammonia toxicity is magnified since the total ammonia concentration is larger and the pH is increased to a greater extent. Thus, the quantity of acid required to alleviate ammonia toxicity depends directly on the wastewater feed TKN. The acid requirements during the second steady-state period were about 330 mL of 6N HCl per 20 L of feed. Since the wastewater TKN concentration was 2,760 mg/L (as N), the relative acid addition was 36 milliequivalent (meq) of acid per gram (as N) of TKN.

Pilot-Scale UASB and UBF Reactors

The data from the pilot-scale treatment units illustrate ammonia inhibition of acetic acid utilization. As was noted in the results section, periods of high reactor effluent COD were accompanied by low reactor pH for both treatment units.

Figure 33 shows the combined observations of the UASB and UBF reactors' pH and COD. The accumulation of volatile fatty acids simultaneously increased the effluent COD and decreased the reactor pH. As shown in Figure 33, when the effluent COD exceeded 7,000 mg/L, the pH decreased to about 7.2. When the reactor effluent COD was below 6,000 mg/L, the pH was usually between 7.4 and 7.8.

When the crab cooker wastewater feed is unamended (not acidified), low effluent COD concentrations are possible only at low F/M ratios. The low F/M ratios are required because when all volatile fatty acids are degraded, the pH increases above 7.8, increasing the concentration of unionized ammonia and decreasing specific methanogenic activity to very low levels. When the pH is 7.9 (at 35° C), about 8.2 percent of the total ammonia concentration is present as unionized ammonia. Thus, if the total ammonia concentration is 2,000 mg/L (as N), the unionized ammonia concentration is 163 mg/L (as N). From Figure 27 in the results chapter, the specific methanogenic activity at a 160 mg/L (as N) unionized ammonia concentration is less than 0.15 g COD/g VSS/day. Thus, when the F/M ratio is increased to 0.3 day^{-1}, the specific activity of the acetate utilizing methanogens is more than doubled.

As acetic acid accumulates within an overloaded reactor, the reactor pH decreases which, in turn, increases methanogenic activity by decreasing the unionized ammonia concentration. The ammonia toxicity is effectively alleviated by the presence of volatile fatty acids which decrease reactor pH. As a result, in highly loaded reactors, such as the UBF and UPF systems reported by Diz and Boardman (1994) and the pilot-scale UBF reactor in this study, reactor effluents will always contain high volatile fatty acid concentrations and therefore high COD concentrations.

Several operational alternatives are available for anaerobic treatment of crab cooker wastewater: high F/M ratios (0.2 to 0.5 day^{-1}) with high effluent volatile fatty acid and COD

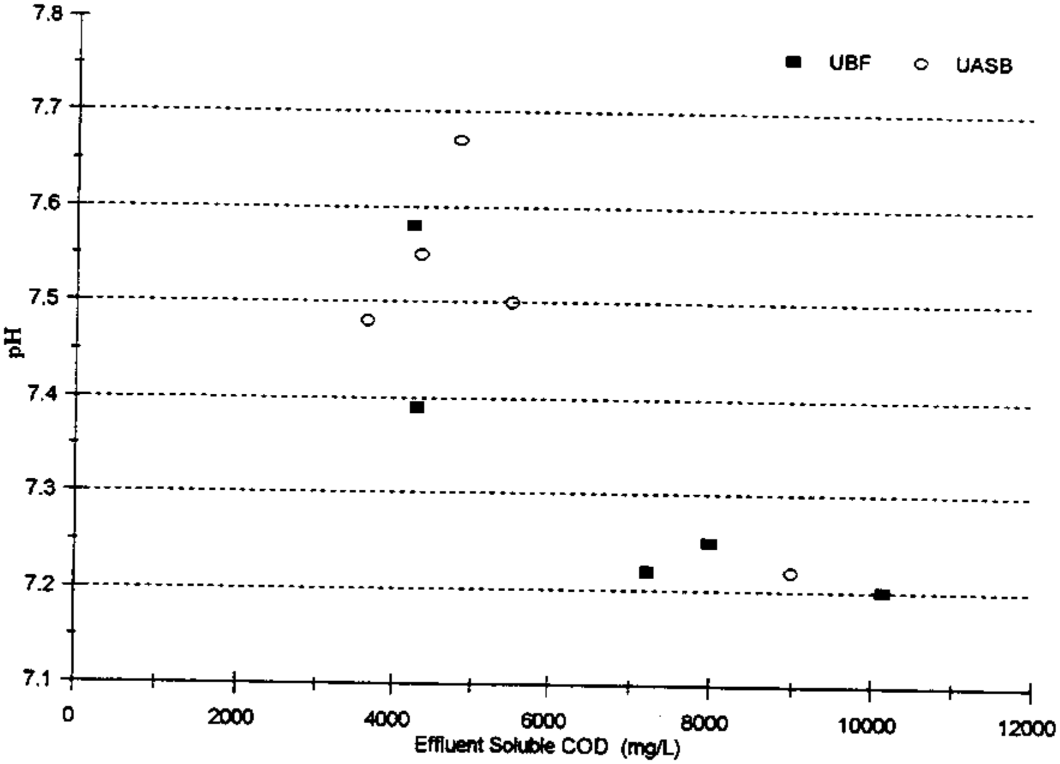


Figure 33. **Relationship Between pH and Effluent COD for Pilot-Scale UASB and UBF Reactors. Observations Over Study Period.**

concentrations; very low F/M ratios (less than 0.15 day^{-1}) and low COD concentrations; and high F/M ratios and low effluent COD concentrations by pH adjustment.

Anaerobic Batch Toxicity Assays

The batch toxicity assays demonstrated that the activity of acetate utilizing methanogens was directly proportional to the unionized ammonia concentration. Previous acclimation to 61 mg/L of unionized ammonia did not prevent a decrease in maximum specific methanogenic activity when the granular sludge were exposed to the acclimation concentration during the batch activity tests; however, the inhibition at a 61 mg/L unionized ammonia concentration may have been more severe if the sludge had not been previously acclimated.

The pH did not appear to effect ammonia inhibition beyond the change in unionized ammonia concentration. The inhibition increased linearly with unionized ammonia concentration above and below the acclimation concentration. Figure 34 shows the variation of percent inhibition with ammonia and sodium concentration.

