University of Alberta

Alternative Treatment Technologies to Deep Well Disposal of Industrial Wastewater

by

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ABSTRACT

The suitability of wastewater disposed of by deep well injection was assessed to identify candidate wastewaters for treatment by other means such that the treated stream could be discharged to surface waters or re-used in an industrial process. The project goal was consistent with the water conservation objective specified in Alberta's Water for Life Strategy. The suitability of wells operated under approval numbers 3924, 8185, 8926, 8713, 9699, and 8784 was not assessed because either inadequate data were available or the volume injected was below the 10,000 m^3/mo minimum established in Phase I of this project.

The most suitable treatment sequence for the well operated under approval number 4779 may be a biofilter followed by nanofiltration/reverse osmosis membrane. This should be verified via bench-scale testing before proceeding to pilot- or full-scale treatment. The appropriate treatment for the well operated under approval number 8951 is most likely an American Petroleum Institute separator followed by demulsification of oil and dissolved air flotation with a membrane or a lagoon. The most feasible option for the well operated under approval number 5737 well is believed to be chemical flocculation followed by dissolved air floatation. The most effective alternative to deep well disposal for the wastes disposed under approval number 7842 well appears to discharge to the municipal sewer system.

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LIST OF ABBREVIATIONS

A^2O^{TM} : Anaerobic/Anoxic/Aerobic BPR
ACWUPP: The Advisory Committee on Water Use Practice and Policy
AENV : Alberta Environment
AF : Air Flotation
AFS : Advanced Filtration Systems
ALR : Airlift Loop Bioreactor
ANAMMOX® : Anaerobic Ammonium Oxidation
API : American Petroleum Institute
ARC : Alberta Research Council
AS : Activated Sludge
ASBR : Anaerobic Sequencing Batch Reactor
AWWA : American Water Works Association
BAF : Biological Aerated Filter
BETX : Benzene, Ethybenzene, toluene, and Xylene
BOD : Biological Oxygen Demand
BPR : Biological Phosphorous Removal
BNR : Biological Nitrogen Removal
CANON® : Completely Autotrophic Nitrogen Removal Over Nitrite
CCME : Canadian Council of Ministers of the Environment
CEQG : Canadian Environmental Quality Guidelines
COD : Chemical Oxygen Demand
CPI : Corrugated Plate Interceptors
CSTR : Continuously Stirred Tank Reactors
DAF : Dissolved air flotation
DNA : Deoxyribonucleic Acid
DO : Dissolved Oxygen
DOC : Dissolved Organic Carbon
EC : Electrocoagulation
EF : Electrofloatation
ER : Enhanced Recovery
EUB : Alberta Energy and Utilities Board
F : Flocculants
FWS : Free Water Surface
GAC : Granular Activated Carbon
HC : Hydrocarbon
HRT : Hydraulic Retention Time
IAF : Induced Air Flotation

IC : Inorganic Coagulants
ID : Identification
KLD : Koch Liquid Detergent
MAP : Magnesium Ammonium Phosphate
MBR : Membrane Bioreactor
MD : Membrane Distillation
MF : Microfiltration
MLSS : Mixed Liquor Suspend Solids
MTBE : Methyl Tertiary Butyl Ether
N/DN : Nitrification/Dentrification
NF : Nanofiltration
NTU : Nephelometric Turbidity Unit
OC : Organic Coagulants
OLAND® : Oxygen Limited Autotrophic Nitrification Denitrification
PAC : Powdered Activated Carbon
PACT® : Activated Sludge with Powdered Activated Carbon Treatment
PAHs : Polycyclic Aromatic Hydrocarbon
RAS : Return Activated Sludge
RBC : rotating biological contactor
RBCs : Rotating Biological Contactors
RNA : Ribonucleic Acid
RO : Reverse Osmosis
SBBR : Sequencing Batch Biofilm Reactor
SBR : Sequencing Batch Reactor or Sludge Blanket Reactor
SCFH : Standard ft^3/hr
SHARON® : Single Reactor System for High Ammonium Removal
SRT : Solids Retention Time
SS : Suspended Solids
SSF : Subsurface Flow
SVI : Sludge Volume Index
TDS : Total Dissolved Solids
TKN : Total Kjeldahl Nitrogen
TN : Total Nitrogen
TOC : Total Organic Carbon
TOC : Total Organic Carbon
TP : Total Phosphorous
TPH : Total Petroleum Hydrocarbons
TPI : Tilted Plate Interceptor

TSS : Total Suspended Solids
TUF : Tubular Ultrafiltration
UASB : Anaerobic Sludge Blanket Reactor
UBAF : Upflow Biological Aerated Filter
UCT : University of Cape Town
UF : Ultrafiltration
USDW : Underground Sources of Drinking Water
US EPA : United States Environmental Protection Agency
UV : Ultraviolet
VOC : Volatile Organic Carbon
VSS : Volatile Suspended Solids
WEF : Water Environment Federation
WO : Wet Oxidation
WWTP : Wastewater Treatment Plant

1. INTRODUCTION

1.1. Background

The demands on water supplies have gradually increased because of population growth and economic development; nevertheless the quantity of available water is limited. Therefore, water conservation has become an issue of increasing importance. The Government of Alberta also has recognized the problem regarding water shortage in the future and has established Water for Life: Alberta's Strategy for Sustainability, in 2002. As a part of the water conservation effort, concerns have been raised regarding the removal of the water from the active natural cycle as the result of underground injection of water or wastewater by the industries. Hence, the Advisory Committee on Water Use Practice and Policy has suggested a review of the use of water for underground injection purposes including the deep well disposal of industrial wastewaters, and subsequent research into treatment technologies that allow this water to be retained in the active hydrologic cycle.

Accordingly, research pertaining to (1) the identification of available data and information on deep well disposal of wastewater in Alberta; (2) the evaluation of the quantity and quality of deep well injected waste streams; and (3) a preliminary assessment of the feasibility of water reuse was conducted by Chen and Kindzierski (2005). Chen and Kindzierski (2005) classified 37 Class Ia wells used for industrial wastewater disposal in Alberta into 8 different categories on the basis of the criteria shown in Table 1.1. The results of this classification and the recommendations regarding the need for further treatability evaluation are presented in Table 1.2 and Table 1.3, respectively.

Among the categories, C, E, F, and G wells were recommended for further study to collect detailed up-to-date information regarding the deep well injected wastewater, or to assess the feasibility of alternative treatment options to reutilize the water. The recommendations for particular wells, along with category and approval numbers, are summarized in Table 1.3. The recommended research was carried out for each individual well during the current project.

Table 1.1. Criteria for Disposal Well Categorization and Recommendations for Each Category (Adapted from Chen and Kindzierski (2005))

Category	Defining Criteria	Recommendations
A	- Low to intermediate disposal rate (<10,000 m^3/month) - Multiple or numerous sources	- Not economical to pursue alternative treatment technologies due to small injection volume
B	- Low to intermediate disposal rate (<10,000 m^3/month) - Discrete or few sources	- Not economical to pursue alternative treatment technologies due to small injection volume
C	- Intermediate to high disposal rate (>10,000 m^3/month) - Discrete or few sources - Unreadable or outdated source characterization data	- Require the updated information on wastewater characteristics to identify the potential of treatability evaluation
D	- Intermediate to high disposal rate (>10,000 m^3/month) - Discrete or few sources - Readable source characterization data with appearance of extensively contaminated source liquids	- Not suitable to pursue economically feasible alternative treatment technologies due to high contamination by dissolved solids
E	- Intermediate to high disposal rate (>10,000 m^3/month) - Discrete or few sources - Indication that individual contaminants present in source liquids would require some form of specific treatment prior to general reuse	- Suitable to assess alternative treatment technologies
F	- Information lacking on disposal rate - Indication that individual contaminants present in source liquids would require some form of specific treatment prior to general reuse	- Require the updated injection volume information to identify the potential of treatability evaluation
G	- Waste liquids being disposed includes contaminated groundwater	- Suitable to assess alternative treatment technologies
H	- Negligible amounts of waste fluids injected during recent years - Infrequent injection periods	- Not economical to pursue alternative treatment technologies due to small injection volume

Table 1.2. Categorization of Existing Disposal Wells (Adapted from Chen and Kindzierski (2005))

Category	Well Approval No.	Well Name or ID
A	6114	NEWALTA MORINV 8-15-54-26
	6660	OKALTA-LEDUC NO. 13 WELL
	7547	NEWALTA PEMBINA 8-23-48-8
	9013	NEWALTA 102 BANTRY 1-25-18-14
B	7070	NEWALTA MORINVILLE 12-19-54-25
	7742	00/13-06-067-08W5/0
		00/13-06-067-08W5/2
	8133	AGEC JOFFRE 6-32-038-25W4/0
	9700	UNIROYAL CHAMBERLAIN 1-17-53-23
C	3924	HUSKY REFINERY NO. 3
		HUSKY REFINERY NO. 5
		HUSKY NO. 6 LLOYD 10C-1-50-1
	5737	SHELL FTSASK 1-31-55-21
		SHELL FTSASK 8-31-55-21
	8713	AIR B7-4 REDW IN 7-4-57-21
	8784	PCI REFINERY DISP EDMT 9-5-53-23
		PCI REFINERY DISP EDMT 15-5-53-23
	8951	IMP 102 STRATHCONA 9-1-53-24
	9699	CHEMCELL DISP CLOVER IN 10-17-53-23
		CHEMCELL DISP CLOVER IN 11-17-53-23
D	8317	DOW 3 FTSASK NACL 10-10-55-22
		DOW 4 FTSASK NACL 7-10-55-22
		DOW 5 FTSASK NACL 15-10-055-22
E	4779	AGU REDWATER 10-17-56-21
		AGU REDWATER 6-17-56-21
F	7842	AT PLASTICS CHEM IN 14-36-52-24
	8926	03/01-10-055-22W4/0
		04/01-10-055-22W4/0
		00/16-10-055-22W4/0
		02/16-10-055-22W4/0
		S0/01-15-055-22W4/0
		03/12-13-055-22W4/0
		04/12-13-055-22W4/0
G	8185	VIRIDIAN FTSASK 4-10-55-22
H	7290	CHEVRON MGSU 1 MITSUE 7-20-72-4
	8251	IMP REFINERY DISPOSAL IN 9-1-53-24
		IMP REF DISP STRATHCONA 8-1-53-24

Table 1.3. Summary of Phase I Recommendations.

Category	Well Approval No.	Recommended Research		
		Update Wastewater Characteristics	Update Injection Volume Data	Evaluate Alternative Treatment Technology
C	3924	Yes	-	-
	5737	Yes	-	-
	8713	Yes	Yes	-
	8784	Yes	-	-
	8951	Yes	-	-
	9699	Yes	-	-
E	4779	-	-	Yes
F	7842	-	Yes	-
	8926	Yes	Yes	-
G	8185	-	-	Yes

1.2. Objectives

The objectives of this project are to:

(1) examine the characteristics of deep well disposed wastewater, and in particular physical and/or chemical analysis data and injection volume, and

(2) identify and evaluate alternative treatment technologies for the wastewaters injected into wells operated under approval numbers 3924, 5737, 8713, 8784, 8951, 9699, 4779, 7842, 8926, and 8185 in order to conserve the water.

The expected contributions of this project in relation to "Water for Life: Alberta's Strategy for Sustainability" are that:

(1) water conservation including a treated water reuse within companies and/or a safe discharge to natural water body could be practiced by applying the proposed alternative treatment technologies by the industries; and

(2) the potential risks of deep well disposal method, such as contamination of underground sources of drinking water and surface environments by migration or escape of wastewater from the well, could be decreased by reducing the overall injection volume.

2. LITERATURE REVIEW

2.1. Alberta Water Reuse Strategy

2.1.1. The Need for a Water Reuse Strategy

Concerns regarding Alberta's water supplies have increased as a result of population growth, agricultural and industrial development and droughts. These pressures also increase potential of risks to Albertan's health and wellbeing, and threaten the economy and aquatic ecosystems (AENV, 2003). Therefore, in 2003, Alberta Environment (AENV) established the guidelines outlined in "Water for Life: Alberta's strategy for Sustainability." Alberta Environment (AENV, 2003) described this guideline as the Government of Alberta's initiative to develop a new water management approach, and outlined specific strategies and actions in order to address the issues related to water reuse and control.

2.1.2. Goals and Directions

Alberta Environment (AENV, 2003) indicated that Albertans had reaffirmed three goals of a provincial water strategy throughout the extensive consultation process. These goals are:

- safe, secure drinking water supply;
- healthy aquatic ecosystems; and
- reliable, high quality water supplies for a sustainable economy.

According to the Water for Life strategy, the key directions and actions are knowledge and research, partnership, and water conservation. Many watersheds have already experienced limitations to availability as a consequence of economic and population growth. The remaining watersheds are predicted to suffer similar water shortages in the future. The solutions proposed in the Water for Life strategy (AENV, 2003) to address this looming problem are (1) a combination of both improving the ability to capture and store water during high flow seasons or periods, where possible and feasible; and (2) improvement of water use practices through significant conservation efforts.

2.1.3. Concerns Regarding Water Use for Underground Injection

Public discussions of "Water for Life: Alberta's Strategy for Sustainability" in 2002 brought to the fore anxieties about water use for underground injection purposes (ACWUPP, 2004b). During the consultation process, Albertans identified the need for an increased emphasis on water conservation, and expressed specific concern about the use of water for underground injection activities, because water disposed of into deep wells could be permanently removed from active water cycle. The Advisory Committee on Water Use Practice and Policy (ACWUPP) was established in 2003 to review the use of water for underground injection, and identify options to reduce the amount of non-saline water used for this purpose (ACWUPP, 2004b). Non-saline water is defined as water that contains less than 4,000 mg/L of total dissolved solids (TDS).

The ACWUPP considered the following industrial activities to be the major sources of non-saline water underground injection:

- deep well disposal of industrial wastewaters;
- water used for creating salt caverns; and
- water used for the enhanced recovery (ER) of oil and bitumen through water and stream injection processes.

The ACWUPP stressed that the reduction of non-saline water injection into underground wells is an important part of conserving water in Alberta (ACWUPP, 2004b).

2.1.4. Strategies to Reduce Underground Injection of Water

The ACWUPP recommended the following principal strategies to decrease subsurface disposal of water (ACWUPP, 2004b):

- The Government of Alberta should revise the regulatory process to address concerns regarding the effects of underground injection of non-saline water.
- Specific targets for underground injection should be included in the provincial water conservation plan.
- Water management plans should be used to determine priority locations within watersheds where every reasonable effort should be made to minimize or eliminate underground injection of non-saline water.
- Increased industry, government, and research group activity to investigate water conservation and recycling of industrial waste, in order to minimize losses of water from the hydrologic cycle.

The ACWUPP (ACWUPP, 2004a) noted that a number of industries use water in the deep well injection processes of industrial wastes. Thus, ACWUPP recommended that the water disposed of in these operations should be examined by improved monitoring and reporting methods in order to maximize water recycling and to minimize reusable water losses. The additional recommendations given to the Alberta Energy and Utilities Board (EUB) and Alberta Environment are reporting (1) the amount of water used, (2) water sources, and (3) substances included in disposed wastes and water.

2.2. Surface Water Quality Guidelines

Alberta Environment (AENV) developed surface water quality guidelines in 1977. The latest edition of the guidelines, *Surface Water Quality Guidelines for use in Alberta*, was compiled in 1999. The document contains three different categories of water quality guidelines in terms of the receiving environment or water usage, including protection of aquatic life, agriculture, and recreation and aesthetics. Since the majority of treated wastewater is discharged to surface waters, water quality requirements introduced in this document focus on guidelines for protection of aquatic life. The water quality guidelines for the protection of aquatic life are summarized in Table 2.1.

Table 2.1. Water Quality Guidelines for Protection of Aquatic Life (Adapted from AENV (1999)).

Substance	Unit	Alberta		CCME [1]
		Acute	Chronic	
Ammonia-N	mg/l			1.37 to 2.2 [2]
Chromium VI	µg/l			1.0
Dissolved oxygen	mg/l	5.0 (1-day min.)	6.5 (7-day mean)	5.5 to 9.5 [3]
Nitrogen (total inorganic and organic)	mg/l		1.0	
Nitrate	mg/l			Follow CEQG[4] guideline [5]
pH	-	6.5 to 8.5	6.5 to 8.5	6.5 to 9.0
Phosphorus as P (total inorganic and organic)	mg/l		0.05	
Phenols	µg/l		4.0	
Suspended Solids	mg/l	Not to be increased by more than 10 mg/L over background value		Increase of 5 mg/l to 25 mg/l [6]

[1] CCME : Canadian Council of Ministers of the Environment

[2] 1.37 mg/L (at pH 8.0, 10°C); 2.2 mg/L (at pH 6.5, 10°C)

[3] For warm water biota: early life stages = 6 mg/L, other life stages = 5.5 mg/L
For cold water biota: early life stages = 9.5 mg/L, other life stages = 6.5 mg/L

[4] CEQG : Canadian Environmental Quality Guidelines

[5] CEQG guideline for nitrate: concentrations that stimulate weed growth should be avoided

[6] For clear flow: Max. increase of 25 mg/L over background levels for any short-term exposure, Max. increase of 5 mg/L for any long-term exposure
For high flow: Max. increase of 25 mg/L over background levels when background levels are between 25 and 250 mg/L, Should not increase more than 10% of background levels when background is >250mg/L.

2.3. Deep Well Disposal

Mogharabi and Ravindran (1992) defined deep-well injection as a method of hazardous waste disposal where liquid or liquefiable waste that has no other potential use is pumped at a controlled rate and pressure into confined formations. Saripalli et al. (2000) reported that deep-well injection of wastewater and liquid hazardous wastes is an important waste disposal practice in most industrialized nations.

Deep well injection of wastewater in the U.S.A. started in the 1930s when oil companies began disposing of oil field brines, and other oil and gas waste products into depleted reservoirs (US EPA, 2001). Most of the early injection wells were converted from oil production to wastewater disposal. Soon, other industries started to consider the deep well disposal method to be suitable for the other wastewaters that were difficult or impossible to treat. Mogharabi and Ravindran (1992) noted that the economics and advantages of deep well disposal made it an attractive solution to the problem of liquid waste disposal.

Injection of hazardous chemicals and steel industry wastes began in the 1950s. At that time, four Class I wells were in use. Thirty wells were established before 1963 and in the period from the mid 1960s to the mid 1970s, the use of Class I injection wells increased sharply at a rate of more than 20 new wells per year (US EPA, 2001).

The disposal of waste fluids into deep wells has been used for a long time in Alberta. The Alberta Research Council (ARC, 1991) indicates that the first disposal occurred in the 1920s with the injection of produced water. Further development occurred in 1951 with the disposal of other industrial process liquid wastes. In 1957, the first water injection occurred to maintain pressure in an oil pool for improved hydrocarbon recovery.

2.3.1. Classification of Disposal Wells in Alberta

Disposal or injection wells in Alberta are classified as 5 different types, depending on the characteristics of injected waste streams to maintain consistent design, operation and monitoring requirements of wells in any category (EUB, 1994). The five classes of disposal wells are:

- Class IV - Well used for injection into a reservoir matrix, of:
  - potable water with no anticipated future conversion to produced water
  - stream from potable water or recycled water.
- Class III - Well used for the injection of hydrocarbons, or inert or other gases, for the purpose of storage in or enhanced hydrocarbon recovery from a reservoir matrix and includes but is not restricted to:
  - solvent or other hydrocarbon products used for enhanced recovery operation
  - sweet gas used for gas storage operations

  - CO_2, N_2, O_2, air or other gases used for storage or enhanced recovery
  - sour or acid gases for disposal, storage, or cycling operations.
- Class II - Well used for the injection or disposal of produced water (brine) or brine equivalent fluids and includes :
  - produced water associated with the recovery of oil, bitumen, gas, or coal bed methane
  - brine from salt cavern of solution mining operations
  - water-based pigging fluids from cleaning of collection and injection lines
  - brine reject or backwash from water softeners associated with enhanced recovery
  - water containing polymers or other chemicals for enhanced recovery
  - waste fluids from circulation during well cementing
- Class Ib - Wells used for the disposal of produced water, specific common oilfield waste streams, and waste streams meeting the following criteria. The waste has:
  - a pH between 6.0 and 9.0
  - a flash point greater than 61°C, unless the waste
    1) is an untreatable sand or crude oil/water emulsion, or
    2) is an antifreeze or dehydration fluid;
  - heavy metal concentrations at or below the levels indicated in Table 2.2.
- Class Ia - Well used for the disposal of oilfield or industrial waste fluids. Waste fluids suitable for deep well disposal, but not meeting the Class Ib criteria, will be classified as Class Ia fluids, and when disposed of by subsurface injection must be injected in an approved Class Ia well.
  - acidic solutions, or alkaline solutions or aqueous solutions with heavy metals above the concentrations given in Table 2.2.
  - metal-finishing solutions
  - solutions containing reactive anions
  - aqueous solutions containing non-halogenated organic compounds in concentrations less than 10 percent by mass
  - aqueous solutions containing halogenated organic compounds in concentrations less than 0.1 percent by mass

2.3.2. Geologic Considerations

The suitability of a formation to receive injected waste fluids at a proposed injection rate is decided by many factors, such as sufficient permeability, porosity, and thickness (US EPA, 2001). Mogharabi and Ravindran (1992) reported that a potential subsurface reservoir for liquid waste should have the following characteristics: (1) a significant volume of porous and permeable reservoir rock containing non-potable water; (2) surrounding rocks that can prevent the escape of waste fluid from the reservoir rock; (3) isolation from the surface environment and from potable groundwater; and (4) economically feasible drilling depths.

The injection zone should be homogeneous and also be of sufficient magnitude to minimize formation pressure buildup and to prevent injected fluids from reaching aquifer recharge areas (US EPA, 2001). The confining zone should have relatively low permeability to prevent upward movement of injected fluids. Brower et al. (1989) noted that injection is feasible where the waste does not interact chemically with the injection zone rock, the confining formations or with the native water in a way that would impede injection; and where no improperly abandoned wells penetrate the injection zone.

Table 2.2. Heavy Metals Criteria for Disposal Well Classification (Adapted from EUB (1994))

Metal	Arsenic (As)	Beryllium (Be)	Cadmium (Cd)	Chromium (Cr)	Lead (Pb)	Uranium (U)
Concentration (mg/Kg)	500	100	100	500	500	100
Metal	Mercury (Hg)	Nickel (Ni)	Selenium (Se)	Silver (Ag)	Thallium (Tl)	
Concentration (mg/Kg)	20	500	200	100	200	

2.3.3. Injection Well Structure

Injection wells typically consisted of three or more concentric layers comprising a surface casing, a long string casing, and injection tubing (US EPA, 2001). The casings which are made of non-corrosive materials, such as steel or fiberglass-reinforced plastic, are used to prevent a borehole depression and to cover an injection tubing. The surface casing covers the outer most layer of an injection well system and extends from the surface to below the lowest underground source of drinking water. The roles of the long string casing which extends to the injection zone are to protect injection tubing and to make the injected fluid enter the receiving formation with a screened, a perforated or an open-hole ending structure (US EPA, 2001). Injection well constructions in terms of the five well classifications are shown in Figure 2.1.

2.3.4. Operational Vulnerability

Sauveplane (1996) stated that compared to other waste disposal methods, deep waste disposal is considered to have the advantages of isolating wastes in a confined aquifer well below the horizon of human activity and potable groundwater resources. This also can mean that the water injected to the deep subsurface cannot be used for any other different purposes. Therefore, deep well injection should be considered as a final option when waste reduction, recycling, and other disposal options are not feasible for technical, environmental, and economic reasons (Brower et al., 1989). The EUB (1994) stated that deep well disposal should remain as an option, but should be guided by the following principles:

- waste minimization shall be implemented prior to using the deep-well disposal option; and
- resource conservation, including surface water and the waste streams themselves, shall be pursued whenever possible.

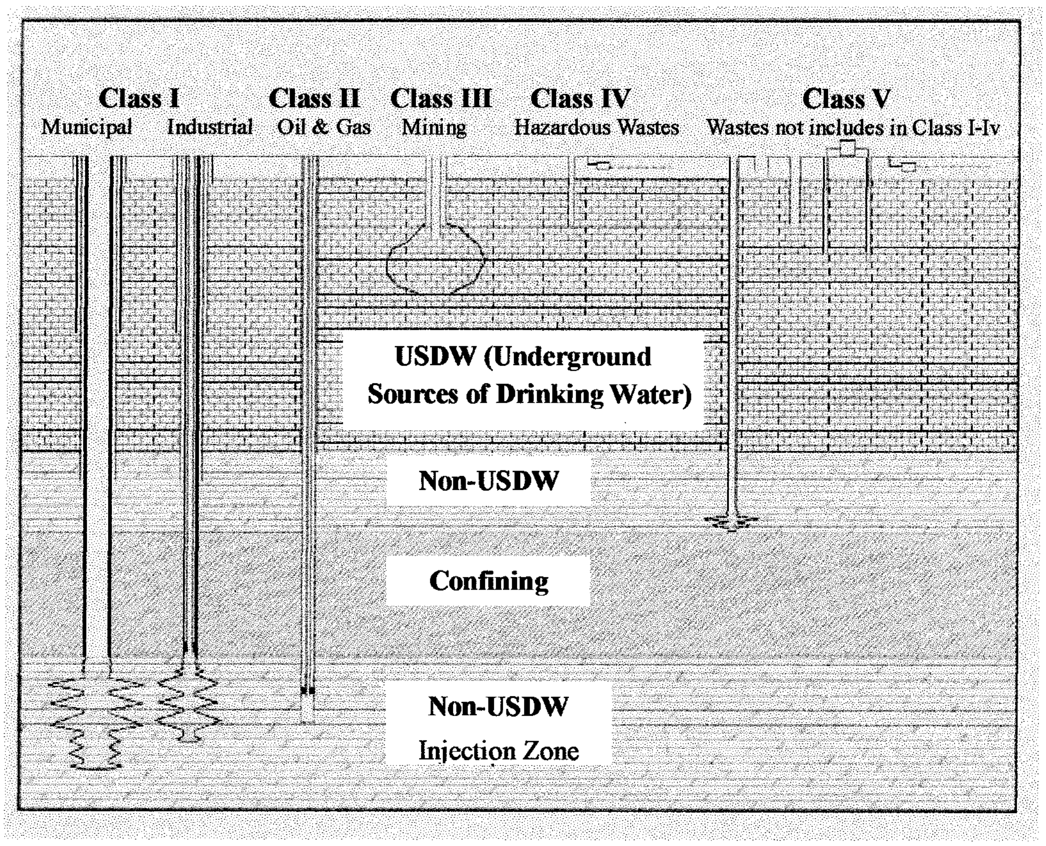


Figure 2.1. Structures of Injection Well for Different Classes (Adapted from Florida DEP (2005))

The principal risk associated with deep-well injection is the contamination of underground sources of drinking water (USDW) by migration of waste components or by displacement of contaminated water into wrong reservoir formations (Mogharabi and Ravindran, 1992). Other risks include contamination of the surface environment and adverse effects on human, animals and plant life by accidental spillage at the wellhead.

Brower et al. (1989) indicated that the major concern associated with deep well disposal is the possibility that injected waste may migrate into and contaminate fresh water aquifers, which can severely harm an aquifer water quality. Poorly constructed or located wells and improperly abandoned wells could result in ground water contamination through the probable pathway formation for wastes migration.

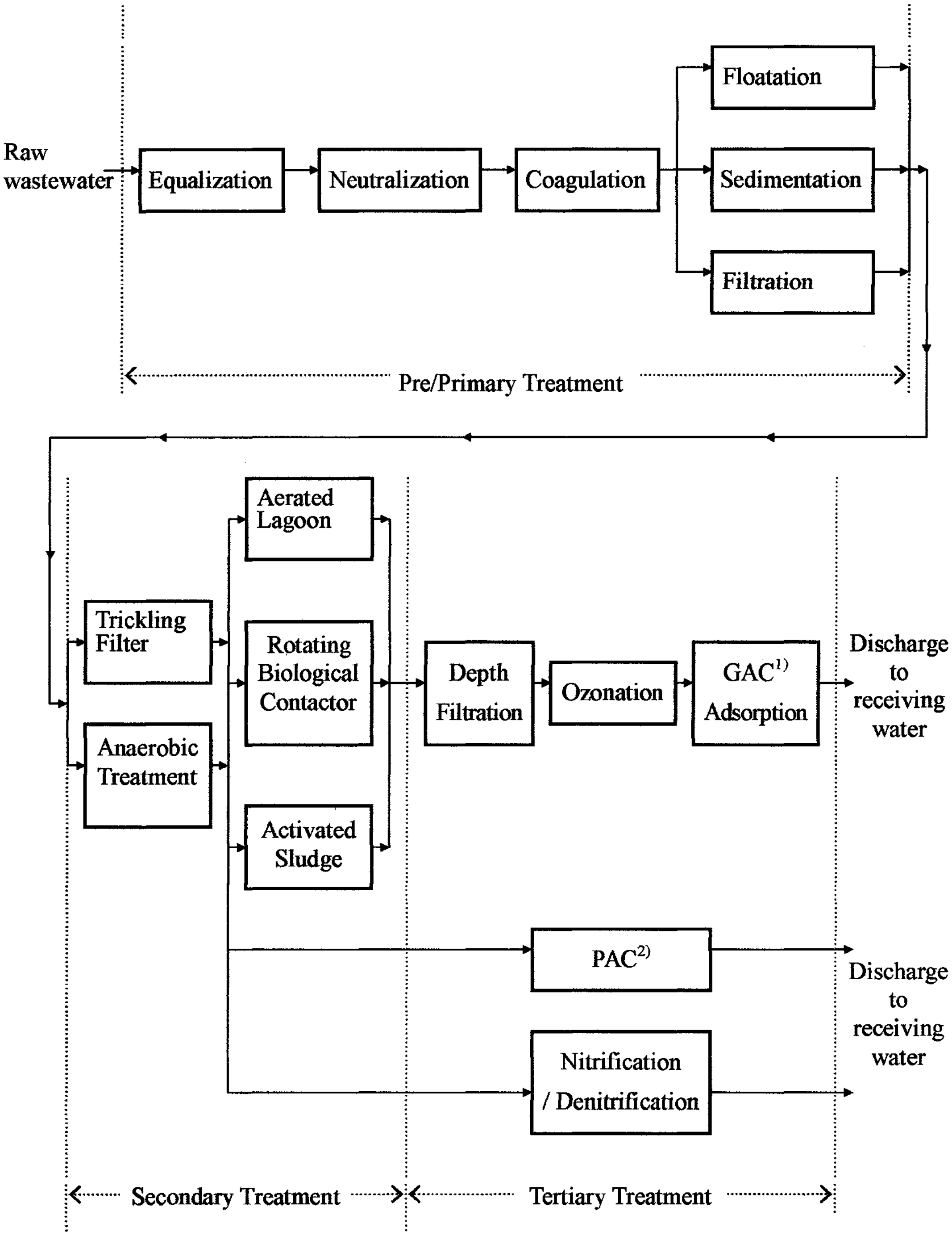
Potential pathways by which fluids can escape the well or injection horizon and enter underground sources of drinking water are (US EPA, 1980; Brower et al., 1989):

- Movement of fluids through a faulty injection well casing;
- Movement of fluids through the annulus located between the casing and well bore;
- Movement of fluids from an injection zone through the confining strata;
- Vertical movement of fluids through improperly abandoned and improperly completed wells;
- Lateral movement of fluids from within an injection zone into a protected portion of that stratum; and
- Direct injection of fluids into or above an USDW.

2.4. Industrial Wastewater Treatment

Methods of industrial wastewater treatment may be classified into preliminary, primary, secondary or advanced treatment (Metcalf & Eddy, 2003; Reynolds and Richards, 1996; Eckenfelder Jr., 2000; Stephenson and Blackburn Jr., 1998). Preliminary treatment is applied to remove gross solids such as large objects, rags and grit that may damage downstream treatment equipment (Metcalf & Eddy, 2003). In primary treatment, a substantial amount of suspended solids is removed from a wastewater through physical operations. These operations generally consist of sedimentation to remove floatable and settleable substances, and flocculation and/or coagulation to enhance the solids removal. Secondary treatment removes most of the organic material from wastewater using biological and/or chemical processes. Advanced or tertiary treatment is used to reduce the concentrations of specific classes of contaminants such as residual suspended solids, refractory organics, or other compounds that are not dealt with adequately by conventional treatment.

Figure 2.2 illustrates the treatment alternatives that are generally considered for the treatment of industrial wastewaters. The diagram shows the conventional series of preliminary and primary treatment processes, as well as secondary and tertiary treatment (Eckenfelder Jr., 2000). A list of the main constituents and major unit operations and processes used to remove theses contaminants from wastewater is presented in Table 2.3 (Metcalf & Eddy, 2003).



[1] GAC : Granular Activated Carbon

[2] PAC : Powdered Activated Carbon

Figure 2.2. Alternative Technologies for the Treatment of Industrial Wastewaters (Adapted from Eckenfelder Jr. (2000)).

Table 2.3. Unit Operations and Processes Used to Remove Constituents Found in Wastewater (Adapted from Metcalf & Eddy (2003))

Constituent	Unit Operation or Process
Suspended solids	■ Screening ■ Grit removal ■ High-rate clarification ■ Coagulation and Flocculation ■ Sedimentation ■ Floatation ■ Filtration
Biodegradable organics	■ Aerobic suspended growth system ■ Aerobic attached growth system ■ Anaerobic suspended growth system ■ Chemical oxidation ■ Advanced oxidation ■ Anaerobic attached growth system ■ Membrane filtration ■ Lagoon
Nutrients (Nitrogen)	■ Chemical oxidation ■ Air stripping ■ Suspended-growth nitrification and denitrification ■ Fixed-film nitrification and denitrification ■ Ion exchange
Phosphorus	■ Chemical treatment ■ Biological phosphorus removal
Nitrogen and Phosphorus	■ Biological nutrients removal
Pathogens	■ Chlorine compounds ■ Ultraviolet (UV) radiation ■ Ozone ■ Chlorine dioxide
Colloidal and dissolved solids	■ Chemical precipitation ■ Carbon adsorption ■ Membranes ■ Ion exchange
Volatile organic compounds	■ Carbon adsorption ■ Advanced oxidation ■ Air stripping
Heavy metals*	■ Chemical precipitation ■ Carbon adsorption ■ Ion exchange ■ Membrane filtration
Oil and Grease*	■ Gravity separation (Floatation) ■ Chemically enhanced separation ■ Dissolved air floatation ■ Centrifugation ■ Ultrafiltration
Odors	■ Chemical scrubbers ■ Carbon adsorption ■ Biofilters ■ Compost filters

* Adapted from WEF (1994).

2.4.1. Physical Treatment

2.4.1.1. Screening and Grit Removal

Screening is the first unit operation generally used in wastewater treatment to remove coarse solid materials in an attempt to prevent damage to subsequent process facilities and the contamination of waterways, and/or to improve overall treatment process reliability and efficiency (Metcalf & Eddy, 2003). The fine screen in place of a coarse screen, or series of coarse and fine screens is used to achieve higher solids removal at the beginning of wastewater treatment process, if required.

Coarse screens and fine screens are two major types of screens used in preliminary treatment of wastewater. Coarse screens have clear openings ranging from 6 to 150 mm, while fine screens have openings less than 6 mm (Metcalf & Eddy, 2003). Most of the screens installed recently in wastewater treatment plants employ mechanical cleaning systems (Reynolds and Richards, 1996). The types of screening devices generally used in wastewater treatment are shown in Figure 2.3.

Wastewater containing large amounts of grit is not a common situation. However, Stephenson and Blackburn Jr. (1998) indicate that high grit loadings can occur in older plants with combined processes and storm sewers, or in those which have poor separation of sewers. In such cases, a grit removal device may be appropriate. A grit chamber or centrifugal solids separating device can be employed to remove grit from wastewater. Grit chambers can remove dense solid materials such as sand, gravel, or cinders according to the greater specific gravities of these substances compared to those of the organic putrescible solids in wastewater (Metcalf & Eddy, 2003).

The most common location for a grit chamber is between the bar screens and the primary sedimentation tanks. Grit chambers are provided to (1) protect moving mechanical equipment from abrasion and the accompanying abnormal wear; (2) reduce formation of heavy deposits in pipelines, channels, and conduits; and (3) reduce the frequency of digester cleaning caused by excessive accumulations of inorganic material (Metcalf & Eddy, 2003).

2.4.1.2. Equalization

Equalization may be required to dampen variations in influent flow rate and contaminant concentrations. The two approaches are illustrated in Figure 2.4. The first approach is to equalize flow and constituent concentration separately (Stephenson and Blackburn Jr., 1998). The use of equalization basins after preliminary treatment (that is screening and grit removal) provides a relatively constant flow rate to the subsequent treatment operations and processes (Reynolds and Richards, 1996). Flow equalization can reduce the variation in mass loadings of constituents as well as dampen the flow variation. Constituent equalization is accomplished by mixing proper amounts of wastewater containing different levels of contaminants. The objective of constituent equalization is to minimize or control fluctuations in wastewater characteristics in order to provide optimum conditions for subsequent treatment processes (Eckenfelder Jr., 2000).

The second approach is the equalization of flow and constituent concentration in a single basin to obtain a more constant mass loading on downstream processes (Stephenson and Blackburn Jr., 1998).

