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**SIMULTANEOUS REMOVAL OF COD AND AMMONIA
FROM HIGH-STRENGTH WASTEWATER
IN
A THREE-PHASE FLUIDIZED BED REACTOR**

By

Li Wan

B.Eng - Chemical Engineering

Northwest University, 1990, Xi'an, China

A thesis

presented to Ryerson University

in partial fulfillment of the requirements for the degree of

Master of Applied Science in

Chemical Engineering

Toronto, Ontario, Canada, 2006

Li Wan, 2006©

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ABSTRACT

Simultaneous Removal of COD and Ammonia from High-Strength Wastewater in a Three-Phase Fluidized Bed Reactor.

Li Wan

Master Applied science2006,

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A major challenge of Environmental Engineering is the efficient treatment of wastewater containing high concentrations of chemical oxygen demand (COD) and ammonia. This work addresses that challenge by designing, building, operating and developing a three-phase fluidized bed reactor (TFBR). The TFBR is designed to aerobically remove COD as well as ammonia from a 1,500 L/day of high-strength synthetic wastewater containing 5,000 mg/L COD and 230 mg/L ammonia in a short hydraulic residence time of 8 h. Experiments with water and air show that the TFBR provides complete fluidization with the designed liquid and gas flow rates. Furthermore, the oxygen transfer is at least an order magnitude higher than that obtained in previous studies. Under the designed condition, it is found that the TFBR removes 91.7% COD and 56.7% ammonia from the high-strength wastewater, and carries the effluent low concentration suspended solids at the same time. The ammonia removal is found to increase to 75% with a higher-than-design influent COD of 6,000 mg/L, which is responsible for more biomass available for ammonia utilization. The corresponding COD removal however decreases to 84.5%. The treatment carried out in this work is the first of its kind, and the developed TFBR is very promising because it offers effective removal of COD and ammonia from heavily polluted wastewaters in shorter residence times with reduced sludge generation.

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NOMENCLATURE

a	The ratio of oxygen transfer of tape water to wastewater
A	the cross section area of TFBR (m^2)
C_{BOD}	BOD (the BOD value at infinite time) (mg/L)
C_{DO}^*	Equilibrium concentration of dissolved oxygen (mg/L)
C_{DO}	Oxygen concentration at the bulk of the liquid phase (mg/L)
C_{Ni}	Ammonia concentration in influent (mg/L)
C_{No}	Ammonia concentration in effluent (mg/L)
C_0	Initial DO concentration (mg/L)
C_{UBOD}	Ultimate BOD (the BOD value at infinite time) (mg/L)
C_{si}	BOD concentration in influent (mg/L)
C_{so}	BOD concentration in effluent (mg/L)
d_b	Sauter mean diameter of air bubble (m)
D_L	Air diffusivity in water (m^2/s)
DO	Dissolved oxygen in water or wastewater (mg/L)
F_B	buoyancy force
F_D	Drag force
F_W	Gravity force
F	Normalized diameter of diffusers (m)
f	Safety factor

H	The height of the TFBR (m)
k	BOD digestion reaction constant (Day^{-1}), Ammonia oxidation Half reaction rate constant ($\text{mg}^{1/2}\text{L}^{1/2}/\text{h}$)
K_d	Decay or maintenance coefficient (Day^{-1})
K_{La}	Volumetric oxygen mass transfer coefficient (s^{-1})
K_s	Saturation constant (mg/L)
N_i	Influent ammonia concentration (mg/L)
N_o	Effluent ammonia concentration (mg/L)
P_A	pressure at diffuser (Pa)
P_G	The gas power input (w)
P_s	Pressure at water surface (Pa)
Q	Flow rate (m^3/s)
Q_m	Maximum specific substrate-utilization rate
R_{O_2}	Required oxygen (g/day)
S	BOD or substrate concentration (mg/L)
V_g	Gas superficial velocity (cm/s)
V_L	Liquid superficial velocity (cm/s)
V_R	Volume of the reactor (m^3)
V_S	Solid phase volume (m^3)
VSS	Volatile suspended solids (mg/L)

X Mass cell concentration (mg/L)

Y Yield coefficient

Greek symbols

ε Phase holdup

μ Viscosity (N.s/m²)

μ Specific growth rate of micro-organisms (day⁻¹)

ρ Density (kg/m³)

σ Surface Tension (N/s)

Subscripts

G(g) Gas phase

in Influent

L(l) Liquid phase

out Effluent

S Solid phase

Abbreviations

ASP Activated Sludge Process

BOD Biological oxygen demand

BOD₅ Biological oxygen demand for 5 days

COD Chemical oxygen demand (mg/L)

CSTR Continuous Stirred Tank Reactor

EAS Extended Aerated Sludge

OTE Oxygen transfer efficiency (%)

GVRD	Greater Vancouver Regional District
HDPE	High Density Poly Ethylene
HRT	Hydraulic Residence Time
LPM	Litter per minute
MBR	Membrane Bioreactor
RBC	Rotating Biological Contactor
SBR	Sequencing Batch Reactor
SCFM	Standard Cubic Feet per Minute
SMP	Soluble Microbial Products
SRT	Solids Retention Time
STP	Secondary Treatment Plant
TF	Trickling Filter
TFBR	Three-phase Fluidized Bed Reactor
TKN	Total Kjeldahl nitrogen
TOC	Total Organic Carbon
UF	Ultra Filtration
USEPA	U.S. Environmental Protection Agency
WTP	Wastewater Treatment Plant

1 INTRODUCTION

Although water amounts to about 70% of our blue planet, only 5% of the water can be used by human beings (Environment Canada, 2006). It is not surprising that to more than two billion people, fresh water is more valuable than gold (Mayell, 2003). Unfortunately, this limitation of usable water has been seriously aggravated by the rapid industrialization and population growth, which have engendered increased rates of wastewater generation. Therefore, wastewater treatment including reuse has become the top agenda for entire world. Our very sustenance depends on the development and utilization of efficient technologies capable of treating wastewaters as quickly as they are produced.

Wastewaters are released from all kinds of domestic and industrial activities. While the compositions of domestic wastewaters are relatively stable with consistent concentrations, those of industrial effluents vary with the associated production process. Nonetheless, almost all wastewaters carry carbonaceous and nitrogen pollutants, which are the major concerns because of their adverse impact on environment, society and economy (Table 1.1). The present work focuses on the treatment of high-strength wastewater that is wastewater having very high chemical oxygen demand (COD) as well as high ammonia concentrations. To this end, a large-scale fluidized bed bioreactor is designed, built, operated and evaluated for the simultaneous removal of COD and ammonia. It is the first time that wastewater treatment of this kind and at this scale has been carried out.

Table 1.1 The Ecological and Socioeconomic Effects of Carbonaceous and Nitrogen Pollutants (Environment Canada, 2001)

Pollutants	Ecological effects			Socioeconomic effects
	Water quality habitat	Plants	Animals	
Carbonaceous	<ul style="list-style-type: none"> • Reductions in dissolved oxygen in water column and sediments due to buildup of oxygen consuming material 		<ul style="list-style-type: none"> • Fish kills, loss of species, reduced biodiversity 	<ul style="list-style-type: none"> • Economic and recreational losses due to reduced fish abundance
Nitrogen	<ul style="list-style-type: none"> • Obnoxious growths of nuisance algae • Degradation of visible water quality (increased turbidity, green coloring) • Depletion of oxygen by decaying organic matter in sewage, industrial, aquacultural, and agricultural inputs and, in bottom waters, by decaying algae. 	<ul style="list-style-type: none"> • Increased and rooted aquatic plants • Changes in aquatic plant species composition 	<ul style="list-style-type: none"> • Increases in the abundance and changes in the composition of aquatic animals (invertebrates and fish) • Smothered lake bottoms, resulting in reduced organisms • Reduced survival of fish eggs due to oxygen depletion 	<ul style="list-style-type: none"> • Degraded shorelines and reduced recreational use due to nuisance algae • Increased costs for drinking water filtration and taste and odor problems • Poisoning of livestock and people by toxins produced by blue-green algae • Reduced aesthetics and recreational use • Cleanup and remediation costs of over fertilized waters • Building of effluent diversions, removal of applies to all aquatic ecosystem types • Economic losses due to fish kills and increased need to import fish — applies to all aquatic ecosystem types

1.1 Wastewaters with High-Strengths in Carbon and Ammonia Nitrogen

Pollutants

High strength COD and ammonia/nitrogen wastewaters are produced in a variety of industries, such as landfill leachates (Dopoulos et al., 1997, Ward et al., 2002), food processing (Demirel et al., 2005), and leather manufacture (Vidal et al., 2004). In addition, industrial streams with a high COD content can lead to highly loaded nitrogen streams if they are first treated in an anaerobic digester. Examples can be found in the pharmaceutical industry (Carrera et al., 2003), tanneries (Murat et al., 2003), slaughterhouse waste processing (Keller et al., 1997), potato processing industries, alcohol and starch production (Abeling and Seyfried, 1992), and formaldehyde production (Campos et al., 2003; Garrido et al., 2001).

Table 1.2 provides the concentrations of carbon and nitrogen in different industrial wastewaters. These data show that the industrial wastewaters with high BOD ($>1,000$ mg/L), and high ammonia concentration (>100 mg/L) are quite common. The BOD, COD and ammonia concentrations are not only different among different industrial effluents, but also dramatically diverse in a same kind of effluent even under same climate conditions. For example, the landfill leachates discharged in a municipal plant in Florida, US had dramatically diverse concentrations of both BOD, COD and ammonia (Ward et al., 2002). The efficient treatment of such wastewaters is a major challenge.

1.2 Environmental Regulations on Wastewater Releases

In North America, most municipalities regulate the limits of organic discharge. Table 1.3a shows the sewer discharge limits for the organic matter in terms of biological oxygen demand (BOD_5) set by various municipalities across Canada.

The municipalities apply strict penalties for non-compliance, and economically burdensome surcharge agreements as shown in Table 1.3b. In the year 2000, Toronto adopted one of the toughest sewer use bylaws, which focuses on pollution prevention and has strict limits on many pollutants. The limits include 18 prohibited classes of chemicals such as radioactive, acutely toxic, hazardous and ignitable wastes, fuels and pesticides, and 55 chemical concentration limits. Standards for discharge to a storm sewer are even more stringent. For a Toronto sewer user, a fine up to \$100,000 per day could be applied for first time offence. In 1998, failures to comply with the bylaw resulted in 52 prosecutions (Toronto, 2006).

Table 1.2 Concentrations of Carbon and Nitrogen in High-Strength Industrial Wastewaters

Wastewater type	COD (mg/L)	BOD ₅ (mg/L)	Nitrogen (mg/L)		References
			Mean	Range	
Detergent Wastewater					
	1,740-4,850	350-830		NH ₃ -NH ₄ ⁺ = 25-316	Dopoulos et al., 1997I
	1,070-2,584	89-204		NH ₃ -NH ₄ ⁺ = 350-830	Horan et al., 1997.
Landfill leachates	522-827	14-30	NH ₃ -NH ₄ ⁺ = 1250		
	242-440	13-21	NH ₃ -NH ₄ ⁺ = 280		
	902-1,616	55-77	NH ₃ -NH ₄ ⁺ = 218		
	416-1,208	13-66	NH ₃ -NH ₄ ⁺ = 410		
			NH ₃ -NH ₄ ⁺ = 380		
			NH ₃ -NH ₄ ⁺ = 1,040		
Resin wastewater	5,000-6,000			TKN= 1,400-1,800	Bae et al., 1997.
	352-1,593			TKN= 118-249	Cheng et al., 1996.
	1,190-3,220			TKN= 228-560	
Rubber factory Wastewater	5,119-18,059	1,463-7,600		NH ₃ -N=354-948	Rakkoed et al., 1999.
				TKN=455-1,686	
Creamery	2,000-6,000	1,200-4,000		TKN=50-60	
Milk product	980-7,500	680-4,500			
Mixed dairy	1,150-9,200			TKN= 14 -272	
Cheese whey	68,814		TKN=1,462		
Cheese	1,000-7,500	588-5,000			Demirel et al., 2005
Fresh milk	4,656				
Cheese	5,340				
Milk powder/	1,908				
Mixed dairy	63,100				

Table 1.2 Concentrations of Carbon and Nitrogen in High-Strength Industrial Wastewaters (continue)

Wastewater type	COD (mg/L)	BOD ₅ (mg/L)	Nitrogen (mg/L)		References
			Mean	Range	
Cheese whey	61,000		TKN=980		Demirel et al., 2005
Cheese			TKN=830		
Fluid milk	950-2,400	500-1,300			
Detergent Wastewater					Dopoulos et al., 1997
Silk and lycra wastewater	1515	590	TKN=164	NH ₃ -NH ₄ ⁺ =25-316	
Cane-molasses alcohol stillage wastewater	45,000	13,000	TKN=1,000		Stern et al., 1996
Leather wastewater treatment	300-1,400	N/A		TKN=50-200	Vidal et al., 2004
	24,089	7,081	TKN=18		
	1,412-1,454	855-965		TKN=311-369	
	800-1,213	510	TKN=66		
Thin fraction piggery manure	N/A	2,912	TKN=707		Hulle, 2004
	3,969	1,730	TKN=1,700		
	9,000-13,000	N/A		TKN= 3,100-4,300	
Slaughter house waste	1,400-2,400	N/A		TKN=170-200	
Starch production	3,000	990	TKN =1,060		
	5,000-1,000	2,000-5,000		TKN= 800-1,100	
Rejected water	232-12,587	81-750		TKN= 260-958	
	390-2,720	N/A		TKN= 943-1,513	

Table 1.3a The Comparison of Sanitary Sewer Discharge Limits for BOD in Canadian Cities (GVRD, 2002)

Cities	BOD (mg/L)
Calgary	1,200
Halifax	300
Red Deer	1,000
Toronto	300
Vancouver	500
Victoria	500
Windsor	400
Winnipeg	300

Table 1.3b Industrial Waste Surcharge Agreements in the City of Toronto
(Toronto, 2003)

Year	1999	2000	2001	2002	2003
Number of surcharge agreements	157	149	149	149	149
Surcharge invoice (in million \$)	8.7	9.8	10.3	8.9	8.5

However, most cities do not restrict the discharge of ammonia or ammonia-nitrogen, even though its concentration in the effluent of a secondary treatment plant is usually high enough (more than 5 mg/L) to kill fish in the receiving water bodies. Only Greater Vancouver Regional District specifies 24 mg/L of ammonia as recommended wastewater limit (GVRD, 2002). Ammonia was added to Canada Environment Protection Agency's (CEPA's) toxic substances list in December 2002. Great Lakes Sustainability Fund (2004) ranks ammonia as one of the two nutrients that needs to be removed from treated Sewage.

The toxicity to ammonia is attributable to the un-ionized form (NH_3), as opposed to the ionized form (NH_4^+). In general, more ammonia and greater toxicity exist at a higher pH condition. The relations between the lethal concentrations of mg/L to freshwater fish with pH under constant temperature of 30°C are listed in Table 1.4. These are concentrations at which

one can expect mortality from half of the animals exposed. (In the scientific literature, these are called LC50 values).

Table 1.4 The Lethal Ammonia Concentration to Fresh Water Fish
(At 30°C, USEPA, 1985)

pH	Duration	Lethal Ammonia Concentration (mg/L)	
		Total Ammonia	Un-ionized NH ₃
6.5	1-hr	14.3	0.036
	4-day	0.73	0.002
7.0	1-hr	11.6	0.093
	4-day	0.74	0.006
7.5	1-hr	7.3	0.181
	4-day	0.74	0.019
8.0	1-hr	3.5	0.26
	4-day	0.47	0.035
8.5	1-hr	1.3	0.26
	4-day	0.17	0.035

The direct and indirect economic loss caused by discharge of ammonia-nitrogen in aquatic ecosystem is huge. The occurrence of toxic algal blooms has forced the closure of many shellfish fisheries in Canada's coastal regions. In British Columbia, Canada, the combined value of all wild commercial shellfish fisheries are estimated at more than \$110 million in 1997. The closure of such a large number of harvesting zones represents a substantial loss in potential earnings to the British Columbia's shellfish industry and the communities depending on it (Environment Canada, 2001).

The above facts reveal the urgent necessity to enforce universally not only ammonia-nitrogen discharge limits but also develop and deploy low-cost, efficient wastewater treatment technologies to remove carbonaceous and ammonia pollutants from the wastewaters.

1.3 Applications of Wastewater Treatment Technologies

Wastewater treatment falls into primary, secondary and tertiary treatment. Primary treatment uses a physical and/or chemical process involving settlement of suspended solids. Secondary treatment includes the processes that employ aerobic or anaerobic microorganisms and result in decanted effluents and separated sludge. Tertiary treatment refers to any treatment process beyond secondary (biological treatments) treatment, and is usually utilized for the removal of nutrients, residual particulate matter, and disinfection. These tertiary treatments involve a variety of chemical methods and biological approaches to achieve treatment objectives.

Table 1.5 Canadian Municipal Wastewater Treatment Plant Overview
(Adopted from Environment Canada, 2003)

WWPT Type	Technology		Number of units
Primary treatment			90
Secondary	Conventional facultative lagoons		762
	Low-rate mechanical systems i.e., aerated lagoons and aerated facultative lagoons		593
	Higher-rate mechanical systems	Conventional activated sludge	212
		High-rate activated sludge	11
		Extended aeration activated sludge	157
		Contact stabilization activated sludge	22
		Oxidation ditch reactor	63
		Sequencing Batch Reactor(SBR)	23
		Membrane Bioreactor (MBR)	4
		Rotating Biological Contactor (RBC)	34
		Trickling filter	29
		Biological Aerated Filter (BAF)	9
Total			2,009

Note: Summary of all treatment plants serving populations more than 500 persons.

The most important treatment is the secondary treatment, which removes practically all the organic and inorganic solids remaining in primary effluent. However, despite the development of new technologies, secondary treatment plants are still dominated by conventional land consuming facultative and aerated lagoons, which are very slow and

inefficient. According to the year 2003 statistics on municipal wastewater treatment facilities (Table 1.5), almost 70% of 2,009 municipal wastewater treatment plants were conventional lagoon-based plants. Only less than 30% used advanced biological treatment. The technologies based on conventional activated sludge process occupy more than 70% of the installations. New technologies such as Rotating Biological Contactors (RBC), Sequencing Batch Reactors (SBR), Membrane Bioreactors (MBR), and Biological Aerated Filter (BAF) technologies play a minor role. (Environment Canada, 2003).

This situation is quite alarming since the conventional technologies, which are based on naturally occurring waste digestion process, are incapable to meet increasingly demanding challenges in the new millennium. Those technologies now need to be replaced by the advanced secondary treatment technologies, all of which are biological in nature.

Figure 1.1 Concentration-Flow Rate Phase Diagram for Application of Different Bioreactors (Nicoletta et al., 2000).

Figure 1.1 shows a general guideline to adopt a suitable secondary wastewater treatment technology. Each technology has its own advantages, and is suitable for special applications. The selection of the technology that is applicable for a specific wastewater mainly depends on the hydraulic and organic loads. From the figure, it can be seen that under high flow demand and lower organic loading conditions, static biofilm processes like trickling filter are

generally suitable. On the other hand, in case of high substrate loading and lower flow rate demand, the processes like Upflow Sludge Blanket (USB) are more appropriate. For intermediate operating condition, suspended floc and particle biofilm technologies, such as Biological Fluidized Bed (BFB), Biofilm Activated Sludge (BAS), Expanded Granular Sludge Bed (EGSB) and Ion Change (IC) are preferred.

Some secondary biological wastewater treatment processes remove organic matter as well as ammonia and nitrogen. The ammonia/nitrogen removal is a sequential two-step process -nitrification followed by denitrification. The capabilities of such processes are listed in table Table 1.6.