From interpolation on Figure 34, the unionized ammonia concentrations leading to 50 and 80 percent inhibition were 85 and 150 mg/L (as N), respectively. Soto *et al.* (1991) reported unionized ammonia concentrations of 41 and 120 mg/L (as N) to cause 50 and 80 percent inhibition of granular sludge methanogenic activity, respectively. The higher relative tolerance of granular sludge to unionized ammonia in this study may have resulted from the higher prior acclimation level. Soto *et al.* (1991) acclimated the granular sludge to 30 mg/L (as N) of unionized ammonia while the granular sludge used in this study was acclimated to 61 mg/L (as N) of unionized ammonia.

Ammonia inhibition was evaluated at high (5,000 mg/L) and low (2,500 mg/L) sodium concentrations. The low sodium concentration was assumed not to effect the specific

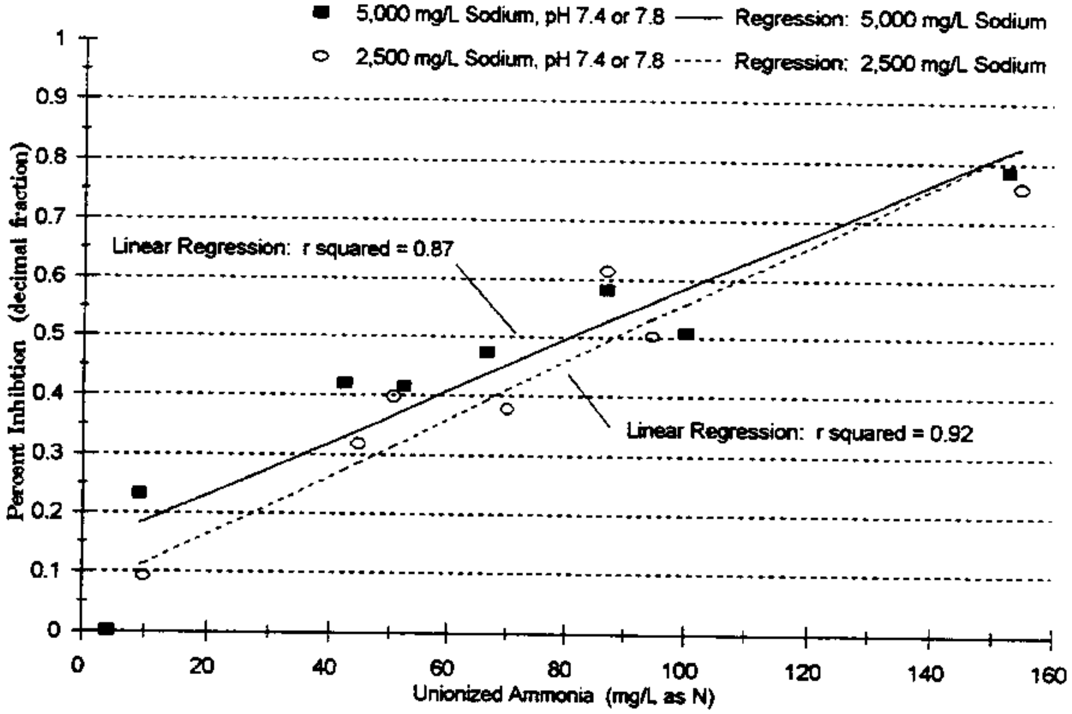


Figure 34. **Anaerobic Toxicity Assay: Effect of Sodium Concentration on Percent Inhibition of Specific Methanogenic Activity at Various Unionized Ammonia Concentrations. Percent Inhibition Calculated From Initial Measurement at pH 7.4, 4 mg/L Unionized Ammonia and Either 2,500 or 5,000 mg/L of Sodium.**

methanogenic activity. Thus, the results at the high sodium concentration were used to draw conclusions regarding the effect of sodium on ammonia toxicity.

The high sodium concentration appeared to inhibit methanogenic activity at the control levels of ammonia (about 4 mg/L as N of unionized ammonia). At pH 7.4, the low sodium specific methanogenic activity was 11 percent greater than the high sodium specific methanogenic activity. At pH 7.8, the low sodium specific methanogenic activity was 25 percent greater than the high sodium specific methanogenic activity. The greater sensitivity of granular sludge to sodium at higher pH levels was also noted by Rinzema *et al.* (1987).

At low concentrations of unionized ammonia, sodium had a synergistic effect on ammonia toxicity. However, the effect of sodium on ammonia toxicity appeared to become less significant as the unionized ammonia concentration increased. Kugelman and McCarty (1965) reported that sodium was antagonistic to ammonium toxicity. However, sodium concentrations reported to be antagonistic were generally below 1,000 mg/L. Since Kugelman and McCarty (1965) performed investigations at pH 7.0 and the concentration of unionized ammonia was below 10 mg/L (as N), the implications of their results on this study are not clear.

At unionized ammonia concentrations greater than 80 mg/L (as N), sodium did not effect the specific activity significantly. This observation could be interpreted as the absence of a synergistic affect from sodium at higher unionized ammonia concentrations; however, a more likely explanation is that the unionized ammonia concentration was far more important in determining the specific activity.

The results suggest that the lab-scale UASB reactors could have maintained higher F/M ratios if the pH had been decreased below 7.3 to further reduce the unionized ammonia concentration.

Full-Scale Treatment System Design

The following section contains a full-scale treatment system design for a model blue crab processing plant. The proposed treatment system includes an equalization tank, a UASB reactor, and pH adjustment equipment. Assumptions made in the UASB reactor design are listed below. The design wastewater feed parameters (COD and TKN) were average values measured at the pilot-scale treatment facilities during the past year.

- Wastewater Feed Daily Flow: 1,000 gallon per day (3,800 L/day) of crab cooker wastewater. According to Harrison (1993), this wastewater flow would result from about 20 cooks or 24,000 pounds of product.
- Average Influent Wastewater COD: 20,000 mg/L.
- Average Influent Wastewater TKN: 1,900 mg/L as N.
- F/M ratio: 0.3 day^{-1}.
- Reactor VSS concentration: 25,000 mg/L.