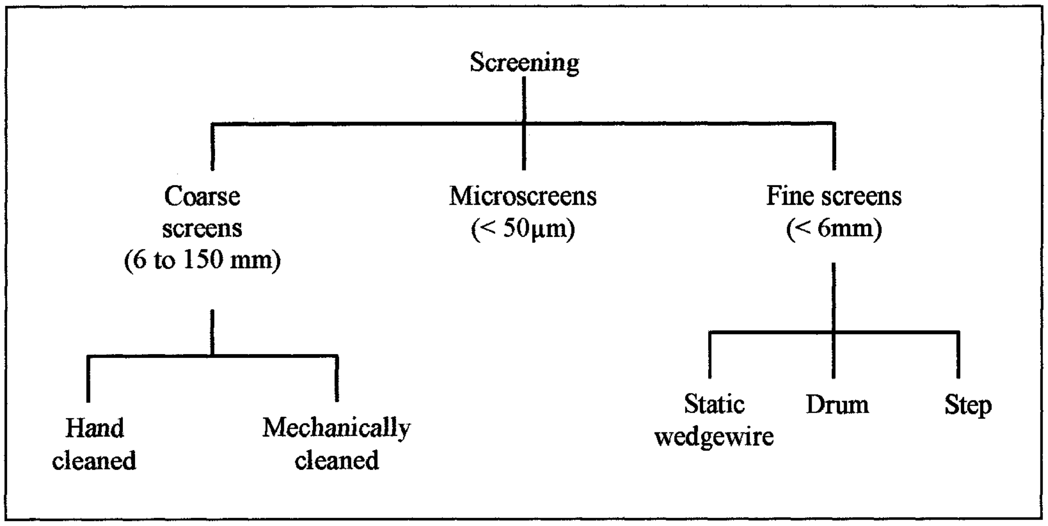


Figure 2.3. Types of Screens Used in Wastewater Treatment (Adapted from Metcalf & Eddy (2003))

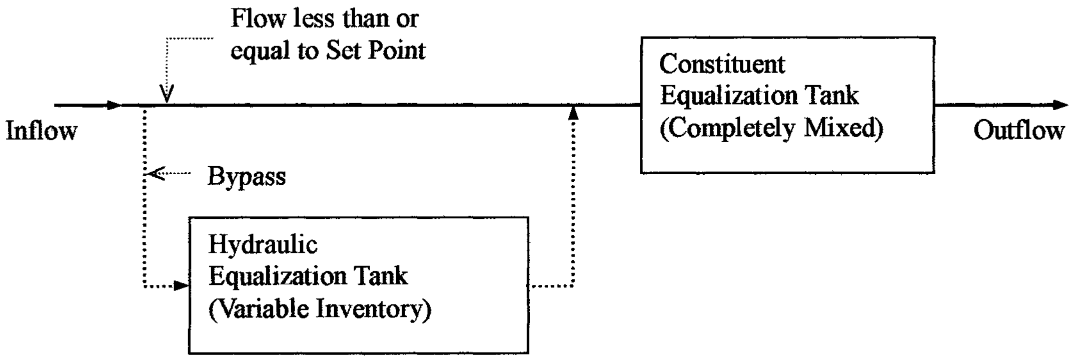
2.4.1.3. Mixing and Flocculation

Mixing is an important unit operation in many phases of wastewater treatment including (1) mixing of one substance completely with another, (2) blending of miscible liquids, (3) flocculation of wastewater particles, (4) continuous mixing of liquid suspensions, and (5) heat transfer. Most mixing operations in wastewater can be classified as either continuous-rapid mixing (less than 30s) or continuous mixing (Metcalf & Eddy, 2003).

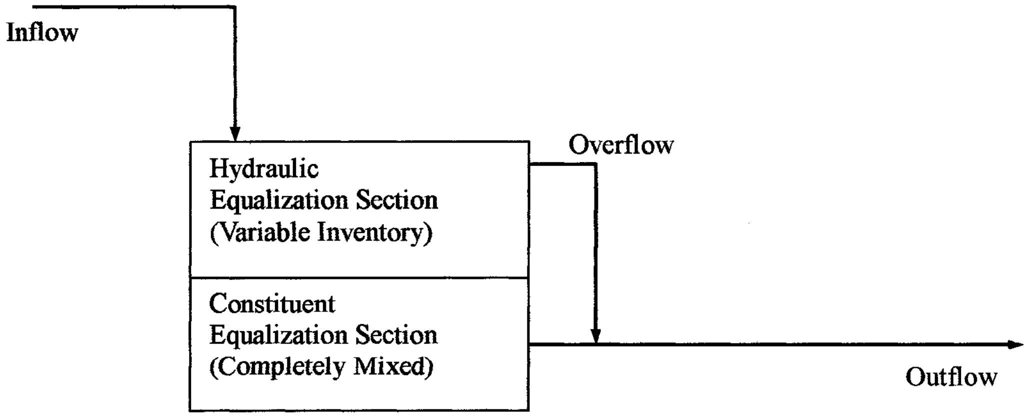
The principal applications of continuous rapid mixing are in (1) the blending of chemicals with wastewater, (2) the blending of miscible liquids, and (3) the addition of chemicals to sludge and biosolids (Metcalf & Eddy, 2003). The rapid mixing basin usually needs intense mixing or agitation devices for the purpose of dispersing chemicals homogeneously throughout the basin (Reynolds and Richards, 1996). The reactors or basins in which the contents must be kept in the suspension, such as equalization basins, flocculation basins, suspended growth biological treatment processes, aerated lagoons, and aerobic digesters, apply continuous mixing (Metcalf & Eddy, 2003). The most common type of mixer is the turbine agitator type in which the rotary action of impellers creates mixing motion in a fluid (Stephenson and Blackburn Jr., 1998).

Wastewater flocculation promotes the formation of aggregates or floc from minute particles and from chemically destabilized solids. Flocculation is a transport step that brings about the collisions between the destabilized particles needed to form larger particles that can be removed readily by settling or filtration (Metcalf & Eddy, 2003).

Although not used routinely, flocculation of wastewater by mechanical or air agitation may be considered for (1) increasing removal of suspended solids and BOD in primary settling facilities, (2) conditioning wastewater containing certain industrial wastes, (3) improving performance of secondary settling tanks following the activated-sludge process, and (4) as a pretreatment step for the filtration of secondary effluent (Metcalf & Eddy 2003). Flocculation process typically follows rapid mixing in which chemicals are added to coagulate (destabilize) the particles.



(a) Bypass of Pump Back System (Separate Equalization for Flow and Constituent)



(b) Dashpot or Inline Accumulator System (Combined Flow and Constituent Equalization)

Figure 2.4. Two Types of Equalization Techniques (Adapted from Stephenson and Blackburn Jr. (1998))

2.4.1.4. Sedimentation

Metcalf & Eddy (2003) describe the objective of sedimentation as the removal of readily settleable solids and floating material to reduce the suspended solids content. The separated material is removed both from the surface and bottom of the basin by suitable devices and is treated further (Fresenius et al., 1989). Mechanically cleaned sedimentation tanks with standardized circular or rectangular design are the most widely used tank type.

Settling is classified into four distinct types or modes. Each type is distinguished by the tendency of interaction among particles and the concentration of the solids. In solids removal processes, any or all of the four types of settling modes can occur at the same time and in any combination (Stephen and Blackburn Jr., 1998). The descriptions and applications of each settling type are given in Table 2.4.

High-rate clarification is applied for solids removal from wastewaters having higher solids concentrations. High-rate clarification employs physical/chemical treatment and utilizes special flocculation and sedimentation systems to achieve rapid settling (Metcalf & Eddy, 2003). Stephenson and Blackburn Jr. (1998) stated that high-rate clarification unit processes are commonly used to concentrate the sludge from the low solids flux rate unit processes, and for situations where the solids concentrations in the influent streams are very high, say over 500 to 1000 mg/L. High-rate clarification has many advantages such as (1) smaller space requirement as a result of compact units, (2) rapid start-up times (usually less than 30 min) which can reach peak efficiency rapidly, and (3) achievement of a high quality effluent (Metcalf & Eddy, 2003).

Cheremisinoff (2002) stated that high-rate clarification is divided into thickening, i.e., increasing the concentration of the feed stream, and clarification, removal of solids from a relatively dilute stream. Cheremisinoff (2002) cites the advantages of a thickener as:

- simplicity of design and economy of operation;
- capacity to handle extremely large flow volumes; and
- versatility, as it can operate equally well as a concentrator or as a clarifier.

A clarification process is usually applied for removing the solids produced during chemical or biological treatment (Edwards, 1995).

2.4.1.5. Floatation and Oil-Water Separation

Industrial wastewaters can contain much larger amounts of low density non-settleable materials than municipal wastewater. Such material may be removed by flotation in which air bubbles become attached to the material (suspended solids or oil) which rises to the surface to form a float that is removed for subsequent treatment (Fresenius et al., 1989).

Table 2.4. Description of Types of Settling

Type	Description	Application[4]
Type I Settling or free settling	The settling of discrete particles in a dilute suspension.[1] The particles settle as separate units.[1] There is no apparent flocculation or interaction between the particles.[1] It generally occurs at the top of a settling tank[2]	Removal of grit or particles from wastewater
Type II Settling or flocculent settling	The settling of flocculent particles in a dilute suspension.[1] It occurs when the particles agglomerate during the settling period with a resulting change in size and settling rate.[3] Most of the suspended solids in industrial wastes are of a flocculent nature.[3]	Removal of a portion of the TSS in untreated wastewater in primary settling facilities Upper portions of secondary settling facilities
Type III Settling or zone or hindered settling	The settling of an intermediate concentration of particles in which the particles are so close together that interparticle forces hinder the settling of neighboring particles.[1] The particles remain in a fixed position relative to each other while settling. As a result, the mass of particles settle as a zone.[1] A Distinct solids-liquid interface will form at the top of the mass and this is known as a sludge blanket.[2]	Secondary settling facilities used in conjunction with biological treatment
Type IV Settling or compression settling	The settling of particles that are of such a high concentration that the particles touch each other.[1] Settling can occur only by compression of the compacting mass.[1] The mass or weight of the upper particles is sufficient to partially overcome the interparticle forces and force water from between the particles.[2]	Usually occurs in the lower layers of a deep solids or biosolids mass, such as in the bottom of deep secondary settling facilities and in solids-thickening facilities

[1] Adapted from Reynolds and Richards (1996)

[2] Adapted from Stephen and Blackburn Jr. (1998)

[3] Adapted from Eckenfelder (2000)

[4] Adapted from Metcalf & Eddy (2003)

Dissolved air flotation (DAF) is one of the oldest and most common method for the removal of low density solids, oil & grease and fibrous materials from wastewater (Cheremisinoff, 2002; Turkman and Uslu, 1989; WEF, 1994). DAF consists of aerating a side stream under pressure and then mixing this stream with influent wastewater. Subsequent reduction of the pressure drives air from solution to form small bubbles that become attached to oil and low-density solids thereby enhancing floatation of those materials to surface of the tank where they are mechanically removed through skimming operation. This allows the material to be separated from the waste stream more completely and in a shorter time that would be possible otherwise (Metcalf & Eddy, 2003).

Non-emulsified oil may be removed from a waste stream by an oil-water separator. Industries that produce oil-contained wastewater, typically employ oil-water separation devices instead of primary clarifiers. An oil-water separator works by providing time for the oil to rise to the surface under relatively quiescent conditions and provides baffles to retain the floating oil in the separator until it is removed by skimming. An oil-water separator must be cleaned out periodically since settleable solids accumulate in the bottom and reduce the effective capacity of separator. The most widely used oil-water separator is the American Petroleum Institute (API) separator (Cheremisinoff, 2002). Corrugated plate interceptors (also known as coalescing separators) include a series of inclined parallel plates to enhance oil removal by providing surfaces on which smaller oil droplets can coalesce to form larger droplets that rise to the surface more quickly.

2.4.1.6. Aeration and Oxygen Transfer

Aeration is a process in which interphase (gas-liquid) mass-transfer occurs by diffusion. Aeration is employed for many purposes in wastewater treatment, including oxygen transfer in biological-treatment processes, solvent stripping from wastewater, and removal of volatile compounds from waste streams (Eckenfelder Jr., 2000).

Maintenance of aerobic conditions in a biological treatment process may require a higher re-aeration rate than can be provided through the natural atmosphere-wastewater interface, because of the low solubility of oxygen and the consequent low rate of oxygen transfer (Metcalf & Eddy, 2003). Therefore, additional interfaces between air and water must be formed in order to transfer the large quantities of oxygen required. The inter-phase transfer of a gas to or from a liquid can be described by the two-film theory. Figure 2.5 shows the schematic drawing of gas-liquid phases in contact. P_G in Figure 2.5 represents partial pressure of the solute gas in the bulk gas and P_{Gi} symbolizes partial pressures of the solute gas at the gas interface. C_{Li} and C_L express the concentrations of the solute gas at the liquid interface and in the bulk liquid, respectively.

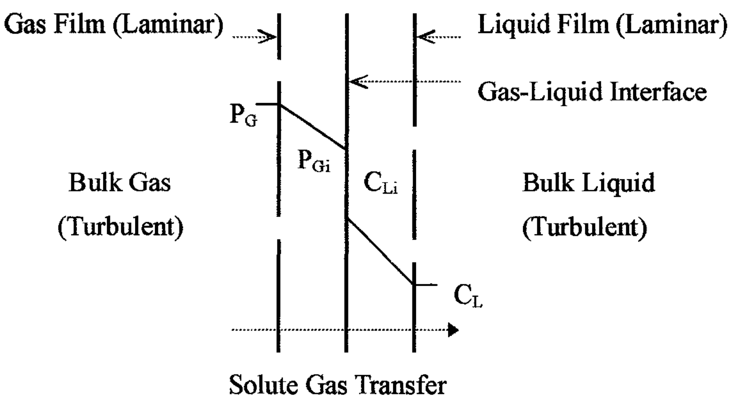


Figure 2.5. Schematic Drawing Illustrating the Two-Film Theory (Adapted from Reynolds and Richards (1996)).

2.4.2. Chemical Treatment

2.4.2.1. Neutralization

Acidic or alkaline conditions are not uncommon in industrial waste streams. This kind of wastewater must be neutralized before being discharged to receiving water, or before chemical or biological treatment. The suitable pH range for the biological treatment is from 6.5 and 8.5 to assure optimum biological activity (Eckenfelder Jr., 2000). Types of neutralization processes suggested by Eckenfelder (2000) are (1) mixing acidic and alkaline waste streams, (2) acid wastes neutralization through limestone beds, (3) mixing acid wastes with lime slurries, and (4) alkaline waste neutralization using strong acid or flue gas containing CO_2.

The convenient chemicals for small quantities of acidic wastewater neutralization are sodium hydroxide (NaOH) and sodium carbonate. However, lime which is cheaper than other chemicals is the most widely used material for neutralization although it is less convenient (Metcalf & Eddy, 2003). General information on the chemicals used most commonly for pH adjustment is given in Table 2.5.

2.4.2.2. Coagulation

Coagulation is applied to destabilize solids in wastewaters that have an appreciable suspended solids content. Colloidal particles found in wastewater typically have a net negative surface charge. The size of colloids (about 0.01 to 1 μm) is such that the attractive body forces between particles are considerably less than the repulsive forces of the electrical charge (unless the particles are extremely close to one another). Under these stable conditions, Brownian motion is sufficient to keep the particles in suspension (Metcalf & Eddy, 2003).

Table 2.5. Chemicals Used Most Commonly for the Control of pH (Adapted from Metcalf & Eddy (2003))

Chemical	Formula	Molecular Weight	Equivalent Weight	Available Form
Chemicals used to raise pH				
Calcium carbonate	$CaCO_3$	100.0	50.0	Powder, granules
Calcium hydroxide (lime)	$Ca(OH)_2$	74.1	37.1	Powder, granules
Calcium oxide	CaO	56.1	28.0	Lump, pebble, ground
Dolomitic hydrated lime	$[Ca(OH)_2]_{0.6}$ $[Mg(OH)_2]_{0.4}$	67.8	33.8	Powder
Dolomitic quicklime	$(CaO)_{0.6}(MgO)_{0.4}$	49.8	24.8	Lump, pebble, ground
Magnesium hydroxide	$Mg(OH)_2$	58.3	29.2	Powder
Magnesium oxide	MgO	40.3	20.2	Powder, granules
Sodium bicarbonate	$NaHCO_3$	84.0	84.0	Powder, granules
Sodium carbonate (soda ash)	Na_2CO_3	106.0	53.0	Powder
Sodium hydroxide (caustic soda)	$NaOH$	40.0	40.0	Solid flake, ground flake, liquid
Chemicals used to lower pH				
Carbonic acid	H_2CO_3	62.0	31.0	Gas (CO_2)
Hydrochloric acid	HCl	36.5	36.5	Liquid
Sulfuric acid	H_2SO_4	98.1	49.0	Liquid

Coagulation involves the reduction of the electrostatic charges on colloidal particle surfaces. Chemicals such as iron or aluminum salts, and organic cationic polymers or polyelectrolytes are used to accomplish coagulation. The most common and widely used inorganic coagulants are (Cheremisinoff, 2002):

- Aluminum sulfate [$Al_2(SO_4)_3$]
- Ferric sulfate [$Fe_2(SO_4)_3$]

- Ferric chloride [$FeCl_3$]
- Sodium aluminate [$Na_2Al_2O_4$]

2.4.2.3. Pathogen Abatement

Pathogen abatement involves the partial destruction or inactivation of disease-causing microorganisms. The four categories of human enteric organisms in wastewater which can cause severe disease are bacteria, protozoan oocysts and cysts, helminths, and viruses. Such pathogens can potentially be found in industrial wastewaters from industrial abattoirs, meat packing, food processing, pharmaceutical and chemical operations (Cheremisinoff, 2002). The proposed mechanisms of the chemicals used for the purpose of pathogen abatement are (1) damage to the cell wall, (2) alteration of cell permeability, (3) alteration of the colloidal nature of the protoplasm, (4) alteration of the organism DNA or RNA, and (5) inhibition of enzyme activity (Metcalf & Eddy, 2003).

The commonly used disinfectants are chlorine, chlorine dioxide, ozone and ultraviolet radiation. Table 2.6 indicates the characteristics of these disinfectants. Chlorine is most widely used disinfectant in drinking water treatment because it is effective at low concentration, is cheap, and forms a residual if applied in sufficient dosage (Reynolds and Richards, 1996). The principal chlorine compounds used at wastewater treatment plants are chlorine (Cl_2), sodium hypochlorite ($NaOCl$), calcium hypochlorite [$Ca(OCl)_2$], and chlorine dioxide (ClO_2). Chlorine dioxide (ClO_2) is not only a powerful bactericide which has equal to or greater disinfecting power than chlorine but also an effective virucide by which inactivation of viruses can be achieved more efficiently (Metcalf & Eddy, 2003).

The decomposition of ozone is thought to proceed as follows (Metcalf & Eddy, 2003):

$$O_3 + H_2O \rightarrow HO_3+ + OH^- \qquad (2.\ 1)$$

$$HO_3+ + OH^- \rightarrow 2HO_2 \qquad (2.\ 2)$$

$$O_3 + HO_2 \rightarrow HO^{\cdot} + 2O_2 \qquad (2.\ 3)$$

$$HO^{\cdot} + HO_2 \rightarrow H_2O + O_2 \qquad (2.\ 4)$$

The free radicals in the form of HO_2 and $HO^{\cdot}$ are probably the active forms in the disinfection process due to their great oxidizing powers. Another possible method for pathogen abatement is ultraviolet radiation with proper dosage, which can prevent the formation of harmful disinfection byproducts (Metcalf & Eddy, 2003).

2.4.2.4. Chemical Oxidation

Eckenfelder Jr. (2000) referred to chemical oxidation as the use of oxidizing agents without the need for microorganisms for the reactions to proceed. The common oxidants are ozone (O_3), hydrogen peroxide (H_2O_2), permanganate (MnO_4), chloride dioxide (ClO_2), chlorine (Cl_2) or ($HOCl$), and oxygen (O_2) (Metcalf & Eddy, 2003). Catalysts are frequently used in oxidation processes to increase the reaction rate to required levels. The types of different catalysts are simple pH adjustment, transition metal cations, enzymes, and a variety of proprietary catalysts of unreported composition (Eckenfelder Jr., 2000). Chemical oxidation is typically applied to situations where organic compounds are non-biodegradable (refractory), toxic, or inhibitory to microbial growth. However, chemical oxidation is also effective for the destruction of many inorganic compounds and the elimination of odorous compounds (Eckenfelder Jr., 2000).

Table 2.6. Characteristics of Commonly Used Disinfectants (Adapted from Metcalf & Eddy (2003))

Characteristic	Chlorine	Chlorine dioxide	Ozone	UV radiation
Cost	Low cost	Moderately low cost	Moderately high cost	Moderately high cost
Deodorizing ability	High	High	High	N/A
Homogeneity	Homogeneous	Homogeneous	Homogeneous	N/A
Interaction with extraneous material	Oxidizes organic matter	High	Oxidizes organic matter	Absorbance of UV radiation
Corrosiveness	Highly corrosive	Highly corrosive	Highly corrosive	N/A
Penetration	High	High	High	N/A
Safety concern	High	High	High	Moderate
Stability	Stable	Unstable	Unstable	N/A
Toxicity to microorganisms	High	High	High	High

The breakpoint chlorination is the chemical oxidation of ammonia to nitrogen gas by chlorine gas or hypochlorite salts. The general reaction steps are as follows (Reynolds and Richards, 1996):

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad (2.5)$$

$$NH_4+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ \qquad (2.6)$$

$2NH_2Cl + HOCl \rightarrow N_2\uparrow + 6HCl + 2H^+$ (2. 7)

Oxidation is usually considered as the last choice for treatment because of its high cost even though it is very effective. However, Stephenson and Blackburn Jr. (1998) noted that the chemical oxidation is used as the first step in the removal of some heavy metals from wastewater and in oxidation of some organics, or as the last step in an oxidation of odorous compounds such as hydrogen sulfide, and the oxidation of inorganics such as cyanide, and in disinfection process. Among various kinds of oxidants as given in Table 2.7, ozone has the highest power of oxidation and oxygen has the least potential. The chemical oxidation applications typically used in wastewater treatment is summarized in Table 2.7.

Table 2.7. Typical Applications of Chemical Oxidation in Wastewater Treatment (Adapted from Metcalf & Eddy (2003))

Application	Chemicals used	Remarks
Grease removal	Cl_2	Added before pre-aeration
BOD reduction	Cl_2, O_3	Oxidation of organic substances
Ferrous sulfate oxidation	Cl_2	Production of ferric sulfate and ferric chloride
Filter-ponding control	Cl_2	Maintaining residual at filter nozzles
Filter-fly control	Cl_2	Maintaining residual at filter nozzles during fly season
Sludge-bulking control	Cl_2, H_2O_2, O_3	Temporary control measure
Control of filamentous microorganisms	Cl_2	Dilute chlorine solution sprayed on foam caused by filamentous organisms
Digester supernatant oxidation	Cl_2	
Digester foaming control	Cl_2	
Ammonia oxidation	Cl_2	Conversion of ammonia to nitrogen gas
Odor control	Cl_2, H_2O_2, O_3	
Oxidation of refractory organic compounds	O_3	

2.4.2.5. Chemical Precipitation

Chemical precipitation involves the removal of aqueous ions through the formation of salts at concentrations that exceed their solubility limits by chemical addition. Typical application of chemical precipitations are (1) a means of improving the performance of primary settling facilities, (2) a basic step in the independent physical-chemical treatment of wastewater, (3) the removal of phosphorus, and (4) the removal of heavy metals. The widely used inorganic chemicals are alum, aluminum chloride, calcium hydroxide (lime), ferric chloride, ferric sulfate, ferrous sulfate and sodium aluminate (Metcalf & Eddy, 2003).

Lime is the primary chemical used in the precipitation reaction to remove solids and heavy metals because lime is an inexpensive and effective precipitant in most cases, especially for the wastewater containing hardness. Lime can contribute efficiently to the removal of most heavy metals by precipitating metals as hydroxide compounds at high pH. Sometimes, other ions such as carbonates, phosphates, and sulfides are also used as precipitants (Stephenson and Blackburn Jr., 1998). Sulfide salts generally have lower solubilities that the corresponding hydroxide or carbonate salts, and so sulfide precipitation is commonly used as a final step in the removal of heavy metals by precipitation.

Sulfide can be removed by chemical precipitation method. The desulfurization by precipitation as FeS can be achieved differently with regard to presence of oxygen (Berné and Cordonnier, 1995). The general reaction without dissolved oxygen is

$$Fe^{2+} + S^{2-} \rightarrow FeS\downarrow \qquad (2.8)$$

and with dissolved oxygen is

$$10S^{2-} + 3O_2 + 4Fe^{2+} + 6H_2O \rightarrow 4FeS\downarrow + 6S\downarrow + 12OH^- \qquad (2.9)$$

The estimation of Fe^{2+} requirement has to take into account the coprecipitation of $Fe(OH)_3$ that will occur.

2.4.3. Biological Treatment

Biological treatment is one of the most commonly applied methods for partial or complete removal of biodegradable constituents in wastewater. The overall objectives of the biological treatment of wastewater, are to (1) transform dissolved and particulate biodegradable constituents into acceptable end products, (2) capture and incorporate suspended and non-settleable colloidal solids into a biological floc or biofilm, (3) transform or remove nutrients, such as nitrogen and phosphorus, and (4) remove specific trace organic constituents and compounds (Metcalf & Eddy, 2003).

Nitrification describes a biological oxidation process for nitrogenous compounds in which ammonia (NH_3-N) is oxidized to nitrite (NO_2^-) and subsequently to nitrate (NO_3^-) by autotrophic nitrifying bacteria such as *Nitrosomonas* and *Nitrobactor* (Metcalf & Eddy, 2003). Since about 7.1mg carbonate alkalinity is consumed to complete ammonia nitrification, sufficient alkalinity must be supplied (Patterson, 1985). The biological oxidation processes can be described by two-step oxidation reactions:

$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$ [*Nitrosomonas*] (2. 10)

$2NO_2^- + O_2 \rightarrow 2NO_3^-$ [*Nitrobactor*] (2. 11)

Denitrification is a biological reduction of nitrate to nitrogen gas in the absence of dissolved oxygen (DO) by denitrifying bacteria which use nitrate or nitrite as an oxygen source (Eckenfelder Jr., 2000). Since denitrifying bacteria requires organic carbon for synthesis and energy source, supplemental addition of an organic carbon source (such as methanol) may be required. The nitrate reduction process includes the following steps:

$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ (2. 12)

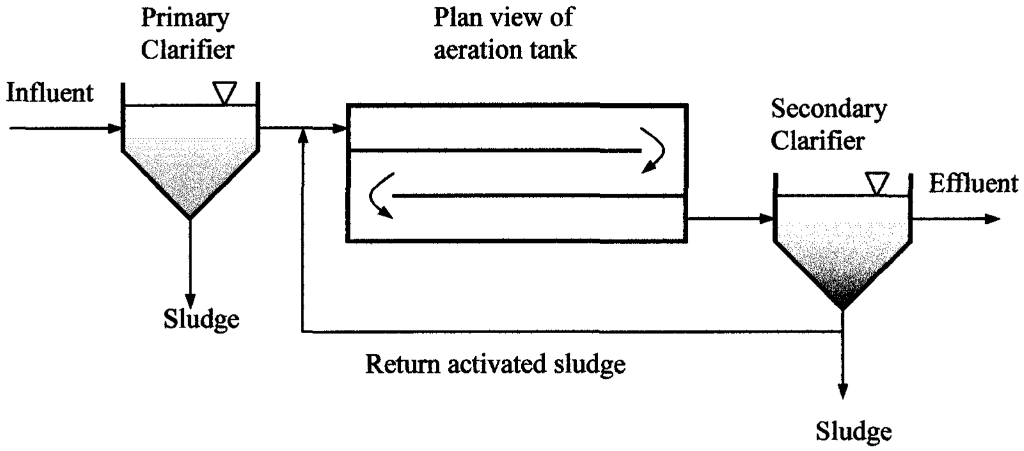
$NO_3^- + \text{Organics} \rightarrow N_2 + CO_2 + H_2O + OH^- + \text{new cells}$ (2. 13)

Classifications of the biological treatment of wastewater by the metabolic function of microorganisms include aerobic processes, anoxic processes, anaerobic processes and facultative processes (Metcalf & Eddy, 2003). Aerobic treatment is a treatment in the presence of oxygen or air and anaerobic treatment is a treatment in the absence of oxygen (Stephenson and Blackburn Jr., 1998). In facultative processes, microorganisms can consume either free molecular oxygen, if available, or combined oxygen (Cheremisinoff, 1994). Denitrification is termed an anoxic process because it occurs in the absence of molecular oxygen, but the metabolic pathways resemble those of aerobic respiration. Biological treatment may also be categorized as suspended or attached growth.

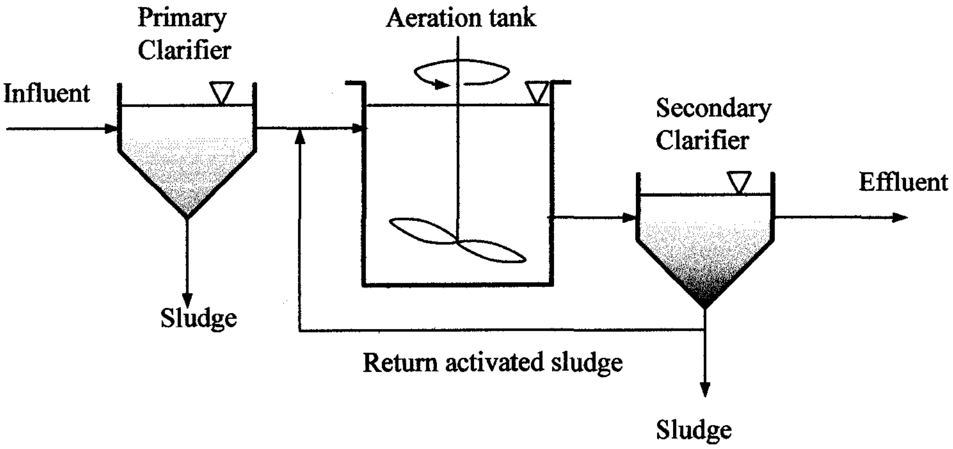
2.4.3.1. Aerobic Suspended Growth Biological Treatment

The microorganisms responsible for suspended growth processes are maintained in liquid suspension by appropriate mixing. The most common suspended biological treatment is the activated sludge process. The objective of the activated sludge process is to remove soluble and insoluble organics from a wastewater stream and to convert this material into a flocculent microbial suspension that is readily settleable and will permit the use of gravitational solid-liquid separation techniques (Eckenfelder Jr., 2000). In the activated sludge process, a high concentration of microorganisms is maintained in an aeration basin by recycling a part of the biomass settled in the secondary clarifier. The microorganisms, primarily bacteria, metabolize organic material in the waste under aerobic conditions to produce new cells, CO_2 and water. Aeration is provided to keep the microorganisms in suspension and to maintain the DO concentration at approximately 2mg/L.

The conventional activated sludge treatment process, as illustrated in Figure 2.6, consists of the following three basic components: (1) a reactor in which the microorganisms responsible for treatment are kept in suspension and aerated; (2) liquid-solids separation, usually in a sedimentation tank; and (3) a recycle system for returning solids removed from the liquid-solids separation unit to the reactor (Metcalf & Eddy, 2003).



(a) Schematic Flow Diagram of Plug-flow process and view of plug-flow reactor



(b) Schematic Flow Diagram of Complete-mix Process and View of Complete-mix Activated-sludge Reactor

Figure 2.6. Typical Activated-sludge Processes with Different Types of Reactors (Adapted from Metcalf & Eddy (2003)).

2.4.3.2. Aerobic Attached Growth Biological Treatment

Attached growth processes utilize microorganisms which are attached to an inert surface for conversion of organic material or nutrients to settleable solids. The materials commonly employed as attachment surfaces rock, gravel, slag, sand, redwood, and a wide range of plastic and other synthetic materials (Metcalf & Eddy, 2003). Two principal aerobic attached growth biological processes are tricking filters and rotating biological contactors (RBCs). The two processes are similar in that both employ cultures of microorganisms that are attached to an inert surface. The difference is the movement of packing media. For trickling filters, the media are stationary while for RBCs the media in the form of disks are rotated (Reynolds and Richards, 1996). Trickling filters have been used for the biodegradation of industrial wastewater for nearly 100 years (Metcalf & Eddy, 2003).

According to Metcalf & Eddy (2003), the trickling filter is a non-submerged fixed-film biological reactor using rock or plastic packing over which wastewater is distributed continuously. Treatment occurs as the liquid flows over the attached biofilm. Reynolds and Richards (1996) stated that the microorganisms grow by sorbing and utilizing the appreciable amount of the organic materials as food substances as a wastewater passes through a filter bed.

RBC units contain a series of closely spaced discs (the medium) that are partially submerged (typically 40 percent) in a wastewater tank. The discs are mounted on a shaft that rotates at 1.0 to 1.6 rpm (Metcalf & Eddy, 2003). A 1 to 4 mm layer of slime biomass is developed on the medium (Eckenfelder Jr., 2000). Oxygen diffuses from the air to the film of wastewater on the medium as the discs rotate. Oxygen and dissolved organics diffuse into the biofilm from the liquid film and the end products diffuse from the biofilm to the wastewater. Biomass sloughs off the media at intervals and is kept suspended in the flow by the motion of the disks until it is carried out of the tank with the bulk flow.

The biofilter system is a combination of filtration and biofilm process. So the biofilm is established on the filter media to enhance biological treatment, clarification and filtration simultaneously (Chen et al., 2000).

2.4.3.3. Anaerobic Biological Treatment

The early applications of anaerobic biological treatment involved the anaerobic digestion of solids (Droste, 1997). Since many industrial wastewaters contain considerably high concentrations of biodegradable materials and warm temperature, anaerobic processes may be economically more feasible methods. Cheremisinoff (1994) explained that the major advantages of anaerobic treatment are: (1) the high degree of waste stabilization which can be achieved with little sludge production, less than 5% of the biodegradable organic matter being converted to cell material, and (2) the production of large quantities of usable end-product in the form of methane gas, which can be used either to heat the waste stream to give a higher rate of stabilization or as a supplement to in-plant power requirements.

Anaerobic treatment of industrial wastewaters was initially limited to suspended growth processes. The three most common types of anaerobic suspended growth treatment processes are illustrated in Figure 2.7: (1) the complete-mix suspended growth anaerobic digester which is the conventional treatment method; (2) the anaerobic contact process in which biomass is separated and returned to the complete-mix or contact reactor; and (3) the anaerobic sequencing batch reactor (Metcalf & Eddy, 2003).

Complete-mix suspended growth anaerobic treatment, as shown in Figure 2.7 (a), consists of a heated reactor in which the solids are suspended and digested under well-mixing conditions without solids recycle (Droste, 1997). Concentrated solids can be added continuously or periodically and mixed with the contents of the reactor to enhance the digestion (Cheremisinoff, 1994).

As shown in Figure 2.7 (b), the anaerobic contact process consists of a reactor and a settling basin, and is similar in configuration and operation to the activated sludge process. In the reactor, a high concentration of biodegradable solids is digested with the feed-waste which contains sludge returned from the settling basin. In the settling basin, digested solids are concentrated in the bottom by gravity. The anaerobic contact process uses solids recycle from a settling basin to increase solids retention time (SRT).

The anaerobic sequencing batch reactor (ASBR) process is operated in a similar manner as the aerobic sequencing batch reactor and includes an anaerobic suspended growth process and solids-liquid separation in the same reactor (Metcalf & Eddy, 2003). The operation of ASBRs consists of four steps as illustrated in Figure 2.7 (c): (1) feed, (2) react, (3) settle, and (4) decant/effluent withdrawal.

2.4.4. Advanced Treatment

2.4.4.1. Filtration

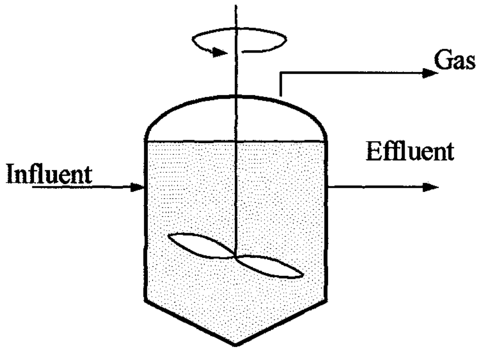
Filtration is defined by Reynolds and Richards (1996) as a solid-liquid separation process in which the liquid passes through a porous medium or other porous material to remove as much fine suspended solids as possible. Solid particles are retained on the medium's surface or within the pores of the medium.

Filtration of effluents from wastewater treatment processes is becoming more common. Depth filtration is now used to achieve supplemental removals of suspended solids from wastewater effluents of biological and chemical treatment processes to reduce the mass discharge of solids and, as a conditioning step that will allow for the effective disinfection of the filtered effluent (Metcalf & Eddy, 2003).

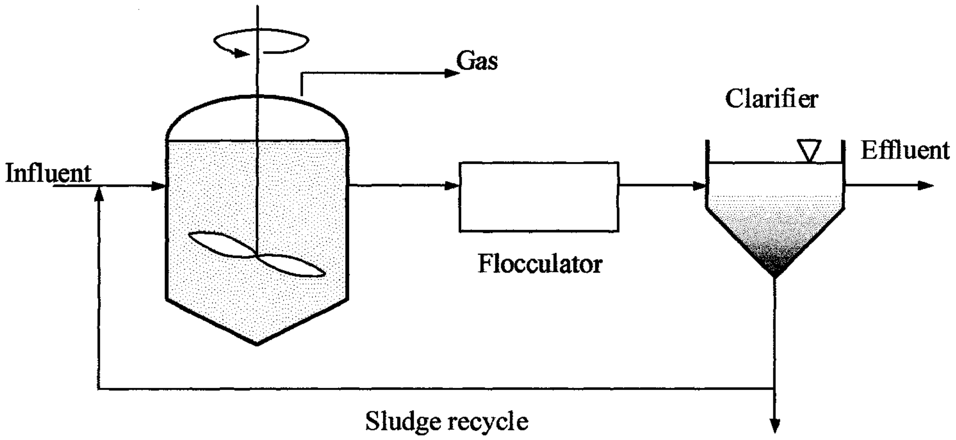
Filters may be classified according to the number of different media used in the filtration column (Reynolds and Richards, 1996):

- Single-medium filters : These have one type of medium, generally sand or crushed anthracite coal.