Table 1.6 Advanced Technologies with Nitrification Potential
(Yang and Hang, 1995)

Technology Name	BOD Removal	Nitrification	Denitrification
Rotating biological contactor (RBC)	x	x	x
Fluidized Beds (FB)	x	x	x
Activated Sludge (AS) at low organic load	x	x	
Extended Aerated Sludge (EAS)	x	x	
Sequencing Batch Rector (SBR)	x	x	
Trickling Filter (TF)	x	x	
Biofilter	x	x	

In terms of bacterial growth pattern, secondary biological wastewater treatment processes are classified into two categories: biological attached-growth (or biofilm), and suspended-growth technologies (Metcalf, 2004). Biofilm technologies have several advantages compared to conventional activated-sludge processes such as high biofilm surface area, high biomass concentration, and small footprints (Nicolella et al., 2000). The advantages and disadvantages of biofilm technologies comparing to suspended growth technologies are listed in Table 1.7.

Activated sludge processes that include Conventional Activated Sludge Process (CASP) and Extended Activated Sludge (EAS), SBR, RBC, and TFBR are among the advanced secondary treatment technologies, which are briefly described next.

Table 1.7 Main Advantages and Disadvantages of Biofilm Process on Granular Medium
(Adopted from Lazarova and Manem, 1994)

No.	Evaluation Conditions		Fixed Bed							Mobile Bed				
			Fixed bed	Floating bed	Fluidized bed			Inverse fluidized bed	Airlift	Turbulent bed	Stirred bed			
					2-Phase	3-phase								
1	High process efficiency		+	+		++	++	++	++	++	+	+		
2	High biomass concentration		++	++		+++	+	+++	++	++	+	++		
3	More active biomass	Thin biofilm					+	++	++	++	++	+		
		Better mass transfer					++	++	++	++	++	+		
4	Stable operation with variations in	concentration	+	+		++	++	++	++	++	++	++		
		Hydraulic loading	++	++						++	+	++		
		toxins	+	+		++	++	++	++	++	+	+		
		temperature	+	+		++	++	++	++	++	+	+		
5	Compact installation	Settling tank superfluous	+++	+++		+	++	+	+	+				
		Tall reactors	+	+		++	++	++	++	++	++			
6	Noise and odour removal		+			+	+	++	++	++	++			
1	Bed clogging	Frequent washing	---	---		-	--	-						
		Large volume of air and water	---	-		-								
2	Sophisticated construction and devices	Influent distribution	-	-		---	---	--						
		Phase separation				---	---		--					
		Oxygenation system	--	-		---		-	-	--	--	-		
3	Reduced filling rate					-	-		--	--	--	--		
4	High energy consumption		--	-		---		--	-	--	--	---		

Note: (+/-): condition partially fulfilled; (+ +/+--): condition fulfilled; (+ + +/---): condition completely fulfilled

Activated Sludge Process

The activated sludge process (ASP) is one of the most widely used secondary treatment processes. There are many modifications of ASP, but all consist essentially of an aerated biological reactor followed by a secondary clarifier. In the reactor, the suspended biomass degrades the influent organic material. The biomass is subsequently separated from the wastewater in the clarifier. Thickened biomass from the clarifier underflow is recycled to the aeration tank to maintain a desired biomass concentration. ASP is classified into Conventional Activated Sludge Process (CASP) and Extended Aerated Sludge process (EASP).

Figure 1.2 Activated sludge process

CASP typically uses a long rectangular aeration basin, with influent and return activated sludge introduced at one end of the basin, and the effluent removed at the other end. Aeration is typically supplied through air diffusers or mechanical aerators. The Mixed Liquor Suspended Solids (MLSS) concentration in the aeration tanks of a conventional ASP is typically within a range of 1,500 - 3,000 mg/L. CASP is well suited for treating low strength domestic waste. The conventional ASP typically removes 90 to 95% of the raw sewage BOD₅, and could be designed to nitrify year round with adequate oxygen transfer, aeration tank, and secondary clarifier capacity. The effluent from a conventional ASP treating municipal wastewater has typically

15 mg/L BOD₅, and 15 mg/L Total Suspended Solids (TSS). The effluent ammonia concentration in a conventional ASP with nitrification typically ranges from 1 - 5 mg/L. With chemical addition, total phosphorus effluent levels less than 1 mg/L are readily attained CASP (Richards XCG, 2004)

EASP(see Figure 1.2), is a variation of the activated sludge process in which there is no primary clarification, and uses longer hydraulic retention time (15 hours) in the aeration step compared to CASP. A longer Hydraulic Residence Time (HRT) provides greater process resilience to shock loading, and the ability to treat high flow rates of wastewater. EASP is preferred for the treatment of high-strength wastewater, and is typically implemented following preliminary treatment such as screening out grit removal. Designed to operate at solids retention time of 15 days or more, EASP may achieve complete nitrification year round.

Sequencing Batch Reactor

The sequencing batch reactor (SBR) is a fill-and draw activated sludge system for wastewater treatment (Figure 1.3). It has a mixed-culture of microorganisms in a suspended growth. Wastewater is added to a single “batch” reactor to remove undesirable components, and then discharged. Equalization, aeration, and clarification can all be achieved using a single batch reactor. To optimize the performance of the system, two or more batch reactors are used in a

Figure 1.3 Sequential Batch Reactor

predetermined sequence of operations. SBRs are uniquely suited for wastewater treatment applications characterized by low or intermittent flow conditions, and have been successfully used to treat both municipal and industrial wastewaters.

The SBR design uses a smaller footprint than the ASP due to the common tall design of the basins. The performance of SBRs is typically comparable to conventional activated sludge systems and depends on system design and site specific criteria. Depending on their mode of operation, SBRs can achieve good BOD and nutrient removal. For SBRs, the BOD removal efficiency is generally 85 - 95%. However, sophisticated controls and skilled labor are required.

Rotating Biological Contactor

A Rotating Biological Contactor (RBC) system (Figure 1.4) usually consists of a flow equalization/solids settling chamber, an RBC unit, and a final settling tank. The RBC unit is typically a once-through flow arrangement comprising multiple passes of disc bundles mounted on rotating shafts in series or parallel, and separated by baffles. The discs are covered by fixed biomass films that alternatively rotate through wastewater and into the air. Typically, about 40% of the discs are submerged in the wastewater. The air-driven submerged biological contactor (SBC) with 75-90% submergence represents a relatively new alternative. One option for this process is to submerge the RBC nearly completely and provide process air through aeration.

This process is referred to as a submerged biological contactor. For maximum efficiency, the RBC system should consist of 4 to 6 stages with baffles between each stage. The diameter of each disc depends upon the amount of media surface area required to treat the wastewater. The RBC should be housed to protect the biological growth from freezing temperatures and avoid excessive loss of heat from the wastewater.

Typically, the organic loading to the first stage standard density media is in the range of 1.7 - 3.0 kg total BOD₅ per square meter. Whether used in small or large facilities, the RBC process is capable to remove more than 85% of the biochemical oxygen demand (BOD) from domestic sewage.

Figure 1.4 Rotating Biological Contactor

Three-Phase Fluidized Bed Reactor (TFBR)

In a three-phase fluidized bed reactor (TFBR) system schematized in Figure 1.5, solids or media are suspended by the action of cocurrent streams of liquid and gas in a tubular reactor. The main component is the vertical column where microbes are immobilized onto individual biomedial media. The media most often used are either sand or granular activated carbon (GAC). The individual biomedial media of the fluidized media provide a vast amount of surface area for biofilm growth. Consequently, high concentration of biomass can be maintained suspended, and reactor sizes can be minimized.

The contaminated influent stream, as shown in Figure 1.5, is fed into the lower portion of the reactor. As the microbes grow on the fluidized biomedial media, the diameter of each particle increases and the effective density is reduced, resulting in a bed expansion. This means that the overgrowth of biofilms can lead to upward elutriation of biomedial media in a conventional fluidized bed or downward elutriation in case density of the media is lighter than that of liquid. This problem is dealt with by the use of a retaining grid at the top of the conventional bed or at the bottom of the

latter. Oxygen needed for the metabolism of the organic contaminants during aerobic operation is usually supplied by outside oxygenator or inside air diffusers. Separation of the excess biomass is commonly carried out either mechanically outside of the reactor or by scouring with air inside the reactor. In the fluidized state, the media provide a large specific surface for attached biological growth and allow biomass concentrations in the range $10\text{--}40\text{ kg m}^{-3}$ to develop. Consequently, more than 90% COD removal rate can be readily achieved.

Figure 1.5 Schematic TFBR Process in Wastewater Treatment

The advantage of high biomass concentration enables TFBR to treat high organic loading influent (more than $6\text{ kg COD/ m}^3\cdot\text{day}$), and long solid retention time allows the slow growth nitrifiers to fulfill ammonia removal. In addition, no mechanical moving parts and small footprints make TFBRs more competitive. Based upon these significant advantages, a TFRB in the present work is chosen as the technology to investigate the feasibility for simultaneous removal of COD and ammonia from high-strength wastewater.

1.4 Objective

The objective of this work is to design a three-phase fluidized bed bioreactor (TFBR) and use it to investigate the simultaneous removal of COD and ammonia nitrogen.

The followings are the milestones of this work

1. Design of a TFBR for the above mentioned purpose
2. Validation of the hydraulic parameters
3. Hydraulic testing with various combinations of superficial liquid and gas velocities
4. Measurement of oxygen mass transfer
5. Evaluation of the performance of the TFBR for simultaneous removal of COD and ammonia from high-strength wastewaters

2 LITERATURE REVIEW

From both research and industries, Three-phase Fluidized Bed Reactors (TFBRs) have received considerable attention due to their high efficiency, and low capital and operating costs. Although TFBRs have been used by Chemical Engineer in hydrocarbon processing since the 1970s, their use in wastewater treatment is more recent. Since 1980, more than 80 full-scale TFBRs have been commissioned in North America and Europe. About two-thirds of those are used for industrial wastewater treatment, and the remainder for municipal applications (Leslie et al., 1998). The applications of the TFBRs include aerobic carbon oxidation, nitrification, denitrification and anaerobic treatment. However, no large scale TFBRs have yet been used for simultaneous removal of carbon and ammonia/nitrogen from high-strength wastewater, which is the focus of the present work. Table 2.1 lists some of the applications of the TFBRs in North America and Europe.

2.1 Fluidization Mechanism in TFBRs

In a fluidized bed, there are three forces acting on a particle: the downward weight of particle F_w (including the weight of biofilm in case biofilm developed on particles), and both upward buoyancy force F_B and drag force F_D (Figure 2.1). The bed hydraulic characteristics are closely related with the densities of both particle and liquid, the superficial velocities of streams, etc.

For a fixed bed where density of particles (ρ_p) is larger than that of liquid (ρ_l), before liquid velocity reaches the minimum fluidizing velocity, the particles stay in a static condition in a fixed bed ($F_B + F_D < F_w$). Along with the increase of liquid superficial velocity (V_l), when the incipient velocity is reached, the fixed bed of particles exists in its loosest possible condition

without expansion. However, the fixed bed does not exert any loading on its original support as the particle weight is balanced by the buoyancy force and Drag force ($F_B + F_D = F_W$). At this point V_l is V_{mf} or minimum fluidizing velocity. When the liquid velocity increases beyond V_{mf} , the upward forces on the particles exceed the downward weight ($F_B + F_D > F_W$), and the particles in the bed get fluidized.

Figure 2.1 Forces on Particle Immersed in a Fluid

On the contrary, in a fluidized bed where the density of solid phase particle is less than that of liquid phase ($\rho_p < \rho_l$), the bed shows a quite different dynamic characteristics. The light particles consist of a floating bed before the gas phase reach a certain superficial velocity, as the sum of the buoyancy force and drag force is larger than the particle weight ($F_B + F_D > F_W$). Only when the superficial velocity of gas (V_g) increases to a certain point ($F_B + F_D \approx F_W$), the floating particles begin to get fluidized. This can be easily shown as a result of expressing F_B , F_D and F_W in terms of the densities, submerge volumes and drag coefficient.

At a given value of V_g , the minimum liquid fluidization velocity tends to zero, which means that the fluidization is determined by the gas. This phenomenon was explained by “pseudo-fluidized state theory” (Comte et al., 1997, Buffiere and Moletta, 1999) based on the assumption that the distribution of the solid within the bed depends on the difference between the density of the solid ρ_s and the overall density of the gas-liquid mixture ρ_m . A simple material balance shows that the density of the mixture can be expressed as equation 2-1:

Table 2.1 Applications of TFBRs in Wastewater Treatment in North America and Europe

Applications	Facility locations	System information	References
Aerobic carbonaceous oxidation of wastewater from coke-making operations	Algoma Steel Plant, Sault Ste, Ontario, Canada	Two reactors, each 65.6 m ² by 8.5 m high	Sutton and Mishra, 1990
Aerobic carbonaceous oxidation of wastewater from automotive manufacturing operation	General Motors Plant, Lansing, MI, USA	One reactor, 18.7 m ² by 6.7 m high	
Aerobic carbonaceous oxidation of wastewater from chemical operations.	Gnndsted Products Plant, Grindsted, Denmark	Two reactors, each 59.8 m ² by 6.1 m high	
Aerobic carbonaceous oxidation of wastewater from coke-making operations	Hoogovens Plant, IJmuiden, Holland	Two reactors, each 84.3 m ² by 8.7 m high	
Aerobic treatment of chemical plant wastewater for organics removal	Formosa, Point Comfort, TX, USA	Two reactors, each 23.6 m ² by 7.3 m high	Sutton and Mishra, 1993
Nitrogen removal by denitrification using methanol as carbon source	Himmerfjärden Bay, Stockholm, Sweden.	Four reactors. Each 38.5 m ² by 6 m high	Alf-Goran.1997
Reduction of Perchlorate from Contaminated ground water	Long Horn Army Ammunitions Plant, TX, USA	One reactors, diameter D=1.5 m height=6.4 m, installed in 2001	CEPA, 2003
Remediation of ground water to reduce high concentrations of perchlorate, chlorate and nitrate	GenCorp Aerojet facility, Rancho Cordova, CA, USA	Four Parallel TFBR, each D=4.2 m, height=6.7 m. built in 1998.	USEPA, 2005.
Anaerobic carbonaceous digestion for the effluent from sugars, starch and animal feeds wastes,	Casco Inc. London, Ontario, Canada	Two ONDEO Degrémont Anaflux @ anaerobic treatment reactors installed in 1998 and 2000.	Natural Resources Canada , 2006

$$\rho_m = \frac{\varepsilon_g \rho_g + \varepsilon_l \rho_l}{\varepsilon_g + \varepsilon_l} \cong \frac{\varepsilon_l \rho_l}{\varepsilon_g + \varepsilon_l} \quad (2-1)$$

In the above equation, ε is the dimensionless hold up of the gas or liquid phase. Subscript l = liquid phase, g = gas phase. It can be seen that as the gas velocity increases, ρ_m decreases. As soon as the biomedica become heavier than the gas-liquid mixture shows in equation 2-1, ($\rho_s > \rho_m$), they start to settle down until they meet a region with a higher amount of liquid when they become lighter than the liquid mixture ($\rho_s < \rho_m$), and consequently begin to move upwards in the bed. The direction of motion can also change due to the friction/collisions with other biomedica, and/or the column wall.

Different hydrodynamic properties of TFBRs with $\rho_s < \rho_l$ have been studied only recently, e.g. critical gas velocity for fluidization (Comte et al., 1997) and pseudo-fluid effect and particle motion mechanism (Buffière et al., 1999). These studies have shed light on various performance characteristics of the above TFBRs. With varying superficial gas and liquid velocities, U_g and U_l , typical changes in the flow regimes are shown in Figure 2.2.

Figure 2.2 Flow Regime Map Based on a Conventional Fluidized Bed where the Media can be Less Dense than the Liquid Phase (adapted from Buffière et al., 1999)

At low gas and liquid superficial velocities, the particle phase floats. As the superficial velocities of both gas phase and liquid phase increase to a certain range, the particle phase becomes a fluidized bed with dispersed bubbles. This fluidized bed develops into a fluidized bed with coalescing bubble if liquid phase and gas phase velocities increase further.

TFBRs can be classified into fifteen types (Fan, 1989), of which three types are used in wastewater treatment as shown in Figure 2.3. The most commonly used TFBR is the conventional E-I-a type, which has solids of density larger than that of liquid, and achieves fluidization using concurrent upward liquid and gas flows. In present study, the third type TFBR is developed for wastewater treatment.

Figure 2.3 Different TFBR Configurations (ρ_p : particle density, ρ_L : liquid density)

TFBRs with light media in wastewater treatment have numerous advantages. They can operate at low liquid superficial velocity, which is compatible with the wastewater treatment industry where long hydraulic residence time is necessary. When only gas is used as the fluidization agent, energy efficiency is significantly increased. Finally, the bottom section can be easily designed as a sludge settler and separator.

2.2 Carbon Oxidation and COD Removal in TFBRs

COD removal through a variety of technologies is the first target in a secondary biological treatment process. An advantage of TFBRs over other biological treatment methods is the high loading capacity, which is made possible by the adhesion and growth of microbiological organisms on the suspended medium. Characteristics of the wastewater, TFBR design, and TFBR operation are all factors in the COD removal. A TFBR can be operated either aerobically or anaerobically (Shrout, 1998). With respect to the performance, many controversial statements exist in literature. Tavares et al. (1995) claimed that the utilization of TFBR should be confined to the treatment of low COD content effluents, generally lower than 300 mg/L. Many studies, however have reported that COD removal rate in TFBR could be very high. Sokół (2003) has claimed that a removal of 90% or higher could be achieved with a COD values as high as 34,525 mg/L by a TFBR with light media as biofilm carrier. Table 2.2 shows the COD removal rates achieved by different TFBR processes.

2.3 Ammonia Removal in TFBRs

Ammonia nitrification in TFBRs depends on the kinetics, and temperature has a very strong influence on the nitrification rate, (Environment Canada, 2003). Some studies however indicate mass transfer as the controlling factor (Rostron et al., 2001). As seen in Table 2.3, the ammonia removal rates can reach $1.5 \text{ kg-N/m}^3\cdot\text{day}$ in TFBR process. This value is about three times higher than those obtained from conventional activated sludge process ($0.4\text{--}0.5 \text{ kg-N/m}^3\cdot\text{day}$). Such a high removal rate of $1.5 \text{ kg-N/m}^3\cdot\text{day}$ was obtained by Tsuneda et al. (2003). In their study, nitrifier granules worked as a solid phase after 300 days of operation. The seed sludge was acclimated in synthetic wastewater for 2 years before putting it into the TFBR. Another study declared an exceptional high ammonia removal rate of $2.5 \text{ kg-N/m}^3\cdot\text{day}$, which is one order higher than that achieved by conventional processes. Botrous (2003) applied a two-column system, where one column was TFBR with sand as biomass media, and the other column was an oxygenation column for the influent.

Table 2.2 COD Removal Rate in TFBRs (Shrout, 1998, Aysegül, 2001)

Reactor configuration	Loading rate (g/L-d)	Influent COD (mg/L)	COD removal (%)	wastewater	HRT (hr)	pH	Temp (°C)	Reference
Anaerobic	70	5,000	80	distillery	na		15	Hoist et al., 1997
Anaerobic/Aerobic	30	3,600	65	industrial	1.4	7	36	Heijnen et al., 1991
Anaerobic	16	5,200	94	ice-cream	8	7.1	15	Borja and Banks, 1995
Anaerobic	10	6,000	41	biological sludge	-		35	Poai-Varaldo et al. 1986
Anaerobic	10*	390	100	municipal	1.5	7.4	10	Sanz and Fdz, 1990
Aerobic	8	188	82	synthetic	0.5	7	29	Tavares et al., 1995
TFBR + oxygenator	3	830	80	dairy	24	na	na	al., 1986
Anaerobic zone/Aerobic zone	0.5	175	80	municipal	24	>7	na	Fdez-Polanco. et al, 1994
TFBR using GAC	14.4	4,350	97	synthetic	-	-	-	Aysegül, 2001

* Total COD: The COD value without filtration. na: Not available.