Based on the design F/M ratio, wastewater strength, and wastewater flow, the HRT of the above system would be 2.8 days. The corresponding reactor volume would be 11,000 L (2,800 gal).

Lettinga *et al.* (1984) estimated installation costs for a 1,000 m^3 UASB at $500,000 to $750,000 1980 dollars. Assuming a 10 percent interest rate, the corresponding cost in 1995 dollars is $1,400,000 to $2,100,000. According to Tisinger (1991) who cited Walker (1990), a full-scale 45 m^3 UASB reactor at the Floyd Agricultural Energy Corp (FAEC) cost $120,000 in 1986. Assuming a 10 percent interest rate, the corresponding cost in 1995 dollars is $280,000. At smaller reactor volumes less economies of scale are realized. Thus, in the absence of better data, the installation costs of a 10.6 m^3 reactor are estimated as half the costs of a 45 m^3 reactor or $140,000 1995 dollars. The above cost is somewhat conservative since the reactor volume is less than one-fourth the FAEC reactor volume. Assuming a 20 year design life and 10 percent interest rate, the annual cost would be $17,000. Averaged over 365 days, the daily cost would be $46.

The proposed treatment system includes an equalization basin with a three day HRT. The equalization basin would provide a degree of wastewater volume and strength equalization while also preventing short term feed interruptions. The wastewater feed pH would be adjusted to 4 or 5 in the equalization basin to induce the coagulation and settling of suspended solids. The equalization basin would thus require solids removal equipment which generates an extra cost; however, the benefits of reduced reactor effluent suspended solids and reduced odors from the holding tank would outweigh the extra investment costs. Based on the design wastewater flow, the equalization basin would require a 11,000 L volume. Overall, the UASB reactor and chemical costs would be more significant than the equalization basin and solids removal equipment costs. Thus, the equalization basin and solids removal equipment costs are not included in this estimate.

The acid requirements of the proposed treatment system are 287 equivalents of HCl per day (76 meq per L wastewater). This acid addition would keep the reactor pH at 7.3. The daily requirement of muriatic acid (35 percent HCl) would be 68 L. The cost of muriatic acid is about $90 for a 55 gallon drum (Waschler, 1995). The corresponding daily chemical cost for the proposed treatment system would be $29 per day ($0.03/gallon). Equipment for pH adjustment, not included in this estimate, would also be required. However, as with the sludge removal equipment, the pH adjustment equipment would probably not be significant compared to the UASB reactor and chemical costs.

Wash water (clean-up water) could be treated in the proposed treatment system without significantly impacting treatment performance. Boardman *et al.* (1993) reported typical daily wash water volumes of 900 L/day that contained 3,800 mg/L of COD. Compared to the high organic loading imposed on the UASB system by the retort effluent, the effect of the wash water waste streams would be small. Since the wash water only contains about 220 mg/L (as N) of TKN (Boardman *et al.*, 1993), the treatment of wash water simultaneously with crab cooker wastewater would reduce the ammonia concentrations within the reactor and subsequently increase specific methane production rates. Harris claw wastewaters could not be treated by the above system since the high sodium concentrations would upset the UASB reactor.

Based on the results of the lab-scale UASB study, the above treatment system would produce an effluent BOD_5 of 300 mg/L.

PILOT-SCALE AIR STRIPPING TOWER

The performance of the air stripping tower in terms of ammonia removals and observed mass transfer coefficients is discussed in the next section. An additional section contains a full-scale air stripping tower design and cost estimate for a model blue crab processing plant.

Ammonia Removal and Mass Transfer

Temperature exerts a strong influence on ammonia air stripping efficiency. The process is more effective at higher liquid temperatures because the Henry's Law constant is increased. The influent liquid temperature is not a reliable indicator of the average Henry's Law constant for an air stripping experiment since liquid is cooled within the tower to a degree determined by the air temperature and air flowrate. Temperature differences caused some variation in the percent removals achieved during the air stripping experiments; however, several trends in ammonia stripping efficiency were noted.

Ammonia removal increased with increasing air flowrate at all liquid loading rates. The higher air flowrates increased the stripping factor and the overall mass transfer coefficient. The combined effect increased overall stripping performance.

Ammonia removal decreased with increasing liquid loading rate. The product of the overall mass transfer coefficient and the specific interfacial area ($K_L \cdot a$) increased with increasing liquid loading rate; however, ammonia removal still decreased. This observation demonstrates the importance of the stripping factor in determining process efficiency. Stripping factors were calculated for each trial using equation 13. The stripping factor during the experiments was between 0.9 and 3.3. In this range, the stripping factor has a large effect on the NTU, as has been demonstrated by Treybal (1980).

The increased liquid loading rate increased HTU which also contributed to the decreased efficiency. At the liquid loading rate of 41 L/m^2/min, 50 and 52 percent ammonia reductions were realized at air flowrates of 15 and 21 m^3/min, respectively. The corresponding stripping factors were 0.89 and 1.1, respectively. To increase the stripping factor to 2 at 11° C (average water temperature), an air flowrate of 38 m^3/min would have been required. As was shown in Figure 29, the air pressure drop approximately quadrupled each time the air flowrate doubled. Thus, extrapolating from Figure 29, the pressure drop at 38 m^3/min would have been about 2 inches of W.C. (water column pressure) per foot of tower height.

Figure 35 illustrates the relationship between the pressure drop and the air flowrate more clearly. The pressure drop was directly related to air flowrate squared (G^2). A linear regression of pressure drop versus air flowrate squared yielded an r squared value of 0.97.