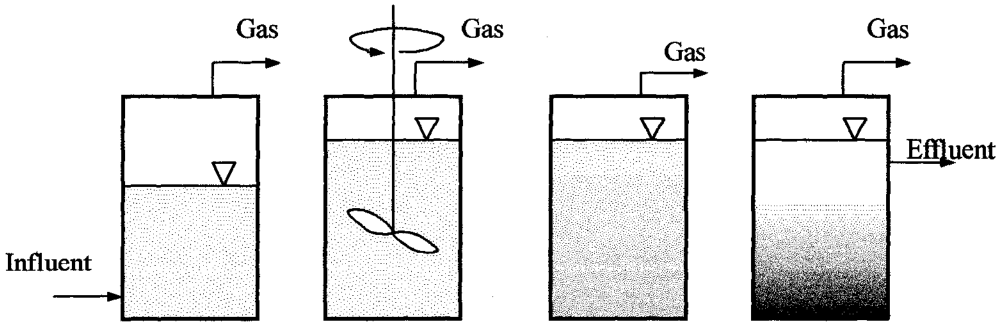
- Dual-media filters : These have two types of media, usually crushed anthracite and sand.
- Multimedia filters : These have three types of media, usually crushed anthracite, sand, and garnet.



(a) Complete-mix Suspended Growth Anaerobic Digester



(b) Anaerobic Contact Process



Feed React Settle Decant

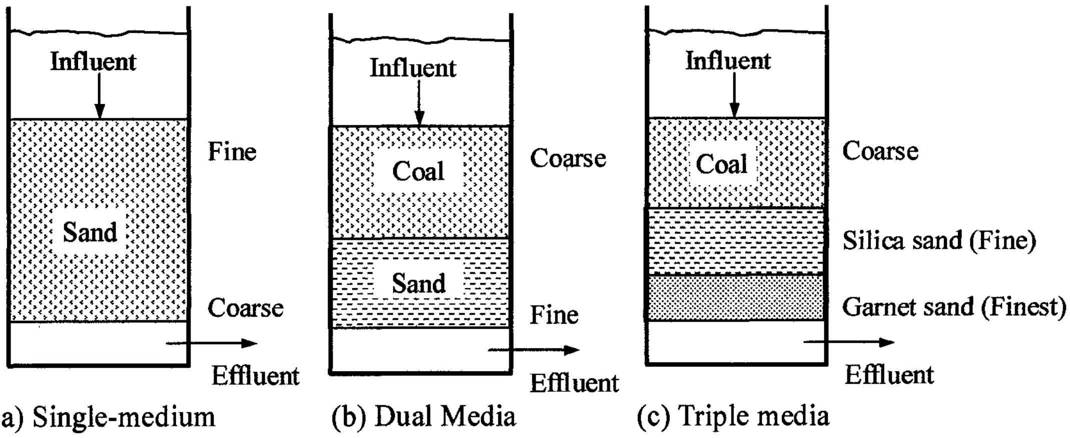
(c) Anaerobic Sequencing Batch React (or ASBR)

Figure 2.7. Anaerobic Suspended Growth Treatment Process (Adapted from Metcalf & Eddy (2003))

The above classification of filters is schematically shown in Figure 2.8. Most of filtration process in advanced and tertiary wastewater treatment apply dual-media or multimedia filters (Reynolds and Richards, 1996).

The most widely used filter types in wastewater treatment in terms of the size of the media for the removal of both organic and inorganic suspended solids are granular media filters. Stephenson and Blackburn Jr. (1998) explained that granular media filters can operate either by gravity flow (gravity filters) or by pressure (pressure filters). Both gravity filters and pressure filters can be used for enhancing water flow by overcoming the frictional resistance in filter bed (Metcalf & Eddy, 2003). The pressure filters operate under pressurized conditions in a closed vessel while the gravity filters are operated under atmospheric pressure using natural gravity flow of water. Because of the operating driving force of pressure filters, they are operated at higher terminal headlosses that allow longer filter runs.

Filters may also be classified by the rate of filtration, which is described by the flow rate per unit area. Granular bed filters can be operated with different rates: rapid granular bed filters operate at higher filtration rates than slow sand filters. Slow sand filter removes particles at the media bed surface, while rapid granular bed filtration, formerly known as "rapid sand filtration," involves depth filtration by which solids become trapped within the filter bed. Commonly used rapid filter media include sand, crushed anthracite coal, granular activated carbon (GAC), and farnet or ilmenite (AWWA, 1999).



(a) Single-medium (b) Dual Media (c) Triple media

Figure 2.8. Schematic Diagrams of Granular Filter Media (Adapted from AWWA (1999))

2.4.4.2. Pressure Driven Membrane

Membrane filtration refers to a broad range of solid-liquid separation processes that include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, as shown in

Table 2.8. The role of the membrane is to serve as a selective barrier that will allow the passage of certain constituents while retaining other constituents (Metcalf & Eddy, 2003). Membrane processes remove dissolved substances and/or finely dispersed particles from wastewater.

Table 2.8. General Characteristics of Membranes

Technology	Structure [1] (pore size)	Membrane [2] Materials	Separation [2] mechanism	Typical Constituents [1] Removed
Microfiltration (MF)	Symmetric macropores (> 50 nm)	▪ Polypropylene ▪ Polyethylene ▪ Polycarbonate ▪ Ceramic	Sieving	TSS, turbidity, protozoan oocysts and cysts, some bacteria and viruses
Ultrafiltraion (UF)	Asymmetric mesopores (2-50 nm)	▪ Polysulfone ▪ Dynel ▪ Cellulose acetate	Sieving	Macromolecules Colloids, most bacteria, some viruses, proteins
Nanofiltration (NF)	Asymmetric micropores (< 2 nm)	▪ Polyvinylidene fluoride	Sieving	Small molecules, some hardness, viruses
Reverse Osmosis (RO)	Dense (no permanent pores)	▪ Cellulose acetate ▪ Polyamide ▪ Nylon	Solution diffusion	Very small molecules, color, hardness, sulfate, nitrate, sodium, other ions

1) Adapted from Metcalf & Eddy (2003)

2) Adapted from Cheremisinoff (2002)

An important phenomenon associated with membrane filtration is membrane fouling. Fouling occurs as a result of deposition and accumulation of constituents in the feed stream on the membrane. For membrane process design, a membrane fouling is needed to be considered prudentially because it affects pretreatment requirements, e.g., cleaning needs, operating conditions, cost and performance. The general forms of membrane fouling are (1) an accumulation of the blocked constituents on the membrane surface; (2) the formation of chemical precipitates due to the chemistry of the feedwater; and (3) damage to the membrane due to the presence of chemical substances that can react with the membrane or biological agents that can colonize the membrane (Metcalf & Eddy, 2003).

The common methods to deal with fouling are (1) pretreatment of the feedwater; (2) membrane backflushing; and (3) chemical cleaning of the membranes (Metcalf & Eddy, 2003). The TSS and bacterial content in the feed water can be reduced by pretreatment, usually achieved by chemical addition. Backflushing with water and/or air is the most widely used of these methods. Backflushing uses a pressurized backflow of water and/or air to dislodge the accumulated material on the membrane surface. The remaining materials after backflushing are typically removed by chemical cleaning.

2.4.4.3. Adsorption

Adsorption is the physical and/or chemical process in which a substance is accumulated at an interface between phases (liquid/solid or gas/solid). Physical adsorption is reversible and is caused by electrostatic attraction between adsorbent and adsorbate due to dipole-dipole interactions (hydrogen bonding) and dispersion interactions (London-van der Waals force). In chemical adsorption, adsorbate is bound more strongly to adsorbent by electrostatic attraction that approaches that of a covalent or electrostatic chemical bond between atoms, and is irreversible (AWWA, 1999). Reynolds and Richards (1996) indicate that activated carbon is an adsorbent that is widely used in advanced wastewater treatment and the treatment of certain organic industrial wastewaters, because it adsorbs a wide variety of organic compounds and its use is economically feasible. The main purposes of adsorption process are to adsorb organic compounds that remain after primary and secondary treatment, and to adsorb toxic organic compounds which are resistant to biological treatment (Reynolds and Richards, 1996; Stephenson and Blackburn Jr., 1998). The classifications of activated carbon by size are (1) powdered activated carbon (PAC) which has less than 0.074 mm diameter, and (2) granular activated carbon (GAC) which has greater than 0.01mm diameter.

2.4.4.4. Ion Exchange

In an ion exchange process, an ion in the wastewater is exchanged for an ion of like charge (positive or negative) in the solid resin through a reversible chemical reaction (Cheremisinoff, 2002). The major roles of ion exchange in wastewater treatment are the removal of nitrogen, heavy metals, and total dissolved solids (Metcalf & Eddy, 2003). Ion exchange can also be employed for the removal of undesirable anions and cations from a waste stream (Eckenfecder Jr., 2000). In an ion exchange column, cations are exchanged for hydrogen or sodium ions and anions are exchanged for hydroxyl ions. Ion exchange resins are composed of the organic or inorganic materials which have attached functional groups and a porous structure. Certain ions in the waste solution are preferentially sorbed by the ion exchange solid, and the exchanger solid releases replacement ions back into the solution in order to maintain electroneutrality (Reynolds and Richards, 1996). The ion exchange reactions are stoichiometric and reversible chemical reactions.

The predominant materials used for the solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins (Cheremisinoff, 2002). The most common ion exchange resins utilize the synthetic organics. Eckenfelder Jr. (2000) noted that most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerization of organic compounds into a porous three-dimensional structure. Ion exchange resins are divided two types: (1) cationic resins when they exchange positive ions, which have acidic functional groups such as sulfonic and (2) anionic resins when they exchange negative ions, which contain basic functional groups, such as amine. Commonly used synthetic ion exchange resins are (1) strong-acid cation, (2) weak-acid cation, (3) strong-base anion, (4) weak-base anion, and (5) heavy-metal selective chelating resins. The characteristics of each type of resin are summarized in Table 2.9.

Ion exchange resins must be regenerated when the exchange capacity of ion-exchange materials is reached. Cation resins are regenerated with an acid or brine solution; while the anion resin is regenerated with a base or brine solution. The cation exchange beds are regenerated by replacing the exchanged ions with hydrogen or sodium, while anion exchange resins are regenerated by replacing the exchanged ions with chloride or hydroxide ions (Stephenson and Blackburn Jr., 1998).

2.4.4.5. Electrical Technologies

Chen (2004) indicates that in electrocoagulation, aluminum or iron ions were generated at the anode through electrical dissolution of aluminum or iron electrodes, while hydrogen gas is released from cathode. The anode reactions are:

Aluminum anode:

$$Al - 3e^- \rightarrow Al^{3+} \qquad (2.14)$$

under alkaline conditions

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \qquad (2.15)$$

under acidic conditions

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (2.16)$$

Iron anode:

$$Fe - 2e^- \rightarrow Fe^{2+} \qquad (2.17)$$

under alkaline conditions

$$Fe^{2+} + 3OH^- \rightarrow Fe(OH)_2 \qquad (2.18)$$

under acidic conditions

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \qquad (2.19)$$

In addition, an oxygen evolution reaction also takes place at the anode

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \qquad (2.20)$$

The reaction at the cathode is

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2.21)$$

The Al^{3+} and Fe^{2+} ions at nascent condition play the role as effective coagulants and the hydrogen gas generated at the cathode can help the floatation of agglomerated particles (Chen, 2004).

Electrofloatation (EF) uses small oxygen and hydrogen gas bubbles generated from water hydrolysis using electrodes such as lead dioxide to induce floatation of particles and oil globules to the surface of water (Patterson, 1985). The hydrogen and oxygen gases evolve from cathode and from anode, respectively.

The electrooxidation process decomposes contaminants either by direct or by indirect methods. The direct anodic oxidation process first involves the adsorption of constituents to the anodic surface and subsequent oxidation through the anodic electron transfer by active oxygen generation which can be the form of physically adsorbed hydroxyl radicals ($OH\cdot$) or chemisorbed oxygen in the oxide lattice (MO_{x+1}) (Rajkumar and Palanivelu, 2004; Chen, 2004). Chen (2004) indicates that the physically adsorbed active oxygen causes the complete combustion of organic compounds (R), and the chemisorbed active oxygen participates in the formation of selective oxidation products as described in the following reactions:

$$R + MO_x\,(OH\cdot)_z = CO_2 + zH^+ + ze + MO_x. \qquad (2.22)$$

$$R + MO_{x+1} = RO + MO_x. \qquad (2.23)$$

The indirect oxidation process produces strong oxidants, such as hypochlorite/chlorine, ozone, and hydrogen peroxide by electrochemical reaction (Rajkumar and Palanivelu, 2004).

Table 2.9. Characteristics of Synthetic Ion Exchange Resins (Adapted from Metcalf & Eddy (2003))

Type of resin	Characteristics	Reactions
Strong-acid cation	Behaves similar to strong acid Highly ionized in both acid (R-SO_3H) and salt (R-SO_3Na) form over entire pH range	$RSO_3H + Na^+ \leftrightarrow RSO_3Na + H^+$ $2RSO_3Na + Ca^{2+} \leftrightarrow (RSO_3)_2Ca + 2Na^+$
Weak-acid cation	Has a weak-acid functional group (-COOH) Behaves like weak organic acids that are weakly dissociated	$RCOOH + Na^+ \leftrightarrow RCOONa + H^+$ $2RCOONa + Ca^{2+} \leftrightarrow (RCOO)_2Ca + 2Na^+$
Strong-base anion	Highly ionized over entire pH range Has strong-base functional groups Used in Hydroxide (OH) form for water deionization	$RR'_3NOH + Cl^- \leftrightarrow RR'_3NCl + OH^-$
Weak-base anion	Has weak-base functional groups in which the degree of ionization is dependent on pH	$RNH_3OH + Cl^- \leftrightarrow RNH_3Cl + OH^-$ $2RNH_3Cl + SO_4^{2-} \leftrightarrow (RNH_3)_2SO_4 + 2Cl^-$

3. EVALUATION METHODS AND PROCEDURES

3.1. Information Collection Procedures

The collection of information associated with the characteristics and volumes of wastewater currently injected to deep wells was begun after reviewing the Phase I report written by Chen and Kindzierski (2005), since this study is building on the results of Phase I. The review of the Phase I report revealed a number of waste streams for which inadequate information existed regarding wastewater characteristics, injected volumes, or both. A meeting was held in September 2005 with Mr. P. Valupadas of Alberta Environment (AENV) to determine a method to obtain the missing information. It was decided that the missing information should be sought by contacting each approval holder individually using the contact information provided AENV. Accordingly, in September and October 2005, letters or emails requesting additional information regarding the deep well injected wastewater characteristics including physical, chemical, biological analyses and disposal volume, and the potential usage of treated wastewater were sent to the contact person identified for each of the companies involved. While some companies responded, responses have yet to be received from most.

Given the companies' poor response rate, alternative sources of information were sought. Records of injected fluid information were also collected from documents reporting the company's contaminant releases or from facility approvals provided by Mr. C. Chan (AENV Northern Region Industrial Approvals). Additional information was also obtained from a query of the annual well injection information by C. Adolf, of the Resources Applications Group at the Alberta Energy and Utilities Board (EUB) during October and November 2005. Table 3.1 shows the date on which information request letters were sent, as well as the type of updated information on subsurface disposal well related wastewaters made available by industry, Alberta Environment, and the EUB.

Table 3.1. Summary of Information Collected from Industry Related to Deep Well Injected Wastewaters.

Category & Well Approval #	Company Operating Deep Well	Request Letter Sent Date	Collected Information From		
			Company	AENV	EUB
C 3924	Husky Lloydminster Refinery	14-Oct-05	-	-	Injection volume
E 4779	Agrium Redwater Fertilizer Plant	2-Sep-05	-	Wastewater analyses data	Injection volume

Category & Well Approval #	Company Operating Deep Well	Request Letter Sent Date	Collected Information From		
			Company	AENV	EUB
C 5737	Shell Canada Limited Scotford Refinery	29-Sep-05	-	Wastewater analyses data	Injection volume
F 7842	AT Plastics Inc.	6-Oct-05	-	Wastewater analyses data	Injection volume
G 8185	▪ Phosphate Pond Inventory ▪ River Road Wells ▪ 119 Street Wells	28-Sep-05	-	-	Injection volume
C 8713	▪ Oil and gas from Redwater field (various sources) including Rice engineering ▪ Dugussa Canada Inc. Hydrogen peroxide plant(Gibbons, Alberta)[1)] ▪ Alberta Environfuels Inc. Edmonton facility	5-Oct-05 29-Sep-05 29-Sep-05	-	-	-
C 8784	Petro Canada Gulf Edmonton Refinery	29-Sep-05	-	-	Injection volume
F 8926	Dow Chemical Canada Inc.	6-Oct-05	Injection volume & Wastewater analyses data	-	-
C 8951	Imperial Oil Strathcona Refinery	29-Sep-05	-	Wastewater analyses data	Injection volume
C 9699	Process WW & groundwater recovery streams (during winter) instead of treating in Edmonton Gold Bar WTP	13-Oct-05	-	-	-

[1)] Dugussa Canada Inc. responded that it does not use deep wells.

3.2. Evaluation Criteria

Based on updated data characterized in Table 3.1 and indicated in detail later, the suitability of further feasibility evaluation was assessed for the wells grouped by approval numbers of deep well operation issued by EUB. This suitability was determined according to either the contaminant levels and injection volumes indicated in the Phase I report (Chen and Kindzierski, 2005) or those collected during the current study. Waste streams containing constituent concentrations higher than can be treated cost-effectively in practice by established technologies (e.g., total dissolved solids greater than 10,000 mg/l, and/or sulphate greater than 1,000 mg/l), were considered to be unsuitable for the further feasibility evaluation. The same minimum injection volume of 10,000 m^3/mon, as set by Chen and Kindzierski (2005), was applied to decide whether the injection flow warranted consideration. All information measured before 1990 was considered to be outdated. Data reported in the 1990s were used for preliminary treatability assessment; however, it was recommended that these data be updated to confirm their applicability before proceeding with any recommendation from the current study. The data reported after the year 2000 was deemed to be relatively representative of current practices and was used in the feasibility assessment with greater confidence.

After identifying those disposal wells (approval numbers 4779, 8951, 5737 and 7842) for which it was reasonable to conduct a treatability assessment, a number of established treatment methods pertaining to physical, chemical, electrical or biological means were reviewed to determine the possible ways of purifying deep well injected waste streams. The broad ranges of the well-established treatment processes and emerging technologies included in the literature review principally targeted removing nitrogen compounds from wastes injected to the approval number 4779 well, which was used for fertilizer plant wastewater disposal, and oil and organics from wastes currently injected to approval number 8951 and 5737 wells, which disposed of oil refinery waste streams.

Each technology was assessed according to its usefulness as a pre-treatment, main treatment or post-treatment method for the particular waste stream. This assessment was based on information available in the literature regarding a particular technology's requirements of influent waste stream quality and the type and extent to which the technology can remove targeted contaminants, coupled with the proposed downstream technologies influent requirements or in the case of a final treatment method, the discharge limits.

The evaluation criteria were developed and applied to conduct a preliminary qualitative assessment (ranking approach) of suitable alternative treatment technology combinations. No standardized approach exists to evaluate treatment technologies.

Therefore, this rational approach based on information available in the literature was adopted. Each possible treatment combination was assessed according to the criteria contained in three primary categories: technical suitability, reliability of technology, and economic feasibility. Within each of these categories, each treatment option was assessed according to several detailed criteria, and to which a score of either 0 for desirable characteristics, or 1 for less desirable characteristics were assigned. The categories and specific criteria are shown in Table 3.2.

The technical suitability category includes operation and maintenance, and residuals (waste streams) as sub-categories. The assessment of operation and maintenance included four detailed criteria consisting of (1) the number of processes, (2) the complexity of operation and maintenance, (3) the expected removal efficiency, and (4) the effect of cold climate. The number of processes is important because a smaller number of processes, that achieves the targeted removal, requires less construction, operation and maintenance effort than one that attains equal removal but which requires a greater number of processes. Therefore, the lower number of processes is considered a more suitable option. The complexity of operation and maintenance was assessed according to the relative complexity of a treatment combination. If the treatment option requires two or less kinds of operation control and maintenance (e.g. pH, or DO control, fouling/scale control, periodic replacement, backwash and/or regeneration of materials), it was assigned the preferred characteristic of "simple" that was scored as 0. Conversely, a score of 1 was assigned to systems requiring three or more kinds of operation and maintenance.

The removal efficiency of each treatment combination was assessed according to reports in the literature of the relative removal ability of the final treatment method. However, testing at bench- or pilot-scale using the actual wastewater would be required to obtain an accurate estimate of removal efficiency. Treatment combinations that included either RO or NF as the final polishing treatment were considered to have high removal efficiency relative to other technologies such as ion exchange or filtration because NF/RO is known to be most effective to remove almost all compounds found in industrial wastewater. The typical removal efficiency of NF/RO membrane is between 90% and 99% for organic compounds, total solids, and typical ions such as NH_3-N, NO_3-N, PO_4^-, SO_4^{2-}, Cl^- (Metcalf and Eddy, 2003).

Climatic constraints especially low temperature in winter has to be considered in technical suitability assessment because a cold climate affects to the chemical and biological systems by decrease a reaction rate or a microorganism growth, respectively. However, the insulation systems such as covering on rotating biological contactor were not considered to decrease the complexity of assessment. The processes which are not affected much by cold climate included steam stripping, and membrane separation.

Production of residuals (waste streams) and their treatability is also an important factor when assessing the technical suitability of a treatment option. The amount of residual production was assessed as either “low” or “high”. The amount of residuals from membrane and biological treatment is considered to be relatively low because membrane processes produce a low volume concentrated retentate, and biodegradation produces a waste biomass stream that can be reduced further via digestion and generally used in a beneficial manner although, the additional treatment cost that may be required for dewatering, conditioning and transportation were not considered in this project. Membrane processes concentrate contaminants, and thereby reduce the volume of wastewater that must be dealt with. Therefore, the concentrate from a membrane process used to polish a waste stream may be injected to a deep well for final disposal, thereby reducing the injected volume considerably. Conversely, for equal flows of the same waste stream, treatment methods such as chemical precipitation, adsorption and ion exchange are considered to produce more residuals because these treatments apply chemicals in the treatment processes or in the regeneration of exhausted materials. The treatability of residuals is deemed to be hard for chemically produced residuals or concentrated waste streams (e.g. chemical precipitates or concentrated ammonia from stripping process).

Reliability is defined by Metcalf and Eddy (2003) as the probability that a system can meet established performance criteria over extended periods of time. Therefore, the reliability of technology was divided by the existence of full-scale application and the reliability of long term operation. Full-scale application was assigned as “many” or “few” depending on the existence of full-scale application of main treatment found in the reviewed literatures. Ion exchange, chemical precipitation and sequencing batch reactor system had relatively few full-scale application for ammonia compounds removal than stripping, membrane and other biological treatment systems, e.g., biofilter, MBR, and partial nitrification/denitrification.

Long-term reliability of operation is also an important factor to apply the treatment technologies with proved operational experience. The technologies have developed and operated for a long time period includes adsorption, ion exchange, and chemical treatments. But other technologies such as membrane, biofilter, MBR, and partial nitrification/denitrification are relatively recently developed methods. According to Manipura et al. (2005) the representative processes of nitration and denitration, e.g., OLAND®, ANAMMOX®, SHARON® and CANON®, has been developing since the middle 1990’s. Given the sparse information available to this assessment, the hydraulic and constituent variability in any waste stream is not available. Therefore, an equalization process is applied at the beginning of each treatment train to minimize shock loading to following processes and eventually to increase reliability of treatment systems.

Table 3.2. Evaluation Criteria for Ranking Alternative Treatment Combinations.

Factor			Score		Possible Treatment Combinations			
			0	1	1	2	...	n
Technical Suitability	Operation and Maintenance	Number of processes	-	-				
		Complexity of operation and maintenance	Simple	Complex				
		Removal efficiency	High	Low				
		Effect of cold climate	Low	High				
	Residuals	Amount of residuals	Low	High				
		Treatability of residuals	Easy	Hard				
Reliability of Technology	Reliability	Existence of full-scale application	Many	Few				
		Long-term reliability of operation	High	Low				
Economic Feasibility	Capital Cost	Capital Investment	Low	High				
	Operation Cost	Operation condition control requirement	Low	High				
		Requirement of periodic maintenance	Low	High				
		Requirement of oxygen or steam addition	Low	High				
		Requirement of chemical addition	Low	High				
Summation								
Rank								

The economic feasibility is also an essential part of the suitability assessment. However, because the detailed evaluation of costs can be pursued only with thorough analysis of in-plant conditions, the required treatment level, and wastewater characteristics, the assessment was done roughly by estimating relative capital and operation costs. The cost factors that were considered include the degree of operational control, the requirement of periodic maintenance, the need for oxygen, steam, or chemical addition. The cost of dealing with waste streams produced by the technologies was not considered. For the capital cost evaluation, biofilter, partial nitrification/denitrification, SBR and chemical treatments were considered to require less capital cost due to their requirement of small volume reactor and simple construction. But, membrane, adsorption and ion exchange need more capital costs because of initial material cost and complexity of construction. The requirement of operation control can consume extensive manpower and materials. Therefore, it was assessed as either "high" or "low" depending on the number of technologies which requires operation control of pH, temperature, pressure and/or DO. If the treatment combination requires two or more operation control it was considered as high operation cost process. The periodic maintenance such as regular backwash, replacement of modules and/or regeneration was also included in operation cost assessment and assigned the character of "low" for one or less periodic maintenance requirement of a treatment combination. Since the addition of oxygen or steam require high energy consumption, the treatment combinations which need to inject oxygen or steam assigned as "high" requirement. The chemical addition for chemical treatment methods such as chemical precipitation also entail high costs for chemicals purchase and residual treatment. But less chemical is required for membrane technology and biological processes. However, membrane processes may require considerable energy input to produce the driving pressure, which was reflected in the operation condition control assessment.

The feasible treatment options were recommended in accordance with the results of the evaluation criteria. The lowest summation score indicates the most promising treatment option. In cases of equal assessment ranking summations, the recommendation of applicable treatment combinations are principally dependent on the wastewater characteristics and/or on-site conditions. Therefore, a more refined assessment should be made when such information becomes available.

The limitations of the evaluation criteria developed are that they do not consider disposal or treatment costs of residuals and retrofit cost of existing treatment facilities, and the system of assigning a score of 0 or 1 to a criterion may not express the exact quality of treatment options. This ranking system produced a single best treatment combination for only the wastewater injected under approval number 4779. In the cases of wastewaters injected under in approval numbers 8951 and 5737, more than one top option was identified because this procedure did not have sufficient power to discriminate among similar potential treatment combinations. In these cases, the simple qualitative comparison of the characteristics of each treatment option could be applied better than ranking approach. Therefore, this ranking approach using the evaluation criteria should be viewed as a preliminary screening to exclude infeasible treatment combinations, but not to identify the optimal combination.

Table 3.3. Description of Evaluation Criteria

Criteria		Score			
Detailed Factors	Standards	0		1	
		Character	Description	Character	Description
Number of processes	Number of processes applied in a treatment combination	-		-	
Complexity of operation and maintenance	Number of operation control and maintenance requirements for a treatment combination (e.g., pH, DO and/or temperature control, fouling/scale control, periodic replacement, backwash and/or regeneration of materials)	Simple	Two or less	Complex	Three or more
Removal efficiency	Relative removal capacity of final treatment technology	High	NF/RO membrane	Low	Filtration and ion exchange
Effect of cold climate	Influence of cold temperature to main treatment	Low	steam stripping, and membrane separation	High	chemical and biological systems
Amount of residuals	Amount of residual production from a treatment combination	Low	Membrane backwash water and biological treatments	High	Chemical treatments, adsorption, and ion exchange
Treatability of residuals	Relative difficulty of residuals treatment	Easy	degraded or diluted residuals	Hard	chemically reproduced residuals or concentrated form
Existence of full-scale application	Existence of full-scale application of main treatment (to remove ammonia compounds)	Many	stripping, membrane and other biological treatment systems	Few	Ion exchange, chemical precipitation and sequencing batch reactor system

Criteria		Score			
Detailed Factors	Standards	0		1	
		Character	Description	Character	Description
Long-term reliability of operation	Reliability of development and operation for a long time period (Relatively low long-term reliability for the technologies developed after 1990s)	High	adsorption, ion exchange, and chemical treatments	Low	membrane, biofilter, MBR, and partial nitrification/ denitrification
Capital Investment	Capital cost investments depending on reactor volume requirements and simplicity of initial construction	Low	biofilter, partial nitrification/ denitrification, SBR and chemical treatments	High	membrane, adsorption and ion exchange
Operation condition control requirement	Number of technologies which requires operation control of pH, temperature, pressure and/or DO	Low	One or less operation control	High	Two or more operation control
Requirement of periodic maintenance	Number of periodic maintenance such as regular backwash, replacement of modules and/or regeneration	Low	One or less periodic maintenance	High	Two or more periodic maintenance
Requirement of oxygen or steam addition	Requirement of oxygen or steam addition in a treatment combination	Low	No oxygen or steam addition	High	Require oxygen or steam addition
Requirement of chemical addition	Requirement of chemical addition in a treatment combination	Low	Less chemical addition for membrane or biological process	High	Large chemical addition in chemical precipitation

4. EVALUATION OF ALTERNATIVE TREATMENT

4.1. Suitability of Available Data for Evaluating Alternative Treatment

4.1.1. Summary of Updated Disposal Well Information

The availability of wastewater characteristic and disposal volume data for the deep disposal wells classified by Chen and Kindzierski (2005) as being suitable for further investigation (Categories C, E, F and G) is summarized in Table 4.1. In this table, the term *original data* refers to data collected during the investigation conducted by Chen and Kindzierski (2005). Some of these wells are found to be unsuitable for feasibility evaluation at this time, because either (1) wastewater characteristics could not be obtained during this or Chen-Kindzierski project; (2) the injected waste is too highly contaminated; or (3) a low monthly volume of waste (less than 10,000 m^3/mon.) is disposed. Evaluation of applicable treatment technologies was conducted for wells which original or updated information pertaining to the wastewater characteristics and injection volumes suggest cost effective treatment by established technologies may be feasible.

A summary of updated disposal volumes for the wells operated under Approval numbers 3924, 4779, 5737, 7842, 8185, 8713, 8784, 8926, and 8951 are presented in Table 4.2.

4.1.2. Disposal Wells Deemed Unsuitable for Further Evaluation at Present

The disposal wells found to be unsuitable for further feasibility evaluation included six wells with approval numbers of 3924, 8713, 9699 (Category C wells), 8926 (Category F well), 8185 (Category G well), and 8784 (Category C wells). No information is available regarding the characteristics of the wastewater injected into the wells operated under approval No. 3924, and the monthly volume of waste disposed into these wells is apparently quite low (less than 10,000 m^3/mon). Chen and Kindzierski reported an injection volume of 10,700 m^3/mon for three wells under this Approval, while updated data indicated an injection volume of 5,981 m^3/mon for two wells.

The wastewater injected into the well operated under Approval No. 8185 (see Table 4.3) contains sulfate and TDS concentrations that suggest it cannot be treated cost-effectively. Additionally, the updated information in Table 4.2, indicates a mean disposal volume of 4,139 m^3/mon, which is below the injection volume of 10,000 m^3/mon. established by Chen and Kindzierski (2005) as the cut-off for economic treatability.

Table 4.1. Summary of Available Disposal Well Information.

Category & Well Approval #	Wastewater Characteristics		Disposal Volume		Suitability of Further Feasibility Evaluation	Remarks
	Existence of Original Data	Existence of Updated Data	Existence of Original Data	Existence of Updated Data		
C 3924	No	No	Yes	Yes	No	No wastewater characteristics data Insufficient disposal volume data
E 4779	Yes	Yes	Yes	Yes	Yes	
C 5737	No	Yes	Yes	Yes	Yes	
F 7842	Yes	Yes	No	Yes	Yes	
G 8185	Yes	No	Yes	Yes	No	Too highly contaminated wastewater Low disposal volume
C 8713	No	No	Yes	No	No	No wastewater characteristics data
C 8784	Yes	No	Yes	Yes	No	Insufficient recent wastewater characteristics data
F 8926	Yes	No	No	Yes	No	Too highly contaminated wastewater Low disposal volume
C 8951	No	Yes	Yes	Yes	Yes	
C 9699	No	No	Yes	No	No	No wastewater characteristics data

Table 4.2. Summary of Updated Deep Well Disposal Volumes.

Approval No. / Year	m^3/yr	Operation period (mon)	m^3/mon	m^3/yr	Operation period (mon)	m^3/mon
No. 3924[1)]	**HUSKY NO. 6 LLOYD 10C-1-50-1**			**HUSKY REFINERY NO. 3**		
2003	24,949	12	2,079	60,185	12	5,015
2004	28,522	12	2,377	39,769	12	3,314
2005	22,483	10	2,248	29,086	10	2,909
Average	25,318	11	2,235	43,013	11	3,746
No. 4779[1)]	**AGU REDWATER 10-17-56-21**			**AGU REDWATER 6-17-56-21**		
2003	307,172	12	25,598	331,223	12	27,602
2004	523,714	12	43,643	282,366	12	23,531
2005	508,744	10	50,874	250,044	10	25,004
Average	446,543	11	40,038	287,878	11	25,379
No. 5737[1)]	**SHELL FTSASK 1-31-55-21**			**SHELL FTSASK 8-31-55-21**		
2003	328,757	12	27,396	-	-	-
2004	323,515	12	26,960	-	-	-
2005	156,598	6	26,100	80,248	4	20,062
Average	269,623	10	26,819	80,248	4	20,062
No. 8784[1)]	**PCI REFINERY DISP DEMT 9-5-53-23**			**PCI REFINERY DISP DEMT 15-5-53-23**		
2003	489,719	12	40,810	419,207	12	34,934
2004	567,421	12	47,285	409,308	12	34,109
2005	591,181	10	59,118	394,006	10	39,401
Average	549,440	11	49,071	407,507	11	36,148
No. 8951[2)]	**Southwell**			**Northwell**		
1988	478,746	12	39,896	174,586	12	14,549
1989	508,593	12	42,383	213,187	12	17,766
1990	456,773	12	38,064	238,928	12	19,911
1991	453,878	12	37,823	242,217	12	20,185
1992	448,707	12	37,392	245,542	12	20,462
1993	442,176	12	36,848	267,099	12	22,258
1994	540,439	12	45,037	221,261	12	18,438
Average	475,616	12	39,635	228,974	12	19,081

Approval No. Year	m^3/yr	Operation period (mon)	m^3/mon	m^3/yr	Operation period (mon)	m^3/mon
No. 7842[1]	**AT PLASTICS CHEM IN 14-36-52-24**					
2003	137,726	12	11,477			
2004	172,550	12	14,379			
2005	146,150	10	14,615			
Average	152,142	11	13,490			
No. 8185[1]	**VIRDIAN FTSASK 4-10-55-22**					
2003	44,362	12	3,697			
2004	37,347	9	4,150			
2005	22,854	5	4,571			
Average	34,854	9	4,139			
No. 8926[3]	**03/01-10-055-22W4/0 & 6 Other Wells**					
2003	266	12	22			
2004	274	12	23			
Average	270	12	22			

[1] Data from EUB (1995)

[2] Data from Alberta Environment and Imperial Oil (12 months operation is assumed)

[3] Data from DOW (2004) and DOW (2005)

No information regarding the wastewater characteristics data could be obtained for wells operated under Approval numbers 8713 and 9699. Thus, the feasibility of waste stream treatment cannot be evaluated for these wells, regardless of the moderate to large injection volumes (10,700 m^3/mon and 118,300 m^3/mon for Approval No. 8713 and No. 9699 wells, respectively) reported for these wells by Chen and Kindzierski (2005).

Dow Chemicals (DOW, 2004; DOW, 2005) indicated that the wells operated under Approval number 8926 have been used for solid waste disposal. Additionally, Chen and Kindzierski (2005) reported that the wastes contained very high constituent levels as shown in Table 4.4. Injection volume information obtained during the present project (mean of 22 m^3/mon) indicated an insufficient volume for further evaluation with respect to the water reuse (see Table 4.2).

Two disposal wells have been operated under approval No. 8784 to dispose of the wastewater generated from the Petro Canada Gulf Edmonton Refinery. The wells are named PCI REFINERY DISP DEMT 9-5-53-23 and PCI REFINERY DISP DEMT 15-5-53-23, with mean monthly injection rates of 49,200 m^3 and 28,200 m^3, respectively, as specified in Phase I report (Chen and Kindzierski, 2005). These wells were classified as category C in the previous report, meaning that updated chemical characteristics of injected wastewater needed to be collected for the purpose of the treatability evaluation. However, other than the volume injected, further information regarding the wastewater properties could not be gathered during the current study. The wastewater characteristics from Phase I report (Chen and Kindzierski, 2005) are summarized in Table 4.5 which includes the average injection rate for the last three years as indicated by updated data. The updated injection volumes have increased slightly for the PCI REFINERY DISP DEMT 15-5-53-23 well while the other well's injection rate remained at almost the same level as that reported in Phase I.

Table 4.3. Characteristics of Wastewater Disposed Under Approval No. 8185 (Adapted from Chen and Kindzierski (2005)).