Table 2.3 The volumetric nitrification rates reached by different fixed film Processes
(Botrous, 2003; Tsuneda et al., 2003)

Nitrification Rate (kg NH₄⁺-N/m³· d)	Influent NH₃-N Concentration (mg/L)	Reactor Type	References
0.42	15.3-20.6	Nitrifying trickling filters	Anderson et al.1994
1.0	50-1,000	Draft tube fluidized bed	Chen et al., 1991
1.0	85-165	CIRCOX® Airlift reactor	Frijters et al., 2000
1.1	50	Circulating floating bed	Garrido et et al., 2000
1.2	50-100	Fluidized bed	Kloep et al., 2000
1.0-1.5	45	Biological aerated filter	Rogalla et al., 1990
1.4	30-100	Up-flow biological aerated filter	Han et al., 2001
1.5	Up to 500	TFBR using nitrifiers as solid phase	Tsuneda et al., 2003
2.5	up to 500	Fluidized bed with external aeration loop	Botrous, 2003

2.4 Simultaneous Removal of COD and Ammonia

In a combined carbon oxidation and ammonia nitrification process, ammonia nitrification is initially suppressed. Table 2.4 lists some of the studies, which have attempted to achieve simultaneous COD and ammonia removal by biofilm processes.

Carbonaceous oxidation occurs immediately after influents are fed into the TFBR, while ammonia nitrification begins quite slowly. Ammonia nitrification does not start until the organics concentration drops to a certain level (Tsuneda, 2004). Ros and Vrtorvsek (1998) found that the nitrification rate drops sharply at a COD loading rate higher than about 3 kg/m³·day in a combined aerobic-anaerobic two-phase (solid-liquid) fluidized bed reactor.

Table 2.4 Some Reported Simultaneous Carbon and Ammonia Removal Rate in Biofilm Processes

Reactor configuration	Influent Composition (mg/L)	Carbon/ NH ₃ Removal (%)	Operating conditions
Horan et al., 1997			
Lab scale Two TFBRs in series. V=1,500 cm ³ . Solid: granular activated carbon	COD=800–2,700 BOD=110 NH ₃ =220–800 Load=0.71 N/m ³ ·d	Removal rate: COD=60% BOD=100% Max.NH ₃ >=90%	The 1 st reactor for carbon removal, the 2nd for nitrification, PH=7.0–7.5 HRT=18 h, T=20°C, Pure oxygen supply.
Welander al, 1998			
Pilot scale Two-stage suspended carrier biofilm process. V1=5 m ³ V2=0.9 m ³ use membrane air diffuser	NH ₃ =400–800 COD=800–2,000 BOD ₇ =30–140	Max. Removal NH ₃ =576 g/day·m ³ COD = 20%	Nitrification in two parallel aerated reactors, filled to 60% (v/v) with two different media, surface areas: 210 and 390 m ² /m ³ HRT=3–4 Days T=10–26°C
Xing et al., 2000.			
Lab scale CSTR with solid media V=10 L Porous 15 mm cubes carrier	C/N ratio 100/40 150/20 200/20	TOC / NH ₃ 93.0 36.8 91.0 59.1 98.7 78.0	N is removed by both nitrification and denitrification in a single continuous TFBR system.
Rostron et al., 2001			
Lab scale CSTR, V=4L with Solids: Linpor: 0.6x0.6x0.6 cm Kaldnes: polyethylene d=1cm PVA: 0.8x0.8x0.8 cm	NH ₃ =500–1,000 COD=1,000–2,000	Nitrification rate: Kg-N/m ³ ·day biomass: 0.36 Linpor: 0.57 Kaldnes:0.53 PVA: 0.70	Reactor filled with different media by V/V= 25% T=16–25°C HRT=0.5–8 h
Tsuneda, 2004			
Lab scale V=3 L Solid: Cement ball d=0.21–0.25 mm	TOC =1480 NH ₃ =372 mg/L	TOC =80 NH ₃ =100 mg/L	Bach experiment. under biomass concentration MLSS=9840 mg/L T=20°C HRT=24 h PH=6.5–7

Besides the suppression effect of organic carbon compounds (COD) over ammonia nitrification, inorganic carbon also has a significant effect on the nitrification rate. According to Biesterfeld (2003), nitrification rate is impaired if inorganic carbon in wastewater is less than 40 mg/L CaCO_3 . It has been found that ammonia removal rate decreases as the COD/TKN ratio increases with the age of the sludge. Further, nitrifiers growth rate is not affected by the presence of heterotrophs (Sharma and Gupta, 2004). In addition to the suppression effect, the oxygen competition becomes another bottleneck for autotrophic nitrifiers, mainly due to its natural slow growth rate (Hirata et al., 2000). As for the nitrification rate, a study showed that in packed bed, it could reach 0.41 kg $\text{NH}_4\text{-N}/\text{m}^3\cdot\text{day}$ (Cecen et al., 1995), and even as high as 0.70 kg $\text{NH}_4\text{-N}/\text{m}^3\cdot\text{day}$ in a CSTR (Sousa et al., 1997). In a later study, Rostron et al. (2001) used different media as biofilm carrier to treat a simulated landfill leachate influent (COD=533-1,067 mg/L, NH_3 = 500-800 mg/L). They found that the reactor lost 35% of its nitrification rate when 533 mg/L COD was fed.

Nitrification rates in a simultaneous carbon oxidation and ammonia nitrification in TFBR are much lower than those obtained in a nitrification only process. Horan et al. (1997) achieved a nitrification rate of 0.63 kg $\text{NH}_4^+\text{-N}/\text{m}^3\cdot\text{day}$ in a system consisting of two TFBR systems in series, in which one was for carbon oxidation and the other for nitrification. In another study by Welander et al. (1998), the system was configured by two bench scale FB reactors, in which one reactor worked for carbon oxidation and nitrification, the other worked for denitrification. The nitrification rate reached 0.29 kg N/ $\text{m}^3\cdot\text{day}$ with 90% of total ammonia nitrogen (TAN) removal rate under a long HRT (3 days), but only a 20% elimination rate of COD was obtained.

The present work targets to treat high-strength synthetic wastewater containing 5,000 mg/L or more COD and 230 mg/L ammonia at the same time. A TFBR is designed and built for this purpose. To support the biomass, the developed TFBR uses a medium that is lighter than the wastewater.

2.5 Biofilm Support Media in TFBRs

In general, the characteristics of the media are closely related to the biofilm immobilization, mass transfer as well as biological kinetics. A thinner biomass encourages endogenous respiration, and minimizes excess sludge production. Removal efficiency is related to the biofilm thickness.

However, if the biofilm is too thick, it will limit the diffusion of substrate, nutrients or oxygen within the film (Safferman and Bishop, 1997). The effect of different parameters on the properties of biofilms is summarized in Table 2.5.

Table 2.5 Operational Parameters Effects on Biofilm (Turan et al., 1996)

Control Parameter	Biofilm Thickness	Biofilm Density	Biofilm Activity	Reference
increase detachment rate	decreases	increases	unchanged	Rittmann et al., 1992
increase substrate flux	increases	increases	increases	Rittmann et al., 1992
increase liquid up flow velocity	unchanged	decreases	unchanged	Araki and Harada, 1994
increase gas up flow velocity	decreases	not examined	increases	Tavares et al., 1995

Sand and glass beads are often utilized due to their simplicity in structure, availability and low cost. However, because of their high density, their application is limited in case longer hydraulic residence time is required, such as in TFBRs for nitrification reactions. At the same time, with those media, more energy consumption is inevitable for achieving a good fluidization. Therefore extensive research has been conducted over a variety of media, such as various types of sands (Wang et al., 1999), granular activated carbon (GAC) (Horan et al., 1997; Pala, 2001), cement ball (Hirata et al., 2000; Tsuneda, 2004), and glassy coke (Dempsey et al., 2005). Some novel media made of polymer have been developed (Sousa et al., 1997) such as polypropylene hollow particle (Sokół, 2003), Linpor polyurethane (foam chips), and hydro gel matrix of polyvinyl alcohol (PVA) obtained by freezing method (Rostron et al., 2001). Experimental results have shown that the PVA media have the highest performance for simultaneous carbon and ammonia oxidation in a lab scale CSTR. However, it is difficult to use them as industrial application due to their complicated manufacturing processes and high costs. Among commercial plastic biomedias, KMT media is extensively used in research (Dalentoft and Thulin, 1997; Sokół, 2003) and industry (AWMC, 1999). The highest COD removal rate (approximately 90%) using KMT media in a TFBR was achieved at a particle loading ratio (bulk media volume to reactor volume) of 55% in the treatment of refinery wastewater (Sokół, 2003).

3

TFBR DESIGN AND EXPERIMENTAL SETUP

This chapter presents the design of the three-phase fluidized bed aerobic bioreactor (TFBR) as well as the accompanying experimental setup and protocol used in this work. Section 3.1 presents the design of the reactor and arrangement of its various components. Section 3.2 includes the tests carried out on the TFBR to determine its hydrodynamic characteristics, oxygen transfer capability and DO profiles. Section 3.3 documents the developed experimental setup, which is used for the simultaneous removal of COD and ammonia from high-strength wastewater.

3.1 TFBR Design

A TFBR was designed and build to study the simultaneous removal of COD and ammonia nitrogen. Table 3.1 shows the completed TFBR system installed in the Water and Wastewater Treatment Technologies Laboratory, Department of Chemical Engineering, Ryerson University.

The scale of the TFBR was carefully selected for future potential industrial applications. Table 3.1 lists the design requirements and conditions for the TFBR.

3.1.1 Design Parameters

The hydraulic residence time (HRT) and air supply rate were chosen as the primary parameters for both the mechanical design of the TFBR, and the selection of air diffuser configuration. Since COD and ammonia need to be simultaneously removed from the wastewater the HRT estimation is based on the longer of times required for BOD removal and nitrification.

Table 3.1 Design Requirements and Conditions

Design requirements			
Treatment capacity	1,500 L/day (1.04 L/min)		
Pollutant	Influent	Effluent	Removal Efficiency
COD	5,000 mg/L	500 mg/L	90%
Ammonia-nitrogen	200 mg/L	10 mg/L	95–98%
Design conditions			
Compressed air	$P_{\max}=100$ psi		
Free space height	3,100 mm from floor to ceiling		
Wastewater feed tank	4.0 m ³ , shared by TFBR and RBC		
Tap water supplying capacity	2 GPM

Front view

Back view

Figure 3.1 The TFBR Bioreactor

Reaction Time Determination

The time required for BOD removal was determined with the help of the following equation based on the first order kinetics:

$$C_{\text{BOD}} = C_{\text{uBOD}}(1 - e^{-kt}) \quad (3-1)$$

where C_{BOD} is the BOD (mg/L) after time t , C_{uBOD} is the BOD value after infinite time (mg/L), and k is first order reaction constant (day^{-1}). Sugar was the source of BOD in synthetic wastewater used in this work. For sugar solutions, BOD_5 is 60–70% of the COD (Soft drink plant, 2005). The BOD_5/COD ratio was assumed at 60%, With $C_{\text{uBOD}} = 300 \text{ mg/L}$, $k = 0.23 \text{ day}^{-1}$ the time required for 90% BOD removal is 0.2 day.

The time required for ammonia nitrification was determined on the basis of the following half rate model

$$\frac{dC_N}{dt} = -kC_N^{1/2} \quad (3-2)$$

where reaction constant $k = 10.96 \text{ mg}^{1/2}\text{L}^{1/2}/\text{h}$, and C_N is ammonium-nitrogen concentration in mg/L.

For nitrification in biological fluidized beds, (Environment Canada, 2003) recommends the above equation with a k value of $10.96 \text{ mg}^{1/2}/\text{L}^{1/2}\cdot\text{h}$ (Bolanos, 2000). With this value, the time required for 95% nitrification is 0.5 h. Therefore, the conservative estimate for the HRT is 0.2 day times a safety factor. A safety factor in the range of 1.5–3 is commonly used for fluidized beds (Environment Canada, 2003). A safety factor of 1.5 was selected, which yielded the HRT of 8 hours.

Table 3.2 Dimensions of the Designed TFBR

Dimension	Size
Number of Sections	3
Column height	2.5 m
Column diameter	60.5 cm
Stand elevation	35 cm
Free space (over head)	50 mm
Gross volume	0.71 m ³

Based on this HRT of 8 h, the required treatment capacity of 1500 L/day, the availability of lab space and fabrication simplicity, a cylindrical reactor was designed with the dimensions that are listed in Table 3.2.

Oxygen Requirement

Like substrate concentration, dissolved oxygen (DO) concentration is also a key kinetic parameter effecting aerobic bioreaction rate. Total oxygen demand includes the demands for both carbonaceous oxidation and ammonia nitrification. The oxygen required for carbonaceous oxidation was deduced from the difference between influent and effluent BOD concentrations, multiplied by the oxygen consumption coefficient. (Water Pollution Control Federation, 1983)

$$R_{o_2} = Q(C_{S_i} - C_{S_o}) * f \quad (3-3)$$

where R_{O_2} is required oxygen for carbonaceous oxidation (g/day), Q is the influent water or wastewater flow rate (m³/d), C_{S_i} and C_{S_o} are the BOD concentrations in the influent and the effluent respectively (mg/L), and f is the factor for oxygen consumption adjustment (1.2–1.3).

Based on ammonia oxidation equations, for each gram of ammonia, 4.57 g oxygen is required out of which 3.43 g oxygen is used for nitrite and the rest for nitrate production (Metcalf, 2003). This requirement is for complete oxidation of ammonia. Mathematically,

$$R_N = 4.57Q(C_{N_i} - C_{N_o}) \quad (3-4)$$

where C_{N_i} and C_{N_o} are the ammonia concentration in the influent and effluent respectively. Thus, the total oxygen requirement for carbonaceous oxidation and ammonia nitrification is given by

$$R_{total} = \underbrace{Q(C_{S_i} - C_{S_o})f}_{\text{Carbon oxidation}} + \underbrace{4.57Q(C_{N_i} - C_{N_o})}_{\text{Nitrification}} \quad (3-5)$$

Using this equation, a total oxygen demand of 6.2 kg/day was estimated for the wastewater treatment experiments.

Oxygen Transfer Efficiency

High oxygen transfer efficiency (OTE) is crucial for high performance of a TFBR. For this purpose, disc and tube type fine bubble membrane air diffusers from FlexAir™ were selected. The diffusers have fine pores on flexible membranes, which supply up to 4 SCFM/disc of air. The disc and tube diffusers used in this work are illustrated in Figure 3.2 and Figure 3.3. Their OTE curves are attached in Appendix C.

Figure 3.2 The FlexAir™ Disc air Diffuser

Figure 3.3 Original T-series and Modified Tube-Shaped Membrane Diffuser

USEPA (1993) recommends using one-half of the clean water transfer rate for the design for biological wastewater treatment processes. Accordingly, three pieces of 9" disc type air diffusers were selected for primary aeration, and installed at the bottom of the TFBR. Three tube type diffusers were selected for secondary aeration, and placed in the middle of the TFBR. This arrangement provides up to 12.1 kg/day oxygen demand, which is almost twice of what is

required. A reason for this over-design was the consideration of very high loadings for future research. Further details of diffuser parameters are provided in Table 3.3.

Table 3.3 The Parameters of the Diffusers

Primary aeration	
Model	9" High Capacity disc type
Diameter (mm)	276.8
Area (m ²)	0.0381
Depth of submerge (m)	2.5
Design capacity (m ³ /hr)	0.8–8.5
numbers of diffusers	3
Air flow rate per diffuser (Sm ³ /hr)	3.0
Estimated efficiency (%)	0.14
Transferred oxygen (Kg)	9.0 kg
Secondary aeration	
Model	62 x 610 T-series tube type
Length x Diameter (mm)	66 x 610
Design capacity (m ³ /hr)	2–8
Number of diffuser	1 (modified into 3)
Air flow rate (Sm ³ /hr.diffuser)	4.0
Estimated efficiency (%)	0.11
Transferred oxygen is (Kg/day)	3.1
Total designed aeration capacity	
Total transferred oxygen (Kg/day)	12.1
the average oxygen transfer efficient	12 %
Total air supplying is (Sm ³ /hr)	13.0

3.1.2 Bio Media

The media in the TFBR should enable stable fluidization with liquid velocity that could vary from the minimum fluidization velocity to the transportation velocity of media. In this study, the liquid superficial velocity is around 0.003 cm/s, which is far below the minimum fluidization velocities of most conventional solid media such as sand, lava rock, and activated carbon. This

situation requires a media that lighter than the liquid phase. Hydroxyl-Pac media was selected as the media for this study. The media provides a large protected surface area for the growth of attached biofilm, and has been used to degrade organic constituents in municipal, industrial and domestic wastewaters. The media can be used in aerobic Fixed-Film Reactors such as TFBRs, Return Activated Sludge Systems, and Anoxic Fluidized Bed reactors (Hydroxyl, 2005). The media is made of two concentric cylinders connected by eight equally spaced radial vanes. Four of these vanes protrude from the inner cylinder toward the center of the element. Figure 3.4 and Table 3.4 show the structure and the physical properties of the media.

Figure 3.4 The Structure of Hydroxyl-Pac Media

Table 3.4 The Physical Characteristics of Hydroxyl-Pac Media (Hydroxyl, 2005)

Parameters	Description
Dimensions	Diameter 22 mm; height 15 mm
Material	high-density polyethylene
Density	0.95 g/cm ³ , the bulk density 113 kg/ m ³
Designed filling ratio	50%
Active specific surface area	Total surface area 588 m ² /m ³ , protected internal surface area will be approximately 402 m ² /m ³
Single medium surface area	Each medium approximately 34.92 cm ² /matrix measured value
Volume ratio	Ratio of medium material volume to volume media occupied is 13.8% (measured)

Hydroxyl-Pac Media has numerous advantages. Lighter density allows lower liquid superficial velocity. Hence, it is suitable for longer HRT, and reduces pumping energy. The media is made from polyethylene and is favorable for micro-organisms to grow and attach. It also has a large

protected specific surface area, as much as approximately $402 \text{ m}^2/\text{m}^3$ with a total surface area of $588 \text{ m}^2/\text{m}^3$. Its structure is open for the passage of water and gas from both ends that facilitates the transfer of substrate and oxygen, and minimizes the risk for “dead zones”. Due to the relatively large size of the media, the media can interact with several air bubbles at a time, and does not simply follow the water movement in the reactor. The media can be used for influents of high solids concentration, as it is not particularly prone to clogging. This relevant large size of the media also allows retaining the carriers in TFBR, and there is no need to employ separation and recycling units in the system.

Sokół (2003) has carried out research work upon the optimum filling ratio of KMT media in fluidized bed for COD removal. In his study, a highest COD removal rate (approximately 90%) was achieved by applying KMT media at particle loading ratio (bulk media volume to reactor volume) of 55%. Since Hydroxyl-Pack media have a similar structure and size, but higher surface area than KMD media do, a 0.5 of solids hold up is chosen in this design.

3.1.3 Construction of the TFBR

The designed TFBR consists of a cylindrical column with inside diameter of 0.605 m and total height of 2.9 m, in which 2.6 m is the effective reactor height. To allow better visual observation, clear poly (vinyl) chloride (PVC) was used as the material of construction for the TFBR column. For easy fabrication and convenient maintenance, the bottom, middle and top sections of the column were built separately and flanged together to form the complete column. The structural details of the TFBR are provided in the Figure 3.5 and 3.6. The design parameters of the TFBR are listed in Table 3.6. Calculations sheets are attached in Appendix 2.