The increased pressure drops associated with stripping factors above 1 at high liquid loading rates (41 L/m^2/min) suggest the use of lower liquid loading rates (20 to 33 L/m^2/min) to

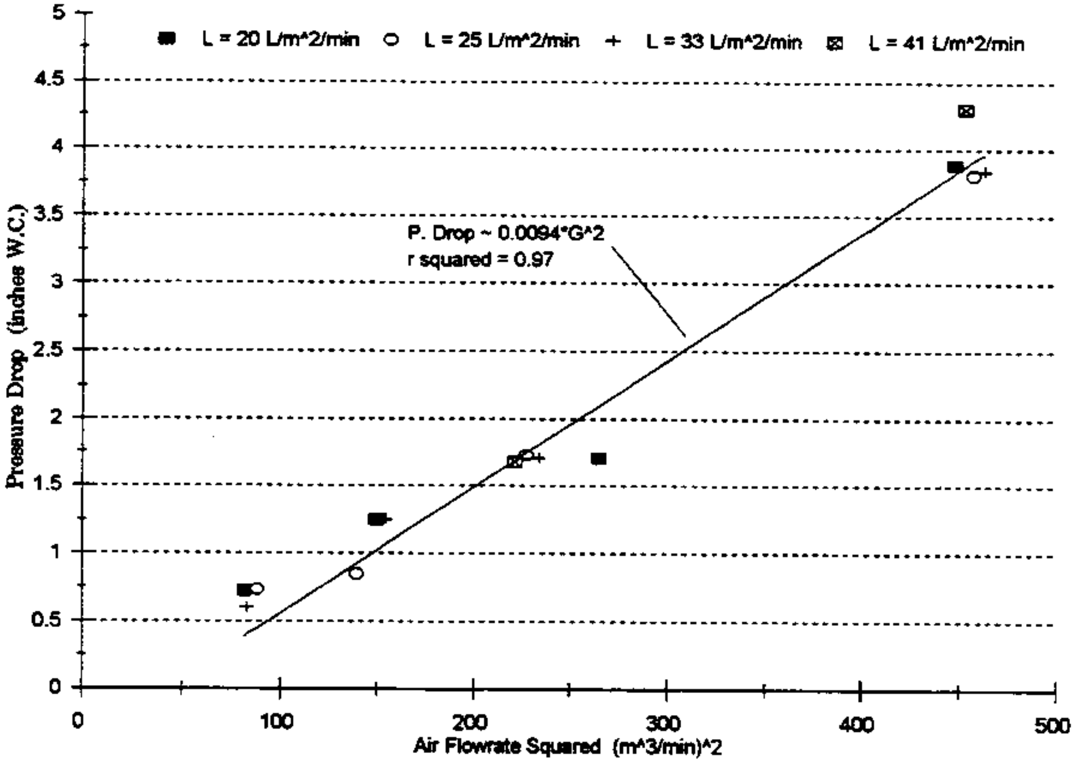


Figure 35. **Variation of Pressure Drop With G^2 (Air Flowrate Squared).**

improve ammonia removal. At low liquid loading rates, stripping factors of 2 or 3 are achievable without excessive pressure drops.

The product of $K_L \cdot a$ increased with increasing air flowrate. At a given liquid loading rate, the increased air flowrate increased air turbulence which caused the local gas side mass transfer coefficient (k_G) to increase. The observation that $K_L \cdot a$ increased with increasing air flowrate indicates that the value of k_G was significant in determining the overall mass transfer coefficient. Thus, gas phase resistance contributed significantly to the overall resistance to mass-transfer.

The product of $K_L \cdot a$ increased with increasing liquid loading rate. Since the liquid loading rates used in this study were very low (below 41 L/m^2/min or 1 gpm/ft^2), the entire packing surface may not have been wetted by the lower liquid flowrates. Thus, increases in the liquid loading rate may have caused the effective specific interfacial area (a) to increase. Since the specific interfacial area may not have been constant, the influence of liquid loading on K_L is impossible to assess.

Although low liquid loading rates may have decreased the wetted packing area, operation at these rates still deserves consideration because of the high air to water ratios needed for ammonia removal. As was stated previously, low liquid loading rates are necessary to allow moderately high air flowrates and therefore moderate pressure drops.

Full-Scale Design and Cost Estimate

Because of the relatively small wastewater volumes produced by crab processing facilities, a reasonable procedure would be to operate an air stripping tower intermittently rather than continuously. Wastewater effluent from a biological treatment system would be collected in a holding tank until the tank was full. The wastewater pH would then be adjusted to 11.5 and the air stripping tower would be operated until the holding tank was empty. The treatment system would adapt easily to different daily wastewater flows.

The following design and chemical costs are based on a wastewater flow of 3,800 L/day (1,000 gpd) of biologically treated crab cooker wastewater. As noted previously, this wastewater flowrate would result from about 20 cooks, or 24,000 pounds of product (Harrison, 1993).

The proposed tower design would reduce ammonia concentrations 96 percent with two nine foot high towers in series. The towers would have a 1 m inside diameter. An ammonia reduction of 96 percent would result from an air flowrate of 113 m^3/m^2/min and a liquid flowrate of 20 L/m^2/min. The pressure drop over each tower would be 4.5 inches W.C., which is within the typical range of 0.25 to 0.5 inches W.C. per foot tower height utilized for air stripping towers (Treybal, 1980).

Little cost data is available for small air stripping applications. However, the annual investment and operating costs (excluding chemical costs) over a 20 year design life for an ammonia air stripping tower designed for 90 percent removal and 95 L/min (25 gpm) of liquid flowrate would be estimated as $4.50/day (Little and Marinas, 1995). The annual interest rate assumed in the cost is 10 percent. Although the estimate was intended for a higher liquid loading rate, lower percent removal, and a single tower, in the absence of better data it is a fair cost estimate for this design. In any case, the investment costs are not as significant as the chemical costs.

The chemical costs depend directly on the feed wastewater volume, ammonia concentration, and bicarbonate alkalinity. After biological treatment, crab cooker wastewater contains high concentrations of ammonia (average: about 1,900 mg/L as N) and alkalinity (average: about 7,000 mg/L as $CaCO_3$). To increase the wastewater pH to 11.5, most of the ammonium (NH_4^+) and bicarbonate (HCO_3^-) are converted to ammonia (NH_3) and carbonate (CO_3^-). Thus, the chemical costs are high per unit volume of biologically treated wastewater.