Substance	Units	Main Contaminants & Level		
		Phosphate Pond	River Road Water Wells	119 Street Water Wells
pH @ 23° C	-	4	7.7	8.45
Carbonate (CO_3^{2-})	mg/l	N/A	N/A	653
Bicarbonate (HCO_3^-)	mg/l	0	6,642	16,407
Chloride (Cl^-)	mg/l	504	1,093	7,167
Sulfate (SO_4^{2-})	mg/l	32,000	17,000	17,000
Calcium (Ca^{2+})	mg/l	338	388	0
Magnesium (Mg^{2+})	mg/l	14	54	0
Sodium (Na^+)	mg/l	1240	510	1,360
Potassium (K^+)	mg/l	245	420	1,000
Total Dissolved Solids	mg/l	344,400	25,100	43,600
Total Iron (Fe)	mg/l	N/A	<0.1	N/A
Total Manganese (Mn^{2+})	mg/l	N/A	1.2	N/A
Total Suspended Solids	mg/l	6	N/A	870

Wastewater from petroleum refineries generally contains various pollutants, including large concentrations of free and emulsified oil, wax, suspended and dissolved solids and dissolved iron, as well as other material such as phenolic compounds, sulfides, chlorides, mercaptans, heavy metals, and ammonium (Patterson, 1985; Nemerow, 1987; Lee et al, 2004; Reyes-Avila et al., 2004). However, only six chemical or physical parameters including pH, COD, Oil, SS, NH_3-N, sulfides, and phenols, which were analyzed over 20 years ago (1984-1985), are available at this time from the Phase I report (Chen and Kindzierski, 2005). Thus, more detailed and updated wastewater characterization is required before a treatability evaluation can be conducted.

Table 4.4. Characteristics of Wastewater Disposed Under Approval No. 8926 (Adapted from Chen and Kindzierski (2005)).

Constituent	Unit	Avg.	Constituent	Unit	Mean
$Mg(OH)_2$	WT%	2.4	Total organic compounds	ppm	211
$CaCO_3$	WT%	2.7	pH	-	12.3-12.5
Iron	WT%	0.2	Total chlorinated organics	N/A	<1.5
NaCl	WT%	11.2	1,2 dichloroethane	ppm	<1.5
Acid Insoluble Components	WT%	8	Dioxins and furans TEQ	ppb	16

Table 4.5. Characteristics of Wastewater Injected Under Approval No. 8784.

<table>
<tr><td rowspan="2">Category & Well Approval #</td><td rowspan="2" colspan="3">Well Name or ID</td><td rowspan="2">WW Source</td><td colspan="2">Injection rate (m^3/mon)</td></tr>
<tr><td>Phase I Report1)</td><td>Updated 2)</td></tr>
<tr><td rowspan="2">C 8784</td><td colspan="3">▪ PCI REFINERY DISP DEMT 9-5-53-23</td><td rowspan="2">Petro Canada Gulf Edmonton Refinery</td><td>49,200</td><td>49,071</td></tr>
<tr><td colspan="3">▪ PCI REFINERY DISP DEMT 15-5-53-23</td><td>28,200</td><td>36,148</td></tr>
<tr><td rowspan="2">WW Analysis</td><td colspan="6">Main Contaminants & Level3)</td></tr>
<tr><td>Name</td><td>Avg.</td><td>Range</td><td>Name</td><td>Avg.</td><td>Range</td></tr>
<tr><td rowspan="9">Phase I Report</td><td colspan="6">Year: 1984-1985</td></tr>
<tr><td colspan="3">PCI REFINERY DISP EDMT 9-5-53-23</td><td colspan="3">PCI REFINERY DISP EDMT 15-5-53-23</td></tr>
<tr><td>pH</td><td>8.8</td><td>8.6-8.9</td><td>pH</td><td>9.1</td><td>8.8-9.4</td></tr>
<tr><td>COD</td><td>9621</td><td>160-19820</td><td>COD</td><td>3176</td><td>575-13061</td></tr>
<tr><td>Oil</td><td>6577</td><td>3-50000</td><td>Oil</td><td>49</td><td>5-78</td></tr>
<tr><td>SS</td><td>294</td><td>22-1200</td><td>SS</td><td>74</td><td>14-176</td></tr>
<tr><td>NH_3-N</td><td>2994</td><td>80-5000</td><td>NH_3-N</td><td>558</td><td>36-2500</td></tr>
<tr><td>Sulfides</td><td>2872</td><td>0-5280</td><td>Sulfides</td><td>87</td><td>25-158</td></tr>
<tr><td>Phenols</td><td>172</td><td>2-630</td><td>Phenols</td><td>127</td><td>1-600</td></tr>
</table>

1) Adapted from Chen and Kindzierski (2005)

2) Adapted from EUB (2005)

3) Unit: mg/l except pH

4.1.3. Disposal Wells Suitable for Further Feasibility Evaluation

Updated information regarding wastewater characteristics and injection volumes are available for the wells operated under Approval numbers of 4779 (Category E well), 5737 (Category C well), 7842 (Category F well), and 8951 (Category C well). This information indicates that a treatment feasibility assessment is warranted. Therefore, a feasibility evaluation for theses wells is conducted based on data given in the sections that follow.

4.2. Wastewater Injected Under Approval No. 4779

4.2.1. Wastewater Characteristics

The two disposal wells operated according to approval No. 4779 are named AGU REDWATER 10-17-56-21 and AGU REDWATER 6-17-56-21. These wells were classified as category E in the Phase I report, which were wells recommended to be investigated further to evaluate the feasibility for water reuse. The injected wastewater has been produced from operations at the Agrium Redwater Fertilizer Plant, at a mean monthly injection rate of 64,900 m^3 (Chen and Kindzierski, 2005).

The wastewater characteristics reported by Chen and Kindzierski (2005) and from the company's report on deep disposal well operations are summarized in Table 4.6. The injection rate for the last three years, indicated by updated data in Table 4.6, has been 65,417 m^3/month which is similar to that reported by Chen and Kindzierski (2005). As described by Patterson (1985) that the main contaminants in the wastewater from fertilizer plants are inorganic nitrogenous compounds. The wastewater contains high concentrations of ammonia nitrogen (1,515 mg NH_3/l) and nitrate (71mg NO_3^-/l). The wastewater also includes intermediate amounts of organic nitrogen (196 mg/l), and low levels of phosphate (5mg/l), and TSS (26 mg/l). However, the company has not measured hexavalent chromium ion (Cr^{6+}), carbonate (CO_3^-) or sulfate (SO_4^{2-}) concentration in recent years. These contaminants were reported in the original deep-well application document on which the Phase I report (Chen and Kindzierski, 2005) was based.

Since the concentrations of all chemical parameters exceed Water Quality Guidelines for Protection of Aquatic Life shown in Table 2.1, alternative treatment technologies need to be evaluated. The evaluation of feasible treatment technologies will focus mainly on methods to remove inorganic nitrogenous compounds such as ammonia, ammonium ion, and nitrate from waste streams, while also considering the removal of phosphate and TSS.

Table 4.6. Characteristics of Wastewater Injected Under Approval No. 4779.

<table>
<tr><th rowspan="2">Category & Well Approval Number</th><th colspan="3" rowspan="2">Well Name or ID</th><th rowspan="2">WW Source</th><th colspan="2">Injection rate (m^3/mon)</th></tr>
<tr><th>Phase I Report1)</th><th>Updated2)</th></tr>
<tr><td>E 4779</td><td colspan="3">▪ AGU REDWATER 10-17-56-21
▪ AGU REDWATER 6-17-56-21</td><td>Agrium Redwater Fertilizer Plant</td><td>64,900</td><td>65,417</td></tr>
<tr><td rowspan="2">WW Analysis</td><td colspan="6">Main Contaminants & Level4)</td></tr>
<tr><td>Name</td><td>Avg.</td><td>Range</td><td>Name</td><td>Avg.</td><td>Range</td></tr>
<tr><td rowspan="5">Phase I Report</td><td colspan="6">Year : 1983</td></tr>
<tr><td>NO_3^-</td><td>545</td><td>34-1,960</td><td>CO_3^{2-}</td><td>395</td><td>72-1,294</td></tr>
<tr><td>NH_3</td><td>856</td><td>23-2,376</td><td>SO_4^{2-}</td><td>8968</td><td>1100-25,100</td></tr>
<tr><td>PO_4^{3-}</td><td>12</td><td>1-115</td><td>SS</td><td>110</td><td>4-1741</td></tr>
<tr><td>Cr^{6+}</td><td>24</td><td>1-57</td><td>pH</td><td>-</td><td>3.1-10.2</td></tr>
<tr><td rowspan="16">Updated 3)</td><td colspan="6">Year : 2003</td></tr>
<tr><td>NO_3^-</td><td>68</td><td>0-238</td><td>Organic N</td><td>190</td><td>4.5-764</td></tr>
<tr><td>NH_3</td><td>1565</td><td>479-4,620</td><td>TSS</td><td>15</td><td>3.6-34</td></tr>
<tr><td>PO_4^{3-}</td><td>4</td><td>0.39-5.8</td><td>pH</td><td>8.9</td><td>8.5-9.8</td></tr>
<tr><td colspan="6">Year : 2004</td></tr>
<tr><td>NO_3^-</td><td>88</td><td>1-352</td><td>Organic N</td><td>343</td><td>4-2,996</td></tr>
<tr><td>NH_3</td><td>1719</td><td>667-5,449</td><td>TSS</td><td>19</td><td>2-60</td></tr>
<tr><td>PO_4^{3-}</td><td>4</td><td>1.2-14.5</td><td>pH</td><td>8.7</td><td>8.5-9.9</td></tr>
<tr><td colspan="6">Year : 2005 (Jan. - Aug.)</td></tr>
<tr><td>NO_3^-</td><td>56</td><td>2-128</td><td>Organic N</td><td>55</td><td>4-242</td></tr>
<tr><td>NH_3</td><td>1261</td><td>932-2,047</td><td>TSS</td><td>45</td><td>14-94</td></tr>
<tr><td>PO_4^{3-}</td><td>6</td><td>1.2-12.0</td><td>pH</td><td>8.5</td><td>8.4-8.9</td></tr>
<tr><td colspan="6">Average (2003 - 2005)</td></tr>
<tr><td>NO_3^-</td><td>71</td><td>0-352</td><td>Organic N</td><td>196</td><td>4-2,996</td></tr>
<tr><td>NH_3</td><td>1,515</td><td>479-5,449</td><td>TSS</td><td>26</td><td>2-94</td></tr>
<tr><td>PO_4^{3-}</td><td>5</td><td>0.4-14.5</td><td>pH</td><td>9</td><td>8.4-9.9</td></tr>
</table>

1) Adapted from Chen and Kindzierski (2005)

2) Adapted from EUB (2005)

3) Adapted from Agrium (2004), Agrium (2005a), and Agrium (2005b)

4) Unit: mg/l except pH

4.2.2. Alternative Treatment Technologies

The technologies used for removing nitrogenous compounds and phosphate from wastewater can be classified broadly as physical, chemical and biological methods.

The possible technologies are reviewed in the following sections. A summary of removal efficiencies published in the literature is given in Table 4.18.

4.2.2.1. Physical Treatments

Physical treatment technologies applied for nitrogen removal include gas or steam stripping, membrane, filtration, and adsorption. A summary of advantages and disadvantages of each physical treatment method is shown in Table 4.8. Gas or stream stripping is used for removing gaseous ammonia dissolved in wastewater by passing air or steam through the waste stream. Since ammonia has to be in the unionized gas form to be stripped, the pH is raised above 10.8 (Reynolds and Richards, 1996). However, if lime is used for pH adjustment, the deposition of calcium carbonate within the stripping tower can cause operational problems. Odour control or ammonia recovery procedures need to be applied to the air stream after the stripping process. Gas stripping is generally used for low concentration of ammonia removal while steam stripping is applied to waste streams containing high ammonia concentrations due to its higher efficiency (Patterson, 1985).

One of the advantages of air stripping is that ammonia removal efficiency can be controlled by pH adjustment (WEF, 1994). Temperature is important operating factor in gas stripping. Especially cold weather negatively affects the stripping tower operation because of ice formation when the wastewater temperature drops below 0 °C, and the increased solubility of ammonia gas with decreasing temperature which induces more stripping air requirement (WEF, 1994; Reynolds and Richards, 1996). Various types of gas stripping equipment are available. These include the induced-draft stripping tower in which the wastewater containing ammonia gas flows downward while stripping gas flows in the upward direction, and the high-pH spray ponds which can be used under cold climates, even though the ammonia removal efficiency is as low as 52%. Siegrist (1996) reported that air stripping towers achieved 97% NH_3 removal efficiency at temperatures between 10°C and 22°C. The process train included pre-treatment to precipitate $CaCO_3$ and absorption of stripped NH_3 by sulfuric acid solution to produce $(NH_4)_2SO_4$ solution. Nevertheless, the author found that the cost of drying ammonia sulfate solution is not economically feasible.

Steam stripping is generally more efficient for ammonia stripping because of the low concentration of ammonia in the stripping gas, elevated temperatures, and absence of other gases in the steam (WEF, 1994). However, steam stripping is more applicable when steam is available from another process in the facility, and when the reuse of recovered high concentration of ammonia is possible (Patterson, 1985). In the stripping process the fouling caused by iron deposition due to elevated water temperature is another operational problem (Metcalf & Eddy, 2003). Patterson (1985) indicated that steam stripping of a fertilizer plant wastewater achieved an effluent ammonia concentration of 20 to 30 mg/l based on influent concentrations of 100 to 1,300 mg NH_3/l. Also, Patterson (1985) explained that the two stage ammonia and hydrogen sulfide stripping process is used for removing ammonia and hydrogen sulfide from petroleum refinery sour water containing high levels of ammonia (2,750 mg NH_3/l), and subsequent recovery of high quality ammonia and hydrogen sulfide from the stripped stream. The ammonia removal efficiency was reported to be 98%. Janus (1997) explained that approximately 70% of the heat in the stripped NH_3 vapor was reusable, which could contribute considerable energy saving.

Membrane separation is also possible for nitrogen and phosphorous compound removal. Because of different operating ranges depending on membrane types, membrane filtration can be broadly divided two groups for nitrogen and phosphorous elimination; microfiltration (MF) and ultrafiltration (UF), and nanofiltration (NF) and reverse osmosis (RO). The various compounds can be removed by different membranes are shown in Table 4.7. Microfiltration is the most widely adapted and most inexpensive membrane technology (Metcalf & Eddy, 2003). Also, MF requires less space for construction and less labor due to easier automatic control. However, MF and UF may require pretreatment for suspended solids reduction. The fouling and scale formation can be serious problems in MF and UF systems. Other disadvantages of MF and UF are requirement of high pressure and periodic membrane replacement every 3 to 5 years. On the other hand, MF or UF can be used as pretreatment for reverse osmosis to prevent fouling of RO elements by suspended or colloidal matter. Reverse osmosis also requires pre-elimination of iron and manganese which can cause scaling at pH values between 4.0 and 7.5.

Table 4.7. Compounds Rejected by Various Membranes (Adapted from Metcalf & Eddy, 2003)

Constituents	MF	UF	NF	RO
Biodegradable organics		Yes	Yes	Yes
Hardness			Yes	Yes
Heavy metals			Yes	Yes
Nitrate			Yes	Yes
Priority organic pollutants		Yes	Yes	Yes
Synthetic organics			Yes	Yes
TDS			Yes	Yes
TSS	Yes	Yes	Yes$^{1)}$	Yes$^{1)}$

$^{1)}$ TSS is removed in pretreatment.

Xu et al. (2001) applied polypropylene hollow fiber membrane to eliminate high strength of NH_3 from a fertilizer factory wastewater. The gaseous ammonia which evaporates and diffuses through the gas-filled micropores in membrane can be removed by sweep gas or by acid solution outside of membrane, but liquid wastewater cannot penetrate the membrane pores. The test resulted in 93.5% NH_3 removal from influents ranging in concentration from 1,000 to 10,000 mg NH_3/l. Fouling, was controlled using a weak acid (Xu et al., 2001). The operation conditions for the stable performance are the pre-removal of hardness and suspended solids prior to the membrane process, and increasing the pH to 11 to obtain gaseous ammonia. Metcalf & Eddy (2003) depicted reverse osmosis as a useful NH_3 and NO_3^- removal process. The full-scale reverse osmosis resulted in a 96% removal efficiency for both NH_3-N and NO_3-N, and almost complete removal of TDS (97%), PO_4^{3-} (99%) and SO_4^{2-} (99%) as well. However, this process required high pressure and consequently entails high operation cost. Karabelas et al. (2001) also studied the feasibility of reverse osmosis application to NO_3^-, NH_4^+ and TDS removal from fertilizer industry wastewater to recycle the treated water within the facility. The bench-scale test results indicated 97% of removal efficiency for both NH_4^+ and NO_3^-. The author suggested adjusting the temperature to between 30 to 35 °C and pH to between 4.5 to 6.5 in order to remove both ions simultaneously.

Patterson (1985) reported the results of a study investigating various methods to remove soluble organic nitrogen. The methods investigated were chemical coagulation, ion exchange, chemical oxidation and activated carbon adsorption. The results showed activated carbon adsorption had the highest organic nitrogen mean removal efficiency (72%) in comparison with other methods having mean removals between 11% and 42%. Prior removal of oil and SS is required to apply carbon adsorption. Metcalf & Eddy (2003) explained that the major disadvantage of carbon adsorption is insufficient definition of regeneration methods.

Filtration technologies proved to be efficient for particulate phosphorous removal as well as suspended solids. Two deep-bed upflow continuous backwash filters employed large size sand and smaller size sand for the first and second filter, respectively, have been considered as effective removal process for suspended solids as well as particulate phosphorous (Metcalf & Eddy, 2003). The first filter used to increase contact time and to reduce clogging problem by applying larger sand. The following second sand filter can remove remaining particles from first filter using smaller-size sand. In full-scale application, the phosphorous concentration in effluent water represented same or less than 0.02 mg/l. A chemical addition using organic polymers, alum, or ferric chloride may be required to improve phosphorous removal efficiency in filtration process depending on the wastewater conditions.

Table 4.8. Advantages and Disadvantages of Physical Treatment Technologies used for Nitrogen and Phosphorous Removal

Treatment Technology	Advantages	Disadvantages
Gas Stripping	- Suitable for low concentration ammonia removal - Easy to control NH_3 removal efficiency by pH control	- Requires pH higher than 10.8 - Ice formation at the temperature below 0°C - More air is required as temperature drops - Deposition of $CaCO_3$ by lime addition to raise pH - Odor and air pollution controls are required - Require following ammonia recovery procedure
Steam Stripping	- Suitable for high strength ammonia removal - Can reuse 70% of heat capacity in NH_3 vapor - Residual ammonia can be sold - More efficient method than gas stripping	- Need to raise pH (by lime) - Require steam production - Fouling by iron deposition due to elevated temperature
Membrane (MF & UF)	- Most widely adapted membrane - Inexpensive among membranes - Require less space & labor - Use as pretreatment for RO	- Require pretreatment of deposits and SS removal - Fouling and scale formation can be serious problems - Require high pressure & replacement membrane every 3-5 years
Membrane (NF & RO)	- Almost complete removal : 97% (TDS), 96% (NH_3-N, NO_3-N), 99% (PO_4^{3-}), 99% (SO_4^{2-})	- Expensive - Require high pressure & pretreatment (pH and Temp. adjustment, and SS, iron and manganese removal) - Need low dissolved matter in influent
Adsorption	- Higher organic nitrogen removal efficiency than chemical methods	- Need pretreatment to remove oil and SS - Insufficient regeneration technologies
Filtration	- Can remove particulate phosphorous and TSS simultaneously	- Require chemical addition to improve efficiency

4.2.2.2. Chemical Treatments

Several chemical treatments are applicable removal methods for inorganic nitrogenous compounds, which include breakpoint chlorination, ion exchange, magnesium ammonium phosphate (MAP) precipitation and chemical reduction. Among these, breakpoint chlorination is used for NH_4^+ oxidation; while chemical reduction is utilized for NO_3^- transformation to N_2 gas. A summary of advantages and disadvantages of each chemical treatment is shown in Table 4.10.

The breakpoint chlorination can convert ammonia to nitrogen gas with an efficiency of up to 99% under proper operating conditions. However, breakpoint chlorination has several potential disadvantages (Reynolds and Richards, 1996; WEF, 1994). First, the formation of harmful or undesirable byproducts such as trihalomethanes, dichloramines, trichloramine and nitrate by complex side reaction may occur. Second, base addition is required if alkalinity in the wastewater is not sufficient to maintain a pH range from 7 to 8. Third, pretreatment is required to reduce the organic or inorganic compounds such as sulfides, sulfates and phenols which increase chlorine demand. Fourth, operating cost may be higher than other that of alternative methods due to high chlorine dosage and increase of dissolved solids.

The typical nitrogenous ions removed by ion exchange are NH_4^+ and NO_3^-. Ion exchange is more suitable for the wastewater with low BOD/N ratio, low temperature, low nitrogen concentration, or which contains nitrification inhibitors (Hedström, 2001). The optimal pH range for nitrogen compound elimination by ion exchange is between 4 and 8 (Patterson, 1985). The suspended solids and carbonaceous material must be removed before ion exchange. The limitations of ion exchange for nitrogen compounds removal in full-scale operations are necessity of well-trained operators due to operational complexity, and high operating cost (Hedström, 2001; WEF, 1994). Additionally Metcalf & Eddy (2003) stated that ion exchange has had limited application to date because of the requirement of extensive pretreatment and concerns about the life of the ion-exchange resins, and the complex regeneration system.

Among various synthetic and natural ion resins, a natural zeolite named clinoptiolite, has proven to have high affinity for NH_4^+, and is inexpensive compared to other resins (Metcalf & Eddy, 2003; WEF, 1994). Exhausted resins need to be regenerated in order to secure continuous ion exchange capacity. Hedström (2001) reviewed chemical and biological regeneration methods applied to saturated clinoptiolite. Chemical regeneration uses sodium chloride (NaCl), a mixture of sodium chloride and sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) or nitric acid (HNO_3) to desorb NH_4^+ ions from exhausted resins. Generally, NH_3 gas is produced after regeneration due to high pH, which must be removed by subsequent processes such as gas or steam stripping, or electrolysis (Hedström, 2001; Reynolds and Richards, 1996; Patterson, 1985).

Biological regeneration which is actually a combination of chemical and biological regeneration as explained by Hedström (2001) applies nitrification to consume ammonia adsorbed to the zeolite resin by nitrifying bacteria. Since the nitrification process requires sufficient amount of alkalinity, sodium bicarbonate is used as the regeneration brine. The part of sodium ions recharge the exhausted resin by displacing adsorbed ammonium ion; while remaining sodium ions produce sodium nitrate. The biological regeneration method can reduce the regenerant consumption. Hedström (2001) introduced three different types of biological regeneration methods including regeneration by nitrifying sludge, by regenerant, and in a single reactor. The principle and properties of each process are given in Table 4.9. Selection of the proper regeneration method depends on the site-specific conditions.

Table 4.9. Biological Regeneration Methods for Exhausted Ion Exchange Resins (Adapted from Hedström (2001)).

Parameter	Biological regeneration of zeolite by nitrifying sludge	Biological regeneration by regenerant	Biological regeneration of zeolite in single reactor
Regeneration principle	Nitrifying sludge with sodium ions is pumped through zeolite column and ammonium ions are desorbed	Nitrified brine solution is pumped through zeolite column and ammonium ions are desorbed	Nitrified brine solution is pumped through zeolite column and ammonium ions are desorbed
Nitrification process	Takes place in aeration tank located after zeolite column; nitrifying bacteria are not separated from regeneration brine	Takes place in aeration tank located after zeolite column; nitrifying bacteria are separated from regeneration brine	Takes place in zeolite column; nitrification bacteria are attached on zeolite grains
Duration of regeneration	Limited by nitrification process	Limited by ion exchange process	Limited by nitrification process

Metcalf and Eddy (2003) described the operational problems when conventional ion exchange is used for nitrate removal. If the wastewater contains a significant amount of sulphate, nitrate removal decreases because ion exchange has lower affinity for nitrate than sulphate. The occurrence of effluent containing high concentration of nitrate named "nitrate dumping" is another problem, which occurs when nitrate breakthrough occurs as a result of sulphate replacing previously adsorbed nitrate.

Patterson (1985) reported that ammonia nitrogen removal efficiency for fertilizer wastewater by ion exchange is from 88% to 94% with influent concentration from 325 mg/l to 719 mg/l. The author also introduced an example of weak cation exchange resin to recover ammonia and hydrogen sulfide from sour water, which yield 5 mg NH_3/l in effluent from 390 mg NH_3/l in influent. Leaković et al. (2000) used a combination of strong acid cation and weak anion ion exchangers to remove NH_4^+ and NO_3^- at the same time from fertilizer wastewater. The chemical regeneration was applied using nitric acid for cation exchanger and ammonium hydroxide for anion exchanger. The author stated that the advantages of ion exchange for fertilizer wastewater treatment are the reutilization of regeneration stream for fertilizer production, reuse of treated wastewater within the facility and on-site chemical production for saturated ion exchanger regeneration. The full-scale industrial application results showed 93% removal efficiency for NO_3^- and 94% for NH_4^+ using 183 mg NH_4^+/l and 100 mg NO_3^-/l in influent. The wastewater was pretreated using a sand filter and activated carbon filter, and diluted to maintain the concentration under 180 mg NH_4^+/l and 100 mg NO_3^-/l prior to ion exchange.

Ion exchange can also be used for recovering ammonium nitrate from the wastewater. Patterson (1985) depicted combination of cation and anion exchange resins to produce concentrated ammonium nitrate from the fertilizer wastewater containing dilute ammonium nitrate. Ammonium ions are first removed by passing the waste through a strong acidic cation exchanger which is regenerated by nitric acid to produce ammonium nitrate. Then ammonia-free effluent flows to an anion exchange resin to remove nitrate. Ammonium hydroxide is used as regenerant for exhausted anion exchange column regeneration to form ammonium nitrate. Patterson (1985) reported a full-scale example of this ion exchange method by which effluent contained 7-11 mg NO_3^-/l using 1,240 mg NO_3^-/l in the influent.

Magnesium-Ammonium-Phosphate (MAP : $MgNH_4PO_4{\cdot}6H_2O$) also known as struvite formed under weak alkaline condition is used for removing NH_4^+, PO_4^{3-} and/or Mg^{2+} from wastewater by chemical precipitation (Altinbas et al., 2002). If the wastewater contains a high concentration of ammonium with a lesser amount of magnesium and phosphate, sufficient magnesium and phosphate must be added to generate MAP. Altinbas et al. (2002) studied MAP precipitation to remove ammonia for the biologically pretreated wastewater with high ammonia and COD in a lab-scale experiment. Due to insufficient Mg^{2+} and PO_4^{3-} in the wastewater, magnesium chloride and sodium dihydrogen phosphate were added to create MAP precipitation. The NH_4^+ removal rate is 61% - 80% at pH 9.2 and at the stoichiometric ratio of Mg:N:P as 1:1:1; while 83% of NH_4^+ was removed above the stoichiometric ratio of Mg:N:P as 1.1:1:1.1. The authors concluded that MAP precipitation can be used as a complementary treatment technology for the wastewater containing high ammonia and phosphorous before biological nutrient removal process.

Janus and Roest (1997) compared MAP precipitation with other technologies such as biofilm, membrane bioreactor, and stripping used for nitrogen compound removal. The ammonium ion removal efficiency by MAP precipitation was higher than 90% at pH values above 9.5. The optimum molar ratio of Mg:N:P is 1.1:1:1. However, the operating cost comparison indicated that MAP precipitation was the most costly among the technologies compared. Siegrist (1996) also compared the ammonia removal techniques within physical, chemical and biological methods including MAP. The physical and chemical methods entailed significantly high operation cost than biological means. The author suggested that MAP precipitation should be considered only when phosphate is available within the facility.

Patterson (1985) demonstrated that ferrous ion addition was an economically feasible chemical treatment for nitrate reduction to nitrogen gas. However, there is no full-scale application of the chemical nitrate reduction method because the process requires catalyst, a large amount of ferrous iron, and alkaline pH. Moreover, chemical reduction showed a maximum of 70% nitrate removal efficiency.

Chemical precipitation is known as the most common and effective practical method for phosphorous removal. The commonly used chemicals are alum and ferric chloride to provide multivalent metal ions (WEF, 1994; Metcalf & Eddy, 2003). The process can remove suspended solids simultaneously but at the same time it produces large amount of sludge. The pH control is very important to maximize precipitation efficiency. The optimum pH ranges for phosphate precipitation with aluminum is from 5 to 7, and with iron is between 4 and 6 (Metcalf & Eddy, 2003). Lime usage is not common due to considerably large sludge production, difficulty of handling the lime and alkalinity coprecipitation in the form of $CaCO_3$ which increases lime consumption.

Table 4.10. Advantages and Disadvantages of Chemical Treatment Technologies used for Nitrogen and Phosphorous Removal.

Treatment Technology	Advantage	Disadvantage
Breakpoint Chlorination	- High NH_4^+ removal efficiency (95-99%)	- Formation of harmful or undesirable byproducts - Require base addition - Require pre-removal of organic/inorganic compounds - High operating cost
Ion Exchange	- Suitable for the wastewater with low BOD/N, low temperature or low nitrogen concentration, or containing nitrification inhibitor	- Require regeneration of resin (consume chemical) - Require pre-removal of SS and carbonaceous matter - Anion exchange has lower selectivity for NO_3^- than SO_4^{2-} (can cause nitrate dumping) - A few full-scale applications - Require NH_3 removal after regeneration - Expensive - Operation is complicated (require well trained operators)
MAP Precipitation	- Can be used as complementary treatment for high NH_4^+ and phosphorous wastewater prior to biological nutrient removal	- Require P and/or Mg addition if insufficient - Require SS removal prior to MAP - High operating cost (only better choice when PO_4^{3-} is available internally)
Chemical Reduction of Nitrate	- Ferrous ion can be used as economically feasible reducing chemical	- No full-scale application - Require catalyst (copper) - Low removal efficiency (<70%) - High chemical demand and cost
Chemical Precipitation of Phosphorous	- Can remove phosphorous and SS simultaneously	- Require chemical addition and pH control - Large sludge production - Lime usage declined due to handling difficulty and $CaCO_3$ deposition

4.2.2.3. Biological Treatments

A number of different biological treatment systems exist to treat nitrogenous compounds. Nitrification and denitrification are the most common processes applied for biological NH_4^+-N and NO_3^- removal. Many alternative technologies using different reactor schemes, integrating two or more treatment methods and/or shorter nitrification/denitrification reactions have been extensively studied in addition to the conventional methods. The conventional methods as well as alternatives are discussed below including broadly adapted technologies such as biofilters, membrane bioreactors, sequencing batch reactors, and partial nitrification and denitrification. A summary of advantages and disadvantages of each biological treatment method is shown in Table 4.17.

Nitrification/Denitrification

The combination of nitrification and denitrification processes contains both an aerobic zone for oxidation of NH_4^+-N to NO_3^- and an anoxic zone to transform NO_3^- to nitrogen gas (Metcalf & Eddy, 2003). The process has an advantageous effect in terms of an internal buffering capacity by hydrogen ions produced during nitrification and hydroxyl ions generated in the denitrification process (Eckenfelder Jr., 2000). However, the activity and growth of microorganisms, especially nitrifying bacteria, can be disturbed by inhibitors which may be contained in industrial wastewater. The most common nitrification and denitrification is conventional activated sludge. The modified methods have been introduced extensively to overcome the limitations of traditional activated sludge process.

Conventional Activated Sludge

Activated sludge system is widely applied nitrification/denitrification process. Eckenfelder Jr. (2000) indicated that wastewater from a fertilizer plant containing high NH_4^+-N and negligible BOD was treated by the activated sludge process using nitrification and denitrification. Siegrist (1996) compared different ammonium removal methods for digester supernatant using pilot scale tests. The results indicated that the nitrification/denitrification process in the activated sludge process with methanol addition as external carbon source for denitrification was a more economical method than chemical or physical ammonium removal.

Carbonaceous material and organic nitrogen compounds are converted biochemically to cell mass by nitrogen assimilation or NH_4^+-N by mineralization during biological treatment (Patterson, 1985; Reynolds and Richards, 1996). Therefore, three-stage nitrogen removal process including carbon removal, nitrification and denitrification process is employed for complete nitrogen removal. Patterson (1985) depicted 90% of ammonia removal and 95-100% oxidized nitrogen removal by a three-stage nitrogen removal system.

The different configurations for nitrification and denitrification are basically classified as single sludge in one reactor and two-sludge in separate basins for aerobic and anoxic condition (Eckenfelder Jr., 2000). The single sludge one reactor system contains an aerobic and anoxic zone or treatment period in one basin, and utilizes raw wastewater as the carbon source for denitrification. On the other hand, two-sludge in separate reactors uses a basin for nitrification and another for denitrification independently. In this system supplemental carbon source such as methanol is added to provide a source of organic carbon for denitrification.

Modified Activated Sludge

Buday et al. (2000) modified the two-stage activated sludge process in DUSLO (a large Central European fertilizer plant) to a pre-dentirification/ nitrification/ post-denitrification system. The front half of the first activated sludge reactor and 1/4 of the total volume of second activated sludge reactor were converted to anoxic condition, which resulted in large energy saving by reducing aeration. The NOx-N removal efficiency reached to 91% in the pre-denitrification step, but the nitrification and denitrification in second activated sludge process achieved only 17% ammonia and 15% NOx-N removal. This was attributed to an inadequate biomass acclimatization period and insufficient retention time in the second anoxic zone.

Roš and Gantar (1998) conducted pilot plant tests to compare conventional activated sludge treatment and combined anaerobic-anoxic-aerobic treatment for the wastewater which was pre-removed suspended solids mechanically and contained high organic loading (COD, BOD_5) and high content of ammonia and organic nitrogen. Both methods showed similar treatment efficiency at similar volumetric loadings (0.8 to 1.99 g COD/l/day) with long hydraulic retention times (1.9 to 4.7 days). However, combined treatment with lower volume loading (0.5g BOD_5/l/day) and long retention time (4.8 days) outperformed the conventional system by reducing ammonia concentration from 224 mg/l to 8.3 mg/l (96% reduction) and COD from 4,073 mg/l to 275mg/l (93% reduction).

The process comparison between anaerobic-anoxic-aerobic and anoxic-aerobic systems conducted by Zhang et al. (1997) for biological treatment of coke plant wastewater containing high ammonia and COD concentrations. The outcomes indicated that anaerobic-anoxic-aerobic scheme achieved 20% more nitrification, approximately twice the denitrification performance and more COD removal. The initial anaerobic treatment was believed to reduce inhibitors and to supply more biodegradable substances in subsequent denitrification and nitrification steps.

Many alternative reactor systems have been developed as alternatives to conventional nitrification/ denitrification processes. These include sequencing bioreactors, attached growth systems such as biofilter reactors, and membrane bioreactors.

Sequencing Batch Reactor (SBR)

In a sequencing batch reactor (SBR), the separate treatment procedures such as complete mixing, aeration and clarification are proceeded stepwise in the same reactor. General sequences include fill, reaction, settlement, decant and idle (Metcalf & Eddy, 2003). The SBR can have very flexible process operation since time or intensity of each step can be adjusted easily (Yilmaz and Oztűrk, 2003). The process does not require a separate clarifier, and of course short-circuiting in the reactor is not possible.

A sequencing batch reactor (SBR) was applied for lab-scale biological nitrogen removal from a sanitary landfill leachate which was characterized by high ammonia and COD concentrations, 886.6mg/l of ammonia and 1,385mg/l of COD (Yilmaz and Oztűrk, 2003). The whole sequence was included fill, aerobic, anoxic, second aerobic, settle, draw and idle periods. The results showed almost complete ammonia removal, and low nitrate (52mg NO_3^-/l) and nitrite (0.59mg NO_2^-/l) concentration in the effluent with 99% denitrification efficiency, when the influent wastewater was anaerobically pre-treated in an up-flow anaerobic sludge blanket reactor, and calcium acetate was used for external carbon source during the anoxic period.

Arrojo et al. (2004) investigated biological granular sludge formation to develop good sludge settling properties and high nitrogen removal in granular sludge using laboratory-scale activated sludge sequencing batch reactors (SBRs) for the wastewater from dairy analysis laboratory. Granules which have good settling properties, SVI 60 ml/g VSS, were observed. 80% of the nitrogen and 70% of the COD were removed in the granular sludge. It is believed that nitrification took place in outer layer of granules with simultaneous denitrification occurring in the inner layer of the granular sludge.

Attached Growth Systems

The attached growth systems are known to be the effective reactor schemes for biological treatment because of the biofilm developing on attached materials. The biofilm reactor is filled with natural or synthetic packing materials or fixed supporters on which microorganisms grow and form a fixed-film (Loosdrecht et al., 2000). Loosdrecht et al. (2000) stated that biofilm reactors are useful when slow growing bacteria such as nitrifiers have to be kept in a wastewater treatment process and when nitrogen removal by nitrification as well as denitrification is required. Since biomass is efficiently retained in biofilm reactor, reactor volume can be reduced and long sludge retention times can be achieved.

The biofilter technology is one of the emerging attached growth biological systems. In biofilter systems, biological treatment and filtration occur at the same time since biofilters have combined properties of a bioreactor and a filter in a single system in which a biofilm develops on filter media (Chen et al., 2000). However, regular backwash using air or water has to be applied to remove retained solids. The aerated biofilter is considered a very promising biological treatment system, which enables stable high-rate nitrogen removal even under fluctuating wastewater conditions, with relatively low operating costs and a low space requirement (Lazarova et al., 2000; Thøgersen and Hansen, 2000). Thøgersen and Hansen (2000) compared full-scale biological aerated filter (BAF) and activated sludge (AS) with recirculation processes for nitrogen removal. The influent wastewater contained 250 mg COD/l, 39 mg TN/l, 4 mg TP/l, 92 mg SS/l, 22 mg NH_4^+-N/l and 1.5 mg PO_4^{3-}-P/l. The BAF system showed similar removal efficiency for TN and SS reduction (88% and 94%, respectively) as AS process (86% and 93%, respectively), while BAF exhibited a higher tolerance to fluctuating hydraulic and chemical loads, and temperature change. However, AS showed better TP removal (81%) than BAF (74%).