Bottom Section of the TFBR

The bottom section in the TFBR is the most important part, as both the air distributor and influent distributor are installed in this part. The bottom section is made from 200 mm high clear PVC with a circular PVC base plate. Three pieces of 9” FlexAir™ fine bubble membrane disc air diffusers were mounted on the bottom plate using 3/4” NPT threaded connections. Diffusers are placed at equal distance from the center to facilitate equal distribution. Outside the reactor, these diffusers are connected to central air supply by a specially designed rotating connection. The connection makes it easy to orient the main air supply pipe around the union. The details of the bottom section are shown in Figure 3.7.

Table 3.5 Complete Design Parameters

1. TFBR Dimensions		
Height (m)	2.90	from floor level
Diameter (m)	0.60	
Fluidized Bed height (m)	2.50	
Total volume (m ³)	0.71	
Effective Reactor volume (m ³)	0.50	
Residence time (hr)	8.0	
Number of Disc type air diffusers	3	
Number of tube type air diffusers	3	
2. Oxygen Transfer Parameters		
Air flow rate (l/min)	200	
Air superficial velocity (cm/s)	1.2	
Air hold up (%)	15	In lower section
Air hold up (%)	20	In upper section
Router mean bubble diameter (mm)	0.68	
Oxygen mass transfer coefficient (1/s)	0.023	Calculated value
Oxygen mass transfer efficiency (%)	14.5	Based on the product OTE curve
Oxygen concentration (mg/l)	9	Calculated value
3. Biofilm Support Media		
Media Density (kg/m ³)	0.95	
Filling ratio (%)	50	
Total specific surface area (m ²)	215	
Protected surface area (m ²)	145	
4. Hydraulic and Organic loading		
Wastewater flow rate (L/min)	1.04	
Ammoni nitrogen loading (kg-N/m ³ ·day)	0.3	
COD loading (kg COD/m ³ ·day)	10.55

Figure 3.6 Details and Perpendicular Cross Section Structure of the TFBR

Figure 3.7 Top View of Bottom Section of TFBR

In addition to the air diffusers, influent distributors are provided in the bottom section of the TFBR. Influent distributors consist of three trapezoid-shaped liquid spray chambers. Each chamber has two perpendicular faces. On each face, there are two rows of 2 mm diameter holes with five holes on the first row and six holes on the second row. These holes allow liquid to enter into the TFBR in a horizontal direction. During the operation, influent wastewater spray exits from these three chambers, and mixes at nearly 90° with the upward flow of fine air bubbles (Figure 3.8).

Figure 3.8 Liquid Phase and Gas Phase Streams in the Bottom Section of TFBR

The perpendicular mixing favors oxygen mass transfer from the gas phase to the water phase. Moreover, the transverse liquid flow prevents the biomedica from stacking, dead zones in the flow region, and the sludge sedimentation on the surface of the liquid spray chamber.

Under the bottom section, there are three influent feed connections, and three branches of compressed air pipes. The sludge discharge and drain line is located at the center of the bottom plate.

A stainless wire mesh protects the membrane surface of the air diffuser from the abrasion of the biomedica, and prevents them going down the drain. The mesh is installed 10 mm above the air diffusers' surface to support the biomedica in non-operational period. The bottom section is designed so that it can be disconnected from the incoming pipes (Figure 3.9) by uncoupling unions at the horizontal section. Hence, during the maintenance, the bottom section can be removed without dismantling the other two top sections of the TFBR.

Figure 3.9 Bottom View of TFBR Bottom Section

Middle Section of the TFBR

The middle section of the reactor consists of two cylindrical sections to facilitate the biomedica loading, unloading and reactor maintenance. Two hand-holes for biomedica loading and unloading are installed on the upper section and lower section, respectively. These two hand holes both have a diameter of 250 mm. The position of the biomedica loading hand-hole can allow up to 70% of the reactor volume to be filled, if required. This feature is very desirable, as some studies (AWMC, 1999, Sokół.2003) recommend 50–67% of biomedica loading to achieve good performance. Those studies have used biomedica similar to the one used in this work. The biomedica-discharging hand-hole is located just above the bottom section of the reactor. Both hand-holes stay closed when the TFBR is in operation. A steel mesh is provided at the top of the column to restrict biomedica entrainment in the TFBR, and allow only effluent to flow out. Three tube type air diffusers are installed in the middle section. Air is supplied through a semi-circular distribution loop, and connected to the section using three unions. The diffusers are connected to this unions inside the section. In case of maintenance, the diffusers are accessible through the hand holes. The structure is shown in Figure 3.10.

Figure 3.10 The Structure of Middle Section of TFBR

Top Section of the TFBR

The top section of the TFBR (Figure 3.11) consists of an octagonal effluent chamber, demister and an off gases vent pipe. The chamber is 200 mm high, and 1300 mm diameter, and allows air to be separated from foam before leaving the TFBR. A high density polyethylene (HDPE) plastic grid is used at the top of the reactor to prevent biomedica from being entrained with the effluent. Two 1½” pipes for effluent discharge and drain are connected to the bottom of the effluent chamber. This chamber is equipped with a sample port just above the reactor column to collect effluent sample. Over the effluent chamber is a 150mm high cone-shaped off-gas vent hood. A demister is also installed between the effluent chamber and vent hood to entrap any water and remove any foam in the air before venting to the atmosphere.

Top view

Front View

Figure 3.11 Top Section Structure of TFBR

For the purpose of emergency discharge and effluent recirculation, a recirculation loop is installed in the TFBR. The loop consists of a 700 L recirculation tank and a recirculation diaphragm pump of 20 L/min capacity. The pump can provide the maximum of 20 times recirculation rate at the influent feed rate of 1.04 L/min. Another function of the recirculation loop is to provide pre-oxygenation during the TFBR start up if at all needed.

3.1.4 Sampling Ports

The TFBR has 12 sample ports and valves to allow wastewater sampling. Ten sampling ports are located along the axial direction of the TFBR as specified in Table 3.6. Sampling Port 0 and 12 are located respectively on the inlet and outlet of the TFBR.

Table 3.6 The axial location of ten sampling ports in the TFBR

Sampling Port	Distance from the Bottom Diffusers (cm)	Sampling Port	Distance from the Bottom Diffusers (cm)
1	1	7	125
2	10	8	155
3	25	9	185
4	45	10	215
5	65	11	245
6	95	12	Out let line

3.2 The Experimental Setup for Hydraulic and DO Tests

After the construction of the TFBR, tests were performed to determine (i) fluidization characteristics, (ii) oxygen transfer rate, and (iii) DO axial profiles.

3.2.1 Determination of Fluidization Characteristics

To determine the fluidization of the TFBR, it was separately operated with biomedica filling ratios of 40%, 50% and 60%. Different water and air superficial velocities were used as shown in Table 3.7

Table 3.7 The Combinations of Velocities Used for Fluidization Tests

Phases	Designed Value		Test Value	
	Flow rate (m ³ /hr)	Superficial Velocity (cm/s)	Flow Rate (m ³ /hr)	Superficial Velocity (cm/s)
Liquid	0.06	0.006	0 – 0.24	0 – 0.20
Gas	13.0	1.32	3.4 – 34.0	0.3 – 3.3
Solid filling ratio: 40%, 50%, 60%.				

Tap water was used as a liquid phase and compressed air as the gas phase. After loading the

biomedia into the TFBR, tap water and compressed air were fed into the TFBR. At a given water flow rate, the gas flow rate was increased step by step. At each combinations of the liquid and gas flow rates, the dead zone height was measured either at the top or at the bottom section of the TFBR.

3.2.2 Determination of Oxygen Transfer Rate and DO Axial Profiles

The DO profiles were examined using the design value of biomedia filling ratio, i.e. 50% and different combinations of gas and liquid superficial velocities as shown in Table 3.8.

Table 3.8 The Combination of Gas and Liquid Velocities Used for DO Profiling

Phases	Designed value		Test value	
	Flow rate (m ³ /hr)	Superficial velocity (cm/s)	Flow rate (m ³ /hr)	Superficial velocity (cm/s)
Liquid	0.06	0.006	0 – 2.1	0 – 0.20
Gas	13.0	1.32	3.4 – 34.0	0.3 – 3.3
Solid hold up: 50%.				

A Hach HQ10 portable DO meter was used to analyze the DO concentrations (Figure 3.12). The DO sensor is factory pre-calibrated and no additional user-calibration required for 1-year lifetime. There is no requirement of warm-up period for the probe polarization. This probe is just required to plug and the meter is ready for use. Specifications are listed in Appendix D1.

Figure 3.12 Hach HQ10 DO Meter

Deaerated water was used to determine oxygen transfer and DO axial profiles. A vacuum system (Figure 3.13)) was used to remove dissolved oxygen from tap water, which was then used as the influent to the TFBR. The DO in the deaerated water was around 0.8-2.0 mg/L. The vacuum system consists of a vacuum column, vacuum pump, and deaerated water transport pump. The vacuum column is a cylindrical column consisting of four sections. The bottom section is a reservoir in which deaerated water is collected and pumped out when required. Two middle sections are packed beds using Tri-Pack plastic packings. Tri-Pack plastic packings are hollow spherical packing media. In the upper packed bed, 25 mm and 50 mm diameter packings are used, whereas only 50 mm diameter packings are used in lower packed bed. To achieve a better degasification performance, water coming from upper bed was redistributed over the lower bed. The top section is a demister, which is provided to entrap the water drops. The vacuum column specifications are shown in Appendix D2.

Figure 3.13 The Vacuum System

When tap water was fed in the vacuum column and distributed by the 16 spray nozzles that arranged above the upper packed bed, a thin water film formed on the packing material resulting in a large mass transfer interfacial area between air phase and the water phase. Consequently, this film facilitated the oxygen transfer from liquid phase to the gas phase. Therefore, when water flowed from top to the bottom in the vacuum column, the dissolved oxygen decreased gradually to a very low level (less than 2 mg/L).

An oil ring vacuum pump connected to the vacuum column provided vacuum in the system. The gauge vacuum in the vacuum column can drop to a pressure as low as the designated value of 27.5 inch Hg. The specifications of vacuum pump are listed in Appendix D3. A schematic diagram for oxygen transfer and DO profile tests is shown in Figure 3.14.

3.3 The Experimental Setup for Wastewater Treatment

In this work, synthetic wastewater was used to simulate wastewater with high COD (around 5,000 mg/L), and high ammonia nitrogen (approximately 250 mg/L) concentrations. The wastewater was treated by the newly designed TFBR. The chemicals and nutrients (

) were first dissolved in a 120 L chemical dosage tank. This concentrated liquid was then was into the feed tank. At the same time, fresh cold and hot tap water was fed into the feed tank to obtain a synthetic wastewater with a temperature of approximately 30°C. The agitator was kept running to achieve complete mixing and homogeneous synthetic wastewater solution. The constituents were calculated based on C:N:P Ratio 110:5:1 (Gray, 2004; Puñal et al., 2003; Jong-Hyun Lee, 1999; Mimma Perneti, 2003). Ratio of P (KH₂PO₄) : P (K₂HPO₄) was maintained at 1:2. (APHA 1995).

Table 3.9 The Synthetic Wastewater Constituents

The Constituent	Concentration (mg/L)
Sugar	3230
(NH ₄) ₂ SO ₄	940
KH ₂ PO ₄	28
K ₂ HPO ₄	72
MgSO ₄ -7H ₂ O	50
FeSO ₄ -7H ₂ O	4
CaCl ₂	30

Figure 3.14 Schematic Diagram of Oxygen Transfer and DO Profile Tests in TFBR

3.3.1 Methods of Analysis

At different stages during the operation of the TFBR, the wastewater was analyzed for COD, ammonia and nitrate concentrations. The ammonia removed, contributes to the cell syntheses, and the conversion to nitrate nitrogen by the nitrifiers. By analyzing the nitrate and TSS concentration in the effluent, the ammonia removal rate by nitrification and cell synthesis can be identified. Therefore, besides nitrate, TSS was chosen as a parameter in this study. Biofilm analysis was also performed to compare the immobilized biomass and suspended biomass in the TFBR.

COD Analysis

The COD analysis was carried out by the standard method: 5220D: *Closed Reflux. Colorimetric Method* (Standard Methods, 1998). The analysis instruments include acid proof auto zero pipettes (Figure 3.15), COD Reactor Block, Orbeco-Hellige 975MP colorimeter (Figure 3.16) and 16mm vials. The analysis procedure followed standard methods 5220D. Digestion solution and sulfuric acid reagent were prepared in the laboratory as per standard methods 5220. The analysis procedure:

Figure 3.15 The COD Digestion Solution Pipettes

Figure 3.16 The COD Reactor Block and Photometer

- A COD vial was filled with 1.5 ml digestion solution and 3.5 ml sulphuric acid reagent, then added 2.5 ml sample (wastewater diluted five times).
- The vial was put in COD reactor block. After 2 hr's digestion at temperature 1500C, then cooled room temperature
- The sample vial was measured in an Orbeco-Hellige 975MP colorimeter under a wavelength of 608 μm .
- The reading of the colorimeter was recorded, which was the COD value of undiluted wastewater samples.

The specifications of COD reactor, colorimeter are listed in Appendix D4

Ammonia Nitrogen and Nitrate/Nitrogen Analysis

To check the ammonia concentration and nitrification rate, a Hach Ammonia Electrode in combination with a Sension™2 meter was used in this study. Essentially, it measures ammonia gas or ammonium ions in aqueous solutions that have been converted to gas by the addition of a strong base. The sension™2 and electrodes shown in Figure 3.17, and the relevant specifications are listed in Appendix D5 and Appendix D6.

Ammonia Analysis

Ammonia electrode is a complete electrochemical cell consisting of a glass pH electrode and a

reference electrode. By checking the difference between ammonia concentrations of influent and effluent, the ammonia removal rate in the reactor could be evaluated. This analysis procedure strictly follows EPA Method 350.3 (Standard Methods, 1998) with reference to Hach Method 10001 (Hach, 2001)

Figure 3.17 Sension™2 Meter, Ammonia and Nitrate Electrodes

Ammonia Concentration

The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode internal solution. Dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any given sample, the partial pressure of ammonia will be proportional to its concentration. Ammonia diffusing through the membrane dissolves in the internal filling solution and, up to a small extent, reacts reversibly with water in the filling solution:

Before each use, the ammonia electrode was conditioned in ammonia ISA storage solution, and then calibrated using 1.0 mg/L, 10.0 mg/L and 100.0 mg/L standard solutions. The calibrated slope was -57 ± 3 mV per ten times difference of standard solution concentrations. 2.0 mL of ammonia ISA solution was added add in 100 ml of sample. The ammonia concentration in feed water was approximately 230 mg/L.

Nitrate Concentration

The nitrate concentration was analyzed by Hach Nitrate Platinum Series Combination Electrode

coupled with a Hach sension™2 Meter. This electrode allows either the direct measurement method or known addition method depending on the analysis situations.

The electrolyte in the electrode is a medium viscosity gel that acts as a restriction device by limiting the release of ammonium sulfate into the sample in the same way a fused glass conjunction does in a conventional electrode. A fresh reference electrolyte is supplied from a replaceable cartridge by depressing the built-in dispenser button. By refreshing the electrolyte at the reference junction, the reference system eliminates junction potential errors caused by clogged frits. The reference half-cell is a silver/silver chloride reference element in a double junction configuration. The gelling agent is non-ionic and does not interfere with the free flow of ions across the reference junction.

For a convenient and quick analysis, a linear calibration method by two standard solutions differing in concentration by 10 times was adapted. The following equation was used to determine the nitrate concentration from the measured potential (Hach, 1999):

$$C_x = C_1 \times 10^{\Delta E/S}$$

$$\Delta E = E_x - E_1$$

Where: E_x is the sample potential, E_1 is the standard potential, C_x is Sample concentration, C_1 is standard concentration and S is the potential slope measured by electrode.

Biomass Analysis

In order to evaluate the attached biomass (biofilm), a biomass test was performed in this study. The test procedure followed the Hydroxyl Pack Biomass Density Test Method (Hydroxyl, 2006). Ten pieces of biomedica were taken out from the reactor, and dipped into a beaker filled with water for 5 minutes to dislodge unattached biofilm. Then biomedica were placed in an oven at 105°C for 24 hours. After drying and cooling to the room temperature, the weight of the biomedica was recorded. The dried biomedica were then thoroughly bleached to clear the attached biofilm. These biomedica were dried at 105°C for 24 hours and weighed again. The difference in the weights was recorded as the total biomass attached to the media.

TSS Analysis

For the evaluation of the suspend biomass in TFBR, the TSS test was performed at 105⁰C. The analysis procedure followed Standard Method 2540 D (Standard Methods, 1998).

pH Control

Hanna HI 9025 (Figure 3.18) was used to measure the pH of the wastewater. The instrument is microprocessor-based pH meter in a waterproof casing. A simple and fast automatic calibration procedure was adopted. The calibration could be performed at 2 points selected from 5 memorized buffers: pH 4.01, 6.86, 7.01, 9.18, 10.01. A 10N NaOH solution was used to adjust the pH of influents in ammonia/nitrogen analysis. The specifications of the pH meter are listed in Appendix D7.

Figure 3.18 The pH Meter

3.3.2 The Experimental Operations

According to the required influent concentration, the concentrated synthetic wastewater was prepared in a chemical/nutrient dosage tank. This concentrated solution was pumped to the 4500 L feed tank using metering pump. At the same time, tap water was fed to this 4500 L feed tank. The solution was stirred to homogenize the wastewater. A metering pump and tap water flow rate were adjusted carefully to control the composition of the synthetic wastewater. Then it was pumped from feed tank into the TFBR and RBC at the same time. In addition, the airflow rate was controlled as required. However, a large quantity of biomass was developed in the feed tank and the pipes due to the high COD concentration and longer holding time in the feed tank. As

results, both pH and DO concentration of the influent dropped to 1–2 and below 2 mg/L respectively. An anaerobic situation developed in the feed tank causing an odor problem. These changes negatively affected the proper performance of both bioreactors. To avoid these problems, the following operational changes were made:

- Synthetic wastewater was prepared continuously instead of batch by controlling flow rates of the metering pump and fresh water taps frequently.
- The large 4,500 L feed tank was replaced by a small 200 L wastewater preparation tank to reduce the residence time of the synthetic wastewater.

By applying these measures, the odor emission and anaerobic situation were eliminated. However, the biomass accumulation in the small feed tank, pipes and flow meters persisted. For better control and reliable influent quality, the influent pipelines were completely flushed with fresh water at least every other day. The influent and effluent samples were collected at least daily. These samples were analyzed for COD, ammonia-nitrogen and nitrate-nitrogen. Major equipments involved in this study include chemicals/nutrients dosage tank, wastewater preparation /feed tank, feed pump and TFBR system. The most important specifications of the equipments are listed in Table 3.10. The schematic process diagram and the equipment layout in the wastewater treatment laboratory are shown in Figure 3.19 and Figure 3.20 respectively.