If anaerobically treated effluent is used as tower feed, the effluent should be aerated prior to pH adjustment. Otherwise, high concentrations of CO_2 will further increase chemical costs. The CO_2 could be removed by aeration of the holding tank. If aerobic treatment is used following anaerobic treatment, no further CO_2 removal would be required. If anaerobic treatment is supplemented by acid addition to reduce alkalinity, more chemicals for air stripping would not neccessairly be required, provided CO_2 removal is incorporated into the treatment train. Acid addition decreases the reactor's bicarbonate alkalinity by converting HCO_3^- to CO_2. If the CO_2 is subsequently removed by aeration, less sodium hydroxide would be required for the conversion of HCO_3^- to CO_3^{-2} since less HCO_3^- is present.

To increase the pH of biologically treated retort effluent, 0.2 equivalents of base per L of wastewater will be required. Based on a sodium hydroxide (15N) cost of $147 per 55 gallons (Waschler, 1995), the chemical cost per L of crab cooker wastewater is about $0.01. The estimate is based on an ammonia concentration of 1,900 mg/L (as N) and an alkalinity of 7,000 mg/L as $CaCO_3$. A chemical cost will also be incurred to readjust the pH. However, since most ammonia is removed from the liquid, the acid requirement will be considerably less than the base requirement. An additional cost of 15 percent of the sodium hydroxide cost is assumed. The resulting chemical cost would be $41 per day for 3,800 L of wastewater flow.

Extra costs would be incurred for the holding tank and pH adjustment equipment. However, the chemical costs would most likely greatly outweigh these extra costs. The holding tank volume would be 1,900 L (500 gal.) capacity. At the design wastewater flowrate and holding tank volume, the air stripping tower would be operated twice daily for approximately 30 minutes.

Costs could be extrapolated for other crab processing facilities based on the installation costs outlined above. Chemical costs could be adjusted based on wastewater flow and TKN concentration. Lime could be used instead of sodium hydroxide to decrease the chemical costs, but increased scale build-up within the tower would probably not favor its use.

The annual air stripping investment and operating costs (except chemical cost) are about $16,000 for a 20 year design life. The chemical costs would be about $41 for 3,780 L of wastewater flow.

Other waste streams could be handled by the air stripping tower. As noted, chemical costs depend directly on the TKN of the wastewater stream since the TKN determines the ammonia concentration and bicarbonate alkalinity of biologically treated crab processing effluents. The impact of other wastewater streams could be assessed by the determining the waste stream TKN. Wash water, for example, has an average TKN of 220 mg/L (as N). The incorporation of this stream into the air stripping tower would not impact treatment performance and would decrease the effluent ammonia concentration by dilution. To some extent, the outlined tower design could incorporate larger wastewater volumes by operating for longer durations; however, a larger tower diameter would be required for much larger wastewater flows.

The ammonia concentration in the tower off-gases would be an area of concern for the application of air stripping technology to biologically treated crab cooker wastewater. The largest ammonia concentration would occur in the gases from the first air stripping tower. The off-gases would contain about 280 mg NH_3/m^3. The second tower's off-gases would contain about 40 mg NH_3/m^3. The average concentration in the discharge from both towers would be 160 mg NH_3/m^3.

The World Health Organization (1986) reported the following data on human exposure to ammonia.

- 35 mg/m^3 odor threshold (most people can identify this concentration in air).
- 280 mg/m^3 caused throat irritation

The tower's off gases would contain a decreased ammonia concentration if the tower influent contained less ammonia. Thus, if other wastewater streams were blended with the crab cooker wastewater, the tower off gases' ammonia concentrations would be reduced. Also, the above design would only require 1 hour of operation per day. Intermittent operation would further reduce the short-term impact of off-gases.

CHAPTER VI. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

The following chapter summarizes conclusions derived from the results of this study. Suggestions for future research topics are also provided.

1. Anaerobic treatment of crab cooker wastewater is constrained by ammonia toxicity. The deamination of amino acids promotes inhibition by producing high ammonia concentrations and elevated pH levels.

2. Treatment of crab cooker wastewater with UASB reactors can substantially reduce wastewater COD (70 percent COD reduction in this study); however, effluent quality fluctuates and effluents contain considerable biodegradable material.

3. When treating crab cooker wastewater, UASB performance appears similar to results reported with Upflow Anaerobic Bed Filter (UBF) and Upflow Anaerobic Packed Filter (UPF) reactors.

4. Acidification of the crab cooker wastewater greatly enhances UASB treatment performance. At comparable feed organic loading rates (OLRs), lower effluent COD concentrations are possible with acidified wastewater than with unacidified wastewater because of the reduced reactor pH. Similarly, at comparable feed OLRs, lower effluent TSS and VSS concentrations are possible with acidified wastewater than with unacidified wastewater because of the reduced wastewater feed suspended solids concentrations.

5. Ammonia inhibition of acetate utilizing methanogens is directly proportional to the unionized ammonia concentration in the range of 8 to 155 mg/L (as N). Prior acclimation to 61 mg/L (as N) of unionized ammonia may lessen the severity of ammonia inhibition; however, specific methanogenic activity may still be inhibited at or below the acclimation concentration.

6. Sodium appears to be synergistic to ammonia toxicity. The synergistic effect appears more pronounced at lower unionized ammonia concentrations (less than 80 mg/L as N).

7. Ammonia stripping efficiency increases as the stripping factor increases from one to three; however, under the conditions of this study (2.3 inch LanPac packing and countercurrent tower), stripping factors from two to three are only possible at low liquid loading rates (less than 41 $m^3/m^2/min$) due to pressure drop considerations.

8. At liquid loading rates less than 41 $m^3/m^2/min$, the product of the overall mass transfer coefficient (K_L) and the specific interfacial area (a) increases with increasing liquid loading rate, probably because more of the packing surface is wetted at higher liquid loading rates. Although liquid loading rates less than 41 $m^3/m^2/min$ may be below the minimum wetting rate of the packing used in this study, ammonia stripping at low liquid loading rates is still preferable because higher stripping factors are achievable.

9. The principal financial consideration for ammonia stripping of biologically treated crab cooker wastewater is chemical costs. Chemical costs are directly related to tower influent ammonia and bicarbonate alkalinity concentrations.

The following list contains suggested areas for further study.