Over 100 Biofor® systems, the upflow biofilter reactor system with Biolite® media, have been operated to produce low ammonia containing effluent water (Lazarova et al., 2000). A summary of full-scale operation for 5 years is shown in Table 4.11. These results indicate that almost complete ammonia removal and very low suspended solids content in the effluent was achieved. The combination of pre-denitrification and Biofor® nitrification system was used to treat COD and nitrogen from primary settled municipal wastewater (Pujol and Tarallo, 2000). When methanol was added in the system, COD and nitrogen removal performance were improved up to 85% TKN, 85% COD and 88% TSS removal.

Table 4.11. Biofor® Biofilter Operating Results (Adapted from Lazarova et al. (2000)).

Compounds (mg/l)	Chevron oil refinery			Mobil oil refinery		
	Influent	Effluent	Removal (%)	Influent	Effluent	Removal (%)
COD	36	26	28%	39	30	23%
NH_4^+-N	23	0	100%	22	0.3	99%
NO_3^--N	6.7	40	-	5.3	42	-
PO_4-P	6.3	6.4	-	6.4	6.4	-
TOC	10.6	8.1	24%	11.2	8.8	21%
TSS	2.1	4	-	2.4	4.3	-

Frijters et al. (2000) reported that a new type of full-scale airlift biofilter reactor with CIRCOX® technology showed successful nitrogen compounds and organic removal for anaerobically pretreated potato-processing factory wastewater. The several full-scale installations proved the process's stable operation for simultaneous nitrification and denitrification. Since the new CIRCOX®-airlift reactor provides the biofilm coated carrier circulation by bottom air supply within the reactor which is partitioned to oxic and anoxic zone, the reactor has many strengths; the reactor is compact and consequently reduce capital cost; the produced sludge is well settled and retained easily in the reactor as a result of dense biomass (500mg VSS/g carrier) on thin biofilm layer (100-300μm); controlling sludge age and periodic back washing are not required; biological sludge production is low. However, the subsequent solids removal process is needed. Full-scale operation resulted almost complete ammonia removal and higher than 90% denitrification efficiency. The similar airlift biofilter scheme which applied internal oxic-anoxic compartment was introduced by Loosdrecht et al. (2000). The compact airlift biofilm reactor was used for integrated nitrogen removal, which contained an extra downcomer to enhance wastewater circulation between oxic and anoxic zone, and to control circulation intensity by head space pressure. This system is simpler than other biofilm suspension reactor since extra air lift pump and recirculation pipe are not required.

The biological aerated filters (BAF) using DeepBed™ sand filter indicated that it is very effective to achieve bio-oxidation, denitrification and SS removal simultaneously (Chen et al., 2000). The operation results for four full-scale DeepBed™ sand filter are given in Table 4.12.

Table 4.12. Operating Results of Full-Scale DeepBed™ Sand Filter (Adapted from Chen et al. (2000)).

Wastewater	Compounds	Inflent (mg/l)	Effluent (mg/l)	Removal Eff. (%)
Coke plant	NH_4^+	168	36	79%
	Phenol	58	0	100%
Semiconductor manufacturing plant	TN	23	2	91%
	NH_4^+	19	0.1	99%
Dairy waste + domestic sewage	BOD	-	-	91%
	COD	-	-	80%

The gas-liquid-solid three-phase flow airlift loop bioreactor was used in lab-scale experiment to remove high strength ammonia from fertilizer wastewater (Wen et al., 2003). The advantages of the process expressed by the authors are better mixture, closer contact between the three phases, faster oxygen transfer rate, higher operational flexibility, shorter reaction time and greater processing capability. The average removal efficiency were 99% and 95% for NH_4^+-N and COD, respectively, under the optimum operating conditions of temperature 35°C, pH 8.0, HRT 8 hours and air influx $0.3m^3/h$. But, Janus and Roest (1997) demonstrated that three-phase (air, water and biomass carrier material) air-lift reactor showed poor denitrification performance while 90% of nitrification rate was achieved in full-scale installation. This implies separate denitrification has to be followed to achieve complete nitrogen compounds removal.

The lab-scale combined anaerobic and aerobic process which was applied an upflow anaerobic sludge blanket reactor (UASB) and an upflow biological aerated filter (UBAF) was used to treat high COD (10,400 mg COD/l) and nitrogen (790 mg TKN/l and 210mg NH_4^+-N) in industrial wastewater (Lacalle et al., 2001). The effluent from UBAF was recirculated to UASB to remove NOx-N compounds formed in aerobic treatment. The almost entire organic nitrogen conversion to ammonia was observed in UASB. The combined process produced the effluent water containing 190 mg/l of COD and 70 mg/l of TN (including 13mg TKN/l and 56 mg NOx-N/l). Hirata et al. (2001) introduced the series of laboratory-scale circulation bioreactor consisted of anaerobic packed bed reactor and aerobic three-phase fluidized bed system for biological nitrogen removal from metal recovery process wastewater. The wastewater hold high strength of TN (3,100mg/l), NOx-N (2,200mg/l), NH_4^+-N (800mg/l) and DOC (1,900 mg/l). The removal efficiency reached between 90 to 98% for TN and from 80% to 92% for ammonia.

To deal with fluctuated ammonium load, the integrated nitrification and ion exchange system containing Filtralite ZL, an expanded clay aggregate filtermedia including zeolite was utilized (Gisvold et al., 2000). The important functions of the Filtralite ZL mentioned by authors were a biofilm carrier for nitrifying biomass, an ammonium ion exchanger and a particle separation filter. The pilot scale four-month experiments in up-flow filters demonstrated stable NH_4^+-N removal capacity even at the peak ammonia load without chemical or biological regeneration.

Another simultaneous biological nitrogen compounds removal and ion exchange were carried out by Chung et al. (2000) through the lab scale modified oxic/anoxic system with natural zeolite recirculation using the wastewater from fertilizer and tannery plants. The influent wastewater was streamed firstly in the anoxic reactor with zeolite powder to enhance organic matter usage in denitrification process in which methanol was also added, and to adsorb ammonium ion in zeolite. The ammonium containing zeolite is introduced to prior oxic reactor for nitrification and biological ion exchanger regeneration. The aerated activated carbon filter was additionally set after oxic/anoxic processes to remove recalcitrant materials remaining in tannery wastewater. The experimental results are given in Table 4.13. The high nitrogen removal efficiency and better sludge settleability were achieved from the experiments.

The PACT® is a combined process between activated sludge and adsorption by powdered activated carbon addition in activated sludge reactor (Eckenfelder Jr., 2000; Matcalf & Eddy, 2003). Generally, PACT® process is accomplished by powdered activated carbon injection into existing activated sludge process with low cost. The process has many advantageous points. The operation is stable even though shock load is introduced to the system. Because of adsorption capacity, PACT® can remove refractory or non-easily biodegradable organics including inhibitors and toxic matters to microorganisms. The produced sludge has well settle characteristics. But, the process requires carbon regeneration, and large amount of carbon addition to achieve higher removal. The full-scale results, reported by Eckenfelder Jr. (2000), represented almost complete removal of COD (99%), TKN (97%), NH_3 (99%) and Phenol (100%) for organic chemicals plant's wastewater containing 10,230mg/l of COD, 120mg/l of TKN, 76mg/l of NH_3 and 8.1mg/l of phenol initially; while, it showed a little lower removal efficiency for the wastewater from textile finishing industry, which indicated 91% removal of COD and 95% NH_3 elimination from the initial concentrations of 1,362mg/l for COD and 74mg/l for NH_3.

Table 4.13. Experimental Results of Combined Oxic/Anoxic and Ion Exchange (Adapted from Chung et al., 2000).

Compounds (mg/l)		NH_4^+-N	TN	COD	TP
Tannary wastewater	Influent	370	392	626	9.1
	Oxic/anoxic Effluent	28	57	175	4
	Removal (%)	92%	86%	70%	65%
	Aerated filter effluent	8	40	58	0.5
	Removal (%)	98%	90%	91%	95%
Fertilizer wastewter	Influent	357	1024	267	2.3
	Oxic/anooxic Effluent	43	91	94	15*
	Removal (%)	88%	91%	64%	-

* P was added for nutrient balance

The nitrification under cold temperature was studied using CAPTOR® which is the attached growth biological ammonium removal process (Golla and Lin, 1992). The process indicated good performance; nitrification rate was only slowly affected by the temperature below 10°C, and up to 50% of denitrification was occurred in deeper layer of attached biomass.

The lab-scale experiment was performed for nitrate removal from the fertilizer wastewater using the bioreactor filled with alginate beads on which denitrifying bacteria were immobilized (Zala et al., 2004). The denitrification efficiency was reached up to 99% after successive 5 batch operations for the influent containing 600-950mg NO_3^-/l with adding methanol as carbon source.

Membrane Bioreactor (MBR)

Membrane bioreactor (MBR) is a suspended biological treatment in conjunction with membrane process by which cleaned wastewater can be separated from biomass (Metcalf & Eddy, 2003). Thus, longer sludge retention time and higher biomass concentration can be achieved in MBR, which lead to less sludge production, high-quality effluent and biological decomposition of non-readily biodegradable compounds (Nakhla et al., 2005; Janus and Roest, 1997; Metcalf & Eddy, 2003). On the other hand, the process requires a high capital cost investment, a periodic replacement of membrane, and a caution to membrane fouling. The biological treatment combined with submerged vacuum ultrafiltration membrane was used to remove organic matter, solids and nutrients in pilot scale experiments (Nakhla et al., 2005). High removal was attained including almost complete removal of suspended solids and colloidal matters, more than 65% NH_3-N and PO_4^{3-} removal, while NOx-N concentration was increased in effluent probably due to nitrification occurred in membrane.

Seo et al. (2002) investigated that ammonia oxidation efficiency when MBR (immersed hollow fiber microfiltration membrane) combining with powdered activated carbon was utilized for synthetic wastewater at the temperature below 4°C. The excellent ammonia oxidation was observed at low temperature (lower than 4°C) with MBR containing high concentration of powdered activated carbon in the bioreactor. The larger amount of activated carbon was preferred to obtain higher ammonia removal. The full-scale MBR integrating to granulated activated carbon adsorber represented high nitrification/ denitrification efficiency, and refractory COD degrading ability (Vasel et al., 2004). However, this process had some limitations such as operation complexity and high operation cost.

Partial Nitrification/Denitrification

Partial nitrification/denitrification is a reduced biological nitrogen removal method accomplished by controlling NO_3^- formation. The process has several advantages compared to traditional complete nitrification system. It can save up to 40% of external organic carbon demand, reduce reactor volume by shorter hydraulic retention time and decrease oxygen requirement (Surmacz-Górska et al., 1997). The Partial nitrification/ denitrification process can be used for the industrial wastewater with low COD/N ratio.

The modification of the existing full scale conventional nitrification/denitrification process to partial nitrification/denitrification also called nitration/denitration system was implemented for the purpose of reducing operating cost and achieving higher nitrogen removal rate. Pedersen et al. (2003) reported that aerated activated sludge process in which complete conversion of NH_4^+ to NO_3^- occurred with pre- and post-denitrification was changed to partial nitrification process as a result of unstable nitrification in conventional activated sludge system. The wastewater conditions were suitable for nitration because of high temperature (38°C - 40°C) and high alkalinity. The nitration/denitration process showed much better performance in terms of effluent nitrogen concentration and operational stability without increasing energy consumption while NO_2^- oxidation to NO_3^- in aeration tank is suppressed by controlling pH, oxygen and temperature.

Ruiz et al. (2003) studied the optimum operating conditions for partial nitrification using synthetic wastewater containing 610 mg NH_4^+/l, in activated sludge reactor. The optimum conditions were found to be DO concentration of 0.7 mg/l in the reactor at which the highest nitrite accumulation with 98% ammonia conversion, and more than 65% of nitrogen loading rate to achieve the best partial nitrification. A laboratory scale sludge blanket reactor (SBR) was tested for nitrogen removal from a pharmaceutical manufacturing facility by applying partial nitrification and denitrification (Peng et al., 2004). The influent wastewater included 250-500 mg COD/l, 130-280 mg BOD/l, 80-200 mg NH_4^+/l, 90-240 mg TN/l, 1-2 mg TP/l, 800-1,400 mg total alkalinity/l and pH 8.8-9.6. The nitrogen removal rate reached 99% with maintaining the temperature at 23°C through ammonia oxidation to nitrite and following nitrite to dinitrogen conversion. The pH in the reactor was found to control the end point for partial nitrification and denitrification, which facilitated on-line control of the process. Surmacz-Górska et al. (1997) also indicated that the pH is the controlling factor for inhibiting the activity of nitrite oxidizing bacteria in partial nitrification/denitrification process based on results from lab-scale activated sludge testing using synthetic wastewater with high ammonia 500 mg NH_4^+/l and 776 mg COD/l.

Hellinga et al. (1998) initially introduced a single reactor system for high ammonium removal named the SHARON® process. SHARON® is based on partial oxidation of ammonium ion to nitrite and subsequent denitrification of nitrite to dinitrogen gas

(Manipura et al., 2005). The nitrite conversion to nitrate is prevented by inhibiting nitrite oxidizing bacteria growth under conditions of high temperature (30°C - 35°C) and short sludge retention times (Hellinga et al., 1998). The related reactions when methanol is added as external carbon source are expressed as follows:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \tag{4.1}$$

$$6NO_2^- + 3CH_3OH + 3CO_2 \rightarrow 3N_2 + 6HCO_3^- + 3H_2O \tag{4.2}$$

Lab scale experiments were performed by Hellinga et al. (1998) in continuously stirred tank reactors (CSTR) to develop principles and feasible operation conditions for the maximum ammonia conversion to nitrite while inhibiting further nitrite oxidation. The influent wastewater from centrifuged sludge digestion effluent contained 1,000 mg NH_4^+/l, 56 mg SS/l, 810 mg COD/l, 230 mg BOD/l and 4,080 mg HCO_3^-/l. The optimum conditions were found at temperature 30 °C to 40 °C and pH between 7 and 8. The process was cost effective since it could reduce the amount of oxygen, external carbon source addition, and reactor size. Also, the process produces smaller amounts of sludge than the conventional nitrification process. Full scale SHARON® processes, operated in the Netherlands since 1997, have demonstrated the SHARON® process to be applicable for complete NH_4^+-N removal (over 99%) at temperatures above 35 °C and pH between 6.5 and 8.0 (Van Kempen et al., 2001).

Anaerobic ammonium oxidation, termed the ANAMMOX®, process was discovered by Mulder et al. (1995) when ammonia consumption was observed in a denitrifying fluidized bed reactor treating methanogenic reactor effluent. In the ANAMMOX® process, nitrite is denitrified to dinitrogen gas using ammonia as the terminal electron donor under anaerobic conditions. Thus, ANAMMOX® is an autotrophic anaerobic process in which ammonium ion is converted to dintrogen gas using nitrite and/or nitrate as the electron acceptor (Manipura et al., 2005). The process can reduce operating cost by up to 90%, and is suitable for inorganic industrial wastewater because carbon source addition is not required. But very high nitrite concentration negatively affects the operation. The overall reaction can be expressed briefly as (Mulder et al., 1995):

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \tag{4.3}$$

Accordingly, Van Dongen et al. (2001) developed a new scheme for treating nitrite formed in SHARON® process by combining it with the ANAMMOX® process. In order to use nitrite formed in SHARON® process as influent for ANAMMOX® process, half of ammonia must remain while the other half is oxidized to nitrite in accordance with reaction (4.4). The pH must be maintained between 6.5 and 7.5, and the temperature above 25°C in order to maintain an adequate ammonia to nitrite conversion rate without nitrate formation.

$NH_4^+ + HCO_3^- + 0.75O_2 \rightarrow 0.5NH_4^+ + 0.5NO_2^- + CO_2 + 1.5H_2O$ (4. 4)

The process has many advantages such as reducing oxygen requirement by 60%, no COD addition needed, less sludge production, and decreased CO_2 emission (Van Dongen et al., 2001). The experimental results of the SHARON® process followed by granular sludge SBR ANAMMOX® system are given in Table 4.14. Overall ammonia conversion to dinitrogen gas was more than 80% with a load of 1.2 mg N/m^3/day.

Table 4.14. Experimental Results for Combination of SHARON® and ANAMMOX® Processes (Adapted from Van Dongen et al. (2001)).

Parameter (mg/l except pH)	SHARON		ANAMMOX®	
	Influent	Effluent	Influent	Effluent
NH_4^+	1180	550	550	-
NO_2^-	0	600	600	0
NO_3^-	0	0	-	-
pH	6.7	-	-	-

Manipura et al. (2005) compared the different partial nitrification/denitrification processes including OLAND®, CANON®, SHARON®, and ANAMMOX® to assess the potential applicability to the treatment of metal industry wastewater in which high ammonium and nitrate are existed. In OLAND® (Oxygen Limited Autotrophic Nitrification Denitrification) process, the ammonium ion is oxidized only to nitrite under limited oxygen conditions and produced nitrite is reduced to dinitrogen gas by ammonium ion consumption according to the following simplified two-step reactions.

$2NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ + NH_4^+$ (4. 5)

$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$ (4. 6)

CANON®, which stands for completely autotrophic nitrogen removal over nitrite, process uses partial ammonia oxidation to nitrite by aerobic ammonia oxidizers and ammonia reduction to dinitrogen gas by consuming nitrite through anoxic ammonia oxidizing bacteria (Manipura et al., 2005). CANON® process differs from OLAND® because anaerobic autotrophic bacteria are utilized to convert the remaining ammonia to dinitrogen gas, as in the ANAMMOX® process. On the other hand, aerobic autotrophic nitrifiers are activated in the OLAND® process to transform ammonia to dinitrogen gas under microaerobic conditions. Reaction (4.7) indicates the overall reaction for the CANON® process:

$NH_3 + 0.85O_2 \rightarrow 0.11NO_3^- + 0.44N_2 + 0.14H^+ + 1.43H_2O$ (4. 7)

Manipura et al. (2005) concluded that CANON® and ANAMMOX® processes which showed advantages such as no supplemental carbon source requirement have more potential to be used for nitrogen compounds removal from inorganic wastewater. However, the authors also stated that a suitable nitrogen removal process should be carefully selected based on the total nitrogen removal efficiency, ammonium and/or nitrate conversion rate, operational cost, capital cost of the system, and effluent requirements. A comparison of properties of each process is given in Table 4.15.

Table 4.15. Comparison of Various Nitrification/Denitrification Processes (Adapted from Manipura et al. (2005)).

System	SHARON®	ANAMMOX®	CANON®	Conventional Nitrification/ Denitrification
# of reactors	1	1	1	2
Conditions	Oxic	Anoxic	O_2 limited	Oxic/Anoxic
O_2 requirement	Low	None	Low	High
pH control	None	None	None	Yes
Biomass retention	None	Yes	Yes	None
COD requirement	None	None	None	Yes
Sludge production	Low	Low	Low	High
Bacteria	Aerobic ammonium oxidizers/ Aanaerobic denitrifying bacteria	Anoxic ammonium oxidizers	Aerobic ammonium oxidizers/ Anoxic ammonium oxidizers	Aerobic ammonium oxidizers/ Anaerobic denitrifying bacteria

Combined Biological Nitrogen Removal and Chemical Treatment

The combined nitrification and chemical treatment methods have been developed to remove nitrogen compounds, COD and phosphorous at the same time. A comparison of biological treatment to integrated chemical oxidation/biological treatment for the removal of COD, TKN, TP and color in laboratory SBRs showed that chemical oxidation prior to biological treatment was the best option (Fongsatitkul et al., 2004). The wastewater from textile plants contained 444 mg BOD_5/l, 1,047 mg COD/l, 89.9 mg TKN/l and 18.4 mg TP/l. The removal efficiency results under the experimental condition of 60-day SRT, Fenton's reagent as a chemical oxidant and pH around 3 for Fenton's reagent addition are given in Table 4.16. In SBRs COD/TKN ratios higher than 7 were required for providing nutrients in biological process. It was also observed that non-readily biodegradable compounds, indicated by a BOD_5/COD ratio of 0.42, could be biologically treated by properly adapted biomass. High removal rate for both phosphorous and nitrogen was explained by simultaneous phosphorous uptake and denitrification under organic substrate limiting conditions and anoxic environment.

Table 4.16. Experimental Results for Three Treatment Methods for Textile Wastewater (Adapted from Fongsatitkul et al. (2004)).

Treatment Method	Removal Efficiency (%)			
	COD	TKN	TP	Color
SBR	83.3	94.1	77.4	35.5
Chemical oxidation + SBR	91.1	91.6	80.6	79.8
SBR + Chemical oxidation	86.9	90.8	79.7	68.0

Pambrun et al. (2004) compared the performance of the simultaneous NH_3 and phosphate removal processes in a lab scale sequencing batch reactor (SBR) and sequencing batch biofilm reactor (SBBR) using synthetic wastewater. The nitration performance resulted 0.95 g NO_2^-/g NH_4^+ in SBR and 0.4 g NO_2^-/g NH_4^+ in SBBR with the temperature 30 °C at which nitrite oxidizing bacteria were inhibited. The phosphate was removed together with ammonia by precipitation in the form of MAP or hydroxyl-apatite. Phosphate removal was between 40 to 90% in SBR and averaged 70% in SBBR depending on remaining free ammonia concentration in the reactor.

Biological Phosphorous Removal

There are several biological phosphorous removal (BPR) technologies with or without nitrogen removal. The most common phosphorous-only removal process is combined anaerobic and aerobic BPR process without nitrification named Phoredox (Metcalf & Eddy, 2003). The commonly applied BPR with simultaneous nitrate removal processes are A^2O and UCT (University of Cape Town), in which the reactors are arranged with same sequence as anaerobic-anoxic-oxic reactors. The main difference between A^2O and UCT is the return activated sludge (RAS) input point; in A^2O RAS containing nitrate is returned to anaerobic reactor, while in UCT RAS is injected to anoxic reactor.

Table 4.17. Advantages and Disadvantages of Biological Treatment Technologies used for Nitrogen and Phosphorous Removal.

Treatment Technology	Removable Compounds	Advantage	Disadvantage
Nitrification/Denitrification		- Inexpensive relative to chemical/physical methods - Combined nitrification/denitrification has internal buffering capacity	- Carbon source addition is required in denitrification - Requires alkalinity addition in nitrification - Industrial wastewater may contain inhibitory compounds
Conventional Activated Sludge (AS)	Org.N, NH_4^+, NO_3^-, NO_2^-	- Widely applied method	- Many modifications are available - Lower efficiency than modified methods
Modified Activated Sludge	COD, Org.N, NH_4^+, NO_3^-, NO_2^-	- Pre-anaerobic is effective to reduce COD and inhibitors - Better efficiency than conventional AS	- Complex operation relative to conventional methods
Sequencing Batch Reactor SBR	COD, Org.N, NH_4^+, NO_3^-, NO_2^-	- High efficiency possible - Produces good settleable sludge - Flexible process operation - Separate clarifier not required - Short-circuiting is not possible	- Require upstream storage system when wastewater is produced continuously

Treatment Technology	Removable Compounds	Advantage	Disadvantage
Attached Growth System (Biofilm and Biofilter Reactor)		- Stable high-rate nitrogen removal - Relatively low operating cost - Combined biological treatment and filtration - Useful when nitrifers have to be kept in the reactor - Useful for simultaneous nitrification/denitrification - Smaller reactor volume with long sludge age - Aerated biofilter is emerging biological method for industrial wastewater treatment	- Regular backwash is required
Biological Aerated Filter (BAF)	COD, SS, TN, NH_4^+ PO_4^{3-}	- Less sensitive to temperature, hydraulic and constituent variation - Stable high rate nitrogen removal - Relatively low operating cost - Low space requirement	- Lower phosphorous removal than conventional AS
Biofor®	COD, TOC, TKN, TSS, NH_4^+	- Many full-scale applications - Reliable operation - High ammonia removal & low SS in effluent	- May require separate post-denitrification process

Treatment Technology	Removable Compounds	Advantage	Disadvantage
CIRCOX®	COD, TN, NH_4^+, NO_3^-, NO_2^-	- High oxygen conversion rate and low capital cost - Compact reactor and low capital cost - Produces low amount of well settling sludge - Several full-scale applications - Sludge age control and periodic backwash are not required	- Subsequent solids removal process is required
DeepBed™ Sand Filter	COD, SS, NH_4^+, Phenol	- Can perform bio-oxidation, denitrification and SS removal at the same time	
Three-Phase Flow Airlift Loop Bioreactor	COD, NH_4^+	- Closer contact between air-wastewater-filter media - Faster oxygen transfer rate - Higher operational flexibility - Shorter reaction time	- May require separate post-denitrification process
UASB (upflow anaerobic sludge blanket) + UBAF (upflow biological aerated filter)	COD, TN, NH_4^+, NO_3^-	- Good organic nitrogen removal - Simultaneous nitrification/denitrification	
CAPTOR®	TSS, Org.N, NH_4^+, NO_3^-	- Good nitrification at temperatures below 10°C	

Treatment Technology	Removable Compounds	Advantage	Disadvantage
Nitrification with Ion Exchange	TSS, TN, NH_4^+	- Filter media used as biofilm carrier, ion exchanger and particle filter	
BNR/Ion Exchange + Adsorption	COD, TN, NH_4^+, TP	- Higher nitrogen removal efficiency - Better sludge settleability	
PACT®	COD, TN, NH_4^+, SS	- Stable operation for shock load - Can remove refractory organics - Produces well settling sludge - Reduce inhibitors and/or toxic material	- Requires carbon regeneration - Requires large amount of carbon addition to achieve high removals
Membrane Bioreactor (MBR)		- Less sludge production - High-quality effluent - Decompose non-readily biodegradable compounds	- Expensive - Require periodic membrane replacement - Require caution to membrane fouling
Submerged Vacuum Ultrafiltration (UF)	COD, SS, NH_3, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}	- Complete SS and colloidal matter removal	
MBR containing Activated Carbon	COD, SS, Org. N, NH_3, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}	- Excellent ammonia oxidation at low temperature (<4°C)	- Requires large amount of activated carbon - Operation complexity - High operation cost

Treatment Technology	Removable Compounds	Advantage	Disadvantage
Partial Nitrification/Denitrification		- Save up to 40% external carbon source - Reduce reactor volume - Decrease oxygen requirement - Useful for low COD/N industrial wastewater	- Requires high temperature - Requires high alkalinity - Requires careful pH, DO and temperature control (operational complexity)
SHARON®	NH_4^+, NO_2^-	- Lower oxygen demand - Reduce organic substrate requirement - Lower biomass production - Not sensitive to high influent TSS - Smaller reactor size	- Requires high temperature (30-35 ℃)
ANAMMOX®	NH_4^+, NO_3^-, NO_2^-	- Can reduce 90% of operation cost - No additional carbon source is required - More suitable for inorganic wastewater treatment	- Process is inhibited by high nitrite concentration
SHARON® + ANAMMOX®	NH_4^+, NO_3^-, NO_2^-	- Reduces 60% of oxygen requirement - No additional carbon source is required - Less sludge production - Decreased CO_2 emission	- Requires careful pH, DO and temperature control (operational complexity)
OLAND®	NH_4^+, NO_2^-	- Oxygen limited autotrophic nitrification/denitrification	

Treatment Technology	Removable Compounds	Advantage	Disadvantage
CANON	NH_4^+, NO_2^-	- Operates as single step process - No need to add external carbon source - Suitable for removing nitrogen from inorganic wastewater	
Combined BNR and Chemical Treatment		- Can remove COD, TSS and/or P simultaneously - High removal efficiency	- Operational complexity - Expensive - Insufficient full-scale application
Bio Nutrient Removal + Chemical oxidation	COD, TKN TP	- Oxidation prior to biological treatment is better to reduce COD, TKN and TP	- Lab scale - Requires low pH as 3
Nitration with MAP Precipitation	NH_4^+, PO_4^{3-}	- Can convert ammonia to nitrite with significant phosphate removal rate	- Used lab-scale reactor & synthetic wastewater for test
Biological Phosphorous Removal	TP, NO_3^-	- Can remove phosphorous and nitrogen at the same time	

Table 4.18. Contaminant Removals Reported for Selected Technologies.

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal Efficiency* (%)	Reference
PHYSICAL TREATMENT					
Gas Stripping High-pH spray ponds	NH_3	-	-	52%	Reynolds and Richards (1996)
Air stripping (Pilot plant)	NH_3	-	-	97%	Siegrist (1996)
Steam Stripping Two-stage ammonia & hydrogen sulfide stripping	NH_3	2,750	50	98%	Patterson (1985)
Steam stripping	NH_3	100-1,300	20-30	>80%	Patterson (1985)
Membrane Microfiltration	COD	24-150	16-53	76%	Metcalf & Eddy (2003)
	TSS	8-46	<0.5	97%	
	NH_3-N	21-42	20-35	7%	
PP hollow fiber membrane	NH_3	1,000-10,000	-	93.5%	Xu et al. (2001)
Reverse Osmosis	NH_3-N	20-35	1-3	96%	Metcalf & Eddy (2003)
	NO_3^-	1-5	0.08-3.2	96%	
	TDS	498-622	10-31	>97%	
	PO_4^{3-}	6-8	0.1-1	99%	
	SO_4^{2-}	90-120	0.5-0.7	99%	

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal Efficiency* (%)	Reference
Reverse Osmosis (Bench-scale)	NH_4^+	272	9	97%	Karavelas et al. (2001)
	NO_3^-	182	6	97%	
Adsorption Activated carbon	Org. N	-	-	71%	Patterson (1985)
Filtration Two deep-bed upflow filters	Particulate P	-	0.02	-	Metcalf & Eddy (2003)
CHEMICAL TREATMENT					
Ion exchange Ion Exchange	NH_3-N	325-719	40	88-94%	Patterson (1985)
weak cation exchange	NH_3	390	5	99%	Patterson (1985)
strong acid cation / anion exchange	NO_3^-	1,240	7-11	99%	Patterson (1985)
strong acid cation / weak base anion exchange	NH_4^+	183	10.1	94%	Leaković et al. (2000)
	NO_3-	100	7.2	93%	
Chemical Precipitation MAP (Pilot-scale, Mg:N:P = 1.1:1:1)	NH_4^+	-	-	>90%	Janus and Roest (1997)
MAP (Lab-scale, Mg:N:P = 1.1:1:1.1)	NH_4^+	-	-	83%	Altinbas et al. (2002)

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal Efficiency* (%)	Reference
BIOLOGICAL TREATMENT					
Conventional Nitrification/Denitrification	TN	39	-	86%	Thøgersen and Hansen (2000)
	TP	4	-	81%	
Activated sludge	SS	92	-	93%	
Three-stage nitrogen removal	NH_4^+	-	-	90%	Patterson (1985)
	NO_3-	-	-	95-100%	
Modified Nitrification/Denitrification Anaerobic-anoxic-aerobic process (pilot-scale)	NH_4^+	224	8.3	96%	Roš and Gantar (1998)
	COD	4,073	275	93%	
Anaerobic-anoxic-oxic process (Lab-scale)	NH_3-N	218	5	98%	Zhang et al. (1997)
	COD	1,121	150	87%	
Sequencing Batch Reactor SBR (Lab-scale)	N	-	-	80%	Arrojo et al. (2004)
	COD	-	-	70%	
SBR (Lab-scale)	COD	1,385	759	45%	Yilmaz and Oztűrk (2003)
	NH_4^+	886.6	2.6	100%	
Biofilm and Biofilter Reactors	TN	39	-	88%	Thøgersen and Hansen (2000)
	TP	4	-	74%	
Biological aerated filter	SS	92	-	94%	

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal Efficiency* (%)	Reference
Biofor®	NH_4^+	23	0	100%	Lazarova et al. (2000)
Biofor®	NH_4^+	22	0.3	99%	
Biofor® with Pre-denitrification (Pilot-scale)	TKN	63	10	85%	Pujol and Tarallo (2000)
	COD	434	62	85%	
	TSS	90	10	88%	
CIRCOX®	TKN	137	79	42%	Frijiters et al. (2000)
	NH_4^+	74	8	89%	
	VSS	264	284	-	
Three phase flow airlift loop bioreactor (Lab-scale)	NH_4^+	447.3	4.5	99%	Wen et al. (2003)
	COD	992.4	49	95%	
Anaerobic packed bed reactor + Aerobic three-phase fluidized bed reactor (Lab-scale)	TN	-	-	90-98%	Hirata et al. (2001)
	HH_3-N	-	-	80-92%	
Upflow anaerobic sludge blanket + Upflow biological aerated filter (Lab-scale)	COD	10,400	190	98%	Lacalle et al. (2001)
	TKN	790	13	98%	
BNR in oxic/anoxic system with Natural zeolite recirculation (Lab-scale)	NH_4^+	357	43	88%	Chung et al. (2000)
	TN	1,024	91	91%	
	COD	267	94	64%	

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal Efficiency* (%)	Reference
Batch Bioreactor with immobilized denitrifying bacteria (Lab-scale)	NO_3^-	-	-	99%	Zala et al. (2004)
BNR in oxic/anoxic system with Natural zeolite recirculation + Adsorption (Lab-scale)	NH_4^+	370	8	98%	Chung et al. (2000)
	TN	392	40	90%	
	COD	626	58	91%	
	TP	9.1	0.5	95%	
PACT®	COD	10,230	102	99%	Eckenfelder, Jr. (2000)
	TKN	120	4	97%	
	NH_3-N	76	0.8	99%	
	Phenol	8.1	0.01	100%	
PACT®	COD	1362	116	91%	
	NH_3-N	74	3.6	95%	
Membrane Bioreactor Nitrification with submerged vacuum UF	SCOD	1,568	37	98%	Nakhla et al. (2005)
	NH_3-N	2.9	1	66%	
	PO_4^{3-}	22.5	7.4	67%	

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal Efficiency* (%)	Reference
Partial Nitrification/Denitrification					
SHARON®	NH_4^+	400-750	5	>99%	Van Kempen et al. (2001)
SHARON + ANAMMOX (Pilot-scale)	NH_4^+	-	-	>80%	Van Dongen et al. (2001)
Sludge blanket reactor (Lab-scale)	TN	90-240	-	99%	Peng et al. (2004)
Combined BNR and Chemical Treatment					
Chemical oxidation + Nitrification in SBR (Lab-scale)	TKN	89.9	-	92%	Fongsatitkul et al. (2004)
	COD	1,047	-	91%	
	TP	18.4	-	81%	
Nitration with MAP in SBR (Lab-scale)	PO_4^{3-}	-	-	40-90%	Pambrun et al. (2004)
Nitration with MAP in SBBR (Lab-scale)	PO_4^{3-}	-	-	70%	

* The removal efficiencies are based on reports from full-scale operation except where noted.

4.2.3. Alternative Treatment Combinations

The wastewater disposed of in the well operated under Approval number 4779 contains various constituents, mainly NH_3-N, and others such as organic N, NO_3^-, TSS and PO_4^{3-}. To treat all compounds, a series of treatment technologies would need to be applied. Therefore, each treatment technology categorized according to physical, chemical or biological was first assessed according its capability for being used as pre-treatment, main-treatment and/or succeeding treatment to polish the main-treatment effluent. The usage of main treatment is prioritized to ammonia nitrogen removal. The evaluation of treatment capabilities is shown in Table 4.19 which also includes the pre-treatment requirements and residual effluent compounds when the technology is utilized for main treatment.

4.2.3.1. Capability of Physical Treatment Methods

The steam stripping method is better suited for main-treatment than is gas stripping, because steam stripping is more efficient for the treatment of high strength ammonia waste streams, and does not have operational problem caused by low temperature. If steam stripping is used as a main treatment, organic nitrogen, NO_2^-, and NO_3^- will remain and need to be removed by subsequent treatment. However, steam stripping may not be a cost-effective and/or simple ammonia removal method for using prior to or following other main treatment technologies due to requirements of steam production and further treatment of concentrated stripped ammonia.

Membrane technologies are divided by two groups, microfiltration/ultrafiltration and nanofiltration/reverse osmosis, based on principal characteristics and removal ability for different constituents. Both methods can be applied for main treatment and post-treatment, but MF/UF treatment cannot remove NO_3^-, NO_2^- and PO_4^{3-}completely while NF or RO can eliminate these compounds. However, NF or RO is more appropriate for polishing treatment because of the requirement for pre-treatment to reduce TSS and scale-causing dissolved materials in the feed stream. NF and RO require considerable energy input to achieve operational pressures, and so are relatively expensive treatment methods.

According to Metcalf & Eddy (2003), the adsorption by activated carbon is used principally for the removal of refractory organic compounds, as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metals. The pre-removal of oil and suspended solids is required before applying adsorption. Therefore, adsorption technology should be used as a pre-treatment method or preferably as a polishing step following main treatment.

The main uses of filtration in full-scale applications are as a complementary treatment following chemical or biological methods, and as pre-treatment before membrane processes (Metcalf & Eddy, 2003). So, filtration should also be used as pre-treatment or polishing step for reducing suspend solids and particulate phosphorous.

4.2.3.2. Capability of Chemical Treatment Methods

Breakpoint chlorination has several potential problems such as harmful byproducts formation, high cost and large amount of dissolved solids production. Breakpoint chlorination process typically should not be selected when ammonia concentrations are greater than 10 to 15mg/l and certain organic compounds are present (WEF 1994). Reynolds and Richards (1996) also indicated that the use of breakpoint chlorination for ammonia removal may decline in the future because of the detrimental residual formation. Therefore, breakpoint chlorination should not be used as any treatment methods despite its high NH_4^+ removal efficiency.