Table 3.10 Equipments Used in This Study

1. Feed Pump	
Dimension	3 m (Diameter)*1.5 m (height)
Name	Continental ultra pump CP33-SSOMT
Speed	4,320/720 RPM
2. Chemical dosage metering pump	
Capacity	0.9–9.4GPM
Motor	1.5HP
3. Three-phase TFBR	
For specification, see Table 3.7

Figure 3.19 The Schematic Flow Diagram for Simultaneous COD and Ammonia Removal

LABORATORY OF WATER AND WASTEWATER TREATMENT TECHNOLOGIES

DEPARTMENT OF CHEMICAL ENGINEERING, RYERSON UNIVERSITY, TORONTO, CANADA

Figure 3.20 The Equipments Layout in the Wastewater Treatment Technologies Laboratory, Ryerson University

3.3.3 The Experimental Program

The experiments conducted in this study are in the following 3 stages:

- The inoculation and biofilm development
- Operation under designed conditions
- Operation under various residential times and concentrations (Table 3.11)

Table 3.11 Experimental Matrix

Hydraulic variables		$\text{NH}_3\text{-N} = 230 \text{ (mg/L)}$	
Flow rate (L/day)	HRT (h)	COD (mg/L)	
		5,000	6,000
1,500	8	Run 3	Run 4
1,725	7	Run 1	-
2,000	6	Run 2	-

Microorganism Inoculation and Biomass Develop

To inoculate microorganism in the reactor, 60 L of wastewater and suspend sludge mixture were pumped as a seed into the reactor. The mixed sludges were collected from effluents of the stabilization tank and the first stage of the RBC at Niagara Municipal Wastewater Treatment Plant, Niagara Falls, Ontario. The TFBR was filled with synthetic wastewater. The aeration was turned on in batch condition, and was continued for about one week, until the liquid in the reactor became white and milky implying that the microorganisms adopted the environment in the reactor. The biomass concentration was high enough to immobilize on biofilm carriers

Immobilization of Biomass and Biofilm Development

In order to immobilize the suspend biomass on the biomedica, the immobilization procedure followed the method recommended by Sokół (2001). Since the media moved very fast even at minimum fluidization with very low airflow rates, the aeration in the TFBR was stopped, and the mixed liquor was recirculated between the reactor and recirculation tank, and aerated using the two diffusers in the recirculation tank. This method increased the dissolved oxygen concentration

to 6–7 mg/L in the influent of the TFBR, and immobilized the biomass on the media within three days. However, it was found that the attached biofilms dislodged if the media moved in the reactor after the aeration starting in the TFBR. This observation made it clear that this method was unsuitable. Consequently, the TFBR operation was changed to continuous mode by continuously feeding the fluidized bed. The rate of aeration was increased from 1 SCFM to 4 SCFM, and slow media movement was maintained. After about 3–4 days, the suspended biomass started immobilizing first on edges, then on inside surface, and finally on the outside surface of the media.

The pH of fresh synthetic water was in the range of 6–8 which is recommended for the optimum growth of microorganisms. However, when the biomass grew on the biomedia, the pH in the reactor dropped below 3. When it was adjusted to little over 6, the biofilm stopped growing and the water in the TFBR gradually became light yellowish, then darkened into light brown, and finally turned reddish within one week of operation with pH control. At the same time, the movement of the air bubbles slowed down indicating the increase in the liquid viscosity. Smaller air bubbles started to coalesce into larger bubbles, and the developed biofilm began dislodging from the biomedia.

With consideration to the fact that biofilm was developed under acidic conditions, the pH changes might be the reason that caused the biofilms to dislodge from the biomedia. Therefore, the biomass immobilization was restarted with pH slightly greater than 6. Other operating conditions such as feed rate, airflow rate, synthetic wastewater composition and reaction temperature were maintained as before. The biomass did not grow on the media even after 6 days of operation, and the liquid color and viscosity changed as before.

Hence, it was decided to stop controlling the pH in the TFBR. When the NaOH feed was stopped, the pH in the TFBR dropped below 3 very quickly within 2 hours. Within 8 hours, the color started normalizing and the biofilm started developing again. The airflow rate was kept high at a superficial velocity of 0.98 cm/s in order to encourage the microorganisms to immobilize on the media and adopt the real operating condition, and at the same time flush out excessive suspended biomass. After one week, noticeable growth of biofilms was observed.

Reactor operation in Steady State under Various Parameters

After the biofilm was fully developed on the media, the study for the removal performance of the TFBR was conducted using different hydraulic and organic loadings as shown in the experimental matrix (Table 3.11).

4 EXPERIMENTAL RESULTS AND DISCUSSION

This chapter presents the results of the experiments carried out with the three-phase fluidized bed reactor (TFBR) designed and built for this study. In this work, The TFBR was first operated with water and air to examine the fluidization characteristics, and the transfer of oxygen. The treatment of high-strength wastewater in the TFBR was carried out in the following step.

4.1 Fluidization Characteristics of the TFBR

Water and air were used to determine the fluidization characteristics for a given solid holdup (ϵ_s), i.e. the ratio of the volume of the biomedica to that of reactor volume. Three ϵ_s of 0.4, 0.5 and 0.6 of hydroxyl media in the TFBR were used. For each ϵ_s , two units of biomedica, one colored red and the other white, placed in the reactor to trace the fluid motion. With low air superficial velocities (V_g), the biomedica moved upwards and downwards in a typical spiral fashion. When the V_g was increased, the turbulence in the column increased. The movement of the biomedica became rapid and more random due to more frequent collisions among the solids and with the column wall.

Complete fluidization was achieved with the liquid superficial velocity (V_l) in the range of 0–0.02 cm/s and V_g = 0.3–3.3 cm/s when ϵ_s = 0.4. Partial fluidization was also achieved at V_l = 0 cm/s and V_g as low as 0.005 cm/s. This negligible influence of V_l is expected given the initial low density of solid. The change in V_g gave rise to three fluidization regimes as depicted in Figure 4.1 at ϵ_s = 0.5.

Figure 4.1 Three-Phase fluidization regimes with $V_l = 0.009$ cm/s, and $\epsilon_s = 0.5$

With V_g less than 0.5 cm/s [Figure 4.1 (a)], only some media got fluidized in the middle and lower part of the column, while a large quantity of media formed a floating bed at the top of the reactor. At the bottom section of the bed, the media were either sparse or absent. The increase in V_g reduced the size of the floating bed. When V_g reached a certain value, all media were uniformly fluidized in the entire TFBR [Figure 4.1(b)]. This state persisted with an increase in V_g until a dead zone appeared at the bottom section of the TFBR [Figure 4.1(c)]. In addition, The size of dead zone was larger than that of floating bed. With further increase in V_g , the size of the dead zone increased, and the fluidization became less uniform in the top of the TFBR. The coalescent air bubbles gradually dominated the top section where the media became sparse. The dead zone appeared at the bottom section of the reactor due to the reduction of gas-liquid mixture density in the reactor, which described by equation 2-1. When V_g increased to certain value, the density of the media became larger than that of the gas-liquid mixture, more and more particles deposited at the bottom of the reactor, and consequently a bottom dead zone appeared.

To investigate the effect of ϵ_s on the dead zone, the TFBR was operated with $\epsilon_s = 0.5$ and $\epsilon_s = 0.6$. It was found that both the size and existing regimes of floating bed and dead zone are closely related to the ϵ_s . As shown in Figure 4.2, the size of the floating bed and the dead zone increased with the ϵ_s increased for a given V_l and V_g .

Figure 4.2 (a)

Figure 4.2 (b)

Figure 4.2 Variation of the Floating Bed and Dead zone in the TFBR
(with (a) $\varepsilon_s = 0.5$ (b) $\varepsilon_s = 0.6$)

With the increase in V_l , the size of the dead zone and floating bed decreased, thereby augmenting the range of full fluidization in the TFBR. The influence of V_g was negligible in this regard. The size of floating bed and dead zone, existing range, and V_g and V_l are plotted in Figure 4.3 for $\varepsilon_s = 0.5$.

Figure 4.3 The Relation among Dead Zone and Floating Bed Size, Existing Range, and Superficial Velocities of Gas and Liquid at $\varepsilon_s = 0.5$

The relation between the size of the dead zone and floating bed, as well as superficial velocities in the TFBR, is of great importance with regards to the operation. In a TFBR, the volume specific surface area, i.e. the total specific area of the media in unit reactor volume, is crucial as it is proportionally related with the biofilm concentration. In order to achieve a high biofilm area, a higher ε_s must be provided. On the other hand, a higher ε_s results in larger floating bed at low V_g condition, or larger dead zone at the bottom section in the case of high V_g condition, where both cases can deteriorate the reactor performance. Thus, for a TFBR with light biomedica, to make sure the operational range falls in full fluidization regime and the TFBR is operated at its utmost advantages, the designed biofilm surface area and hydraulic parameters of the bed operation need to be well balanced. In this study, the both V_g and V_l operating ranges have resulted in full fluidization.

4.2 Oxygen Transfer in the TFBR

To examine oxygen transfer, the TFBR was fed with deaerated water with low dissolved oxygen (DO) concentration about 1.5 mg/L. DO analysis was carried out on the samples extracted from different sampling ports on the TFBR as listed in Table 3.6.

Figure 4.4 Initial Oxygenation in the TFBR
(with $\epsilon_s=0.5$, $V_f=0.009$ cm/s, $V_g=1.0$ cm/s, $T=15-17^\circ\text{C}$)

Two separate tests with $\epsilon_s=0.5$ and 0.6 were conducted with the designed V_f and V_g of 0.009 and 1.0 cm/s, respectively. The results showed that there was no significant difference in terms of the required time to reach saturation in the TFBR under experimental conditions. As observed from Figure 4.4, DO saturation in the TFBR was a quick process. The DO concentration in the whole column reached steady state within 4 minutes.

4.2.1 Oxygen Volumetric Mass Transfer Coefficient in the TFBR

Because liquid superficial velocity was extremely low in experimental condition, so we can assume the mass transfer conducted in batch regime and described by equation 4-1. Therefore

from the data obtained at the initial oxygenation experiment, the volumetric mass transfer coefficient of oxygen (K_La) can be calculated using the equation.

$$\frac{dC_{DO}}{dt} = K_La(C_{DO}^* - C_{DO}) \quad (4-1)$$

where C_{DO}^* is the saturation concentration in the liquid phase, and C_{DO} is the DO concentration in the liquid phase at any time t . Integrating Equation 4-1 yields

$$\ln\left(\frac{C_{DO}^* - C_{DO}}{C_{DO}^* - C_{DO,0}}\right) = K_La \cdot t \quad (4-2)$$

This equation can be used to calculate the oxygen volumetric mass transfer coefficient based on the experimental data. Table 4.1 provides the data and calculated values of the coefficient.

The measured K_La from this study is in good agreement with the calculated value by using Joshi gas hold up correlation (Joshi and Sharma, 1979) and Kawase equation (Kawase et al, 1987). Detailed work sheet for calculation is listed in Appendix 3B.

It is observed that the K_La values are almost the same from the three sample ports above air diffusers in the TFBR. That means that the oxygen transfer rate in this TFBR is nearly uniform in contrast to appreciable oxygen mass transfer rate gradient (Alvarez-Cuenca and Nerenberg, 1981; Alvarez-Cuenca et al.1983 and Alvarez-Cuenca et al.1984). This difference of the K_La uniformity in TFBR resulted from different flow conditions. In their studies, both V_g and V_l are much higher than those used in present study. The oxygen volumetric mass transfer rate gradient in their study is due to the kinetic energy of high liquid flow rate which makes bubble-breakage rate very high. Therefore, the interfacial area reduce dramatically in the bulk zone, and great reduction of volumetric mass transfer results.

The uniformity of oxygen transfer coefficient in the TFBR developed in this work provides the possibilities of sufficient oxygen supply in the entire column, thereby eliminating any oxygen limitations.

Table 4.1 The Oxygenation and Oxygen Transfer Rate

(V_g=1.0 cm/s, V_l=0.009 cm/s, T=15-17°C)

Time	DO Concentration		
	Distance above primary air diffusers		
	1 cm	25 cm	95 cm
0:00	1.4	1.4	1.6
0:30	3.1	3.4	3.2
1:00	5.7	6.9	7.4
1:30	9.1	9.2	9.3
2:00	10.0	10.3	10.3
2:30	10.7	10.9	10.7
3:00	11.4	11.3	11.3
4:00	11.5	11.3	11.4
5:00	11.5	11.4	11.4
6:00	11.6	11.4	11.4
11:00	11.6	11.5	11.4
16:00	11.6	11.5	11.4
Calculated mean volumetric mass transfer coefficient K_La (s ⁻¹)			
	0.023	0.022	0.025

Furthermore, it is remarkable that the volumetric mass transfer coefficient values in the TFBR are at least an order of magnitude higher than those obtained in other studies with similar air phase superficial velocities and much lower liquid superficial velocity. The coefficient values have the same order of magnitude than that obtained by Alvarez-Cuenca (1984) in TPFBR (Table 4.2) even though liquid superficial velocity in this study was much lower (around 500 times lower). This excellent mass transfer rate can be attributed to fine bubble membrane diffusers used in the present work.

The high oxygen mass transfer in the developed TFBR can be attributed to following factors. First, the tall TFBR results in a high hydraulic pressure, which leads a high DO concentration. Secondly, a complete mixing among the three phases caused by fast moving media contributes to a high mass transfer rate. Thirdly, the use of advanced air diffuser, as the smaller air bubble, the larger interfacial area (which is a in K_La), thus the higher oxygen mass transfer coefficient.

Table 4.2 Comparison of the Volumetric Oxygen Transfer Coefficients in Fluidized Beds

Experiment conditions				K_La (1/s)	References
V_l (cm/s)	V_g (cm/s)	Solid phase	Size (mm)		
0.3	1.3	Granular activated aluminum particle	$d_p=1-2.5$	$3.0 \times 10^{-5*}$	Quiñones Bolano, 2000
1.8	2.0	Glass beads	$d_p=0.4$	2.8×10^{-3}	Yang et al., 2001
2.8	2.0	Polystyrene beads	$d_p=3.5$	0.9×10^{-2}	Nikolov et al., 2000
5	4	Glass beads	$d_p=1$	0.015	Aivarez-Cuenca et al., 1984
This study					
0.009	1.0	Polyurethane matrix	$D=22 \times 15$	0.23×10^{-1}	Wan, 2006

* The value is oxygen transfer coefficient just above diffuser.

4.2.2 DO Profiles in the TFBR

The axial DO profiles in the TFBR had small gradients, and the DO concentrations varied in an operation were within $\pm 3\%$. The average DO concentration in the TFBR was higher than the standard values at the same temperature and pressure conditions (Figure 4.5).

Figure 4.5 Axial DO Profile in the TFBR at Various V_g ($V_l = 0.019$ cm/s, $\theta = 4$ h, $T = 16-17^\circ\text{C}$)

The water was over saturated with DO by more than 16%. This is coherent with a very low V_l and therefore long residence time and high DO concentrations.

With low V_l (0.005–0.023 cm/s) corresponding to 0.048–0.240 m³/h of volumetric flow rate, the axial DO profiles were examined by increasing the air superficial velocity from 0.3 cm/s to 1.6 cm/s. The results are plotted in Figure 4.6. The following phenomena were observed:

When liquid superficial velocity is very low, e.g. $V_l = 0.003$ – 0.009 cm/s, the DO concentration varied with air superficial velocity as shown in Figure 4.6 (a,b). With low air velocity, $V_g = 0.3$ cm/s, the DO in the TFBR generally increased with the axial distance from the air diffusers. As soon as the V_g increased more than 0.7 cm/s, this trend reversed. This result was possibly due to less turbulence at the lower section of the bed in the TFBR. As discussed in the previous section, the solid phase was observed to be sparse in the bottom section of the TFBR with low V_l and V_g . As the distance from the air diffusers increased, the solid phase became denser and the biomedica became agitated. The elevated turbulence improved the oxygen transfer from air phase to water phase, thereby increasing the DO concentration.

Figure 4.6 (a) ($V_l = 0.005$ cm/s, $\theta = 15$ h, $T = 16$ – 17°C)

Figure 4.6 (b) ($V_l = 0.009$ cm/s, $\theta = 7$ h, $T = 15-16^\circ\text{C}$)

Figure 4.6 (c) ($V_l = 0.014$ cm/s, $\theta = 5$ hr $T = 16-17^\circ\text{C}$)

Figure 4.6 (d) ($V_l = 0.023$ cm/s, $\theta = 3$ h, $T = 15-16^\circ\text{C}$)

Figure 4.6 Axial DO profiles at various gas phase superficial velocities in TFBR

When the liquid phase superficial velocity was increased to 0.014 cm/s, the DO profiles displayed a similar tendency. The DO concentration declined as the distance from the air diffusers increased. At the same time, the average DO concentration jumped to a higher level [Figure 4.6 (b,c)], which could be related to enhanced bubble break by the turbulence of the higher liquid flow rate. Even though the increase of V_l reduces residence time (θ), this effect far less important with regards to that oxygenation that is so fast in the TFBR. When V_l was further increased to 0.023 cm/s [Figure 4.6 (d)], the tendency of DO profiles remained the same, but they came closer to each other.

Variation of DO Profiles with V_l for a Constant V_g

The axial DO profiles with a given air superficial velocity and different liquid superficial velocities in the TFBR displayed similar characteristics, except at very low gas superficial velocities ($V_g < 0.3$ cm/s).

Figure 4.7 (a) ($V_g = 0.3 \text{ cm/s}$, $T=15-17^\circ\text{C}$) Figure 4.7 (b) ($V_g = 1.0 \text{ cm/s}$, $T=15-17^\circ\text{C}$)

Figure 4.7 (c) ($V_g = 1.6$ cm/s, $T = 15-17^\circ\text{C}$)

Figure 4.7 Axial DO profiles at various liquid phase superficial velocities in the TFBR

The DO concentrations varied with different V_l (Figure 4.7). When the air superficial velocity was higher than 0.7 cm/s, the influence of the liquid superficial velocity on the axial DO concentration was not significant. However, the distance from sample ports to air diffusers had a remarkable effect. When the distance increased, the DO level declined. This is because oxygen mass transfer was more intense near the distributors at the bottom of the column, which confirms previous work by Alvarez-Cuenca et al (1984) with two dimensional TFBR.

DO Profiles at high liquid superficial velocities

The DO profiles were also examined by operating the TFBR in the high-than-design liquid superficial velocity range of 0.058–0.203 cm/s. Figure 4.8 shows the results obtained from the experiments. When $V_l = 0.058$ cm/s, the DO profiles in the TFBR displayed the same trend as observed earlier in Figure 4.6 (d). The axial DO level was not significantly affected by the gas phase superficial velocities. The DO concentration declined as the distance to the air diffusers increased. This characteristic is illustrated by Figure 4.8 (a), this similarity occurred because the hydraulic conditions did not change too much (V_l increase from 0.023 cm/s to 0.058 cm/s).

As liquid superficial velocity was increased to 0.116 cm/s, the DO concentrations with low gas velocities (0.3–0.7 cm/s) dropped as shown in Figure 4.8 (b). With higher V_g (more than 0.7 cm/s), the DO concentrations were higher, and did not change much along the length of the TFBR.

With $V_l=0.174$ cm/s and $V_g=0.3$ cm/s, the DO concentration declined, and became almost constant in the axial direction [Figure 4.8 (c)]. When V_l was increased to 0.203 cm/s [Figure 4.8 (d)], the DO profile with $V_g=0.3$ as well as 0.7 cm/s became flat and uniform. In addition, the average DO concentration decreased to around 9.5 mg/L. This is explained by the liquid phase residence time and V_g effect on the mass transfer.

Based on the aforementioned results, the following conclusions can be made:

- a) For a given liquid superficial velocity, the average DO concentration is related to gas phase superficial velocity
- b) The average DO concentration decreases with the increase in the liquid superficial velocity. This phenomenon can be attributed to lower oxygen transfer rate under shorter hydraulic residence time. As an example, when $V_l=0.005$ cm/s, the hydraulic residence time (HRT) is around 14 h. When V_l is increased to 0.203 cm/s, the HRT decreases to 0.5 h, which significantly reduces the time for interfacial mass transfer, and thus in turn reduces the DO concentration.
- c) With a given gas superficial velocity, the DO concentration decreases with the increase in V_l . Take $V_g=1.6$ cm/s as an example. When the liquid superficial velocity increased from 0.058 cm/s to 0.203 cm/s, the corresponding average DO concentration in the TFBR decreased from 11.70 mg/L to 10.18 mg/L. This phenomenon can also be explained by shortened time for interphase mass transfer.
- d) The DO profiles for various V_l show high DO concentrations. Close to uniform DO concentrations are attainable with the liquid superficial velocities in the range, 0.023–0.058 cm/s.