1. Two acetate utilizing methanogenic species are prevalent in anaerobic treatment systems: *Methanothrix and Methanosarcina*. Since the effluent acetic acid concentration is very high in the pilot-scale treatment units, is the predominant acetate utilizing methanogen *Methanosarcina*, as the relative kinetic considerations would suggest? Do the two species have different sensitivities to ammonia?

2. Does unionized ammonia inhibit anaerobic microorganisms other than the acetate utilizing methanogens? Specifically, are the hydrogen utilizing methanogens inhibited, as has been suggested in the literature?

3. If the UASB reactor pH had been reduced to 7.0, would higher loading rates have been possible?

4. Countercurrent ammonia stripping is limited by pressure drop considerations. Could crossflow stripping increase overall efficiency?

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CHAPTER VII. APPENDICES

APPENDIX A

THEORETICAL COD EQUIVALENT OF VOLATILE FATTY ACIDS

The theoretical oxygen demand of the volatile fatty acids is summarized below.

Acetic Acid: $CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$

Propionic Acid: $CH_3CH_2COOH + 3.5O_2 \rightarrow 3CO_2 + 3H_2O$

Butyric Acid: $CH_3CH_2CH_2COOH + 5O_2 \rightarrow 4CO_2 + 4H_2O$

From the above stoichiometry:

Volatile fatty acid	Theoretical Oxygen Demand
Acetic Acid	1.1 mg O_2/mg Acetic Acid
Propionic Acid	1.5 mg O_2/mg Propionic Acid
Butyric Acid	1.8 mg O_2/mg Butyric Acid

APPENDIX B

CALCULATION OF MAXIMUM SPECIFIC METHANOGENIC ACTIVITY

The maximum specific methanogenic activity was calculated from the slope of cumulative methane production versus time. The methane production during each one hour interval was calculated from the sum of methane accumulated in the headspace and lost from the headspace during each hour.

The calculation is summarized below.

Acc. CH_4 = $V * (m_2 - m_1)$

Lost CH_4 = $L * (m_2 + m_1)/2$

where:

Acc. CH_4 = accumulated methane

Lost CH_4 = lost methane

m_1 = methane concentration at beginning of interval

m_2 = methane concentration at end of interval

V = headspace volume

L = total volume of biogas generated during interval

APPENDIX C

LIQUID DISTRIBUTOR DESIGN

The liquid distributor was a gravity feed type distributor. The distributor area was divided into three equal area radial sections. Six holes (approximately 1/8 inch diameter) were drilled in each equal area section for the liquid distribution. Overall, the holes were chosen evenly spaced over the entire area of the distributor. Three 2 inch PVC pipe sections and four 1.5 inch PVC pipe sections were placed through the distributor to allow air to flow freely out from the tower.

APPENDIX D

CALCULATION OF AIR VELOCITY FROM MANOMETER READING

Air velocity was calculated from manometer readings using the following equations.

$$V_a = 1096.2 * (P_v/D)^{-0.5}$$

$$D = 1.325 * P_b/T$$

where:

V_a = Air Velocity in ft/min

P_v = Manometer reading, inches water column

D = Air Density

P_b = barometric pressure in inches of mercury

T = absolute temperature (°F + 460)

APPENDIX E

LOCATION OF AIR VELOCITY SAMPLING POINTS

The velocity sampling points were chosen according to product literature from Dwyer Instruments, Inc. A total of twenty measurements were made in addition to the centerline measurement. Ten sampling points were located across the horizontal and vertical axis. Points along either axis, were located at one of five distances on either side of the centerline. The points were located at the following distances from the centerline (r = pipe radius): 0.316•r; 0.548•r; 0.707•r; 0.837•r; and 0.949•r.

The average of the above sampling locations provided an average air velocity.

APPENDIX F
CALCULATION OF AVERAGE VSS DURING SECOND STUDY PERIOD

DAY 69

	Reactor A	Reactor B	
VSS (mg/l)	31500	29700	VSS IN SLUDGE BED
TSS (mg/l)	38900	35200	TSS IN SLUDGE BED
% volatile	81	84	
Volume (ml)	760	560	SLUDGE BED VOLUME
VSS (mg)	23940	16632	TOTAL VSS

DAY 140

	Reactor A	Reactor B	
VSS (mg/l)	46840	45620	VSS IN SLUDGE BED
TSS (mg/l)	56880	57790	TSS IN SLUDGE BED
% volatile	82.3	78.9	
Volume (ml)	1000	700	SLUDGE BED VOLUME
VSS (mg)	46840	31934	TOTAL VSS

Growth From day 69 to day 140

	Reactor A	Reactor B
VSS (mg)	22900	15302
COD Removed (mg)	833000	368000
Yield (mg VSS/mg COD)	0.027	0.042

Growth Yield was Used to Calculate VSS Between Days 69 and 140

	Reactor A VSS (mg)	Reactor B VSS (mg)
Day 69	24000	17000
Day 97	35000	24000
Average During SS#1	29500	20500

Since Reactor Volume was 2 Liters

Average VSS (mg/L)	14800	10300

Growth Yield was Used to Calculate VSS Between Days 69 and 140

	Reactor A VSS (mg)	Reactor B VSS (mg)
Day 105	35183	24192
Day 142	40418	29311
Average During SS#1	37801	26751

Since Reactor Volume was 2 Liters

Average VSS (mg/L)	18900	13400

APPENDIX G
CALCULATION OF F/M RATIO
SECOND STUDY PERIOD

Food/Microorganism (F/M) Ratio = g COD / g VSS / day

or

F/M Ratio = OLR (g COD/L/day) / VSS (g/L)

Steady-State Period #1

	Reactor A	Reactor B
Avg. OLR (g COD/L/day)	5.7	2.5
Avg. VSS (mg/L)	14800	10300
F/M Ratio (day^-1)	0.4	0.2

Steady-State Period #2

	Reactor A	Reactor B
Avg. OLR (g COD/L/day)	6.4	2.8
Avg. VSS (mg/L)	18900	13400
F/M Ratio (day^-1)	0.3	0.2