Ion exchange, which can remove various ionic compounds principally NH_4^+, NO_3^-, and SO_4^{2-}, can be adapted for main treatment technology with pre-treatment to remove TSS and/or TOC. When ion exchange is used for both anion and cation removal, organic nitrogen and phosphate will remain in the effluent. Ion exchange can be employed for post-treatment rather than pre-treatment since ion exchange is an expensive process and requires pre-removal of TSS accordingly it is more suitable treatment for low concentration of nitrogen.

If the MAP precipitation is used for NH_4^+ removal in main-treatment for this wastewater, a considerable amount of PO_4^{3-} and Mg^{2+} would have to be added to satisfy stoichiometric requirements for MAP formation. This would lead to high operating costs. Therefore, MAP precipitation should not be considered for main treatment. However, MAP precipitation can be used as a complementary treatment for high NH_4^+ and phosphorous wastewater prior to other main NH_4^+ removal processes so as to reduce NH_4^+ and phosphorous concentrations considerably. Also, the MAP precipitation technology can be used as a supplemental method for polishing tertiary treatment when NH_4^+ concentration is reasonably decreased by a main treatment and PO_4^{3-} is still left in the treated wastewater. Similar reasoning indicates that chemical precipitation of phosphate also should be used for pre-treatment and/or for polishing step. The possible chemicals are alum or ferric chloride.

Chemical reduction of nitrate requires high cost reducing chemicals and does not have sufficient full-scale applications. Thus, this process should not be considered as an alternative method for the effective nitrate removal.

4.2.3.3. Capability of Biological Treatment Methods

Biological treatment can be used for main treatment. In case the wastewater is not produced continuously, the flow equalization process may be required to keep active biomass. The nitrification and denitrification method represented by conventional or modified activated sludge process can remove nitrogen compounds including organic nitrogen, NH_4^+, NO_3^- and NO_2^- as well as COD. The activated sludge process may not be as suitable method as a number of the modified reactor systems and improved nitrogen removal technologies, such as partial nitrification/denitrification.

The sequencing batch reactor, one of the decant batch process, requires upstream storage to retain continuously produced waste streams. Nevertheless, the method has advantages such as high nitrification/denitrification efficiency, flexible operating control, and no requirement for a separate clarifier. Since the continuity of wastewater production cannot be confirmed from the data available, a SBR with proper flow control systems such as a flow equalization pond may be a more appropriate main treatment method than activated sludge system. Also, activated sludge systems are generally preferred to treat relatively large flows, but may not be economical when treating moderate to low flows of wastewater.

The biofilm and/or biofilter systems, one of the representative attached growth biological treatment technologies, have the combined functions of biological treatment and filtration in one reactor. Because of this property many full-scale applications of biofilter and/or biofilm systems have been developed. The biofilter systems usually entail relatively low operating costs compared to conventional means to produce a stable and high nitrogen removal efficiency. The better known biofilter systems include biological aerated filters, Biofor®, CIRCOX®, DeepBed™ and three phase airlift bioreactors. Since most of these systems apply only nitrification without denitrification to remove NH_3-N, the treatable constituents include TSS, organic carbon, NH_4^+ and organic nitrogen. However, the remaining NO_3^- or PO_4^{3-} also may be eliminated in the biofilter systems depending on the specific reactor operation conditions, e.g., biological aerated filter can remove PO_4^{3-}, and CIRCOX® or deep inside of biofilm can reduce NOx-N compounds by denitrification. The systems may require prior influent denitrification to enhance nitrification by reducing nitrate and organic compound concentrations in the influent.

Metcalf & Eddy (2003) stated that the MBR process is one of the most promising methods for wastewater treatment, and produces good quality effluent which is ideal for a number of reuse applications or for further processing by nanofiltration or reverse osmosis. Therefore, a membrane bioreactor can be applied as main treatment for removal of dissolved nitrogen compounds and phosphate as well as suspended materials. High quality effluent can be produced by this system due to constituent separation by membranes and long biomass retention time. However, the primary reduction of TSS may be required to prevent heavy fouling on membrane.

The techniques that combine biological nitrogen removal and chemical treatment require a large amount of chemical addition. Also, because the combined methods have little field application to date, these processes may not be suitable for use as main treatment methods.

The partial nitrification/denitrification process termed nitration/denitration can reduce external carbon source requirements and oxygen demand. Other advantages of this process are reduced reactor size and decreased sludge production. Additionally, there are many different types of available technologies such as SHARON®, ANAMMOX®, OLAND®, and CANON®. On the basis of these merits, nitration and denitration processes may be used as main treatment methods. Nevertheless, the residual constituents such as TSS, PO_4^{3-}, NO_3^- or NO_2^-, which can differ according to the technology employed, would have to be removed by subsequent treatment. In addition to follow-up treatment, reduction of nitrate by denitrification prior to nitration/denitration process can improve performance.

Biological phosphorous removal in which phosphorous is mainly treated cannot be considered as main treatment because the wastewater studied in question contains a low level of phosphate (5 mg/l) compare to nitrogen compounds (1,515 mg NH_3/l).

4.2.3.4. Technically Feasible Treatment Combinations

On the basis of above discussion, several treatment combinations have been identified to remove NH_4^+, organic N, TSS, NO_3^- and PO_4^{3-}. These combinations of technologies are summarized in Figure 4.1. Each sequence of treatment processes contains at least one applicable main-treatment. It is assumed all treatment combinations would include an equalization system at the beginning of the process, which was omitted in the figure to reduce the complexity of evaluation. Compounds removed by the process are indicated under each treatment option. Further treatment of process waste streams (e.g., sludges, regeneration waste streams) has not been included in the figure to improve clarity.

Table 4.19. Evaluation of Suitability of Selected Technologies to Treat Waste Injected Under Approval No. 4779.

Treatment Technology	Compounds Treated	Requirement of Pre-treatment	Suitability for use as pre-treatment	Main-treatment		Suitability for use as post-treatment
				Suitability for use as main-treatment	Compounds not affected	
PHYSICAL METHODS						
Gas Stripping	NH_3	Yes (TSS Removal, pH)	No	No	-	No
Steam Stripping	NH_3	Yes (TSS Removal, pH)	No	Yes	Org.N, NO_3^-, PO_4^{3-}	No
Membrane (MF & UF)	TDS, TOC, COD, TSS, NH_3	Yes (TSS Removal)	No	Yes	NO_3^-, NO_2^-, PO_4^{3-}	Yes
Membrane (NF & RO)	TDS, TOC, Org.N, NH_3, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-},SO_4^{2-}	Yes (pH, Temp. and TSS,TDS Removal)	No	No	-	Yes
Adsorption	COD, Org. N	Yes (TSS, Oil)	Yes	No	-	Yes
Filtration	TSS, Particulate P	No	Yes	No	-	Yes
CHEMICAL METHODS						
Breakpoint Chlorination	NH_4^+	Yes (Organic/Inorganics Removal)	No	No	-	No
Ion Exchange	NH_4^+, NO_3^-, SO_4^{2-}	Yes (TSS,OC Removal)	No	Yes	Org.N, PO_4^{3-}	Yes

Treatment Technology	Compounds Treated	Requirement of Pre-treatment	Suitability for use as pre-treatment	Main-treatment		Suitability for use as post-treatment
				Suitability for use as main-treatment	Compounds not affected	
MAP Precipitation	SS, NH_4^+, PO_4^{3-}, Mg^{2+}	Yes (pH)	Yes	No	-	Yes
Chemical Precipitation	SS, PO_4^{3-}	Yes (pH)	Yes	No	-	Yes
Chemical Reduction	NO_3^-, PO_4^{3-}	No	No	No	-	No
BIOLOGICAL METHODS						
Conventional Activated sludge	TSS, COD, Org.N, NH_4^+, NO_3^-, NO_2^-	No	No	No	-	No
Sequencing Batch Reactor	TSS, COD, Org.N, NH_4^+, NO_3^-, NO_2^-	No	No	Yes	PO_4^{3-}	No
Biofilm and Biofilter Reactor	COD, TOC, TSS, NH_4^+, Org.N	Maybe (Denitrification)	No	Yes	NO_3^-, PO_4^{3-}	No
Membrane Bioreactor (MBR)	COD, TSS, Org. N, NH_3, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}	Maybe (TSS removal)	No	Yes	None	No
BNR+ Chemical Treatment	COD, TKN TP	No	No	No	-	No
Partial Nitrification/ Denitrification	COD, Org.N, NH_4^+, NO_3^-, NO_2^-	Maybe (Denitrification)	No	Yes	TSS, PO_4^{3-}, (NO_3^-, NO_2^-)	No
Biological Phosphorous Removal	TP, NO_3^-	No	No	No	-	No

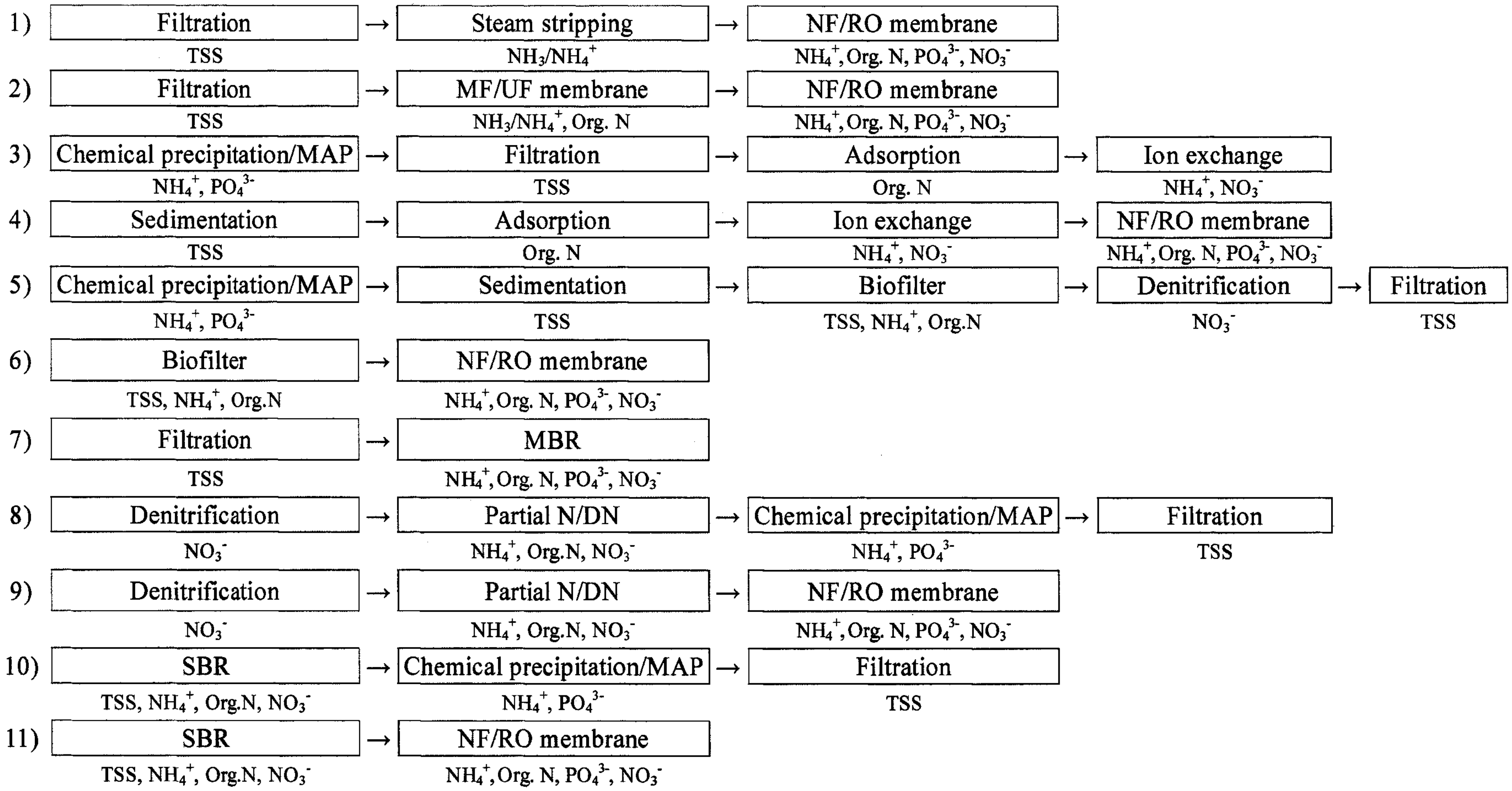


Figure 4.1. Possible Treatment Combinations for the Wastewater Disposed Under Approval No. 4779.

4.2.4. Evaluation of Potential Treatment Combinations

Each potential treatment combination (1 through 11) is assessed below according to the evaluation criteria as given in Table 3.2. The results of the evaluation of each potential treatment combination are given below. The overall outcome of this evaluation is shown in Table 4.20.

- Complexity of Operation and maintenance
  1) Complex: pH adjustment for stream stripping, steam production, and fouling/scale control and periodic replacement of membrane
  2) Complex: fouling/scale control, periodic backwash and periodic replacement of both membranes
  3) Complex: periodic regeneration of ion exchangers and adsorbents, and pH adjustment for chemical process
  4) Complex: periodic regeneration of ion exchangers and adsorbents, and fouling/scale control and periodic backwash/replacement of membrane
  5) Simple: relatively simple operation of biofilter even though pH adjustment for chemical treatment
  6) Simple: relatively simple operation of biofilter even though fouling/scale control and periodic backwash for one membrane
  7) Simple: relatively simple operation of MBR although fouling/scale control and periodic backwash are required for one MBR
  8) Complex: complicated DO, pH and temperature control for partial nitrification/ denitrification, and pH adjustment for chemical precipitation
  9) Complex: complicated DO, pH and temperature control for partial nitrification/ denitrification, and fouling/scale control and periodic backwash for one membrane
  10) Simple: relatively simple operation of SBR even though pH adjustment for chemical precipitation
  11) Simple: relatively simple operation of SBR even though fouling/scale control and periodic backwash for one membrane

- Removal Efficiency
  1) High: almost complete removal in NF/RO membrane
  2) High: almost complete removal in NF/RO membrane
  3) Low: relatively low removal efficiency of ion exchange (May require further treatment)
  4) High: almost complete removal in NF/RO membrane
  5) Low: relatively lower removal efficiency of filtration compare to membrane
  6) High: almost complete removal in NF/RO membrane

7) High: high removal efficiency of MBR
8) Low: relatively lower removal efficiency of filtration compare to membrane
9) High: almost complete removal in NF/RO membrane
10) Low: relatively lower removal efficiency of filtration compare to membrane
11) High: almost complete removal in NF/RO membrane

- Effect of Cold Climate
    1) Low: stream stripping, main removal process, is not affected by low temperature although NF/RO membrane process requires temperature control
    2) Low: MF/UF membrane, main removal process, is not affected by low temperature although NF/RO membrane process requires temperature control
    3) High: low temperature affects chemical treatment because of reaction rate decrease, and adsorption capacity
    4) High: low temperature affects adsorption capacity
    5) High: low temperature affects chemical treatment because of reaction rate decrease
    6) High: low temperature affects microorganism growth and oxygen uptake rate in biofilter
    7) High: low temperature affects microorganism growth and oxygen uptake rate in MBR
    8) High: partial nitrification/denitrification require high temperature
    9) High: partial nitrification/denitrification require high temperature
    10) High: low temperature affects microorganism growth and oxygen uptake rate
    11) High: low temperature affects microorganism growth and oxygen uptake rate

- Amount of Residuals
    1) High: concentrated ammonia in stripping gas
    2) Low: relatively low residuals in backwash water from membranes
    3) High: large sludge from chemical precipitation and concentrated ion exchange regeneration solution
    4) High: concentrated ion exchange regeneration solution even though relatively low residuals in backwash water from membrane and adsorption
    5) High: large sludge from chemical precipitation although relatively low residuals in biofilter
    6) Low: relatively low residuals in biofilter and membrane
    7) Low: less sludge in MBR process
    8) Low: less sludge production from chemical precipitation for pre-treated wastewater and from partial nitrification/denitrification process

9) Low: less sludge production from partial nitrification/denitrification process and low residuals in backwash water from membrane
10) High: large sludge production from chemical precipitation and SBR
11) Low: large sludge production from SBR, but less residuals in backwash water from membrane

- Treatability of Residuals
  1) Hard: need to treat concentrated ammonia from steam stripping
  2) Easy: relatively easy to treat sludge from membrane backwash water
  3) Hard: need to treat chemical precipitates and concentrated ammonia from ion exchange regeneration
  4) Easy: relatively easy to treat sludge from membrane backwash water even though concentrated ammonia from ion exchange regeneration is hard to be treated
  5) Hard: need to treat chemical precipitates
  6) Easy: relatively easy to treat sludge from biofilter and membrane
  7) Easy: relatively easy to treat sludge from filtration and MBR
  8) Hard: need to treat chemical precipitates
  9) Easy: relatively easy to treat sludge from partial nitrification/denitrification and membrane
  10) Hard: need to treat chemical precipitates
  11) Easy: relatively easy to treat sludge from SBR and membrane

- Existence of Full-Scale Application
  1) Many: many field applications of steam stripping for ammonia removal and membrane
  2) Many: a number of full-scale membrane applications
  3) Few: a few full-scale ion exchange system for NH_4^+ and NO_3^- removal and less full-scale chemical precipitation process
  4) Few: a few full-scale ion exchange system for NH_4^+ and NO_3^- removal
  5) Many: many filed application of biofilter even though less full-scale chemical precipitation process
  6) Many: many filed application of biofilter and membrane
  7) Many: many filed application of MBR
  8) Many: a lot of full-scale application of partial nitrification/denitrification even though less full-scale chemical precipitation process
  9) Many: a lot of full-scale application of partial nitrification/denitrification and membrane

10) Few: less full-scale application of SBR and chemical precipitation
11) Few: less full-scale application of SBR even though many filed applications of membrane

- Long-term reliability of operation
  1) Low: membrane process is relatively new technology and still developing
  2) Low: membrane process is relatively new technology and still developing
  3) High: adsorption, ion exchange and chemical treatment have been introduced for a long time
  4) Low: membrane process is relatively new technology and still developing
  5) Low: biofilter process is relatively new technology
  6) Low: biofilter process is relatively new technology
  7) Low: MBR is relatively new technology
  8) Low: partial nitrification/denitrification process is relatively new technology
  9) Low: partial nitrification/denitrification process is relatively new technology
  10) High: SBR, chemical treatment and filtration have been introduced for a long time
  11) Low: membrane process is relatively new technology and still developing

- Capital Investment
  1) High: generally NF/RO membrane requires high initial capital cost
  2) High: generally membranes require high initial capital cost
  3) High: packing materials are required for adsorption and ion exchangers
  4) High: packing material is required for adsorption and ion exchangers, and generally membrane requires high initial capital cost
  5) Low: generally biofilter needs smaller reactor volume with packing materials and relatively simple reactor design for chemical treatment and filtration
  6) High: generally biofilter needs smaller reactor volume with packing materials, but NF/RO membrane requires high initial capital cost
  7) High: generally filtration requires simple reactor design with filter media, but MBR requires high initial capital cost
  8) Low: smaller reactor volume is required for partial nitrification/denitrification
  9) High: smaller reactor volume is required for partial nitrification/denitrification, but NF/RO membrane requires high initial capital cost
  10) Low: generally SBR and chemical process require lower capital cost
  11) High: generally SBR requires lower capital cost, but NF/RO membrane requires high initial capital cost

- Requirement of Operation Condition Control
  1) High: steam stripping require pH control, and membrane process requires high pressure and also may need pH and temperature control
  2) High: both membrane processes require high pressure and also may need pH and temperature control
  3) High: pH control is required in chemical treatment and ion exchange
  4) High: ion exchange requires pH control, and membrane process requires high pressure and also may need pH and temperature control
  5) Low: relatively less control is required in biofilter even though chemical process needs pH control
  6) Low: relatively less control is required in biofilter even though one membrane process requires high pressure and also may need pH and temperature control
  7) Low: relatively less control is required for one MBR even though it needs high pressure and also may need pH and temperature control
  8) High: partial nitrification/denitrification needs temperature, DO and pH control, and chemical process requires pH control
  9) High: partial nitrification/denitrification needs temperature, DO and pH control, and membrane process needs high pressure, pH and temperature control
  10) Low: relatively less control is required in SBR even though chemical precipitation needs pH control
  11) Low: relatively less control is required in SBR even though membrane process requires high pressure and also may need pH and temperature control

- Requirement of Periodic Maintenance
  1) High: membrane requires periodic backwash and replacement of modules
  2) High: both membrane require periodic backwash and replacement of modules
  3) High: periodic regeneration is required for adsorption and ion exchanger
  4) High: membrane requires periodic backwash and replacement of modules, and regular regeneration is needed for adsorption and ion exchanger
  5) Low: regeneration of media may not be required for biofilter due to natural bio-regeneration
  6) High: membrane requires periodic backwash and replacement of modules even though regeneration of media may not be required for biofilter due to natural bio-regeneration
  7) High: membrane in MBR process requires periodic backwash and replacement of modules

8) Low: relatively less periodic treatment requires for partial nitrification/ denitrification even though backwash is needed for filtration
9) High: membrane requires periodic backwash and replacement of modules
10) Low: relatively less periodic treatment requires for SBR even though backwash is needed for filtration
11) High: membrane requires periodic backwash and replacement of modules

- Requirement of Oxygen or Steam Addition
  1) High: steam has to be provided in stream stripping
  2) Low: no oxygen or steam addition is required
  3) Low: no oxygen or steam addition is required
  4) Low: no oxygen or steam addition is required
  5) Low: relatively low oxygen requirement in biofilter systems due to high oxygen transfer rate in smaller reactor volume
  6) Low: relatively low oxygen requirement in biofilter systems due to high oxygen transfer rate in smaller reactor volume
  7) High: oxygen provision is required for nitrification in MBR
  8) Low: lower oxygen demand in partial nitrification/denitrification
  9) Low: lower oxygen demand in partial nitrification/denitrification
  10) High: oxygen provision is required for nitrification in SBR
  11) High: oxygen provision is required for nitrification in SBR

- Requirement of Chemical Addition
  1) Low: relatively less chemical is required for chemical backwash for membrane
  2) Low: relatively less chemical is required for chemical backwash for membrane
  3) High: high chemical addition is required for chemical precipitation
  4) Low: relatively less chemical is required for ion exchanger regeneration and chemical backwash for membrane
  5) High: high chemical addition is required for primary chemical precipitation
  6) Low: relatively less chemical is required for chemical backwash for membrane
  7) Low: less chemical is required for MBR
  8) High: less external carbon source addition is needed in partial nitrification/ denitrification, but high chemical addition is required for chemical precipitation
  9) Low: less external carbon source addition is needed in partial nitrification/

denitrification and relatively less chemical is required in membrane backwash

10) High: high chemical addition is required for chemical precipitation
11) Low: relatively less chemical is required for chemical backwash for membrane

Table 4.20. Evaluation Results for Alternative Treatment Combinations (Approval No. 4779 Wells).

Factors			Score		Possible Treatment Combinations										
			0	1	1	2	3	4	5	6	7	8	9	10	11
Technical Suitability	Characteristics of Operation	Number of processes	-	-	3	3	4	4	5	2	2	4	3	3	2
		Complexity of operation and maintenance	Simple	Complex	1	1	1	1	0	0	0	1	1	0	0
		Removal efficiency	High	Low	0	0	1	0	1	0	0	1	0	1	0
		Effect of cold climate	Low	High	0	0	1	1	1	1	1	1	1	1	1
	Production of Residuals	Amount of residuals	Low	High	1	0	1	1	1	0	0	0	0	1	0
		Treatability of residuals	Easy	Hard	1	0	1	0	1	0	0	1	0	1	0
Reliability of Technology	Reliability	Existence of full-scale application	Many	Few	0	0	1	1	0	0	0	0	0	1	1
		Long-term reliability of operation	High	Low	1	1	0	1	1	1	1	1	1	0	1
Economic Feasibility	Capital Cost	Capital Investment	Low	High	1	1	1	1	0	1	1	0	1	0	1
	Operation Cost	Operation condition control requirement	Low	High	1	1	1	1	0	0	0	1	1	0	0
		Requirement of periodic maintenance	Low	High	1	1	1	1	0	1	1	0	1	0	1
		Requirement of oxygen or steam addition	Low	High	1	0	0	0	0	0	1	0	0	1	1
		Requirement of chemical addition	Low	High	0	0	1	0	1	0	0	1	0	1	0
Summation					11	8	14	12	11	6	7	11	9	10	8
Rank					7	3	11	10	7	1	2	7	5	6	3

4.2.4.1. Most Suitable Treatment Combinations

According to the evaluation results, the most promising treatment options are given in Figure 4.2. All treatment combinations require an equalization process at the beginning of treatment train because homogeneity of wastewater production cannot be expected. The various biological treatment methods are more appropriate than are the physical and/or chemical processes. However, because the biodegradability of the wastewater cannot be assessed from the available information, the preference of biological methods is based on the assumption that the organic material in the waste stream can be oxidized biologically.

The most promising of the alternative treatment combinations is a biofilter followed by NF or RO membrane separation. A biofilter may be the more appropriate biological treatment method, because it can perform biological treatment and filtration in a compact reactor and achieve stable nitrogen removal at a moderate operating cost. The NO_3^- remaining to be removed in the subsequent process can be reduced significantly in a biofilter system because of simultaneous denitrification which may occur in a deep biofilm, depending on the specific reactor or operation scheme. The effluent from membrane filtration (NF or RO) would be of very high quality with less than 3 mg/l of NH_3-N, 3 mg/l of NO_3^-, 30 mg/l TDS, 1 mg/l of PO_4^{3-} and 1mg/l of SO_4^{2-} which can be inferred from full-scale reverse osmosis performance results (Metcalf & Eddy, 2003)

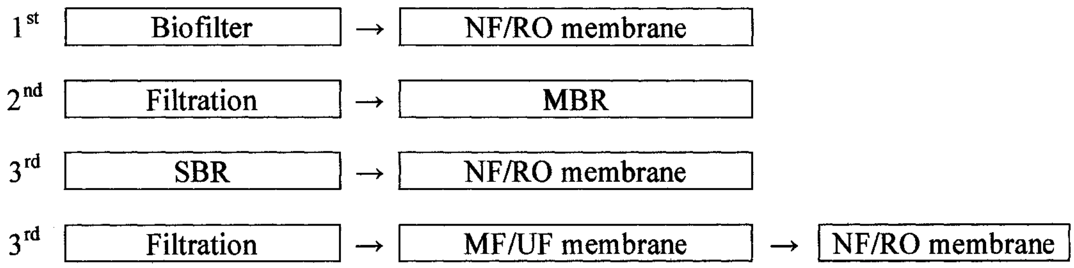


Figure 4.2. Ranked Treatment Options for Wastewater Disposed under Approval No. 4779.

Another biological process, combinations of filtration and a MBR is ranked as the next most applicable treatment option. If site-specific conditions are not suitable for biofilter treatment and if the biofilm formation in biofilter system is not sufficiently facilitated during lab- or pilot- scale experiments, the MBR can be considered as more feasible biological treatment methods. The MBR process can decompose non-readily biodegradable compounds with the production of high quality effluent. The MBR process can produce good quality effluent with less than 40 mg/l of soluble COD, around 1 mg/l of NH_3-N, and about 7 mg/l of PO_4^{3-}, based on information from a full-scale MBR process using UF membranes (Nakhla et al., 2005).

The third ranked option was another biological-physical treatment combination. This would involve a SBR followed by and NF or RO membrane. This combination should be investigated if the previously mentioned biological treatment options are not suitable for this wastewater treatment. If the wastewater is found to contain little biodegradable components or the plant's physical constraints are not suitable for a biological treatment process, the physical treatment combinations of filtration, MF/UF and NF/RO membrane would be the most applicable option. Filtration is relatively simple to manage compared to biological processes.

The choice of the more suitable treatment train using a biological or physical/chemical technology depends on an in depth analysis of the waste streams and an assessment of the plant's unique conditions. In addition, bench- or pilot-scale testing would be required to determine the more feasible treatment option for full-scale application. Metcalf & Eddy (2003) stated that the purpose of conducting pilot-plant studies is to establish the suitability of the process in the treatment of a specific wastewater under specific environmental conditions and to obtain the necessary data on which to base a full-scale design.

4.3. Wastewater Injected Under Approval No. 8951

4.3.1. Wastewater Characteristics

Chen and Kindzierski (2005) indicated that one disposal well has been used for the injection of wastewater produced from Imperial Oil Strathcona Refinery under Approval No. 8951. The name of the well was given as IMP 102 STRATHCONA 9-1-53-24, and the injection rate was reported to be 23,300 m^3/mon. Because no chemical and/or physical wastewater parameter data could be obtained, Chen and Kindzierski classified the well as category C, meaning that information on wastewater characteristics was required to evaluate the feasibility of treatment. Recently obtained information represents that two different disposal wells, indicated by names of Southwell and Northwell are used from the company under Approval number 8951. The Strathcona Refinery Approval Renewal Application (Imperial Oil, 1995) indicates that the South well is used for the disposal of brine wastewater from the crude unit desalter and the wastewater from the asphalt units. The North disposal well is utilized for the injection of all other process wastewater streams including spent caustic and sour waters. However, the information does not indicate whether the well, IMP 102 STRATHCONA 9-1-53-24, reported by Chen and Kindzierski (2005) well is the South well or the North well, or some other well.

The parameter values and injection volumes reported in the Renewal Application

(Imperial Oil, 1995) are summarized in Table 4.21. Although these data represent the most recent data that could be obtained during the present study, they were collected from 1988 to 1994. Therefore, more recent data are required to identify the characteristics of the wastes that are currently disposed of to these wells.

Given the injection volumes and contaminants levels shown in Table 4.21, an assessment of treatment feasibility is warranted. The following assessment should be considered as preliminary, and subject to change when current information becomes available. The treatment methods considered for this wastewater will primarily target oil, COD and SS reduction, as well as ammonia.

Table 4.21. Characteristics of Wastewater Injected Under Approval No. 8951.

<table>
<tr><td rowspan="2">Category & Well Approval #</td><td rowspan="2" colspan="2">Well Name or ID</td><td rowspan="2" colspan="2">WW Source</td><td colspan="2">Injection rate (m^3/mon)</td></tr>
<tr><td>Phase I Report[1]</td><td>Updated[2]</td></tr>
<tr><td>C 8951</td><td colspan="2">IMP 102 STRATHCONA 9-1-53-24</td><td colspan="2">Imperial Oil Strathcona Refinery</td><td>23,300</td><td>39,635 (Southwell)
19,081 (Northwell)</td></tr>
<tr><td rowspan="2">WW Analysis</td><td colspan="6">Main Contaminants & Level[3]</td></tr>
<tr><td>Name</td><td>Avg.</td><td>Range</td><td>Name</td><td>Avg.</td><td>Range</td></tr>
<tr><td>Phase I Report</td><td colspan="6">Updated contaminant information required</td></tr>
<tr><td rowspan="7">Updated[2]</td><td colspan="6">Year : 1988 – 1994</td></tr>
<tr><td colspan="3">Southwell</td><td colspan="3">Northwell</td></tr>
<tr><td>COD</td><td>1,281</td><td>950-2,289</td><td>COD</td><td>27,366</td><td>17,561-54,500</td></tr>
<tr><td>Total Solids</td><td>111</td><td>31-210</td><td>Total Solids</td><td>63</td><td>33-718</td></tr>
<tr><td>Oil</td><td>386</td><td>105-1,237</td><td>Oil</td><td>521</td><td>41-9,151</td></tr>
<tr><td>NH_3</td><td>20</td><td>-</td><td>NH_3</td><td>4,125</td><td>-</td></tr>
<tr><td>pH</td><td>7.4</td><td>6.8-8.0</td><td>pH</td><td>9.1</td><td>8.8-9.4</td></tr>
</table>

[1] Adapted from Chen and Kindzierski (2005)

[2] Adapted from Imperial Oil (1995)

[3] Unit: mg/l except pH

4.3.2. Alternative Treatment Technologies

One of the major contaminants in oil refinery wastewater is oil itself, and comprises two categories: free oil and emulsified oil. Free oil can be distinguished from emulsified oil by its ability to float to the surface of water within approximately 30 minutes, and has droplet sizes larger than 150μm (Cheremisinoff, 2002; Cheryan and

Rajagopalan, 1998; Aymong and Abbott, 2004). Emulsified oil is characterized by droplet diameters smaller than 20μm and will not float to the water's surface without additional treatment because it is retained in suspension by surface active agents (surfactants).

The COD in oil refinery wastewater mainly comes from aliphatic and aromatic hydrocarbons, phenols, sulfides and mercaptans. Hence, a reduction in the COD is directly related to the removal of these compounds (Berné and Cordonnier, 1995; Tyagi et al., 1993; Gulyas and Reich, 1995).

As reported in Oil and Gas Journal, 89% of the European oil refinery plants surveyed employ three levels of treatment (Anonymous, 1999): (1) gravity separation using American Petroleum Institute separators (API), corrugated plate interceptors (CPI) or simple tank separation; (2) advanced treatment such as flocculation, air flotation, sedimentation and filtration; and (3) biological treatment including biofilters, activated sludge or aerated ponds. The combination of different categories of treatments can produce significantly improved effluent in terms of oil, ammonia, sulfide and phenols.

The technologies used for oil refinery wastewater treatment are typically primary removal of oil in order to eliminate non-emulsified free oil, followed by the removal of demulsified oil, and finally biological treatment and/or advanced treatment to polish final effluent. The possible technologies for purifying the refinery wastewater are discussed in the following sections. The advantages and disadvantages of the various methods of oil refinery wastewater treatment are given in Table 4.37. The removal efficiency of each method is shown in Table 4.38.

4.3.2.1. Preliminary Removal of Oil

The most commonly applied method to remove non-emulsified oil from a wastewater consists of simple gravity separation followed by chemical addition and flocculation of the wastewater and dissolved air flotation (WEF, 1994).

Free and non-emulsified oil, as well as granular suspended solids, are removed in preliminary treatment by gravity separation (Patterson, 1985; WEF, 1994; Stephenson and Blackburn Jr., 1998; Berné and Cordonnier, 1995). The American Petroleum Institute separator is the gravity separation method commonly used to remove readily settleable solids and free oil from refinery wastewater (Huchler, 2003). Patterson (1985) reported that the effluent from an API separator included 8 to 20 mg/l of oil when the influent of oil refinery wastewater contained from 30 mg/l to 100 mg/l oil. Cheryan and Rajagopalan (1998) indicated that the API technology is widely accepted as an effective and low cost preliminary oil reduction step for a variety of oily wastewaters.

Corrugated plate interceptors (CPI), also called tilted plate interceptor (TPI) represent an alternative technology for the removal of non-emulsified oil. A CPI unit employs inclined plates to decrease vertical rise of free oil (Patterson, 1985; Stephenson and Blackburn Jr., 1998). CPI requires less maintenance due to having no submerged moving parts and require 15 to 20% less space than API. However, the smaller size of the unit may provide insufficient volume to retain oil slugs, the shorter retention time may not be adequate to break oil emulsions, and the inclined plates may become fouled. Eckenfelder Jr. (2000) indicated that the oil droplets larger than 0.006 cm can be separated by CPI units, and effluent from CPI generally contains as little as 10 mg/l of free non-emulsified oil.

4.3.2.2. Removal of Residual Oil

The wastewater from oil refinery is mainly polluted by petroleum emulsions consisting of oil, water and emulsifying agent. The emulsifying agent hinders agglomeration of oil droplets by reducing the interfacial tension (Hafiz et al., 2005). The effluent from preliminary oil removal (API or CPI separator) generally contains between 30 to 150 mg/l of fine emulsion state hydrocarbons, sulfides, and dissolved or colloidal matter (Berné and Cordonnier, 1995). The emulsified oil which remains after preliminary treatment needs to be broken by a demulsification process that applies physical, chemical and/or electrical methods (Patterson, 1985; Berné and Cordonnier, 1995). The demulsified oil and fine suspended solids can be separated from water by gravity or by various flotation techniques such as air flotation or electroflotation.

Physical Methods

Air flotation is the common alternative to gravity separation for removing non-emulsified oil and suspended solids (Patterson, 1985; Cheremisinoff, 2002). The commonly applied air flotation techniques are dissolved air flotation (DAF) and induced air flotation (IAF). DAF employs high pressure to dissolve air in the wastewater and following pressure release to create air bubbles with diameters in the range of 40 to 70 μm (Cheremisinoff, 2002). In IAF, also known as dispersed air flotation, the air bubbles are formed by contacting air directly with wastewater by a spinning impeller (Eckenfelder Jr., 2000; Metcalf & Eddy, 2003). The IAF process requires less space and hence significantly lower capital cost than DAF units. However, IAF has disadvantages such as a higher power requirement and production of more float skimmings compared to DAF. IAF units have not been employed frequently to treat refinery wastewaters (Berné and Cordonnier 1995).

Filtration is one of the most common physical methods of oil and solids removal (Patterson, 1985). Filtration efficiency depends on oil concentration, droplet size, solids contents, and hydraulic variations. Filtration media can experience clogging problems that may necessitate frequent backwash or media replacement. Patterson (1985) reported that oil removal efficiency by multimedia filtration varied from 0 to 83% when the influent petroleum refinery wastewater contained from 8 to 35 mg oil/l. Generally, high removal was achieved with higher initial concentration. Eckenfelder Jr. (2000) indicated that upflow filtration with graded silica medium performs the dual role of filtering and coalescing. In this process, oil rises to the top of the separator by buoyancy and by water flow, and can be removed by backwashing. Berné and Cordonnier (1995) demonstrated that the filtration efficiency in a hydro-skimming refinery with the influent containing from 90 to 270 mg/l of hydrocarbons (average 139 mg/l) was 84 to 91% (average 87%), while the efficiency increased over 90% with addition of organic chemicals for coagulation. However, coagulant addition caused rapid pressure drop in the filter.