Figure 4.8 (a) ($V_l = 0.058$ cm/s, $\theta = 1.2$ h, $T = 15-19^\circ\text{C}$)

Figure 4.8 (b) ($V_l = 0.116$ cm/s, $\theta = 0.6$ h, $T = 12-14^\circ\text{C}$)

Figure 4.8 (c) ($(V_l = 0.174$ cm/s, $\theta = 0.4$ h, $T = 13-15^\circ\text{C}$)

Figure 4.8 (d) ($(V_l = 0.203$ cm/s, $\theta = 0.3$ h, $T = 13-14^\circ\text{C}$)

Figure 4.8 Axial DO profile under high liquid superficial velocity in the TFBR

4.3 Simultaneous COD and Ammonia Removal

This section presents the effects of hydraulic residence time (HRT), and influent concentrations on the removal rates of COD as well as ammonia. The effects of COD and ammonia loadings on the concentrations of both the suspended and immobilized biomass are also included.

4.3.1 COD Removal

In this study, the relation of COD removal rate with hydraulic residence time was investigated in the range of 6-8 hours residence time. In order to encourage the biomass immobilizing on biomedica, the reactor was operated at a shorter residence time of 7 h. The flow rate was kept at 1.2 LPM ($1.725 \text{ m}^3/\text{day}$). The COD concentration varied slightly around 5,000 mg/L, and ammonia concentration maintained about 230 mg/L, as shown by the little variation in Figure 4.9. After around 3 weeks of operation, the reactor reached steady state. The variation of COD concentration in effluent was less than 5% in two consecutive days (less than 800 mg/L), which is equal to 84.6% removal rate.

Subsequently, the feed flow rate was increased to $2 \text{ m}^3/\text{day}$ in relation to the HRT decreasing from 7 h to 6 h. Within a few hours, noticeable biomass dropped from the biofilm biomedica. At the same time, TSS in the TFBR increased 50%. After 24 h of operation, the COD in the effluent increased to more than 1,400 mg/L. Accordingly, the COD removal rate dropped to 65%, from 84% with a flow rate $1.725 \text{ m}^3/\text{day}$.

The phenomena of biofilm shedding could be due to the process exceeding its maximum loading, which is $12 \text{ kg COD/day}\cdot\text{m}^3$. Under 6 h residence time and influent conditions, the organic loading was as high as $13.1 \text{ Kg COD/day}\cdot\text{m}^3$. If it were kept at this loading rate, the TFBR would reach its new steady state. That would take about another 2 weeks time. This was when the flow rate was reduced to $1.5 \text{ m}^3/\text{day}$, and gradually the TFBR regained its new steady state after 10 days. In two days, the average COD in the effluent was less than 450 mg/L, and the related COD removal reached 91.7%. The COD removal with residence time is displayed in Figure 4.9

Figure 4.9 COD Removal Rate with Various HRT

The TFBR performance of removal with residence time was well established with a loading of $10.55 \text{ Kg/m}^3 \cdot \text{day}$, which exceeds its design value. This high efficiency could be the results of the following factors:

1. High oxygen transfer efficiency. During the complete experimental period, the DO concentration in the TFBR was more than 5 mg/L with an airflow rate of $12 \text{ m}^3/\text{h}$.
2. Enough nutrients in the influent guaranteed the demand for cell synthesis.
3. High temperature, The temperature in the whole experiment was kept between $27\text{--}30^\circ\text{C}$

As illustrated in the experimental matrix ((Table 3.11)

Table 3.11), the study for the COD removal rate and its dependence on influent concentration were conducted with two influent COD concentrations of $5,000 \text{ mg/L}$ and $6,000 \text{ mg/L}$. The ammonia concentration kept constant at around 230 mg/L , and the hydraulic residence time was 8 h . When the COD in the influent increased to $6,000 \text{ mg/L}$, the COD removal rate reduced sharply from more than 90% to less than 60% . After 6 days of operation, the TFBR reached a new steady state with 85% COD removal. The biomass in the biofilm was then analyzed. However no significant biofilm change was observed from the analytical data or by visual check.

The TSS however increased obviously as a result the reactor to adapting to a new operating condition. Figure 4.10 shows the relation of the COD concentration with time.

Figure 4.10 COD Removal Rate with Influent COD Concentration

As shown in Figure 4.10, the TFBR reached a new steady state after one week. That is a quite short transition time compared to the case when the TFBR regained its normal performance from 6 h residence time to 8 h (Figure 4.9), likely because of the biofilm shedding resulting from the loading shock.

4.3.2 Ammonia Removal

relation between ammonia removal and different HRT is presented in

Figure 4.11. During this stage of the experiment, the influent COD: $\text{NH}_3\text{-N}$ ratio was kept around 5000:230. At a HRT of 7 h, the ammonia removal rate reached 54.9% at steady state, when the HRT increased to 8 h, it increased slightly to 58.6% at a new steady state. the average removal rate increased from 52.9% to 56.7%. However, the nitrate concentration in the effluent was low. This means that the increase of the ammonia removal rate was not due to the increase in the nitrification rate, but due to the increase of cell synthesis in the liquid phase as confirmed by the change in TSS during the operations with two different HRTs. The ammonia removal rate was

related to the HRT to some extent, but did not show a strong dependence.

Figure 4.11 The Concentration Changes of Ammonia for Different HTR and COD:NH₃ Ratio of 22:1

Compared to the effect of HRT, the COD: NH₃-N ratio showed a more significant impact on ammonia removal rate. At a constant HRT of 8 h, when the COD concentration increased from 5,000 mg/L to 6,000 mg/L and ammonia remained constant (around 230 mg/L), the ammonia removal rate increased from 56.7% to 73.2%. During this period, the biofilm density on media did not change, and remained around 15 mg/particle. However, the TSS in the effluent of the TFBR increased from 1,190 g/L to 1,460 g/L. The nitrification rate did not show any noticeable change. That is the ammonia eliminated from the wastewater converted into cellular mass as indicated by the TSS increase. Figure 4.12 shows the relation of the ammonia removal rate with the change in the COD: NH₃-N ratio.

Figure 4.12 Ammonia Removal Rate for Different COD: NH₃-N Ratios

During this process the temperature was kept at 27-29 °C and the DO was kept higher than 4 mg/L. Both conditions are favorable for ammonia nitrification. However, nitrification was still very low even though ammonia removal was 73.2%. This means there was no temperature or oxygen limitation to achieve a high nitrification rate. The most likely reason for low nitrification could be the pH effect (less than 3) and the suppressing effect from a high COD concentration.

Ammonia Nitrification

Eventhough the ammonia removal varied between 52.9% and 73.2% for different influent conditions, the nitrification rate was very throughout the experimental period. Figure 4.13 shows the variation of nitrate concentration and ammonia removal with time.

To confirm the rate of nitrification, nitrate analysis for the influent was performed. The concentration of nitrate was found to be less than 0.5 mg/L, which means nitrification did exist in the TFBR but was limited.

Figure 4.13 Nitrate at various COD/NH₃ ratio and HRT

As was indicated before, because of the biofilm immobilization problem, the TFBR in this study was operated with a pH lower than 3, which is favorable for heterotrophs but could be problematic for achieving a satisfactory nitrification.

Another possible reason for the low nitrification is likely the high COD suppression effect. In one study of simultaneous COD, ammonia removal (Tsuneda, 2004), the ammonia nitrification did not start until the carbon organics concentration dropped to a certain low concentration. It may be noted that in the present study, the lowest COD concentration in the effluent was higher than 350 mg/L even at the best COD removal performance. In another study (Ros and Vrtorvsek, 1998) it was found that the nitrification rate dropped sharply at a COD loading higher than 3 kg/m³·day in two combined aerobic-anaerobic FBRs. In the present study, the COD loading rate was always more than 10 kg COD/m³·day.

Nitrogen Balance in the TFBR

Theoretically, the total ammonia/nitrogen removed in the TFBR can be striped, converted to nitrate, nitrogen gas and cellular nitrogen. Since the Ph in the reactor is always under 3, so there

should be no ammonia gas stripping happened. and at the same time, aerobic condition was maintained in the TFBR, there was very little chance for denitrification to occur. Therefore, the ammonia/nitrogen in the TFBR was very likely transferred into two different forms. Most of it assimilated into cell synthesis, and less than 4% was oxidized into nitrate. This hypothesis could be proven by the ammonia nitrogen balance shown in Table 4.3. in which The calculation of nitrogen percentage in biomass is based on the biomass formula: $C_5H_7NO_2P_{0.075}$ (Bashaar, 2004).

Table 4.3 The Ammonia-Nitrogen Balance in the TFBR System

Run number	Nitrogen in (g/day)	Nitrogen out (g/day)			Total	Unaccounted (g/day)
		NH ₃ -N	NO ₃ -N	N in biomass		
Run 1	387.1	188.87	3.72	202.15	391.02	-3.94
	368.1	182.30	2.76	182.06	364.36	3.70
	370.3	165.89	4.92	192.94	358.83	11.48
Run 2	452.2	204.83	4.23	375.97	580.80	-128.61
Run 3	323.3	133.49	4.61	216.06	349.55	-26.27
	331.2	138.82	3.60	207.69	346.51	-15.31
	333.8	137.23	3.31	211.88	349.11	-15.32
Run 4	344.6	82.51	3.30	260.18	342.69	1.90
	335.1	86.83	3.46	257.39	344.22	-9.13
	331.2	81.65	3.89	265.41	347.06	-15.86

Based on the data provided in Table 4.3, the possibility due to ammonia gas stripping and nitrogen gas losses resulting from denitrification could be eliminated. The unaccounted nitrogen in the table is mostly negative, and very likely due to the analysis errors occurred during biomass tests. Thus, most of the ammonia nitrogen is converted to cellular material.

4.3.3 Biomass Concentration in the TFBR

In this study, the suspended biomass concentration measured by total suspended solid (TSS) was closely related with TFBR performance and showed different correlations with HRT and influent COD concentration. On the other hand, the immobilized biofilm was more or less stable and unaffected in the TFBR. Figure 4.14 displays the immobilized biofilm and dried biofilm sampled

from the TFBR.

Figure 4.14 Biomedia with biofilm and Dried Biofilm

The TSS was analyzed daily, and its concentration throughout the experiment period is shown in Figure 4.15. From this graph, it is observed that along with the biomass immobilization on the media, the suspended biomass concentration decreased gradually before the TFBR reached its first steady state. After around 2 weeks of operation, the biofilm immobilization on media was accomplished. Corresponding to this phenomenon, TSS in the liquid phase decreased to its lowest level, from 1,065 g/L to 922 g/L. Simultaneously, the biomass on the biomedia increased by 55%, from 409 g to 635 g. At the same time, the TFBR achieved its steady state COD removal rate of 85% at 7 h HRT. This result implies that most of the COD removal was not accomplished by the suspended biomass but by the immobilized biomass (biofilm). When the HRT increased to 8 h, the TSS were increased to 1,191 mg/L but the biofilm concentration did not increase as expected. This mean that the TFBR system adjusted its treatment capability by adjusting the amount of suspended solids.

Figure 4.15 Variation of the TSS with HRT and COD Concentration

When the influent COD increased from around 5,000 mg/L to 6,000 mg/L, the TSS in the effluent of the TFBR jumped from 1,191 mg/L to 1,476 mg/L and the biofilm displayed a relatively stable concentration. That is the increased COD removal rate was closely related with the suspended biomass when the reaction condition changed.

Table 4.4 presents this change in entire testing period in which the equivalent concentration of biomass in biofilm is calculated based on the total media specific area of 145 m². The total biomass concentration is the sum of the concentrations of TSS and biofilm in the TFBR.

Table 4.4 The Biomass Change in the TFBR

Sampling date	Biomass per particle (mg)	Mass of biofilm in the TFBR (g)	Equivalent concentration of biofilm (mg/L)	TSS in the Reactor (mg/L)	Total biomass concentration (mg/L)
14 days	10.2	409	569	1065	1634
19 days	15.9	635	882	922	1804
31 days	14.7	590	819	1191	2010
38 days	15.3	613	851	1476	2277

4.4 Sources of Errors

Errors might occur in the following aspects in any analytical operations: methods for analysis, analytical instruments, and personal skills. Errors from personal skills cannot be eliminated, and exist in any analytical operation. Experience and expertise can reduce human error and it is unpredictable. However, the errors produced by the instruments can be eliminated up to a certain extent by adopting proper calibration and careful operation practices as suggested in instruction manuals. The overall error can be estimated. In this work, the errors occurred in the following analyses, and are estimated as follows:

DO Analysis

HQ10 Hach Portable LDO Dissolved Oxygen Meter was used in this study, its accuracy is: ± 0.1 mg/L for 0–8 mg/L, and ± 0.2 mg/L for 8–20 mg/L. In this study, both low and high concentrations are involved. So the maximum error for DO value should be ± 0.2 mg/L.

COD Analysis

In the COD tests, all samples were doubly diluted. Therefore, the analytical range was 300–4,000 mg/L, which was measured by high COD mode. By testing with standard digested COD solutions, it was found that the maximum photometer-reading errors were: ± 13 mg/L for 1,000 mg/L COD (related error of 1.3%), and ± 113 mg/L for 2,500 mg/L COD (related error of 4.5%).

Nitrogen Analysis

Nitrogen analysis was performed by ammonia electrode and nitrate electrode. As the analyzed samples were in linear range of the electrode, so the errors coming from the electrode could be ignored. Therefore, the possible errors came from SensionTM 2 meter. According to the instruction manual, this error should not more than 0.2 mV or 0.05% of the readings.

TSS and Biofilm Analyses

These two analyses strictly followed the manual of Standard Methods (Standard Methods.1998). Based on the nitrogen balance, the maximum error in the biofilm and TSS analyses was 7.3%.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A three-phase fluidized reactor (TFBR) was designed, built and operated to study simultaneous removal of COD and ammonia from high-strength synthetic wastewater. The TFBR showed superior fluidization and oxygen transfer characteristics. With solids hold up of 0.5, the TFBR demonstrated full fluidization with the water and air superficial velocities in the ranges, 0–0.023 and 0.8–2.0 cm/s, respectively. The volumetric oxygen mass transfer coefficient in oxygen transfer tests was at least an order of magnitude higher than that reported in the past TFBR studies. The dissolved oxygen (DO) concentrations along the length of the TFBR were close to uniform with less than $\pm 3\%$ deviations. Furthermore, the water inside the TFBR was supersaturated with DO by more than 16%. This shows excellent mixing and oxygen transfer in the reactor.

The TFBR was designed to simultaneously remove COD and ammonia from 1,500 L/day of synthetic wastewater containing 5,000 mg/L BOD and 230 mg/L ammonia in a short HRT of 8 h. In the operation under the design conditions, the TFBR successfully removed 91.7% COD and 58% ammonia from the wastewater. With a higher-than-design influent COD of 6,000 mg/L, and thus more biomass availability for ammonia utilization, the ammonia removal rate increased to more than 75%. The COD removal however dropped to 84.5% when operating with influent COD=6,000 mg/L over the design capacity. In addition to its high COD and ammonia removal

efficiency, the TFBR carried out effective wastewater treatment with low concentration of suspended solids. In the TFBR operation under design conditions, total biomass concentration was about 2,010mg/L out of which 819 mg/L comprised the biofilms. Thus, in addition to delivering high rates of simultaneous removal of COD and ammonia from high-strength wastewater, the developed TFBR lowers the costs for sludge treatment.

The good performance for simultaneous removal of COD and Ammonia obtained in the TFBR showed its potential commercial value, it can be applied to treat industrial wastewater contains high COD and ammonia nitrogen pollutants.

5.2 Recommendations

Based on the results obtained in this study, the following are the recommendations for future work:

1. As the next step, the developed TFBR should be tested with industrial high-strength wastewaters.
2. The cell immobilization procedure developed in Chapter 3 should be used in order to accomplish the seeding process in a shorter time of two weeks.
3. A media of smaller size than that employed in this study will give a higher specific area, and likely a better performance of the TFBR. The smaller-sized media should be tried with the TFBR.
4. An opening in the top section of the TFBR will facilitate sample extraction. In the present TFBR, the particle sampling port is located on the particle-loading flange.

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APPENDIX A

Fundamentals of COD Removal and Nitrification

Carbonaceous and ammonia pollutants are one of the biggest concerns in wastewater treatment. This section presents a brief literature survey of the work published on COD removal and ammonia nitrification.

A.1 The Theory of Carbonaceous Organics Oxidation

In aerobic heterotrophic oxidation, an organic substrate is used as both the electron donor and the carbon source. Oxygen is the electron acceptor, and NH_4^+ (if present) or NO_3^- can be the nitrogen source combining with phosphorus to provide nutrients for cell synthesis. This situation provides a high-energy yield advantage. Therefore, aerobic heterotrophs are characterized by their high specific growth rate e.g., 9/day and high yield e.g., 0.45 gVSS/gBOD_L (Rittman, 1987). During aerobic wastewater treatment, in case the oxygen supply is sufficient, three basic phenomena occur when organic matter is removed from solution by heterotrophic oxidation (Metcalf, 2004). First, a portion of organic matter is oxidized by the organisms for energy, the organic materials are then digested into simple end substances like water and carbon dioxide. Second, new biomass cell is synthesized through partial absorbing of energy produced in the oxidation process. In this biochemical process, organic substrate is used as the electron donor and as the carbon source. Finally, when the organic substance is used up, the new cells start to consume themselves for cell maintenance, this process is also called endogenous respiration. These biological processes can be summarized as three processes:

- Oxidization
- Cell synthesis
- Endogenous respiration

The metabolism pathway in a biological oxidation process can be illustrated by Figure A.1

Figure A.1 Pathway of biological oxidation process (Adopted from Lindblom, 2003)

As the exact stoichiometry involved in carbonaceous organic oxidation in real wastewater is impossible to be determined, a symbolic average composition of organic matter in wastewater is adopted for calculation. Thus if organic matter is $C_{18}H_{19}O_9N$, then the heterotrophic oxidation can be represented as the following (Metcalf, 2004):

Similarly, if the average composition $C_5H_7NO_2$ represents the biomass cell, then the aerobic oxidation of biomass occurs as follows:

A. 2 The Theory of Ammonia Nitrification

The nitrification process is defined as a two-step chemoautotrophic process where NH_4^+ serves as the electron donor, O_2 as the electron acceptor, and inorganic carbon as the carbon source under the metabolism of nitrify bacterial. Two sequential steps accomplish this process: ammonia is oxidized into nitrite and nitrite is oxidized into nitrate by ammonia oxidizing and nitrite oxidizing microorganisms respectively. Ammonia

oxidizing bacterial and nitrite oxidizing bacterial are often referred as nitrosomonas and nitrobacters. Nitrosomonas are autotrophic organisms whereas nitrobacters are facultative ones as they can utilize organic carbon (Environment Canada, 2003). Comparing to relatively simple stoichiometry, the energy reactions occur in a stepwise fashion, each step involving removal of two electrons. The intermediates and their oxidation states are given in Figure A.2

Figure A.2 Biochemical pathway of nitrification (adopted from Silva, 1997)

Two consequential biological nitrification reactions can be presented by:

The total reaction can be written as:

Based on the above-mentioned reactions, two moles of oxygen are required to oxidize one mole of ammonium nitrogen to nitrate. This is equivalent to the consumption of 4.57g of oxygen per gram of $\text{NH}_4^+\text{-N}$ oxidized. Meanwhile two moles of H^+ are produced from the oxidation of 1 mole of ammonium, that equals to 7.1mg CaCO_3 alkalinity depleted per mg of ammonia nitrogen oxidized (USEPA, 1993).

If the empirical formula $\text{C}_5\text{H}_7\text{NO}_2$ stands for the formation of biomass, the following reaction can be written to represent the growth of nitrosomonas and nitrobacters (Sørensen and Jørgensen, 1993).

Combine the equation A-6 and equation A-7, the overall synthesis and oxidation reaction for ammonia to nitrate can be simplified as:

Equation A-8 predicts that 1mole ammonium can produce 0.021 mole of nitrifying biomass, and needs 1.98 moles of HCO_3^- , which is equivalent to an alkalinity reduction of 7.07 g $\text{CaCO}_3/\text{g NH}_4^+\text{-N}$ consumed. This means in the nitrification process, when the wastewater does not have enough alkalinity, the pH drops. So in order to maintain a favorable process condition, the addition of a base might be necessary if large quantity of ammonia need to be removed.