APPENDIX H
LAB-SCALE UASB REACTOR DATA

FIRST STUDY PERIOD DATA

Day	Effluent Soluble COD (mg/L) Reactor A	Effluent Soluble COD (mg/L) Reactor B	Unfiltered Feed COD (mg/L)
18	1270	800	9200
19	1400	1320	10000
26	1500	1680	10600
32	2120	2090	22000
39	2420	2610	
45	5000	4370	17400
53	4740	4000	19600
56	5170	6220	20400
59	4240	5200	21000
64	5040	8080	20800
70	6420	12100	
74	6270		
75			

Period	COD Loading (g COD/L/day) Reactor A	COD Loading (g COD/L/day) Reactor B
Day 1-30	0.5	0.5
Day 30-43	1	1
Day 44 - 55	3	3.5
Day 55 - 75	3	5.7

FIRST STUDY PERIOD DATA

	Alkalinity (mg/L as CaCO3)		
Day	Reactor A	Reactor B	Feed
16	950	720	
18	1270	1425	
20	1410	1500	
22	2240	2300	
23	2170	2430	
28	3040	3000	
33	3220	3000	2860
35	4060	3900	3110
40	4200	4230	
43	4420	4990	3100
48	5200	5140	3300
50	6110	6060	
56	7200	7180	
65	7030	7000	
87	8440	7280	

OTHER DATA

		Value (mg/L)		
Day	Measurement	Reactor A	Reactor B	Feed
51	TKN	1140	1200	2670
56	TKN	1740	1900	2900
69	TKN	1760	1710	1900
69	Ammonia	1650	1620	1570
76	Chloride	6850	6860	6600
76	Sulfate	314	227	323
80	Sodium	3810	3480	3470
80	Potassium	869	899	857
80	Calcium	437	513	524
80	Magnesium	272	285	333
80	Ammonia	1270	1600	2240
81	TSS	730	520	
81	VSS	370	380	
82	Chloride	6850	6860	6600
82	Sulfate	314	227	323

SECOND STUDY PERIOD DATA
COMPARISON OF REACTOR START-UP ALTERNATIVES
DAYS 1-45

Reactor Effluent = Soluble COD
Watstewater Feed = Unfiltered COD

	COD (mg/l)		
Day	Reactor A	Reactor B	Feed
8	1770	650	7120
12	1130	673	5660
18	850	493	4860
24	167	197	3780
29	258	137	
37	761	761	27400
41	1120	931	

Day 1.
Feed COD = 6,750 mg/L

Full-Strength Feed From
Day 30 on.

	ml biogas/g COD	
Day	Reactor A	Reactor B
4	114	398
8	90	386
11	130	529
13		392
18	463	782
22	301	574
24	278	611
30	230	511
37	474	471
40	523	551
41	488	509

SECOND STUDY PERIOD DATA
REACTOR OPERATION AFTER START-UP PERIOD
DAY 45 - DAY 151

		Effluent Soluble COD (mg/L)		Unfiltered
DATE	DAY	Reactor A	Reactor B	Feed COD (mg/L)
1/13	45	2020	1280	
1/17	49	1350	2504	24700
1/22	54	3040	2290	22600
1/28	60	3576	4389	23760
1/31	63	1470	1880	11840
2/5	68	828	745	10510
2/8	71	1170	924	11000
2/11	74	1030	945	12900
2/15	78	1120	997	10130
2/18	81	1140	1100	11600
2/21	84	903	763	6340
2/24	87	711	646	6950
2/27	90	1160	873	5380
3/2	93	644	604	5730
3/6	97	916	700	
3/10	101	993	715	23200
3/14	105	1210	977	24600
3/17	108	1260	1060	23800
3/20	111	1400	1130	24200
3/23	114	1225	938	
3/26	117	1150	1000	
3/30	121	1150	1010	
4/2	124	1230	1130	25300
4/5	127	1190	1110	
4/8	130	1190	1050	23300
4/11	133	970	1050	23900
4/14	136	1220	965	23400
4/17	139	1150	941	
4/20	142	1330	1120	
4/23	145	1370	1140	
4/26	148	1280	950	22300
4/29	151	1330	935	

DAY 68 - 97 STEADY-STATE PERIOD #1
DAY 105 - 151 STEADY-STATE PERIOD #2

	COD Loading (g COD/L/day)	
Period	Reactor A	Reactor B
Day 45 - 63	7.6	5.3
Day 63 - 97	5.7	2.5
Day 97 - 151	6.4	2.8

APPENDIX I
PILOT-SCALE UASB DATA

	COD (mg/L)		Reactor	VFA-COD	Volatile Fatty Acid (mg/L)	
Day	Soluble Effluent	Unfiltered Feed	pH	mg/L	Acetic	Propionic
41	9000	19664	7.22	5680	4770	290
52	12850	17959				
66	4820	15600	7.67	2980	1460	919
83	3420	18875		870	<100	580
98	2840	16100				
107			7.8			
150	5500	24300	7.5			
174	4340	19800	7.55	2330	1840	201
201	3660	24400	7.48	1940	1680	60

Period	Organic Loading (g COD/L/day)
Day 1 - 95	0.7
Day 95 - 1	Feed Interrupted
Day 142 -	2.7

APPENDIX J
PILOT-SCALE UBF REACTOR

	COD (mg/L)		Reactor	VFA-COD	Volatile Fatty Acid (mg/L)	
Day	Soluble Effluent	Unfiltered Feed	pH	mg/L	Acetic	Propionic
21	11080	21400				
27	9519	21900				
42	9859	19100				
55	8080	18500				
70	12706	22300				
80	12000	22500				
85	14100	23700				
102	9520	21300				
118	6330	14800				
141	8000	19700	7.25	4520	3860	180
152	8163	18000		4041	3080	435
175	7220	15600	7.22	3560	2350	653
186	7810	18900		5455	3200	1290
201	6580	16100				
207			7.7			
253	4230	24300	7.58			
277	10140	19800	7.2	7140	4020	1810
304	4300	24400	7.39	2070	1440	326

Period	Organic Loading (g COD/L/day)
Day 1 - 20	1.4
Day 20 - 1	3.5
Day 119 -	1.2
Day 200 -	Feed Interrupted
Day 247 -	2.3