Aymong and Abbott (2004) introduced the advanced filtration systems (AFS) followed by oil-water separation with coalescing plates for the removal of oil and petroleum hydrocarbons. The AFS employ surface modified substrates as the filtration materials to remove oily hydrocarbons permanently and rapidly, while it preventing flow reduction and desorption of filtered substances. AFS media can capture insoluble, semi-soluble and mechanically emulsified components and attain greater than 99% removal efficiency of various hydrocarbons.

Membrane filtration methods have been applied to separate oil from water. Oil globules and/or oil aggregates are rejected at the membrane surface, while water molecules pass through the membrane (Patterson, 1985). Membrane separation has the advantages of (1) being a widely applied technology that has been shown to produce a uniformly high quality permeate without the need of chemical addition; (2) requiring little space; (3) being amenable to automation; and (4) not requiring highly skilled operators. However, membrane technologies are generally not economical when applied to treat large wastewater flows and polymeric membranes require relatively frequent membrane replacement if adequate pre-treatment is not provided. More than 3,000 polymeric and 75 inorganic ceramic membrane separation systems have been constructed throughout the world for the oily wastewater treatment (Cheryan and Rajagopalan 1998). Therefore, membrane separation is a technology that should considered along with other polishing treatment methods.

Ultrafiltration is able to break oil-water emulsions and concentrate the oil rather than destroying it, so UF is generally used for oil recovery and/or reuse (WEF, 1994). Since oil recovered by UF does not contain chemical additives, it can be recycled effectively or reused without additional sludge production. Also the UF requires little operational control compare to complex chemical dosage determination in coagulants addition and shows excellent oil removal capabilities (Vaughan Jr. et al., 2001).

Vaughan Jr. et al. (2001) designed and operated a full-scale tubular ultrafiltration unit (TUF) for oily wastewater treatment based on the results of a 30 month pilot study. The wastewater from an aluminum producer contained approximately 5% oil. Initial treatment was provided in a lined gravity separation pond that removed the majority of the free oil under quiescent conditions. Pond effluent was treated in full-scale tubular UF modules with softened water containing 0.5% Koch Liquid Detergent (KLD) cleaning as well as sponge ball cleaning that achieved 99.9% removal of oil and grease and resulted in an average of 3 mg oil/l in the effluent. The authors decided to utilize a lined permeate holding pond as the final polishing step instead of unlined hybrid wetlands because of the excellent performance of the full-scale UF system. The residual from TUF system was transported to a free-oil holding tank in which the free-oil was separated naturally because of thermodynamical instability of concentrated oil emulsion. The skimmed free oil in holding tank was sent to offsite recycler.

A pilot study conducted by Reed et al. (1998) compared alternative methods to treat an oily wastewater. These included dissolved air flotation with cationic polymer addition (DAF), a tubular UF system, and a biological aerated filter. The results of this investigation are presented in Table 4.22. Based on the results of this study, the tubular UF membrane system was selected to upgrade the existing oily wastewater treatment facility because the DAF unit produced significantly more sludge and entailed high operating cost, and the biological aerated filter exhibited unreliable operation due to frequent clogging, while the UF system consistently produced high quality effluent with relatively simple operation.

Table 4.22. Results of a Pilot-scale Comparison Between Chemical Addition-DAF and Tubular Ultrafiltration (Summarized from Reed et al. (1998)).

Parameter	Item	CA-DAF	Tubular UF
Oil & Grease	Influent (mg/l)	2,360-3,240	920-5,600
	Effluent (mg/l)	9-41	<50
	Removal Eff. (%)	98-99	97
TSS	Influent (mg/l)	-	150-2,100
	Effluent (mg/l)	-	<25
	Removal Eff. (%)	-	97

Murphy et al. (2003) surveyed the diverse existing and emerging technologies for oily wastewater treatment including biological methods, DAF, chemical oxidation, filtration, membranes, parallel-plate oil separators. It was determined that a ceramic ultrafiltration membrane was the best suited to treat effluent from a CPI separator used to remove non-emulsified oil from ship bilge water. The choice was based on operating cost, reliability, long term permeate flux, resistance to chemicals, and manpower requirements.

Centrifugation is a possible method to enhance the removal of non-emulsified oil from water by mechanically created centrifugal force when the satisfactory separation of coagulated oil particles is not achieved by other gravity separation methods (WEF, 1994). However, centrifugation has limitations that include high maintenance and energy requirements.

Chemical Methods

Oil-water emulsions can be broken by chemical methods that utilize coagulants to reduce the static repulsion between emulsified oil bodies and by destroying the emulsion-water interface (Song et al., 1998). Chemical addition is an effective method to break oil-water emulsion, but generally requires more labour and skilled operators to determine proper chemical dosages; is sensitive to changes of influent quality; increases the dissolved solids in the effluent; and increases treatment costs because of the chemical addition (Cheryan and Rajagopalan, 1998; Vaughan Jr. et al., 2001).

The chemicals commonly used for oil demulsification are coagulating salts such as aluminum salts or iron salts, and acids such as hydrochloric acid or sulfuric acid. These chemicals can be added alone or in conjunction with heating, electrical treatment or organic cleaving agents. The application of coagulating salt is a widely used and effective method of demulsifying oil-water emulsion (Patterson, 1985). Sulfide can be removed by formation of FeS precipitates when iron salts are added as a coagulant Sulfide removal by FeS precipitation can be used for the wastewater containing from 10 to 50 mg/l of sulfide. (Berné and Cordonnier 1995). However, the co-production of iron hydroxide precipitates increases sludge production (Patterson, 1985). Demulsification by acid is commonly more efficient than by using coagulating salt for aggregating oil emulsions, although acid is more expensive and requires effluent neutralization (Patterson, 1985; WEF, 1994). Polymers are frequently added with coagulating salts or acids to enhance the flocculation.

Song et al. (1998) studied demulsification efficiency at a bench-scale batch reactor (the volume was not specified) by addition of ozone and natural salt to a simulated wastewater containing 18,200 ppm of oil emulsion prepared by the cutting oil containing 80% mineral oil. The results indicated that the combination of ozone (29 mg/min) and 3% salt addition enhanced the demulsification efficiency by 98 %, and increased the reaction rate, while lower than 40 % demulsification was achieved by either salt or ozone addition. The authors suggested that the synergetic effects of demulsification was induced by the destabilization of oil-water interface through salts, and by the following emulsifier oxidation with ozone.

Specialty coagulants and/or coagulating agents have been introduced for chemical demulsification of oil-water emulsion. Diethanolamine polyether, a cationic polymer, was synthesized by Hafiz et al. (2005) and used in a lab-scale experiment to destabilize oily refinery wastewater containing 200 ppm of oil and 250 NTU of turbidity. The turbidity removal efficiency indicated that 4 mol of diethanolamine polyesthers showed higher turbidity removal rate (45%) than 7mol demulsifier was used (41% of turbidity removal) probably due to re-emulsification of oil under demulsifier overdose condition. Turbidity removal increased by approximately 65% with 5 ppm $FeCl_3$ addition. Also the diethanolamine polyethers showed good biodegradability by microorganisms in river fresh water as indicated by complete biodegradation within 6 to 7 days.

Physicochemical Methods

The addition of coagulating chemicals to break oil-in-water emulsions can significantly improve the flotation unit efficiency (Patterson, 1985; Eckenfelder Jr., 2000; Cheremisinoff, 2002; Metcalf & Eddy, 2003; Huchler, 2004). Patterson (1985) indicated that using both coagulating salts and air flotation yielded better oil removal efficiency for oil refinery wastewater on the basis of the comparison study of removals obtained using air flotation alone to using air flotation in conjunction with coagulating chemicals. The results are shown in Table 4.23.

Table 4.23. Comparison of Oil Removal Efficiency by Air Flotation (AF) and Coagulants Addition (Adapted from Patterson (1985)).

Wasewater	Treatment	Oil Removal (%)
Oil refinery wastes I	AF	70%
	AF + Polyelectrolyte + Bentonite clay	95%
Oil refinery wastes II	AF	79%
	AF + Aluminum sulfate (25 mg/l)	87%
Oil refinery wastes III	AF	70-80%
	AF + Aluminum sulfate (30-70 mg/l)	90%
	AF + Lime (75-100 mg/l)	95%

Patterson (1985) also reported that coagulating a refinery wastewater containing 50-100 mg oil/l with 35 mg/l of alum resulted in an API separator effluent oil concentration of 15 mg/l. Berné and Cordonnier (1995) compared hydrocarbon (HC) and TSS removal from a petrochemical wastewater using alum and anionic polyelectrolyte to results obtained when an organic coagulant (same as cationic polymer coagulant) was used. The comparison results represented that organic coagulant produced much lower sludge and better removal of oil and SS as given in Table 4.24.

Table 4.24. DAF Performance Using Different Coagulants (Adapted from Berné and Cordonnier (1995)).

Coagulants	Flotation influent (mg/l)		Flotation effluent (mg/l)		Removal (%)		Sludge volume (m^3/day)
	HC*	TSS	HC*	TSS	HC*	TSS	
10 mg/l aluminum sulfate and 1mg/l anionic polyelectrolyte	150	70	21	24	86	66	18-30
	120	59	18	20	85	66	
	130	63	16	28	88	56	
0.7 mg/l active matter of organic coagulant	160	173	13	17	92	90	3-5
	112	70	18	17	84	76	

*HC = hydrocarbon

Zhong et al. (2003) used microfiltration using a ceramic membrane (zirconia: ZrO_2) combined with flocculation to treat a refinery wastewater. The prior flocculation with polymer (a derivative of polyacrylamide) resulted in a decrease of permeate oil and COD concentration and membrane fouling, with increased membrane flux at the optimum conditions of 70 mg/l polymer, 40 °C temperature, 90 minute stirring time and another 90 minute holding time. As the results shown in Table 4.25 indicate, flocculation and subsequent MF reduced the permeate oil and COD dramatically.

Table 4.25. Comparison of MF to Combined Flocculation and MF for the Removal of Oil and COD from Refinery Wastewater. Influent concentrations were 3,000 mg COD/l, and 6,000 mg oil/l (Adapted from Zhong et al. (2003)).

Treatment		Flux ($l/m^2 \cdot h$)	COD	Oil
MF	Effluent (mg/l)	120	154	34.7
	Removal (%)	-	94.9	99.4
Flocculation + MF	Effluent (mg/l)	173.5	108	8.8
	Removal (%)	-	96.4	99.9

Electrical Methods

Electrocoagulation and electroflotation have been applied to demulsify and removal oil from wastewater (Patterson, 1985). In electrocoagulation, a metallic coagulant, such as ferrous ion, is produced by oxidation of anode material when voltage is applied. Electrocoagulation and electroflotation are efficient methods for the removal of suspended solids and oil. The electrocoagulation has several strengths such as fast particulate removal with high efficiency, compact reactor size, relatively low capital and operation cost, simplicity of operation, relatively low sludge production, and low manpower requirement through operation automation (Xu and Zhu, 2004; Chen, 2004; Adhoum and Monser, 2004). The optimum pH for electrocoagulation is near 7, and higher temperature causes lower energy consumption through a conductivity increase. The laboratory electro-coagulation by sacrificial aluminum electrodes for reducing COD, phenol and colour from olive mill wastewater indicated effective removal capacity of 76% for COD, 91% for polyphenols, and 95% for dark colour in 25min (Adhoum and Monser, 2004). The full-scale electrocoagulation process has been operated since 2000 to treat emulsified oily bilge wastewater from fleet and shipyards (Stephenson et al., 2003). By electrocoagulation, almost complete removal of hydrocarbons can be achieved as shown in Table 4.26. The concentrated solid residuals from electrocoagulation were dewatered by pressure filter and then disposed of as solids wastes.

Table 4.26. Emulsified Oily Wastewater Treatment by Electrocoagulation at Full-scale (Adapted from Stephenson et al. (2003)).

Contaminants	Influent (mg/l)	Effluent (mg/l)	Removal Efficiency (%)
Total PAHs	5.25	N.D.	100
Total BETX	2.37	0.014	99.4
MTBE	0.17	<0.00005	100
Hydrocarbon Oil and Grease	2,350.0	<2	99.9

The gas bubbles generated by electroflotation are either smaller or do not coalesce as easily compared to the bubbles produced in DAF or IAF units (Chen, 2004). The bubble sizes are distributed from 1-30 µm for EF, from 50-100 µm for DAF and 0.5-2 µm for IAF. Although the bubbles generated by IAF are smaller than by those produced by EF, the oil and SS removal efficiencies of IAF are lower than EF probably because of rapid agglomeration of gas globules (Chen, 2004). Flotation efficiency improves as median gas bubble size decreases due to larger surface area for attachment of pollutants. A comparison of various flotation technologies for oily wastewater treatment is shown in Table 4.27. EF is considered as the most effective and economical separation method for the removal of oil and light suspended solids by flotation. But because electrical methods of coagulation or flotation are still developing techniques, full-scale field applications are not widespread.

Table 4.27. Comparison of Various Flotation Technologies (Adapted from Chen (2004))

Treatment Type	EF	DAF	IAF	Settling
Bubble size (μm)	1-30	50-100	0.5-2	
Specific electricity consumption (W/m^3)	30-50	50-60	100-150	50-100
Air consumption (m^3 air/m^3 water)		0.02-0.06	1	
Chemical conditioning*	IC	OC+F	OC	IC+F
Treatment time (min)	10-20	30-40	30-40	100-120
Sludge volume as percent of treated water	0.05-0.1	0.3-0.4	3-5	7-10
Oil removal (%)	99-99.5	85-95	60-80	50-70
TSS removal (%)	99-99.5	90-95	85-90	90-95

* IC : Inorganic Coagulants, OC : Organic Coagulants, F : Flocculants

4.3.2.3. Biological Treatments

The effluent from oil removal processes generally contains COD, BOD, phenols, and ammonia with considerably low concentrations of hydrocarbon and sulfide if the pretreatment steps are operated properly (Berné and Cordonnier, 1995). The biodegradable substances including oil, phenols, sulfur compounds, and NH_4^+ remaining after pre-removal of free oil and demulsification-gravity separation can be decomposed by microorganisms and/or removed with sludge flocs in subsequent biological treatments. Such treatment may be in the form of activated sludge, biofilm or biofilter reactor, membrane bioreactors, or lagoons (Patterson, 1985; Berné and Cordonnier, 1995; Nemerow, 1987). Since oil concentrations higher than 30 mg/l will disturb biological process, the oil contents in bioreactor influent must to be controlled (Huchler, 2004). Nutrient addition, particularly phosphorous, may be required to maintain biological activity (Berné and Cordonnier, 1995).

Conventional Activated Sludge

The activated sludge process is seldom used for refinery wastewaters due to their relatively low content of readily biodegradable organics (Berné and Cordonnier, 1995). Patterson (1985) indicated that phenol concentrations less than 500 mg/l can be treated by biological treatment. The author summarized the phenol removal performance of various biological treatment schemes for refinery wastewater as shown in Table 4.28. The phenol concentration in the biological systems ranged from 0.01 to 3.8 mg/l, which indicates the possibility of phenol removal by microorganisms. However, since the treatability and inhibition of biological process is extensively depended on wastewater characteristics and presence of other toxic chemicals, the efficiency of phenol removal is strongly related to influent phenol loading rate and coexistence with sulfate or sulfide.

Table 4.28. Phenol Removal from Refinery Wastewater by Biological Treatment Methods (Adapted from Patterson (1985)).

Treatment Process	Influent Phenol (mg/l)	Effluent Phenol (mg/l)
Biooxidation Pond	30	1
Trickling Filter	30-40	0.5-0.7
	9-25	0.6-3.8
Activated Sludge	80	<0.5
	8-10.5	<0.01-0.055
	0.3-1.1	<0.01-0.6
	3-8	0.007-0.05
	40-80	<1.0
	15-20	0.01-0.03
Activated Sludge + Trickling Filter	8-11	<0.01-0.5
Activated Sludge + PAC*	6	0.01
	6	0.01
	2.4	<0.01
	1.4	0.01
	55	0.06

* Results from pilot-scale, other results are from full-scale operation

Attached Growth Systems

There are many different schemes of advanced fixed film bioreactors such as rotating biological contactors, fluidized beds, packed beds, rotating fibre discs and microporous membrane (Jou and Huang, 2003). The main strengths of fixed film bioreactors include simplicity of operation, easy control of shock loading, less sludge production, lower energy requirement, effective performance for low influent substrate load and small reactor volume (Jou and Huang, 2003; Israni et al., 2002). However, Vaughan Jr. et al. (2001) stated that for the application of fixed film bioreactors, the drawbacks of frequent clogging, and difficulty in backwashing have to be considered, depending on the reactor type.

Jou and Huang (2003) carried out the pilot-scale experiment using unique fixed film bioreactor which was equipped with 4-chamber fiber-glass reinforced plastic horizontal tank containing cylindrical plastic pall rings for biomass support frame to treat oil refinery wastewater. The results indicated higher and more rapid removal of COD and phenol with the removal efficiencies of 85% to 90% for COD and almost 100% for phenol when fixed film bioreactor was applied with 8-hour HRT than when traditional activated sludge was used with a 25-hour HRT which resulted 50 to 60% of COD reduction and 99% phenol removal. The authors concluded that by using a fixed film bioreactor, higher removal efficiency and stable operation can be achieved since high biomass concentration can be maintained in the reactor, and the growth and activities of slow growing bacteria, such as nitrifiers, can be enhanced.

Sekoulov and Brinke-Seiferth (1999) recommended the fixed bed biofiltration process for crude oil refinery wastewaters which were pretreated by activated sludge system or by flocculation via pilot-plant study because the biofiltration of low-loaded wastewater can significantly sorb refractory organics, colloidal particles and suspended solids on the biofilm surface, and fixed bed systems are effective for treating hard to remove organics such as phenols. The recommended packing material for microorganism carrier was burned clay with a diameter of 8 to 16 mm to prevent clogging. The suggested treatment sequence for two different refinery wastewaters included activated sludge (with powdered activated carbon) – fixed bed biofiltration – sand filtration – activated carbon filter, or flocculation – fixed bed biofiltration – sand filtration – holding tank. The authors emphasized the importance of the biofiltration process because it is less sensitive to toxic shock loadings and can be applied as either the main treatment or polishing method. The lab-scale experiment was also conducted using a fixed film biofilm reactor for the purpose of phenol reduction from sterilized petroleum plant wastewater by Hsien and Lin (2005). Phenol was effectively reduced from a 72 mg/l initial concentration to a 4 mg/l effluent concentration.

Tyagi et al. (1993) employed a pilot-scale modified 4-stage rotating biological contactor (RBC) with polyurethane foam disks in order to study biodegradability of oil containing wastewater collected from API and DAF effluent in a petroleum refinery. The RBC system has many advantages such as low operating cost, tolerance of shock and toxic loadings, simplicity of process control and low energy requirement. Based on the performance results of RBC units for four different hydraulic loadings given in Table 4.29, the modified RBC showed high removal for all measured parameters including oil, COD, Phenol, NH_4-N and SS though the reduction efficiency decrease as hydraulic loading increases. The proportional increase of average organic removal rate to the organic loading increments reflected that COD removal is substrate limiting reaction and substantially the process has a good shock loading absorbing capacity. Therefore, the authors explained that polyurethane foam played an important role as a porous biomass support media to improve biological reduction of oil refinery wastewater.

Table 4.29. Performance of a Modified RBC at Various Loadings (Adapted from Tyagi et al. (1993)).

Parameter	Values			
Hydraulic loading (m^3/m^2·day)	0.01	0.02	0.03	0.04
Organic loading (g/m^2·day)	2.3-5.3	4.7-10.7	9.5-18.8	12.7-25.1
Average organic removal rate (g/m^2·day)	3.6	6.9	11.8	15.5
Oil Removal (%)	>80	>80	>80	>80
COD Removal (%)	87.5	84.9	81.5	80.2
Phenol Removal (%)	93.6	90.8	83.3	87.6
NH_4-N Removal (%)	99.6	96.9	91.6	88.9
SS Removal (%)	81.6	80.4	78.2	69.0

The gas-liquid-solid three phase airlift loop bioreactor (ALR) was tested for oil refinery bio-treatment in a study conducted by Xianling et al. (2005). The ALR had several advantages of faster oxygen transfer, flexibility of operation, no requirement of pre-aeration, and compact size. Additional strengths indicated by Garibay-Orijel et al. (2005) are that the ALR allows treatment of low strength wastewater, biofilm thickness can be controlled, and the system can dilute the influent using treated effluent to provide alkalinity and adequate pollutants level. Veeresh et al. (2005) stressed drawbacks of the fluidized bed reactor include the requirement of biofilm support media, very high recycle ratio, and high operating cost. The pilot-scale ALR with synthetic resin carriers produced highly purified effluent from oil refinery wastewater pre-treated by oil removal in a flotation process (Xianling et al., 2005). The effluent from the ALR contained less than 100 mg/l of COD and less than 15 mg/l of NH_4-N, while the influent included 250-613 mg/l of COD and 56-125 mg/l of NH_4-N. The performance of the ALR is compared to that of an activated sludge system in Table 4.30. These results indicate the ALR system to operate at a shorter HRT, produce less sludge and achieve lower effluent pollutant concentrations.

Sokół and Korpal (2005) also used a lab-scale three-phase fluidized bed bioreactor containing polypropylene particles as support media to remove COD and phenolic compounds from refinery wastewater. By this process, approximately 90% of the COD was removed from an influent containing 5,475 mg COD/l, and phenol was eliminated almost completely (99.9%) from initial concentration of 567mg/l under optimum operating conditions.

Table 4.30. Comparison of an Airlift Loop Bioreactor to Activated Sludge (Adapted from Xianling et al. (2005)).

Item	Airlift Loop Bioreactor	Activated Sludge
Hydraulic Residence Time (hrs)	6.5	24
Effluent COD (mg/l)	<100	100-120
Effluent NH_4-N (mg/l)	<15	20-30
Sludge Production (ton/100ton treated water)	1.8	6.4
Land Usage (m^2/m^3/hr water treating)	16.7	60.8

Dalmacija et al. (1995) investigated a lab-scale biosorption system that used granular activated carbon columns as a tertiary treatment for oil-field brine wastewater treated by activated sludge. The AS effluent contained 29,000 mg/l of mineral matter (mostly NaCl), 0.025 mg/l of phenols, and 0.3 mg/l of crude oil. The non-biodegradable organics, which was remained after oxidation of readily biodegradable substances in the activated sludge system, were adsorbed by the GAC. Microorganisms consumed the organics accumulated on the carbon surface, contributing to the biological regeneration of the GAC. The minimum 77% COD removal records indicated biosorption with GAC was effective for organics removal as given in Table 4.31.

Table 4.31. COD Removal by Biosorption with GAC at Various Flow Rates (Adapted from Dalmacija et al. (1995)).

Parameter	Values			
Flow rate (l/day)	40	70	95	130
Flow per unit cross-section area of column ($l/cm^2 \cdot day$)	2.0	3.6	4.8	6.6
Influent COD (mg/l)	120	115	105	110
Effluent COD (mg/l)	3	7	20	25
COD removal (%)	98	94	81	77

Membrane Bioreactor

The membrane bioreactor (MBR) is one of the applicable technologies to remove oil and other organic components from wastewater. Scholz and Fuchs (2000) used a lab-scale MBR to treat a synthesized oil-water emulsion composing of either fuel oil or lubricating oil and a surfactant. The MBR consisted of an activate sludge reactor and external tubular cross-flow ultrafiltration system using simulated oil-water emulsion containing either fuel oil or lubricating oil with a surfactant. The comparison between UF only and MBR resulted that the MBR process produced the better quality permeate when similar initial oil concentration was introduced. The removal efficiency of all measured parameters, HC, surfactant, TOC and COD, indicated the good performance of MBR system even at the final periods of experiment with shorter retention time of 6.75 hours and higher pollutants level in the bioreactor than other stages of experiment as summarized in Table 4.32. The MBR system can minimize the formation of excess biomass (sludge) because the energetic substrate could be used for other purposes than cellular growth due to long SRT. Thus the amount of required nutrient addition in MBR decreased correspondingly. The nutrients requirements for effective biodegradation of 1kg oil were 6.7g of nitrogen and 0.8g of phosphorous in MBR, while 120g nitrogen and 20g phosphorous was required in traditional bioreactor (Scholz and Fuchs, 2000). Since the contents of microorganisms as well as pollutants in MBR can accumulated and stayed longer through mixed liquor suspend solids (MLSS) rejection by membrane, the bioavailability of nutrients and biodegradability of pollutants significantly increased in MBR system, which resulted in almost complete oil-free permeate production.

Table 4.32. Summary of MBR Removal of Fuel Oil or Lubricating Oil (Adapted from Scholz and Fuchs (2000)).

Introduced Oil		Fuel Oil	Lubricating Oil
Retention time (hr)		6.75	6.75
Oil biodegradation rate (g/l/d)		9.39	3.24
Concentration in reactor (mg/l)	HC	18,307	6,504
	TOC	22,788	5,381
Concentration in permeate (mg/l)	HC	0.29	0.05
	Surfactant	4.2	1.16
	TOC	58.3	18.7
	COD	243	131
Removal Efficiency (%)	HC	99.99	99.99
	Surfactant	97.8	98.3
	TOC	97.8	97.9
	COD	96.3	95.3

Seo et al. (1997) carried out a pilot-scale experiment using combined activated sludge and hollow fibre polysulfone UF membrane for the purpose of evaluating the biodegradability and the organic matter rejection efficiency for the oily wastewater from an automobile engine manufacturing plant which was primarily treated by chemical precipitation, flotation and sedimentation. The MBR, consisting of activated sludge and an external membrane separation unit, showed stable high removal ability as 95.3% for organic contents at 3.67-day HRT with the average effluent concentration of 40.8 mg COD/l even when the organics in the influent fluctuated from 780 mg/l to 1,960 mg/l (average 1,333 mg/l). The 18.4 mg/l of oil in the influent also could be removed to the average concentration of 4.4 mg/l.

Sequencing Batch Reactor

A lab-scale two-stage SBR was applied to remove oil and COD from an oil refinery wastewater (Lee et al., 2004). The first stage SBR, operated with a 9.6 hour HRT, was used for oil and grease removal and the second stage SBR with a 16 hour HRT reduced the remaining COD. The experimental results indicated that the two-stage SBR was an effective method for oil refinery wastewater purification as shown in Table 4.33.

Table 4.33. Average Performance of a Two-Stage SBR Treating Oil Refinery Wastewater (Adapted from Lee et al., 2004).

Stage	Influent (mg/L)		Effluent (mg/l)		Removal (%)	
	Oil & Grease	COD	Oil & Grease	COD	Oil & Grease	COD
1st stage	5,840	3,962	6	2,103	99.8	47.0
2nd stage	6	2,090	N.D.*	97	100.0	95.3

* N.D. : Not Detected

Anaerobic Treatment

Anaerobic treatment is generally used for the wastewater with high organic contents and toxic compounds. Thus, the anaerobic biodegradation of oil refinery wastewater may be applicable (Lee et al., 2004). Anaerobic processes have many advantages compare to an aerobic treatment for example lower operating cost, smaller reactor volume, production of methane gas that can be used in energy recovery, and less sludge production. However, many drawbacks, such as the requirement of longer start-up time to develop proper biomass, low quality effluent, and potential problems caused by odor or corrosive gas formation, have to be considered before utilizing the anaerobic treatment (Metcalf & Eddy, 2003).

Reyes-Avila et al. (2004) applied anaerobic denitrification process to decompose nitrate-nitrogen, carbon (acetate) and sulfide simultaneously using synthetic wastewater simulated as refinery waste stream. The author found that the removal efficiencies were reached to around 100%, 69% and 100% for nitrate, acetate and sulfide, respectively. Sulfide was mostly removed by partial oxidation to elemental sulfur which can be accumulated in the reactor without inhibition of denitrification performance rather than consumed as energy source for nitrate reduction.

Another lab-scale biological phenol elimination applied the anaerobic treatment for the effluent of oil-water separator in the petroleum refinery plant (Charest et al., 1999). The reactor scheme was upflow fixed film anaerobic bioreactor. After biomass attached on the biofilm had adapted to the oil refinery wastewater, more than 97% of phenol was removed from the 150 mg/l of initial phenol concentration, while oil and grease contents remained almost same.

Lagoons and Wetlands

Lagoons are an option for polishing of pretreated wastewater. Reynolds and Richards (1996) stated that aerated lagoons are widely used in industrial wastewater treatment because they are less expensive than the activated sludge process. However, lagoons principally occupy more land per unit mass of BOD removed, and may require further polishing step to remove biomass solids and oxidation end products, such as sulfate and nitrate. Sublette et al. (1998) investigated biocatalyzed treatment of sulfide laden wastewater produced from refining industries in a full-scale partially aerated earthen pit system. The existing pit was bio-augmented by seeding sulfide oxidizing bacteria, *Thiobacillus denitrificans* strain F. The author indicated that among the many technically possible sulfide removal options such as chemical oxidation, air stripping, precipitation, air oxidation and biological treatment, the biological method is the most economically feasible option to effectively remove sulfide. A sulfide containing wastewater with around 100 mg/l of sulfide and 4,800 mg/l of TDS was observed to be almost completely treated indicated by approximately 99% sulfide removal without H_2S emission due to rapid sulfide oxidation to sulfate.

Constructed wetland treatment systems have increased in popularity because of operational simplicity, low maintenance requirements, low construction costs and environmental friendliness (Yang and Hu, 2005). Also the systems have shown good capacity of final purification for various kinds of sewage and industrial wastewater including secondary treated oil refinery wastewater. However, wetlands may not be suitable for cold climates because of minimal bio-oxidation during the winter. Yang and Hu (2005) conducted a pilot scale wetlands comparison study for the effluents from oil refinery with different substrata and flow regimes, but with the same plant life to evaluate reusability of wetland effluent within the refinery. The subsurface flow (SSF) wetland system performed better than free water surface (FWS) in terms of higher COD and TP removal due to the high porosity of gravel substratum and lack of cover on media surfaces which can enhance oxygen transfer. The results are summarized in Table 4.34. The effluent from wetlands contained an oil and grease concentration of 17.9 mg/l and 13.6 mg/l for FWS and SSF, respectively. The SSF wetland systems performed better than FWS system. Also, since the SSF wetland effluent included 15.7 mg/l of Cl^-, 20.5 mg/l of SO_4^{2-}, 1,930 mg/l of TDS, 1,672 mg/l of alkalinity and 280 mg/l of hardness (the influent analyses data were not provided), the authors suggested that the treated water could be reused for cooling, cleaning and miscellaneous purposes in the plant.

Moreno et al. (2002) also investigated the use of a constructed wetland with vertical flow as a method for ammonia removal from biological tricking filter effluent in the oil refinery plant in a lab-scale column test. The result proved planted wetland was an effective technique to remove 90% of ammonia with 3 to 20 mg/l ammonia in influent to less than 3mg/l in effluent.

Table 4.34. Comparison of Constructed Wetlands for Polishing Biologically Treated Oil Refinery Wastewater (Summarized from Yang and Hu (2005)).

Flow Regime		Free Water Surface (FWS)	Subsurface Flow (SSF)
Substratum		Sand	Gravel
Removal Efficiency (%)	COD	30	50
	TN	60	80
	TP	50	60
	Oil and Grease	57	48

4.3.2.4. Tertiary Treatments

A number of advanced treatment technologies associated with the removal of residual oil, phenols, ammonia nitrogen and/or sulfides have been developed and can be classified by physical, chemical, and electrical methods. Seo et al. (1997) stated that although the existing physicochemical treatment facility could remove most of the free and emulsified oil from the wastewater, soluble organic matter was still discharged at high concentration from the oily wastewater producing plants.

Physical Methods

Adsorption is a possible polishing step for the removal of remaining oil and organic constituents before discharge. Activated carbon adsorption was reported as a possible method for oil removal from refinery waste streams, even though it requires high energy for the regeneration of exhausted adsorbents (Patterson, 1985; Nanoti et al., 1997). A pilot-scale granular activated carbon column system showed oil removal efficiencies from 5 to 85% when applied to treat petroleum refining wastewater (Patterson, 1985). Mueller et al. (2003) evaluated the adsorption capacity of five different adsorbents including PAC, amine-modified bentonite clay, anthracite and two organically modified montmorillonite clays. Test results were evaluated on the basis of oil and COD removal capacity and estimated costs. The tests were in the form of batch isotherm experiments. The oily automotive industry wastewater was pre-treated by chemical demulsification. PAC showed not only much better removal efficiency for both oil and COD but also lower cost compared to the other adsorbents tested. Phenol also can be effectively removed by activated carbon adsorption, although rapid phenol breakthrough is a potential problem. It was reported that more than 99% of 44 mg/l initial phenol was removed by activated carbon to the level of 0.001mg/l (Patterson, 1985). Eckenfelder Jr. (2000) also demonstrated that activated carbon adsorbed 80.6% of phenol in an batch column test, reducing the initial 1,000 mg/l concentration to 194mg/l.

The steam or gas stripping can be used for the removal of sulfide, ammonia and phenols, although phenol stripping efficiency is usually lower than sulfide and ammonia (Eckenfelder Jr., 2000). However, since gas stripping only transfers the pollutants from the aqueous to gaseous phases, further treatment of the air stream is required (Sublette et al., 1998). Also, pH adjustment is needed before and after air stripping (Berné and Cordonnier, 1995). The oil content has to be sufficiently reduced prior to stripping since co-stripped oil compounds in off-gases can be dangerous. Many drawbacks of air stripping such as low ammonia removal efficiency, treatment difficulty of residual air and polluted off-gas production have hindered the application of the process (Berné and Cordonnier, 1995).

The results of both air and steam stripping to treat sour condensates in refineries, indicated steam stripping has higher sulfide reduction capacity (96 to 99%) given a 1,000 to 10,000 mg/l sulfide in influent, while air stripping showed from 90 to 96% removal efficiency from a 200 to 500 mg/l initial sulfide concentration (Berné and Cordonnier, 1995). The removal efficiencies by steam stripping reported by Berné and Cordonnier (1995) were between 90% to 98% for sulfide at the temperature ranges between 75 to 100 ℃ and from 92% to 97% for volatile ammonia when higher temperature was applied for ammonia stripping. Because of the higher solubility and higher temperature requirement of ammonia, Chevron Research Company introduced two-stage stripping to separate H_2S and ammonia removal, which resulted in the effluent containing less than 5 mg/l of H_2S and 50 mg/l of NH_3 (Eckenfelder Jr., 2000).

Membrane technologies are commonly used if final effluent polishing is required (Chang et al., 2001). Elmaleh and Ghaffor (1996) used a lab-scale inorganic ultrafiltration membrane in cross-flow mode to remove hydrocarbons and suspended solids from an artificially produced mixture of crude oil and suspended solids which were obtained from activated sludge process. The concentration was similar to the effluent of conventional biological treatment at an oil refinery with 20 mg/l total HC and 30 mg/l SS. The UF showed total rejection of HC and solids by size exclusion at

35 °C, because the sizes of oil droplets and solids (2 µm and 60 µm, respectively), were less than the membrane mean pore size (0.02 µm). The importance of temperature control in oil emulsion filtration was also noted by the authors, since oil droplet size reduced considerably as the temperature increased.

The rotary ultrafiltration was applied for in-plant recycling of die lubricant wastewater (Peterson et al., 2005). A stainless steel-ceramic composite ultrafiltration membrane with 0.1 µm pores was selected in the pilot-scale experiment to prevent the damage of membrane by rotation. The UF was preceded by oil removal steps including rope skimmers and DAF to prevent membrane fouling and clogging by oil and suspended solids. The tests showed concentration of die lube components from 3.3 to 20 fold was possible with stable high quality permeate production indicated by clear and colourless permeate having a low COD.

Gryta et al. (2001) applied combined UF and membrane distillation (MD) for the final purification of oily wastewater from typical bilge wastes. In membrane distillation the water vapour evaporated from the wastewater by vapour/liquid equilibrium transfers through the hydrophobic membrane by the partial pressure difference between inner and outer sides of membrane which is derived by temperature disparity (Gryta et al., 2001). As the purification results of UF and following MD by pilot-scale experiment presented in Table 4.35, the combined UF and MD process can remove oil, TOC and TDS very effectively. However, when high oil content is introduced to the UF, the permeate flux becomes lower.

Table 4.35. Permeate Quality of Ultrafiltration, and Ultrafiltration Combined with Membrane Distillation (Adapted from Gryta et al. (2001)).

Process/ Feed	Oil (mg/l)	TOC (mg/l)	TDS (mg/l)	Removal Efficiency (%)		
				Oil	TOC	TDS
Bilge water	3.6	4	37.9	-	-	-
UF	0.049	0.086	37	98.6	97.9	2.4
UF/MD	0	0.018	0.014	100	99.6	99.96

Duyvesteijn (1998) assessed the feasible oil refinery wastewater treatment for water reuse as fresh make-up water within the plant. Because the wastewater effluent contained suspended solids and chloride ions, the series of sand filter to remove SS, UF to reject biological contaminants and RO to reduce dissolved salts level was selected to be the best treatment option. The salt rejection was recorded higher than 95% in the RO unit. The pilot scale experiment proved this process is technically applicable for water reuse.