A.3 Kinetics of BOD Removal and Ammonia Nitrification

A.3.1 Carbonaceous Oxidation

If biological oxygen demand (BOD) presents organic carbon compound, then the change of BOD value can therefore evaluate the degree of organic carbon oxidation by microorganism. As this process is considered a first order reaction, BOD removal

kinetics can be expressed by the following expression (Metcalf, 2004):

$$C_{BOD} = C_{uBOD} (1 - e^{-kt}) \quad (A-9)$$

Here C_{BOD} is the BOD value after time t

C_{uBOD} is the ultimate BOD (ie. The value of BOD at $t=\infty$)

t is reaction time (day).

K is the reaction constant, typically its value is in the range of 0.23–0.3 (1/day)

A.3.2 The Nitrification

The rate of growth of nitrifiers is affected by a number of variables. This makes theoretical modeling complicated. These affecting factors include ammonia concentration, temperature, pH, organic content and dissolved oxygen concentration. The Monod Model is the basic formula to describe the kinetics of biological growth of nitrifiers in nitrification process (Sørensen and Jørgensen, 1993)

$$\mu = \mu_{\max} \frac{S}{K_s + S} \quad (A-10)$$

Where μ = growth rate of micro-organisms (day⁻¹)

$\mu_{\max}$ = Maximum growth rate of microorganisms (day⁻¹)

K_s = Saturation constant equal to substrate concentration (mg/L), at half the maximum growth rate

S = Growth limiting substrate concentration (mg/L) for the nitrification process

This expression could be simplified for different situations. When substrate concentration is high enough ($S \gg K_s$), there will be no diffusion limitation and the microorganisms grow at the maximum growth rate $\mu_{\max}$, and the reaction rate becomes zero order. When the reaction is proportional to the substrate concentration, then the reaction can be considered as a first order reaction. In this case, the reaction rate will be directly governed by the ammonia concentration (S).

In a simultaneous carbon oxidation and ammonia nitrification process, the heterotrophic and autotrophic microorganisms co-exist and they digest carbon organics and nitrogen compounds.

(a) Relationship between the Nitrifiers Growth Rate and the Ammonia Oxidation Rate

The ammonia oxidation rate can be related to the nitromonas growth rate by the following correlation (Sørensen and Jørgensen, 1993).

$$\frac{dS}{dt} = -\frac{1}{Y} \frac{dX}{dt} \quad (\text{A-11})$$

Its Michaelis-Menten differential form is described as:

$$\frac{dS}{dt} = -\frac{\mu_{\max}}{Y} \cdot X \cdot \frac{S}{K_s + S} \quad (\text{A-12})$$

Where $\mu_{\max}$ = Maximum nitrosomonas growth rate (day^{-1})

dS/dt = Ammonia oxidation rate, $\text{mg NH}_4^+\text{-N oxidized /mg VSS}\cdot\text{day}$

Y = Nitrifiers yield coefficient ($\text{mg. nitrosomonas growth VSS/mg NH}_4^+$ removed)

S = Growth limiting substrate concentration (mg/L)

K_s = Saturation constant, NH_4^+ (mg/L)

X = Nitrifying mass cell concentration (mg/L)

In case the substrate concentration S is much higher than K_s , the above equation can be simplified into:

$$\frac{dS}{dt} = -\frac{\mu_{\max}}{Y} \cdot X \quad (\text{A-13})$$

an overview of the main physiological and kinetic characteristics of both types of nitrifying organisms is summarized in Table A.1.

Table A.1 (X_{NH}) and nitrite oxidizing bacteria (X_{NO}) (adopted from Hulle,2004)

Parameter	Unit	X_{NH}	X_{NO}
Maximum specific growth Rate ($\mu_{\max}$)	Day ⁻¹	0.3–2.2	0.2–2.5
Biomass yield (Y)	g VSS /g N	0.04–0.13	0.02–0.08
Affinity constant for TAN (K_{TAN})	mg TAN/L	0.06–27.5	
Affinity constant for TNO ₂ (K_{TNO_2})	mgTNO ₂ /L		0.1–15
Affinity constant for oxygen (K_{O_2})	mg O ₂ /L	0.03–1.3	0.3–2.5
Temperature range	°C	4–42	4–46
pH range		4.5–8.5	4.5–9

In Table A.1, the varying value for TAN and TNO₂ affinity constant can be explained by the fact that ammonia (NH₃) rather than ammonium (NH₄⁺) and nitrous acid (HNO₂) rather than nitrite (NO₂⁻) are the actual substrates for ammonium oxidizer and nitrite oxidizer growth, respectively (Suzuki et al.1974.)

(b) Relationship between Dissolved Oxygen and growth Rate of Nitrifiers

In nitrification processes, DO levels have a significant effect over nitrifiers growth rate and nitrification efficiency. If oxygen is regarded as a limiting substrate, then Monod model can be used to illustrate the relationship between nitrifiers growth rate and dissolved oxygen concentration.

(A-14)

where K_{O_2} is the half saturation constant for oxygen.

Equation A-14 is a substrate limiting model, in which only one substrate is taken into account. However in a biofilm process, either ammonia or oxygen can be concentration limiting components in the reaction. Therefore, a comprehensive model was developed (Sørensen and Jørgensen, 1993)

$$\mu = \mu_{\max} \cdot \frac{DO}{K_{O_2} + DO} \cdot \frac{S}{K_s + S} - K_d \quad (A-15)$$

All parameters are same as in Eq. (A-15), K_d is the decay or maintenance coefficient (day^{-1}).

The following table lists some of the specific growth rate equations obtained by other researchers to model carbon and ammonia oxidation respectively.

(c) Factors affecting Nitrification Processes

The most important parameters affecting nitrification include: the inhibition from the free ammonia (NH_3), free nitrous acid (NO_2^-), temperature, pH and DO.

Inhibition Effect

In the liquid phase, uncharged nitrogen forms are considered as the actual inhibitor for ammonium and nitrite nitrification. The amount of ammonia and nitrous acid present in the liquid phase can be described by the following equilibrium equations.

Free ammonia is in equilibrium with ammonium in the liquid phase, the concentrations of

free ammonia nitrogen (NH₃-N) can be expressed as follows (Yun and Kim,2003):

Table A.2 Reported specific growth rate equations used for carbon and ammonia oxidation. (adapted from Tsuneda, 2004)

Model	Equation for hetero trophic specific growth rate	Equation for autotrophic specific growth rate
Equation for autotrophic specific growth rate	$\mu_H = \frac{\mu_{\max H} S}{K_{MH} + S} - k_{eH}$	$\mu_A = \frac{\mu_{\max A} N}{K_{MA} + N} - k_{eA}$
Haldane with endogenous metabolism	$\mu_H = \frac{\mu_{\max H} S}{K_{MH} + S + S^2/K_{iH}} - k_{eH}$	$\mu_A = \frac{\mu_{\max A} N}{K_{MA} + N + N^2/K_{iA}} - k_{eA}$
Edwards with endogenous metabolism	$\mu_H = \frac{\mu_{\max H} S}{K_{MH} + S} \cdot \frac{1}{1 + S/K_{iH}} - k_{eH}$	$\mu_A = \frac{\mu_{\max A} N}{K_{MA} + N} \cdot \frac{1}{1 + N/K_{iA}} - k_{eA}$
Yano-Kogawith endogenous metabolism	$\mu_H = \frac{\mu_{\max H} S}{K_{MH} + S + S^3/K_{iH}^2} - k_{eH}$	$\mu_A = \frac{\mu_{\max A} N}{K_{MA} + N + N^3/K_{iA}^2} - k_{eA}$
Competitive inhibition with endogenous metabolism	$\mu_H = \frac{\mu_{\max H} S}{K_{MH} + S + S^2/K_{iH}} - k_{eH}$	$\mu_A = \frac{\mu_{\max A} N}{K_{MA} + N + N^2/K_{iA}} - k_{eA}$

$$NH_3 = \frac{NH_4^+ + 10^{pH}}{\frac{6344}{e^{273+T}} + 10^{pH}} \quad (A-18)$$

Basically, a higher temperature and/or a higher pH results in a higher ammonia concentration. this equilibrium relation ship can be visualized by Figure A.3

Figure A.3 The relations between ammonia and ammonium (Metcalf ,2004).

The concentrations of NH_3 and HNO_2 , as function of total ammonia nitrogen ($\text{NH}_4^+ + \text{NH}_3$), total nitrite concentrations ($\text{NO}_2^- + \text{HNO}_2$) and pH are presented in Figure . From the diagram, boundary conditions of zones of nitrification inhibition can be determined. The dashed lines mark the lower limit and the solid lines mark the upper limit of the range of boundary conditions of zones of nitrification inhibition.

Because the concentrations of these two forms depend on the solution pH, therefore NH_3 is the main inhibitor of nitrification at high pH (>8), whereas HNO_2 is the main inhibitor at low pH range.

Figure A.4 The inhibition effect of free ammonia and nitrite acid

pH Effect

According to USEPA, nitrification process is sensitive to pH. The nitrification can happen at a pH range of 6 to 10. However, the ideal pH range is between 7.5 and 8.0. (Metcalf, 2004). This preference of nitrifiers for slightly alkaline environments could be the fact that the nitrosomona and nitrobactor bacteria organisms use NH_3 as substrate, meanwhile the optimum pH range is also linked with the pH dependent $\text{NH}_4^+/\text{NH}_3$ and $\text{HNO}_2/\text{NO}_2^-$ equilibria, where NH_3 and HNO_2 can exhibit inhibitory effects starting from a certain pH, as explained above (Hulle, 2004). Figure A.5 depicts this dependence relations.

Figure A.5 Effect of pH on the activity of nitrification bacteria (The activity at pH 8.0 was used as the reference activity) (Grunditz and Dalhammar, 2001)

Temperature

Temperature is a key parameter in the nitrification process as it affects the growth rate of nitrifiers. Nitrification can occur at 4–45°C, but the optimal range is 30–35°C. In the range of 5–30 °C, the reaction rate will double with each 7°C increase in temperature (Environment Canada, 2003). Other studies have shown that nitrification was inhibited by a low temperature of 10°C or less. In addition, this inhibitory effect was greater for nitrobacters than for nitrosomonas, as this was proved by build-up of nitrite at lower temperatures (Sørensen et al., 1993).

Regarding the effect of temperature on the growth rate. Faup.G.M suggested the following Arrhenius type correlation between the saturation constant K_s , and the temperature in °C (Sørensen et al. 1993).

$$K_s = K_{20} \cdot e^{b \cdot (t-20)} \quad (\text{A-19})$$

In which b is the temperature coefficient and it varies with the bacterial concentration (MLVSS), if X presents the bacterial concentration, and then the correlation can be expressed as:

$$b = 0.00044 \cdot X^{0.69} \quad (\text{A-20})$$

This effect can be illustrated by minimum residence time under different temperatures by the following diagram.

Figure A.6 Temperature effect on minimum residence time (Philips et al. 2002)

Dissolved Oxygen (DO) Availability

DO can be a limiting factor of nitrification. A DO concentration of 0.4–2.0 mg/L can reduce the maximum rate to half (Environment Canada, 2003). Some workers recommend a DO greater than 2 mg/L for nitrification (Metcalf, 2004).

The dissolved oxygen concentration is of utmost importance for both ammonia nitrifiers and nitrite nitrifiers. However, the latter seems to be more sensitive towards low DO than ammonia nitrifiers. Accumulation of NO_2^- at low DO is usually explained by the difference in oxygen half saturation constant (K_O) for ammonia nitrifiers and nitrite nitrifiers (Philips et al. 2002). This means that oxygen deficiency due to a low DO influences the activity of nitrite nitrifiers more significantly than that of ammonia nitrifiers. Therefore, maintaining a high dissolved oxygen level is a prerequisite for eliminating insufficient ammonia oxidation in the nitrification process.

APPENDIX B

Calculations for the TFBR Design

B.1 Reaction Time and Reactor Dimensions

B.1.1 Reaction Time

(a) Ammonia Nitrification

According to half rate model, the reaction rate for ammonia

$$\frac{dC_{NH_3}}{dt} = -kC_{NH_3}^{1/2} \quad (\text{Quiñones-Bolanos, 2000})$$

Where $k = 10.96 \text{ mg}^{1/2} \text{ l}^{1/2} / \text{h}$

Influent ammonia concentration $C_{NH_3 \text{ in}}$: 200 mg/L

Desired removal efficiency: 95%

Effluent ammonia concentration $C_{NH_3 \text{ out}}$: 10 mg/L

Integrate above equation to get:

$$t = \frac{1}{2k} (\sqrt{C_{NH_3 \text{ in}}} - \sqrt{C_{NH_3 \text{ out}}})$$

Thus the reaction time is $t = 0.39 \text{ h}$

Given that the inhibition effect over nitrification by high BOD, adopt a safety factor.

Factor $f = 3.0$ (usually 1.5–3).

Then a realistic reaction time is 1.2 h

(b) BOD Removal

In a synthetic wastewater prepared with sugar, it is generally believed that the BOD₅ is 60–70% of the COD, thus assume BOD₅ = 60% COD,

Then according to BOD reaction kinetic equation.

$$C_{BOD} = C_{uBOD}(1 - e^{-kt})$$

here $C_{uBOD} = 3,000 \text{ mg/L}$

$$C_{\text{BOD}} = 300 \text{ mg/L} \quad (\text{assume } 90\% \text{ percent removal})$$

$$K = 0.23 \text{ 1/day}$$

Calculated reaction time $t = 0.2 \text{ day} = 5.4 \text{ h}$

As mentioned above, this reaction time should be multiplied by a safe coefficient f , it's value usually is 1.5–3.

Take $f = 1.5$ h

Then a realistic reaction time is 8.0 h

Thus, the designed reaction time is 8.0 h

The residence time of the liquid phase in the TFBR is chosen between the hydraulic residence time and reaction residence time. Here it is chosen by reaction residence basis as hydraulic time is very difficult to determine.

B.1.2 Reactor Volume and Dimensions

According to the residential time and influent flow rate in design requirement $Q = 62.5$

$$\text{L/hr} = 1.7 \times 10^{-5} \text{ m}^3/\text{s}$$

So required reactor volume: 0.5 m^3

Reactor diameter and liquid superficial velocity

If presume the effective reactor volume ratio is: 70 m^3

The gross reactor volume should be: 0.71 m^3

The maximum the reactor height: 2.5 m

Then the diameter of the reactor should be: 0.60 m

And cross section area: 0.29 m^2

Corresponding liquid superficial velocity is: 0.006 cm/s

Calculated dimensions of the TFBR is listed in the table of below.

Calculated TFBR dimensions:

Number of Sections:	3
Column height:	2.5 m
Column diameter:	60.5 cm
Stand elevation:	35 cm
Free space (over head):	0.50 mm
Gross volume:	0.71 m ³

The circulation ratio

As the residential time might need to be adjusted in various experiment, it is desirable that residence time can be adjusted to meet the future study.

Therefore put part of effluent into circulation is necessary. The hydraulic residence time $HRT = V/Q = H.A/Q = H/V_l$

A : the cross section area of TFBR (m²)

H : the height of the TFBR (m)

Q : the total fluent flow rate (m³/s)

V_l : liquid superficial velocity (m/s)

Based on calculated superficial velocity = 0.006 cm/s. In order to get a various residence time, the superficial velocity should be larger, the difference between the influent and required velocity can be make up by circulation. Thus following table should be followed for a different HRT.

Table B.1 The Relationship between HRT and Circulation Ratio

HRT (h)	7	6	5	4	3	2
Circulation ratio	0.63	0.90	1.286	1.857	2.81	4.71
Total feed flow rate (LPM)	1.70	1.98	2.377	2.971	3.96	5.94

Based on above table, the minimum HRT = 2 h, correspondingly the Max. recirculation ratio is 4.71, corresponding feed flow rate will be 5.9 LPM. So required recirculation pump capacity should be more than 6 LPM.

B.2 The DO Requirement for TFBR and Supply

B.2.1 Oxygen Requirement Calculation

Required oxygen (kg/day):

$$Q*(f*(S_i - S_o) + 4.57(N_i - N_o))/1000 \quad (\text{Water Pollution Control Federation, 1983})$$

The Parameter of Influent and Effluent list in followings

Q = flow rate:	1.5 m ³ /day
S_i = influent BOD5 concentration:	3,000 mg/L
Required BOD removal percentage:	95%
S_o = effluent BOD5 concentration:	150 mg/L
f = factor for the oxygen consumption:	1.2–1.3 takes 1.3 in this design
N_i = the influent ammonia	200 mg/L
Required ammonia removal percentage:	95%
N_o = the effluent NH ₃	10 mg/L

B.2.2 The Air Requirement

The total oxygen requirement for BOD removal and ammonia nitrification = 6.2 Kg/day

That equal to air:	27.0 kg/day = 20.9 m ³ /day
The standard air density:	1.29 kg/m ³
Assume the oxygen transfer efficiency:	12%,
Then needed air quantity:	174.1 m ³ /day = 7.3 m ³ /hr

B.2.3 The Configuration of Air Diffusers

If set safety factor as 2, then transferred oxygen should be: 12.4 kg/day. Based on the structure of reactor and specifications of EDI air diffuser, Reactor is configured in two different groups. the detailed specifications and operating parameters listed in Table 1.3

in Chapter 3.