APPENDIX K
BATCH TOXICITY ASSSAY DATA

Raw Data at pH 7.4

Bottle	Na	Total NH3	Unionized NH3	Specific Activity g COD/g VSS/day
1	2500	150	4.1	0.85
2	2500	1650	44.9	0.58
3	2500	2580	70.2	0.53
4	2500	3200	87.0	0.33
5	5000	150	4.1	0.76
6	5000	1560	42.4	0.44
7	5000	2450	66.6	0.40
8	5000	3200	87.0	0.32

Raw Data at pH 7.8

Bottle	Na	Total NH3	Unionized NH3	Specific Activity g COD/g VSS/day
1	2500	151	9.9	0.77
2	2500	773	50.7	0.51
3	2500	1445	94.7	0.42
4	2500	2360	154.7	0.21
5	5000	140	9.2	0.58
6	5000	801	52.5	0.44
7	5000	1530	100.3	0.37
8	5000	2330	152.7	0.16

Data was rearranged as follows to calculated percent inhibiiton
All percent inhibitions were calculated versus the activity at pH 7.4 and 2,500 mg/L sodium
Also, regression outputs for the activities and percent inhibition are shown below
Both regressions were versus unionized ammonia concentraiton

Low Sodium

	Specific Activity (g COD/g VSS/day)		Percent Inhibition	
Un-N	Measured	Regression	Measured	Regression
4.1	0.85	0.78	0.0%	0.0%
9.9	0.77	0.75	9.2%	11.4%
44.9	0.58	0.61	31.8%	26.6%
50.7	0.51	0.58	39.8%	31.5%
70.2	0.53	0.50	37.9%	41.1%
87.0	0.33	0.43	61.4%	49.4%
94.7	0.42	0.40	50.2%	53.2%
154.7	0.21	0.15	75.8%	82.7%

High Sodium

	Specific Activity (g COD/g VSS/day)		Percent Inhibition	
Un-N	Measured	Regression	Measured	Regression
4.1	0.76	0.64	0.0%	
9.2	0.58	0.62	23.3%	18.2%
42.4	0.44	0.51	41.8%	33.0%
52.5	0.44	0.48	41.6%	37.4%
66.6	0.40	0.43	47.4%	43.7%
87.0	0.32	0.36	58.2%	52.8%
100.3	0.37	0.31	50.8%	58.6%
152.7	0.16	0.14	78.7%	81.9%

APPENDIX L
AIR STRIPPING DATA

Experiments with diluted wastewater at pH 12.0.

Air Flow (cfm)	Liq. Flow (gpm/ft^2)	% red.	Cin/Cout	Liquid Temp. Deg. C. Influent	Effluent	Average	H	Air Temp Deg. C	P Drop (in W.C.)	S	Air/water ft^3/gal	NTU	HTU	Kl*a gal/ft^3/mi	Kl*a min^-1	Date	Run #
418	0.34	65.2	2.87	17.3	12.7	15.0	0.00043	16.8	0.78	2.25	696	1.28	4.67	0.07	0.58	3/11	3
749	0.46	77.1	4.37	19.2	14.5	16.9	0.00047	23	3.88	3.26	922	1.74	3.45	0.13	1.07	3/12	8
584	0.47	60.8	2.55	12.3	12.6	12.5	0.00038	16.6	1.6	2.01	703	1.15	5.23	0.09	0.72	3/12	5
568	0.47	67.7	3.10	20.9	15.1	18.0	0.00050	23	1.8	2.56	684	1.35	4.44	0.11	0.85	3/12	9
556	0.44	61.6	2.60	18.7	14	16.4	0.00046	19	1.6	2.47	715	1.13	5.33	0.08	0.66	3/11	2
433	0.48	61.9	2.62	21.3	15.6	18.5	0.00051	22.9	1.24	2.04	533	1.18	5.07	0.09	0.73	3/12	10
324	0.47	53.2	2.14	12.9	12.2	12.6	0.00038	16	0.84	1.12	390	1.07	5.59	0.08	0.67	3/12	6
318	0.45	56.5	2.30	20	14.5	17.3	0.00048	18.4	0.6	1.44	400	1.09	5.49	0.08	0.66	3/12	11
757	0.52	76.9	4.33	18	15.2	16.6	0.00047	25.5	3.98	2.88	824	1.77	3.39	0.15	1.23	3/12	7
757	0.55	72	3.57	18.3	12.5	15.4	0.00044	19	3.8	2.57	779	1.55	3.88	0.14	1.14	3/11	1
534	0.58	52.4	2.10	12.7	5.3	9.0	0.00032	13	1.73	1.25	521	1.00	6.03	0.10	0.77	4/5	5
418	0.56	57.4	2.35	16.9	11.9	14.4	0.00042	16	0.84	1.33	423	1.16	5.16	0.11	0.87	3/11	4
334	0.58	49.1	1.96	12.4	6.9	9.7	0.00033	15	0.073	0.81	326	1.10	5.47	0.11	0.85	4/5	6
702	0.78	71.3	3.48	19.9	15	17.5	0.00049	24.4	3.84	2.01	553	1.61	3.72	0.21	1.68	4/4	1
541	0.8	57.2	2.34	21.1	16.8	19.0	0.00052	24.4	1.71	1.50	383	1.11	5.43	0.15	1.18	4/4	2
440	0.75	60.2	2.51	21.05	16.3	18.7	0.00052	24.4	1.25	1.28	332	1.31	4.60	0.16	1.31	4/4	3
324	0.81	49.3	1.97	21.1	17.1	19.1	0.00053	24	0.6	0.89	226	1.03	5.80	0.14	1.12	4/4	4
753	1.01	53.3	2.14	14.4	7.7	11.1	0.00036	11.8	4.3	0.94	422	1.19	5.06	0.20	1.60	2/26	4
533	1.01	50.4	2.02	17.2	9.4	13.3	0.00040	16.3	1.68	0.73	299	1.27	4.71	0.21	1.72	4/5	7
520	0.99	48.7	1.95	17.5	9.4	13.5	0.00040	16.1		0.73	297	1.17	5.13	0.19	1.55	4/5	8

Experiment using 556 cfm air flowrate and 0.44 gpm/ft^2 liquid loading rate not used in data analysis since liquid loading rate was far below target loading rate.