B.3 Oxygen Transfer Coefficient Calculation by Bubble Bed model

According to Joshi gas hold up correlation (Joshi and Sharma,1979)

$$\varepsilon_G = \frac{V_G}{0.3 + 2 \cdot V_G}$$

In designed reactor, the Qg:	0.0033 m ³
Superficial velocity V _G :	0.012 m/s
Calculated air hold up:	3.6%

According to the Kawase equation (Kawase et al.1987)

$$K_{L_a} = 2 \cdot \sqrt{\frac{D_L}{\pi}} \cdot \sqrt{\frac{V_G \cdot g}{\mu_L}}$$

Here V _G is superficial gas velocity:	0.012 m/s
D _L is air diffusivity in water:	3.721E - 05 m ² /s
u _L is water viscosity:	0.00089 s.N/m ²

From this equation, the calculated K_{La}=0.023 1/s

APPENDIX C

The OTE curves of EDI Flex Air diffusers

C.1 EDI FlexAir™ 9" Disc Diffuser OTE Curves

C.2 EDI FlexAir T-Series Diffuser OTE Curves

APPENDIX D

Specifications of Equipments and Instruments

D1 Specifications of LDO HQ10 Portable Dissolved Oxygen Meter

General Characteristics	
Display	Dot matrix LCD with electroluminescent backlight
Inputs	5-pin Hach dissolved oxygen probe locking connector
Outputs	RS232 via Docking Station optional
Power requirements	4 AA alkaline batteries, or power through the Docking Station
Dissolved Oxygen Measuring Mode	
Measuring Range	0–20 mg/L (ppm) 0–200% saturation
Accuracy	0.1 mg/L for 0–8 mg/L, 0.2 mg/L for greater than 8–20 mg/L
Temperature	0–50°C (32 –122 F)
Measuring Unit	Oxygen Concentration: 0.01 or 0.1 mg/L (ppm), % Saturation: 0.1% , Temperature: 0.1°C(0.1F)

D2 The Vacuum Column and Specifications

Column Structure	
Material	Clear PVC
Consisting sections	Reservoir, lower packed bed, upper packed bed, demister.
Dimensions	1030 mm (Diameter) x 2430 mm (height) 10 mm(wall thickness)
Column Packing	
Packing material	Tri-Pack
Packed height	1,100 mm
Packing Media size	Diameter (D) = 25 mm and 50 mm
Specific surface area	279 m ² /m ³ (D=25mm), 157m ² /m ³ (D=25mm)
Void Space	90% (D=25mm) and 93%(D=50mm)
Bulk Density	99.4 kg/m ³ (D= 25 mm) 64.4 kg/m ³ (D = 50 mm)
Packing factor	15
Operation parameters	
Maximum vacuum	30 In W.C.
Operating vacuum	27.5 In W.C.
Loading capacity	150 LPM
Inlet DO level	7–10 mg/Lvary with the temperature
Outlet DO level	0.8–2.0mg/L@vacuum =27.5 and water temperate =12°C

D3 Vacuum Pump Specifications

Type	Oil Ring Vacuum Pump
Free Air Displacement	5.3 CFM
Ultimate Vacuum	27 In W.C.
Oil requirement	2.37 L
Efficiency	60%@ 1µm Hg
Manufacturer	Precision Pump Co.
Motor	5KC38RN4x, ¾ Hp, 1725RPM

D4 COD Test Instruments and Reagents

1. COD Reactor Block	
Name	Accu-TEST ® COD Reactor Block
Capacity	30 vials, 16mm diameter
Operating Temperature	150±2°C
Power requirement	110 V or 220 V
2. Colorimeter	
Name	Orbeco-Hellige 975MP Portable Water Analysis colorimeter
Wavelength	608um
Particle size	Diameter = 25 mm and 50 mm
Calibration	Plant preloaded
3. Reagents	
1)	Standard potassium dichromate digestion solution
2)	Sulphuric acid reagent

D5 Specifications of Ammonia Electrode and Nitrate Electrode

1. Ammonia selective electrode	
Methodology	Ammonia Gas Sensing Combination Electrode
Concentration Range	0.06 to 17,000 mg/L NH ₃ . 0.05 to 14,000 mg/L NH ₃ -N
Temperature Range	Operating: 0 to 50 °C Storage: -40 to 60 °C
pH Range	> pH 11; Ionic Strength Adjustor raises pH above 11
Slope	-57 ± 3 mV/decade in linear concentration range
Response Time	95% response in three minutes or less in linear range
Electrode Connector	BNC twist type
Ammonia Membrane Modules	Replaceable membrane modules
2. Nitrate Platinum electrode	
Methodology	Nitrate Platinum Series Combination Electrode
Reference Electrolyte	Ammonium Sulfate Reference Electrolyte
Concentration Range	0.05 mg/L 3.5×10^{-6} N to 14,000 mg/L (NO ₃ ⁻ -N)
Linear Region	4 mg/L to 14,000 mg/L NO ₃ ⁻ -N
Temperature Range	Routine Use: 10 to 30 °C Occasional Use: 10 to 50 °C Storage: -40 to 50 °C
Sample pH Range	3 to 11 ISA should bring to 3.6
Slope	58 ± 3 mV/decade
Response Time	In linear range, 10 to 60 seconds
Cable Connector	BNC twist type

D6 Technical Specifications of Sension™2 Meter

General Characteristics		
Display	Custom LCD	
Inputs	1BNC; 5-pin Hach pH/temperature or Hach temperature probe	
Output	Display or One-way RS232	
Input Impedance:	>10-12 ohms	
Instrument Drift	< 40μV/°C	
Input Bias Current	< 1 picoamp at 25°C , v< 4 picoamp over full range	
Application	0 to 50°C at 85% non-condensing relative humidity	
Functions and Analysis Modes		
PH mode	Range	-2.00 to 19.99
	Resolution	0.001/0.01/0.1 selectable
	Slope range	58 ±3 mV/decade
ISE mode	Range	0.000 to 19,900
	Resolution	0.1/0.01/0.001 selectable
Millivolt mode	Range	-2,000 to 2,000 mV
	Resolution	0.1 mV
	Accuracy	0.2 mV or 0.05% of reading
Temperature mode	Range	-10.0 to 110 0C can also display °F
	Resolution	0.1 °C
	Accuracy	1.0 °C

D7 The Specifications of the pH Meter

Parameters	Value	
PH probe	HI 1230B	
Temperature compensation	automatic or manual, -5 to 105°C 23°F to 221°F	
pH measurement	Range	0.00 to 14.00 pH
	Resolution	0.01 pH
	Accuracy	±0.01 pH
mV measurement	Range	±399.9 mV; ±1,999 mV
	Resolution	0.1 mV; 1 mV
	Accuracy	±0.2 mV; ±1 mV

APPENDIX E

Unit Operations at the Water Treatment Technologies

Laboratory

Chemical Engineering Department, Ryerson University

E.1 Vacuum System

E.1.1 Start up Procedure

1. Check vacuum column, the inside water distributors and all valves. Close all the outlet valves including the drain valve at the bottom.
2. Check level alarm controller and make sure it is in working order.
3. Check discharge pump and pump controller.
4. Check oil level in vacuum pump and connection pipes, make sure it is in good working conditions.
5. Open tap feed water valve start feeding water into the vacuum column.
6. Open valve on the vacuum pipe and start the vacuum pump, check the vacuum pump working conditions without strong vibration and noise.
7. Check the pressure change in the vacuum column gauge. The vacuum in the vacuum column should increase to 27 inch water column (In W.C.) within a half hour. If not, check leakage with soap solution.
8. When the deaerated water level in the reservoir of the vacuum column is higher than low alarm level, start outlet pump. Take a sample and analyze the DO

concentration in the sample. If the DO concentration is lower than 2 mg/L, the vacuum system is already working under normal conditions and the deaerated water can be discharged out of system for other operations. Otherwise start the recirculating valve on recirculating line. Let part of the deaerated water go back to the column. At the same time, reduce the opening of the discharge valve slowly until the DO concentration meets required value of 2 mg/L or less. Then readjust the discharge valve to feed related equipment (RBC, FBRs).

9. The deaerated water level in the vacuum column need be monitored carefully to prevent that the level is too high to uppack the Tri-Pack particles in the vacuum column, especially in the situation when system is operated without the using of alarm controller.

E.1.2 Shut down Procedure

1. Firstly, stop the feed water by closing the feed water valve.
2. Stop the discharge pump.
3. Stop vacuum the pump and close the valve on the vacuum line to prevent the water flowing into vacuum pump or oil in the vacuum pump flow into vacuum column.
4. Slowly open the valve on the recirculation line that connect to the recirculation tank. Let air come into the column slowly. When the pressure in the vacuum column restores to atmospheric pressure (the reading of vacuum gauge drop to zero), open the drain valve to drain out the residual water in the vacuum column.

E.2 The operation of Three-Phase Fluidized Bed (TFBR) System

E.2.1 Start up Procedure:

1. Close the valve on the drain line and open the valve on the effluent line, then feed the TFBR with tap water until the reactor is full (water comes out from the effluent line).
2. Check for leakages on the feed line, TFBR column and effluent line. If there are no leakages, start compressed air slowly, check if there is any leakage on the air diffusers (coarse air bubbles will come out if there is any leakage around diffuser membrane). If any leakage is found, empty the TFBR and fix the leakage. Redo leakage test otherwise go to the next step.
3. Empty the TFBR, open the hand-hole flange located on the upper section of the TFBR, load the biomedica solids until the required amount. seal the hand-hole flange.
4. Feed the seeding sludge into the TFBR through the particle sampling port located on particle loading flange. Close the sampling port valve. Feed synthetic wastewater into the TFBR until all the biomedica solids emerge in the liquid. Then open the compressed air valve and start the aeration. The flow rate can be half of the designed airflow rate or even lower. The particle will move slowly in the TFBR.
5. When the suspended biomass in the TFBR increases to certain concentration, the liquid phase color will become milky. Then feed the TFBR with synthetic water (or real wastewater). At the same time, increase the air flow rate so that all biomedica in the TFBR is fully fluidized.
6. The liquid flow rate increases in small steps by inching up every 2-3 days until it reach the designed flow rate.
7. Keep the TFBR in continuous operation, and the biofilm will develop on the biomedica after 2-3 weeks time.
8. The TFBR can be operated under various parameters for a specific research.

E 2.2 Operation and Sampling:

1. The feed pump is located near the 4.5 m³ feed tank. The rate of influent wastewater can be adjusted with either the feed pump or feed rate control valve located after the feed pump.
2. The effluent can be discharged into the recycling or directly into drain system by the control valves located on the recycling line and effluent line.
3. The flow rate of compressed air to the primary and secondary air diffusers can be controlled independently according to specific purposes.
4. in the TFBR has a total of total 12 sampling ports, of which two are located on the influent line and effluent line respectively, the others ten are arranged longitudinally on the TFBR. Detailed information is listed in Table 3.6, thus samples can be take from the influent, effluent and different positions on the TFBR column.
5. when high high liquid superficial velocity is needed in the TFBR, the circulating tank and circulating pump can be put into use to achieve this purpose. The available circulating ratio can as high as 20 times the designed influent flow rate (see appendix B.)
6. When biomass sediment accumulates in the influent distributor (located around air diffusers in the bottom section of the TFBR), back flush becomes necessary. Connect the compressed air hose to sampling port on the inlet line. Open and close the compressed air a few times. Then the clogged biomass will be cleaned.
7. To start aeration, the airflow rate is increased slowly. If the air increases too fast, the liquid in the TFBR will over flow into the vent hood.

E.2.3 Shut down Procedure

1. When the TFBR operation needs to be discontinued, stop influent and start to feed tap water and keep the reactor running continuously.
2. Increase the air flow rate so that the turbulence produced in the reactor will wash out the biofilm dislodging rate from the media.

3. Keep the TFBR running with tap water for around one week. The water in the column will become clear and there will be no visible biomass presented in the water phase in the TFBR. That means the biofilm have been removed from the media.
4. Stop water and air supply. Dry for one week the media in the TFBR, then the residual water will evaporate naturally.
5. Open the hand-hole flange that close to bottom section, discharge the clean media to a proper container.
6. If residual biomass still exists in the influent distributor or the bottom area in the reactor bottom, put some NaOH solution and keep the area submerged in the NaOH solution for a few hours. Next drain the NaOH solution to a container for proper disposal. Flush with clear water the parts or area treated by the NaOH solution. The TFBR should be now clear completely clean.
7. Clear the outside of TFBR and relevant equipment. Keep them in clean and good properly conditions.

APPENDIX F

Complete Raw Data in the Synthetic Wastewater Treatment Tests in This Study

Date	Flow rate (LPM)	COD _{in}	COD _{out}	Rem (%)	TSS (mg/0.1L)	DO (mg/L)	PH	Temp (°C)	DO in Influent	Loading Rate		
										kg COD /day.m ³	Kg COD /day.m ³ removed	SLR g/m ² /d
8-Jul	1.2	4833	987	80.1	101.0	5.7	2.5	28–29	2.3	12.0	9.6	47.84
8-Jul		5047	883	81.7								
9-Jul	1.2	5625	1084	78.5	91.2	5.8	2.7	27–28	1.2	13.3	10.5	51.93
9-Jul		5319	740	86.8								
10-Jul	1.2	4879	1048	80.3	96.6	5.7	2.8	28–29	3.5	12.5	10.1	49.96
10-Jul		5417	1118	77.1								
11-Jul	1.2	4849	938	82.7	87.0	5.2	2.4	29–30	4.2	12.0	10.0	49.43
11-Jul		5045	554	88.6								
12-Jul	1.2	5316	865	82.9	92.2	5.4	2.5	27–28	3.7	12.8	10.6	52.85
12-Jul		5241	790	85.1								
13-Jul	1.4	4810	1657	68.4	154.0	5.3	2.6	27–29	6.2	14.4	9.9	48.96
13-Jul		5345	1466	69.5								
14-Jul	1.0	4992	1400	73.8	127.7	5.3	2.4	28–29	5.8	10.4	7.6	37.94
14-Jul		5217	1476	70.4								
15-Jul	1.0	4739	1191	77.2	112.2	5.3	2.4	28–29	1.2	10.2	7.8	38.90

Complete Raw Data in the Synthetic Wastewater Treatment Tests in This Study (continue 1)

Date	Flow rate (LPM)	COD _{in}	COD _{out}	Rem. (%)	TSS (mg/0.1L)	DO (mg/L)	PH	Temp (°C)	DO in Influent	Loading Rate		
										kg COD /day.m ³	Kg COD /day.m ³ removed	SLR g/m ² /d
15-Jul		5272	1265	73.3								
16-Jul	1.0	4663	1339	74.6	117.2	5.4	2.3	28–29	2.3	10.3	7.7	38.20
16-Jul		5506	986	78.9								
17-Jul	1.0	5233	882	84.0	110.4	5.6	2.6	28–29	6.5	10.8	9.1	45.07
17-Jul		5424	797	84.8								
18-Jul	1.0	4927	923	83.0	114.3	5.3	2.5	28–29	3.5	10.3	8.5	42.40
18-Jul		5219	829	83.2								
19-Jul	1.0	4625	985	81.1	108.8	5.8	2.5	27–30	7.0	10.2	8.3	41.15
19-Jul		5449	904	80.5								
20-Jul	1.0	5616	689	87.4	125.1	5.5	2.5	28–29	4.8	10.7	9.3	46.28
20-Jul		4905	762	86.4								
21-Jul	1.0	5406	698	85.8	124.7	5.6	2.4	28–29	5.9	10.7	9.2	45.50
21-Jul		5130	796	85.3								
22-Jul	1.0	5660	771	85.0	123.3	5.1	2.4	29–30	5.4	10.8	9.2	45.58
22-Jul		4994	680	88.0								
23-Jul	1.0	5555	731	85.4	123.9	5.2	2.3	29–30	2.6	11.2	9.6	47.51

Complete Raw Data in the Synthetic Wastewater Treatment in This Study (continue 2)

Date	Flow rate (LPM)	COD _{in}	COD _{out}	Rem (%)	TSS (mg/0.1L)	DO (mg/L)	PH	Temp (°C)	DO in Influent	Loading Rate		
										kg COD /day.m ³	Kg COD /day.m ³ removed	SLR g/m ² /d
23-Jul		5497	600	89.2								
24-Jul	1.0	4960	365	93.4	119.1	5.3	2.5	29-30	6.4	10.2	9.5	47.18
24-Jul		5077	491	90.1								
25-Jul	1.0	5420	402	92.1	121.5	5.2	2.5	28-30	5.0	11.2	10.3	51.01
25-Jul		5581	480	91.1								
26-Jul	1.0	6351	2306	58.7 [#]	122.9	4.8	2.5	27-30	6.5	12.4	7.3	36.28
26-Jul		5924	1605	74.7								
27-Jul	1.0	5872	1185	80.0	149.4	5.2	2.4	28-30	3.7	12.2	9.7	48.33
27-Jul		6125	1237	78.9								
28-Jul	1.0	6032	1049	82.9	153.4	4.9	2.4	28-30	6.2	12.6	10.5	51.93
28-Jul		6412	1187	80.3								
29-Jul	1.0	6379	1161	81.9	147.6	5.3	2.5	29-30	6.1	13.0	10.7	53.02
29-Jul		6479	918	85.6								
30-Jul	1.0	5959	942	85.5	149.2	5.2	2.5	28-30	5.6	11.9	10.2	50.60
30-Jul		5800	1028	82.7								

Complete Raw Data in the Synthetic Wastewater Treatment in This Study (continue 3)

Date	Flow rate (LPM)	COD _{in}	COD _{out}	Rem (%)	TSS (mg/0.1L)	DO (mg/L)	PH	Temp (°C)	DO in Influent	Loading Rate		
										kg COD /day.m ³	Kg COD /day.m ³ removed	SLR g/m ² /d
31-Jul	1.0	6167	887	84.7	147.6	5.2	2.4	29-30	5.2	12.2	10.3	51.13
31-Jul		5820	904	85.3								
1-Aug	1.0	5865	948	83.7	152.2	5.3	2.6	28-30	2.8	12.5	10.5	52.01
1-Aug		6473	920	84.3							0.0	

APPENDIX G

The Nitrogen Balance in the TFBR System

Date	Flow rate (LPM)	NH ₃ -N _{in} (mg/L)	NH ₃ -N _{out} (mg/L)	Effluent NO ₃ -N	Biomass (mg/0.1L)	Nitrogen in (g/day)	Nitrogen out (g/day)			Δ	Perc. (%)*
							NH ₃ -N	NO ₃ -N	N in biomass		
July 7	1.2	227	102.0	2.6	106.5	392.3	176.3	4.5	222.9	399.1	-6.9
July 8	1.2	227	106.2	1.6	101.0	392.4	183.5	2.8	211.4	394.9	-2.4
July 9	1.2	216	104.8	2.0	91.2	373.2	181.1	3.5	190.8	371.9	1.3
July 10	1.2	224	109.3	2.2	96.6	387.1	188.9	3.7	202.1	391.0	-3.9
July 11	1.2	213	105.5	1.6	87.0	368.1	182.3	2.8	182.1	364.4	3.7
July 12	1.2	214	96.0	2.9	92.2	370.3	165.9	4.9	192.9	358.8	11.5
July 13	1.4	224	101.6	2.1	154.0	452.2	204.8	4.2	376.0	580.8	-128.6
July 14	1.0	219	118.7	3.1	127.7	315.4	170.9	4.5	222.7	393.6	-78.3
July 15	1.0	226	107.1	3.4	112.2	325.4	154.2	4.9	195.7	349.9	-24.4
July 16	1.0	229	105.3	3.0	117.2	329.8	151.6	4.3	204.4	356.0	-26.3
July 17	1.0	217	94.1	2.9	110.4	312.5	135.5	4.2	192.5	328.0	-15.5
July 18	1.0	223	95.0	2.5	114.3	321.1	136.8	3.6	199.3	336.1	-15.0
July 19	1.0	230	93.2	3.0	108.7	331.2	134.2	4.3	189.7	323.9	7.3
July 20	1.0	237	92.2	2.7	125.1	341.9	132.8	3.8	218.2	350.9	-9.1
July 21	1.0	232	96.9	3.0	124.7	334.1	139.5	4.3	217.5	357.0	-22.9
											-6.86

The Nitrogen Balance in the TFBR System (continue)

Date	Flow rate (LPM)	NH3 -N _{in} (mg/L)	NH3 -N _{out} (mg/L)	Effluent NO ₃ -N	Biomass (mg/0.1L)	Nitrogen in (g/day)	Nitrogen out (g/day)				Δ	Perc. (%)
							NH ₃ -N	NO ₃ - N	N in biomass	total		
July 22	1.0	232	92.2	2.5	123.3	335.1	132.8	3.6	215.0	347.8	-12.7	-3.79
July 23	1.0	224	92.7	3.2	123.9	323.3	133.5	4.6	216.1	349.5	-26.3	-8.13
July 24	1.0	230	96.4	2.5	119.1	331.2	138.8	3.6	207.7	346.5	-15.3	-4.62
July 25	1.0	232	95.3	2.3	121.5	333.8	137.2	3.3	211.9	349.1	-15.3	-4.59
July 26	1.0	228	91.6	2.6	122.9	328.3	131.9	3.7	214.3	346.2	-17.9	-5.45
July 27	1.0	236	54.0	2.2	149.4	339.1	77.8	3.2	260.5	338.3	0.8	0.24
July 28	1.0	222	50.2	2.4	153.4	320.3	72.3	3.5	267.5	339.8	-19.5	-6.10
July 29	1.0	235	59.8	2.0	147.6	339.1	86.1	2.9	257.4	343.5	-4.4	-1.29
July 30	1.0	239	57.3	2.3	149.2	344.6	82.5	3.3	260.2	342.7	1.9	0.55
July 31	1.0	233	60.3	2.4	147.6	335.1	86.8	3.5	257.4	344.2	-9.1	-2.73
Aug. 1	1.0	230	56.7	2.7	152.2	331.2	81.6	3.9	265.4	347.1	-15.9	-4.79

Note: 1. The calculation of nitrogen percentage in biomass is based on the biomass formula: C₃H₇NO₂P_{0.075}

2. The percentage (%) mean the unaccounted N in percentage of total Nitrogen come in the TFBR.

3. Δ is the difference between the amount of nitrogen and nitrogen came out of the TFBR system.