Chemical Methods

Sulfide can be removed by several different methods such as stripping, chemical oxidation, biological treatment and precipitation (Berné and Cordonnier, 1995). Since sulfides can inhibit biological purification by some extent, or retard the destruction of BOD exerting compounds such as phenols and CN^-, chemical precipitation of sulfide prior to flocculation-gravity separation process is generally used for the wastewater containing sulfide between 10 and 50 mg/l to decrease the sulfide concentration to less than 1 mg/l after gravity separation. When ferric chloride ($FeCl_3$) is added to precipitate sulfide, the process can cause some problems regarding chloride ion residual which need to be removed and possibly disturbs subsequent biological treatment, and sludge production (Schenk et al., 1999).

Gunukula and Tittlebaum (2001) conducted pilot-scale testing of ozonation to reduce oil and grease, total petroleum hydrocarbons (TPH) and COD from a barge cleaning industrial wastewater. Ozone can extensively decompose toxic recalcitrant chemicals such as phenols, cyanides, alcohols, pesticides and sulfides. Ozonation can be utilized either before or after biological treatment. The results in Table 4.36 indicate that the removal efficiency increased significantly as the ozone application rate increased. The ozone flow rate of 0 represents the case where oxygen was applied.

Table 4.36. Oxidation by Ozone (Summarized from Gunukula and Tittlebaum (2001)).

Parameters		Values		
Ozone flow rate (SCFH*)		0	6	12
Oil and Grease	Initial (mg/l)	45-55	45-100	57.2
	Final (mg/l)	-	-	8.2
	Removal Efficiency (%)	50	83	86
TPH	Initial (mg/l)	35-50	50-75	56.1
	Final (mg/l)	-	-	7.8
	Removal Efficiency (%)	50	82	86
COD	Initial (mg/l)	360	330	265
	Final (mg/l)	-	-	129
	Removal Efficiency (%)	15	28	51

* SCFH : Standard ft^3/hr

Hydrogen peroxide is a very effective oxidant for phenol destruction in the presence of ferrous ion (Fe^{2+}) as a catalyst (Fenton's reagent). Fenton's reagent (the combination of ferrous salts and hydrogen peroxide, $Fe(II)/H_2O_2$) is considered to be a very effective phenol oxidation chemical because the Fenton system generates hydroxyl radicals ($OH\cdot$) and perhydroxyl ($HO_2\cdot$) radicals which are very strong oxidants, and ferrous ion is used in a catalytic manner. The advantages of the Fenton process are that the residual iron is non-toxic and abundant in the environment, and hydrogen peroxide is not harmful (Carriazo et al., 2005), disadvantages of the process are mainly related to the cost of reagents. Sheu and Weng (2000) used Fenton's reagent (Fe^{2+}/H_2O_2) in the lab-scale oxidation of H_2S, phenol and COD from spent caustic wastewater which was characterized by high hydrogen sulfide and some mercaptans, phenols and emulsified hydrocarbons. The optimum pH was found to be around 2. The COD removal rate was higher than 99.5% (less than 100mg/l of final COD) using initial COD concentrations of from 30,000 to 45,000mg/l with 50min reaction time, 90℃ temperature, 100mg/l of Fe^{2+} and H_2O_2/COD ratio of 1.1. Downing et al. (1997) reported efficient phenol oxidation by chlorine dioxide (ClO_2) in oil refinery wastewater which was treated by steam stripper to remove VOC and H_2S, and DAF with coagulants to eliminate oil. The average phenol concentration in DAF effluent was between 250 to 350 mg/l. The reaction between ClO_2 and phenol was performed at pH between 6 and 7 and resulted in the production of organic acids. The almost complete phenol elimination was achieved by applying chlorine dioxide at two-points. The first application resulted in approximately 90% phenol conversion when a 2:1 ClO_2 to phenol molar ratio was used. The remaining phenol was oxidized by a second ClO_2 injection at a 5:1 molar ratio (ClO_2:phenol).

Zerva et al. (2003) demonstrated that among various advanced treatment technologies, wet oxidation (WO) is a very effective technique to mineralize highly polluted wastewater although the process requires high operating cost and complex safety conditions. The effectiveness of wet oxidation for the oily wastewater containing a large amount of organic matter (mainly alcohols and phenolic compounds) represented by 11,000 mg/l of COD from lubricant production unit of petroleum company was studied by Zerva et al. (2003). The water temperature was found to be the main factor for wet oxidation. Almost 50% of COD was removed within 10 minutes at the temperature of 260°C and 30 bar of oxygen pressure.

Recently the catalytic wet oxidation by peroxide or air has been introduced for phenol removal using various catalysts such as Fe-exchanged pillared beidellite (Catrinescu et al., 2003), pillared clays containing Al-Ce-Fe (Carriazo et al., 2005), extrudates of Al-Fe pillared clay (Guo and Al-Dahhan, 2003), and activated carbon (Suarez-Ojeda et al., 2005). The advantages of the process as stated by Guo and Al-Dahhan (2003) included treatment under lower temperature and pressure conditions, the catalyst can be easily recovered, regenerated, and reused, and the process can treat individual contaminants or a group of similar pollutants within complex mixtures of pollutants.

Electrical Methods

A bench scale experiment of indirect electrochemical treatment by Ti/TiO_2-RuO_2-IrO_2 anode was conducted by Rajkumar and Palanivelu (2004) using different phenolic wastewaters including oil refinery waste. COD was reduced from an initial concentration of 602 mg/l to final levels of 152 mg/l, while 160 mg/l of initial TOC decreased to 83 mg/l with 2,400 mg/l of supplemental chloride ion addition and 24 Ah/l charge. The authors stated that the electrochemical treatment of oil refinery wastewater consumed considerable electrical energy and represented less current efficiency mainly due to a low TDS level and conductivity even though it achieved 75% COD removal and 48% TOC reduction.

Table 4.37. Advantages and Disadvantages of Oil Refinery Wastewater Treatment Technologies.

Treatment Technology	Compounds Removed	Advantage	Disadvantage
PRELIMINARY REMOVAL OF OIL			
American petroleum Institute (API)	Free oil, SS	- Widely used technology - Effective and low cost preliminary oil reduction step	- Oil droplets smaller than 0.15 mm not removed
Corrugated plate interceptor (CPI)	Free oil, SS	- Removes smaller oil droplets than API - Require 15-20% less space than API	- Plates can be fouled
REMOVAL OF EMULSIFIED OIL			
Physical Methods			
Filtration	Emulsified oil, SS	- One of the most common methods for oil and solids removal	- Frequent backwash or media replacement may be required
Advanced Filtration System (AFS)	Oil, COD, BOD, TOC	- Can remove insoluble, semi-soluble and mechanically emulsified components - High removal efficiency (>99%)	- Not proven for the full-scale operation
Adsorption	oil		- Low oil removal efficiency by powdered bentonite organoclay

Treatment Technology	Compounds Removed	Advantage	Disadvantage
Centrifugation	Emulsified oil	- Occupies small area	- Requires more maintenance and higher energy consumption
Membranes	oil	- Can be used for oil reuse/recovery with minimal sludge production - Requires little operational control - Excellent oil removal capabilities - Widely applied technology - Uniform high quality permeate - Little or no chemical addition need - Compact size - Easy automation and simple operation - Highly skilled operators not required.	- Requires high capital cost with large effluent volumes - May require frequent replacement of membrane as a result of fouling and membrane degradation especially for polymeric membranes
Dissolved Air Flotation (DAF)	Non-emulsified oil	- Commonly used method in refineries	
Induced Air Flotation (IAF)	Non-emulsified oil	- Requires less space and less capital cost than DAF	- Higher power requirement - More float skimmings production - Not used commonly for refinery wastes
Chemical Methods			
Chemical addition	Emulsified oil	- Effective to break oil-water emulsion	- Requires skilled operators to determine proper chemical addition dosage - Sensitive to influent quality - Produces large sludge and high TDS - Expensive due to chemical addition

Treatment Technology	Compounds Removed	Advantage	Disadvantage
Coagulating by salts	Emulsified oil	- Widely used and effective method - Sulfide can be removed by FeS precipitation (when iron salts used)	- Produces aluminum or iron hydroxide precipitates - Requires pH adjustment
Coagulating by acids	Emulsified oil	- More effective than coagulating salts	- Expensive - Requires neutralization of effluent
Electrical Methods			
Electrocoagulation	Oil, SS, COD, phenol	- Fast particulate removal with high efficiency - Compact reactor size - Relatively low capital/operational cost - Simplicity of operation - Less sludge production - Less manpower requirement	- little full-scale application
Electroflotation	Non Emulsified oil	- Most effective and economical among various flotation methods	- Little full-scale application
BIOLOGICAL TREATMENT			
Conventional Activated Sludge			
Activated Sludge (AS)	COD, Oil, Phenol, SS, NH_4-N	- Inexpensive - Relatively simple operation	- Hard to biodegrade recalcitrant or non-biodegradable constituents

Treatment Technology	Compounds Removed	Advantage	Disadvantage
Attached Growth Systems			
Fixed Film Bioreactors	COD, Oil, Phenol, SS, NH_4-N	- Simple to operate - Higher removal efficiency for biodegradable organics - Stable operation - Tolerance to shock load - Less sludge production - Less energy requirement - Higher oxygen transfer in carriers - Compact reactor size - Effective for low influent substrate load	- Frequent clogging of biofilters - Difficulty in backwashing - Need to develop proper biofilm
RBC	COD, Oil, Phenol, SS, NH_4-N	- Low operating cost - Tolerance of shock and toxic loadings - Simplicity of process control - Low energy requirement	
Three phase airlift loop bioreactor (ALR)	COD, Oil, Phenol, SS, NH_4-N, S^{2-}, TP	- Faster oxygen transfer - Flexibility of operation - Compact size and shorter HRT - Less sludge production - Better pollutants removal efficiency - Allows low strength wastewater treatment - Can control biofilm thickness - Can dilute the influent using treated effluent to provide alkalinity	- very high recycle ratio - high operating cost

Treatment Technology	Compounds Removed	Advantage	Disadvantage
Biosorption with GAC	COD (Refractory organics)	- Can regenerate GAC biologically - Can oxidize non-readily biodegradable organics	
Membrane Bioreactor			
MBR	COD, Oil, Phenol, SS, NH_4-N, S^{2-}, TP, Surfactants	- Can degrade xenobiotic substrates to less toxic material - Requires less nutrient - Less sludge production - Produce almost complete oil-free permeate	
Sequencing Batch Reactor			
SBR	COD, Oil, Phenol, SS, NH_4-N, S^{2-}, TP	- Good oil & COD removal	- May require flow control for continuous wastewater production
Anaerobic Treatment			
Anaerobic Treatment	Oil, COD, Phenol, SS, NH_4-N, S^{2-}, TP	- Lower operating cost - Smaller reactor volume - Production of methane gas that can be used in energy recovery - Less sludge production	- Require longer start-up time to develop proper biomass - Low quality effluent - Odor causing or corrosive gas formation
Lagoon and Wetland			
Lagoon	Oil, phenol, COD, NH_4-N, SS, S^{2-}, TP	- Economic sulfide removal method - Can control formed H_2S odour - Less expensive than AS	- Requires much greater land area - May need to polish effluent from lagoon

Treatment Technology	Compounds Removed	Advantage	Disadvantage
Constructed Wetland	COD, TN, TP, Oil	- operational simplicity - low maintenance requirements - low construction costs - environment friendly system	- Not suitable for 12 month treatment in cold climates
ADVANCED TREATMENTS			
Physical Methods			
Adsorption	COD, phenol	- High removal efficiency	- Rapid phenol breakthrough can occur - Energy-intensive for regeneration
Air Stripping	H_2S, NH_3		- Requires pre- and post pH adjustment and upstream oil removal - Air stream scrubbing is required
Membrane Separation	Oil, SS, COD, phenol, S^{2-}, NH_4-N	- Higher separation efficiency - Obtain high quality permeate - Low operating costs - No chemical additives required - High COD removal efficiency - Compact and easily automated system - Produces high quality permeate	- Requires temperature control to maintain proper oil droplet size - Require high pressure
UF + MD	Oil, TOC, TDS	- Almost complete removal of oil, TOC and TDS	- Low UF permeate flux with high oil content

Treatment Technology	Compounds Removed	Advantage	Disadvantage
Chemical Methods			
Chemical Precipitation by iron ion	S^{2-}	- Relatively simple method to remove sulfide	- Chloride ion residual when ferric chloride ($FeCl_3$) is added - Large sludge production
Ozonation	Oil, COD, phenol, NH_4-N, S^{2-}	- Decomposes recalcitrant chemicals - Can be utilized either before or after biological treatment	- Expensive (high capital & operating cost)
Fenton's reagent	Phenol, S^{2-}	- Reagent is environmentally friendly and safe to handle - Hydrogen peroxide is not harmful	- High cost - Few full-scale applications
Wet Oxidation (WO)	COD	- Can mineralize highly polluted wastewater	- High operating cost - Requires complex safety procedures - Requires high temperature and pressure
Electrical Methods			
Direct Electrooxidation	TOC, COD	- Simple mineralization technology	- Little full-scale experience
Indirect Electrooxidation	TOC, COD	- Can remove toxic or refractory organics	- High energy input - Less current efficiency - Requires supplemental oxidant addition - Forms chlorinated intermediates - Requires complex facility to apply hydrogen peroxide and ozone - Requires high chloride concentration

Table 4.38. Removal Efficiency of Various Refinery Wastewater Treatment Technologies.

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal (%)	Reference
PELIMINARY REMOVAL OF OIL					
API Sperator	oil	30	12	64	Patterson (1985)
	oil	50	8	84	
	oil	100	20	80	
CPI Seperator	oil	150-500	50-86	-	Patterson (1985)
SECONDARY REMOVAL OF DEMULSIFIED OIL					
Physical Methods					
Multimedia Filtration	oil	8	8	0	Patterson (1985)
	oil	35	6	83	
	oil	10	8	20	
	oil	12	12	0	
	oil	18	11	39	
	oil	27	17	37	
Filtration in hydroskimming refinery	oil	90-270	10-43	84-91	Berné and Cordonnier (1995)
Tubular UF	oil		1-9	99.9	Vaughan Jr. et al. (2001)
Tubular UF (Lab-scale)	oil	2,460	<50	97	Reed et al. (1998)
	TSS	645	<25	97	
Adsorption by bentonite organoclay (Lab-scale)	oil	25.7		55	Moazed et al. (2005)

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal (%)	Reference
Chemical Methods					
Ozone + salt (Lab-scale)	Emulsified oil			98 (demulsification)	Song et al. (1998)
Synthsized diethanolamine polyethers + $FeCl_3$ (Lab-scale)	Turbidity	250 NTU		65-66	Hafiz et al. (2005)
Physicochemical Methods					
Coagulation/Gravity sedimentation	Oil	50-100	15	70-85	Patterson (1985)
DAF	Oil	125	13	72	Patterson (1985)
DAF + Alum	Oil	100	10	90	Patterson (1985)
DAF	Oil	154	40	74	Patterson (1985)
DAF + $FeCl_3$	Oil	34	3	95	Patterson (1985)
DAF + Polyelectrolyte	Oil	410	27	93	Patterson (1985)
Biological oxidation pond	Oil	40	18	55	Patterson (1985)
DAF + organic coagulant	Oil	112-160	13-18	84-92	Berné and Cordonnier (1995)
	SS	70-173	17	76-90	
Polymer + DAF (Lab scale)	Oil	2,950	30	99	Reed et al. (1998)
Polymer + MF (Lab-scale)	COD	3,000	108	96.4	Zhong et al. (2003)
	Oil	6,000	8.8	99.9	
Electrical Methods					
Electrocoagulation (Lab-scale)	COD			76	Adhoum and Monser (2004)
	Phenol			91	
Electrocoagulation	PAHs	5.25	N.D.	100	Stephenson et al. (2003)
	Oil	2,350	<2	99.9	

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal (%)	Reference
BIOLOGICAL TREATMENTS					
Attached Growth Systems					
fixed film bioreactor (Pilot-scale)	COD	510		85-90	Jou and Huang (2003)
	Phenol	30		100	
Fixed film bioreactor (Lab-scale)	Phenol	72	4	94	Hsien and Lin (2005)
Modified RBC (Pilot-scale)	COD	234-926	<10	80-88	Tyagi et al. (1993)
	Oil	45-65	5-7	>80	
	Phenol	6.4-88	2-3.2	83-94	
	NH_4-N	23-30	0-4.2	89-99.6	
	SS	64-110	20-26	69-82	
Three phase airlift loop bioreactor (ALR) (Pilot-scale)	Oil	30-55	4-6		Xianling et al. (2005)
	Phenol	10.7-40.6	0.3-0.4	96-99	
	COD	250-613	<100	60-84	
	NH_4-N	56-125	<15	73-88	
	SS	108-159	40-60	44-75	
	S^{2-}	<2.0	0.5-0.7	65-75	
	TP	<0.5	0.2-0.3	40-60	
Three phase fluidized bioreactor (Lab-scale)	COD	5,475	645	88	Sokół and Korpal (2005)
	Phenol	567	0.37	99.9	
Biosoption with GAC (Lab-scale)	COD	110-120	3-25	77-98	Dalmacija et al. (1995)

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal (%)	Reference
Membrane Bioreactor					
MBR (AS + UF) (Lab-scale)	HC	18,307	0.29	99.99	Scholz and Fuchs (2000)
	TOC	22,788	58.3	97.8	
	COD	-	24.3	96.3	
MBR (AS + Membrane) (Pilot-scale)	Oil	18.4	4.4	76.1	Seo et al. (1997)
	COD	1,333	40.8	95.3	
Sequencing Batch Reactor					
Two-Stage SBRs (Lab-scale)	Oil	5,840	N.D.	100.0	Lee et al. (2004)
	COD	3,962	97	97.6	
Anaerobic Treatment					
Denitrification (Lab scale)	NO_3-N			100	Reyes-Avila et al. (2004)
	Sulfide			100	
Upflow fixed-film anaerobic bioreactor (Lab-scale)	Phenol	150		97	Charest et al. (1999)
Lagoon and Wetland					
Lagoon	S^{2-}	100		99	Sublette et al. (1998)
Concstructed Wetland with Subsurface flow (Pilot-scale)	COD			50	Yang and Hu (2005)
	TN			80	
	TP			60	
	Oil		13.6	48	
Concstructed Wetland with Vertical flow (Lab-scale)	NH_3-N	3-20	<3	90	Moreno et al. (2002)

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal (%)	Reference
TERTIARY TREATMENTS					
Physical Methods					
GAC (pilot-scale)	Oil	8.5	7.5	12	Patterson (1985)
	Oil	8.3	7.1	14	
	Oil	6.3	6.0	5	
	Oil	12.0	8.7	28	
	Oil	17.0	13.0	24	
	Oil	12.0	1.8	85	
Adsorption by AC	Phenol	44	0.001	99	Patterson (1985)
Adsorption by AC (Lab-scale)	Phenol	1,000	194	80.6	Eckenfelder Jr. (2000)
Steam stripping	S^{2-}	1,000-10,000	20-100	96-99	Berné and Cordonnier (1995)
Air stripping	S^{2-}	200-500	5-15	90-96	Berné and Cordonnier (1995)
Steam stripping	S^{2-}			90-98	Berné and Cordonnier (1995)
	NH_3-N			92-97	
Membrane (MnO_2 membrane) (Lab-scale)	Turbidity	91	1	99	Cai et al. (2000)
UF + MD (Pilot-scale)	Oil	3.6	0	100	Gryta et al. (2001)
	TOC	4	0.018	99.6	
	TDS	37.9	0.014	99.96	

Treatment Process	Compound	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal (%)	Reference
Chemical Methods					
Oxidation by ozone (Pilot-scale)	Oil	57	8	86	Gunukula and Tittlebaum (2001)
	TPH	56	8	86	
	COD	265	129	51	
Fenton's reagent (Lab-scale)	COD	30,000-45,000	<100	99.5	Sheu and Weng (2000)
Wet oxidation (Lab-scale)	COD	11,000		50	Zerva et al. (2003)
Electrical Methods					
Electrochemical treatment by Ti/TiO_2-RuO_2-IrO_2 anode (Pilot-scale)	COD	602	152	75	Rajkumar and Palanivelu (2004)
	TOC	160	83	48	

* The removal efficiencies are based on full-scale operation unless otherwise specified.

4.3.3. Alternative Treatment Combinations

The wastewater injected into the Northwell under Approval No. 8951 contains a high level of COD and ammonia, 27,366 mg/l and 4,125 mg/l, respectively (see Table 4.21). These levels of contaminants suggest that treatment may not be cost effective (or technically feasible) by established technologies. Additionally, the contaminants that contribute to the COD cannot be inferred based on the data, because the concentrations of the reported constituents that are known to contribute to COD are not sufficient to explain the high COD concentrations. Therefore, a feasibility assessment of the treatment of this wastewater cannot be conducted at this time. However, an assessment can be performed when current and more detailed wastewater characteristics data become available.

The wastewater disposed of to Southwell seems to be treatable, assuming that the parameters shown in Table 4.21 adequately describe its quality. Additionally, the mean monthly injection volume is approximately twice that of the Northwell waste stream, rendering the recovery of the Southwell wastewater more beneficial. In order to treat all identified pollutants (COD, solids, oil and ammonia), a train of treatment technologies needs to be applied. The anticipated treatment train will include preliminary elimination of oil and subsequent removal of the remaining constituents. This approach is generally applied to treat oily wastewater. Evaluation of the suitability of each technology for use as preliminary, main, or tertiary treatment is summarized in Table 4.39.

4.3.3.1. Capability of Physical Treatment Methods

The American Petroleum Institute (API) separator is widely used for free oil removal in refinery plants because it is simple and more economical technique with less fouling problem. But, Corrugated Plate Interceptor (CPI), the other representative free oil separator, has less application in refinery plants and severe fouling problem. Therefore, API is more suitable preliminary treatment than CPI to remove free oil from the wastewater. Floatable suspended solids also can be removed by API.

Filtration is the most common technology to remove particulate matter, and has suggested to be effective for retaining emulsified oil as well. So it can be used as one of the demulsified oil removal techniques in conjunction with proper oil demulsification and coagulation/ flocculation methods. Filtration also can be used as tertiary polishing treatment to reduce particulate levels in the effluent. However, the Advanced Filtration System (AFS) cannot be considered as an appropriate emulsified oil removal technique since little information regarding its full-scale application exists.

Membrane filtration has shown excellent rejection of oil with proper chemical pretreatment such as oil demulsification and flocculation. Thus, it can be used as one of the effective emulsified oil removal methods. Also, membranes can be used effectively as a polishing step. If an appropriate membrane is selected for the tertiary treatment, virtually complete removal of all measured contaminants can be achieved.

Adsorption can reduce oil, COD and phenols from the waste stream. However, when it is applied for emulsified or chemically demulsified oil removal, frequent regeneration of exhausted adsorbents cannot be avoided and results high operating costs. Additionally, the oil removal efficiency is not fully proven yet. Thus, adsorption may not be considered as an applicable method.

Centrifugation is one of the alternative emulsified oil removal techniques. But since it requires frequent and thorough maintenance and entails high energy consumption, it cannot be regarded as a suitable option.

Flotation is the most common technique for emulsified oil removal. Dissolved air flotation (DAF) is more commonly applied in refinery plants than Induced air floatation (IAF) because IAF consumes more energy and produces larger skimming materials. The oil and light suspended solids can be more efficiently floated and skimmed off in DAF with appropriate demulsification and flocculation of emulsified oil.

4.3.3.2. Capability of Chemical Treatment Methods

It is well known that the removal efficiency of emulsified oil significantly increases when coagulating chemicals are added to the oil-water emulsion before a physical separation process. Thus, a coagulation or flocculation process should be utilized before demulsified oil separation using floatation or filtration. The choice of suitable coagulant and flocculant depends on wastewater characteristics and oil-water emulsion condition.

Chemical oxidation and advanced oxidation processes should not be applied as preliminary or main treatment because of high operation cost. In addition, the use as tertiary treatment for ammonia removal also should be avoided because chemical oxidation (mainly breakpoint chlorination) of NH_3 is not a preferred way due to possible chlorinated byproduct formation.

The catalytic wet oxidation is still in the development stage, although it has shown a good potential to mineralize highly polluted wastewater. Most of the cited wet oxidation results are obtained from lab-scale experiments using synthetic wastewater. Therefore, the process needs more development before it is implemented at full-scale (Guo and Al-Dahhan, 2003).

4.3.3.3. Capability of Electrical Treatment Methods

Several electrical processes have been emerged as cost-effective methods for coagulation, floatation, and/or oxidation. Both electrocoagulation and electrofloatation may be more effective and economical methods to remove emulsified oil than are the more widely used chemical or physical treatments. However, since electrical coagulation and flotation are recently developed techniques, little information exists regarding full-scale application. So the utilization of these technologies should be avoided at this stage.

Electrooxidation by either direct or indirect mechanisms is also not well established at full-scale. Although good oxidation capacity for toxic or refractory organics has been demonstrated, many problems remain to be solved before full-scale application. These include the development of economical and effective anodes, and prevention of intermediate toxic material formation.

4.3.3.4. Capability of Biological Treatment Methods

Activated sludge has not been commonly applied for oil refinery wastewater treatment because the waste stream contains extensive toxic or non-biodegradable materials such as phenol and sulfide, and lower BOD contents. Thus, activated sludge should not be used as a main biological method.

Sequencing batch reactors have shown high removal efficiency for COD and oil treatment under optimum operating conditions. If the wastewater is produced continuously or at a variable flow rate, an appropriate flow control system has to be utilized prior to a SBR. With proper flow rate management, a SBR can be an alternative biological treatment.

A number of different reactor schemes have been introduced for attached growth biological treatment systems, such as fixed film bioreactors, modified RBC, three-phase airlift loop bioreactor and biosorption with GAC. Attached growth systems have shown high removal efficiency for refractory and other organics, tolerance of variable influent loadings, low sludge production, and compact reactor size, although some systems require pH control and nutrient addition. Therefore, the attached growth systems can be used as efficient biological treatment, while a subsequent tertiary treatment for residual COD, TSS, and nitrate removal may need to be applied.

A membrane bioreactor is another possible biological method. Since biomass has a relatively long retention time in a MBR, refractory or non-easily biodegradable organics can be biologically decomposed to low levels. The fact that biofilm formation is not required in a MBR is one of the advantages compared to an attached growth system. Hence, a MBR can be a suitable alternative biological treatment method for biodegradable oily wastewater.

Anaerobic treatment is generally most applicable to wastewaters having very high BOD concentrations. Since the refinery wastewater generally have low BOD concentrations, this method should not be considered as an appropriate biological treatment technique, unless a further analysis of the wastewater in question indicates it to have a very high BOD.

A lagoon can be considered as a final polishing treatment. Many full-scale applications of lagoons in Alberta and elsewhere have shown them to be a cost effective biological polishing step provided sufficient land is available. A constructed wetland may not be suitable due to harsh winter conditions.

Table 4.39. Evaluation of the Suitability of Various Technologies for Use as Preliminary, Main, and/or Tertiary Treatment (Approval No. 8951).

Treatment Technology	Compounds Treated	Suitability for use as preliminary treatment	Secondary treatment		Suitability for use as tertiary treatment	Compounds not affected
			Requirement of Pre-treatment	Suitability for use as main-treatment		
PHYSICAL METHODS						
API	Free oil, SS	Yes	-	No	No	COD, NH_4-N
CPI	Free oil, SS	No	-	No	No	COD,NH_4-N
Filtration	Emulsified oil, SS	No	Yes (Coagulation)	Yes	Yes	NH_4-N
Membrane	Oil, SS, COD, NH_4-N	No	Yes (Coagulation)	Yes	Yes	None
Adsorption	Oil, COD	No	-	No	No	NH_4-N
Centrifugation	Emulsified oil, SS	No	-	No	No	COD, NH_4-N
Floatation (DAF)	Emulsified oil, SS	No	Yes (Demulsification)	Yes	No	COD, NH_4-N
Floatation (IAF)	Emulsified oil, SS	No	-	No	No	COD, NH_4-N
CHEMICAL METHODS						
Coagulation/Flocculation	Emulsified oil, SS	Yes	-	No	No	COD, NH_4-N
Chemical Oxidation	Oil, COD, NH_4-N	No	-	No	No	None
Catalytic Wet Oxidation	Oil, COD, NH_4-N	No	-	No	No	None

Treatment Technology	Compounds Treated	Suitability for use as preliminary treatment	Secondary treatment		Suitability for use as tertiary treatment	Compounds not affected
			Requirement of Pre-treatment	Suitability for use as main-treatment		
ELECTRICAL METHODS						
Electrocoagulation	Emulsified oil, SS	No	-	No	No	COD, NH_4-N
Electrofloatation	Emulsified oil, SS	No	-	No	No	COD, NH_4-N
Electrooxidation	Oil, COD, NH_4-N	No	-	No	No	None
BIOLOGICAL METHODS						
Conventional AS	COD, Oil, SS, NH_4-N	No	-	No	No	NO_3^-
SBR	COD, Oil, NH_4-N, SS	No	Yes (Flow control)	Yes	No	NO_3^-
Attached Growth Systems	COD, Oil, NH_4-N, SS	No	Yes (pH adjustment, nutrient addition)	Yes	No	NO_3^-
MBR	COD, Oil, NH_4-N, SS	No	Yes (pH adjustment, nutrient addition)	Yes	No	None
Anaerobic Treatment	COD, Oil, SS	No	-	No	No	NH_4-N
Lagoon	COD, Oil, NH_4-N, SS	No	-	No	Yes	NO_3^-

4.3.3.5. Possible Treatment Combinations

The potentially suitable treatment combinations for removing COD, solids, oil, and ammonia are presented in Figure 4.3. A preliminary equalization system may be required for all treatment combinations. To remove free and emulsified oil from the wastewater primarily, combination of API separator, chemical flocculation, and dissolved air flotation or filtration can be applied. To further purify the wastewater in question by reducing the ammonia concentration, membrane separation or a biological treatment such as MBR, SBR, attached growth system or lagoon can be utilized based on the evaluation of various possible combinations for refinery wastewater treatment.

1)	API Free oil, SS	→	Flocculation Oil, SS	→	DAF Oil, SS	→	Membrane Oil, SS, COD, NH_4-N
2)	API Free oil, SS	→	Flocculation Oil, SS	→	Filtration Oil, SS	→	Membrane Oil, SS, COD, NH_4-N
3)	API Free oil, SS	→	Flocculation Oil, SS	→	DAF Oil, SS	→	MBR Oil, SS, COD, NH_4-N
4)	API Free oil, SS	→	Flocculation Oil, SS	→	Filtration Oil, SS	→	MBR Oil, SS, COD, NH_4-N
5)	API Free oil, SS	→	Flocculation Oil, SS	→	DAF Oil, SS	→	SBR Oil, SS, COD, NH_4-N
6)	API Free oil, SS	→	Flocculation Oil, SS	→	Filtration Oil, SS	→	SBR Oil, SS, COD, NH_4-N
7)	API Free oil, SS	→	Flocculation Oil, SS	→	DAF Oil, SS	→	Attached Growth Oil, SS, COD, NH_4-N
8)	API Free oil, SS	→	Flocculation Oil, SS	→	Filtration Oil, SS	→	Attached Growth Oil, SS, COD, NH_4-N
9)	API Free oil, SS	→	Flocculation Oil, SS	→	DAF Oil, SS	→	Lagoon Oil, SS, COD, NH_4-N
10)	API Free oil, SS	→	Flocculation Oil, SS	→	Filtration Oil, SS	→	Lagoon Oil, SS, COD, NH_4-N

Figure 4.3. Possible Treatment Combinations for the Wastewater Disposed Under Approval number 8951.

4.3.4. Evaluation of Potential Treatment Combinations

Evaluation of possible treatment combinations according to the criteria in section 3.2 (Table 3.2) according to the many factors including technical suitability, reliability of technology and economic feasibility may not have enough power of discrimination because all 10 treatment combinations shown in Figure 4.3 employ API as the preliminary oil removal method followed by chemical coagulation/flocculation. The major differences among the combinations are (1) chemically demulsified oil removal methods either DAF or filtration; and (2) a final polishing step comprising a membrane separation technology, a MBR, a lagoon, or an attached growth biological treatment method.

DAF may be preferred over filtration for the removal of de-emulsified oil, SS and COD, since DAF does not entail the operational problems that may be incurred by filtration systems such as clogging. However, a DAF system may cause volatilization of ammonia from the wastewater, resulting in an air stream that may require further treatment (although the reported ammonia concentration is only 20 mg/l).

The potential polishing steps have been identified as membrane separation, a membrane biological reactor (MBR), a sequencing batch reactor (SBR), an attached growth biological treatment or a lagoon. Each has its own advantages depending on wastewater characteristics and site-specific constraints. If the wastewater contains low BOD (not specified in the waste stream quality report), and treated wastewater is to be reused for in-plant water make-up purposes, membranes may be more suitable than a biological treatment method. However, in cases where BOD contents are moderate to high and the wastewater does not need to be reused directly, a lagoon may be a preferable alternative. Generally, a lagoon is a more economical and simple method compared to other biological methods in cases where sufficient land area can be provided for lagoon construction. Where lagoon construction is not practicable on site, other biological treatment systems can be alternative options in relation to site-specific conditions and/or required effluent quality. Generally, a MBR can produce highly purified water compared to a SBR or an attached growth system that may require a subsequent clarification step.

4.3.4.1. Most Suitable Treatment Combinations

The more promising treatment options for Southwell wastewater are shown in Figure 4.4. The most applicable combination of treatment processes are deemed to be API to remove non-emulsified oil, followed by chemical addition to demulsify and coalesce residual oil (flocculation) prior to treatment in a DAF unit, and finally a membrane separation process to polish the effluent. A filtration step may be substituted for DAF depending on the waste stream properties. Similarly, a lagoon can be the more feasible alternative to membrane treatment if the biodegradable organic content warrants such treatment.

Detailed analyses of wastes currently injected to Southwell are essential in order to select the most appropriate treatment option, since refinery wastewater generally contains a number of different recalcitrant and toxic pollutants along with oil and ammonia. Because these recommendations of feasible treatment options are based on limited information, they should be re-assessed when more detailed current information becomes available. A complete characterization of the waste stream injected to the Northwell is also recommended to allow a treatability assessment.

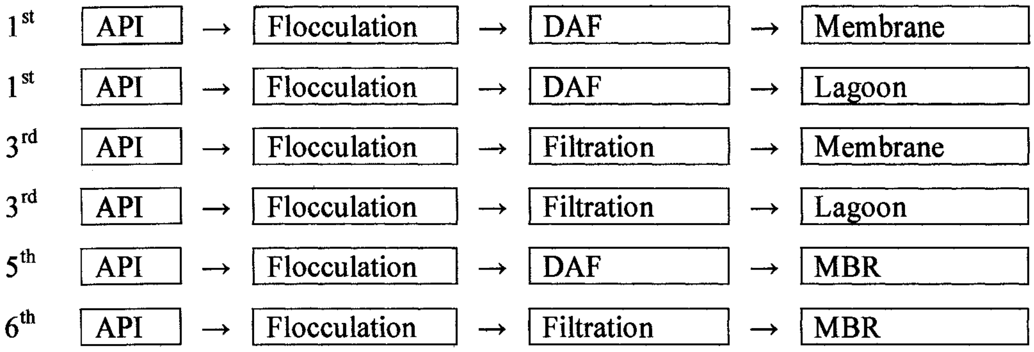


Figure 4.4. Ranked Treatment Alternatives for Wastewater Disposed to the South well Under Approval Number 8951.

4.4. Wastewater Injected Under Approval No. 5737

4.4.1. Wastewater Characteristics

The two wells, named SHELL FTSASK 1-31-55-21 and SHELL FTSASK 8-31-55-21, have been used for the disposal of the wastewater produced from the Shell Canada Scotford Refinery under Approval No. 5737. These wells were classified as category C in the Phase I report, which indicated that recent wastewater analysis data were required in order to evaluate treatment alternatives. The volumes of waste injected into the wells were 35,800 m^3/mon and 36,800 m^3/mon for SHELL FTSASK 1-31-55-21 and SHELL FTSASK 8-31-55-21, respectively.

A report submitted to Alberta Environment (Shell, 1993) indicated that de-oiled water and refinery processed sour water are disposed of into one or the other of the wells (only one well is used at any one time). The injection volumes provided by EUB (2005) indicate mean injection rates of 26,819 m^3/mon for SHELL FTSASK 1-31-55-21, and 20,062 m^3/mon for SHELL FTSASK 8-31-55-21 for the years 2003 to 2005, as shown in Table 4.40. The available waste stream data report only four parameters, oil and grease, TSS, TOC and pH, although wastewater from a refinery generally contains various pollutants. The mean concentrations of the parameters are reported to be 14.3 ppm of oil and grease, 521 ppm of TSS, 57.7 ppm of TOC, and a pH of 9.3. Since the wastewater contains a dilute level of oil and grease and relatively high TSS, the removal technologies will primarily focus on oil and grease, and TSS reduction, with subsequent TOC removal.

4.4.2. Alternative Treatment Technologies

The parameter values shown in Table 4.40 indicate a relatively low level of wastewater pollution, suggesting that the source waste stream is definitely treatable if the reported parameters are the major constituents of the wastewater (sulfur compounds would be expected in a sour water waste stream). The possible treatment technologies for oil and grease and simultaneous TSS removal have been discussed previously in section 4.3.2. Because the waste stream has been "de-oiled" presumably in an API unit, the remaining oil is probably emulsified. Flocculation combined with subsequent demulsified oil separation may be sufficient to deal with the 14.3 ppm of oil and grease, as well as the TSS. Potential technologies for combined demulsified oil and TSS removal are flotation or filtration.

Table 4.40. Wastewater Injected under Approval No. 5737.

<table>
<tr><td rowspan="2">Category & Well Approval #</td><td rowspan="2" colspan="3">Well Name or ID</td><td rowspan="2">WW Source</td><td colspan="2">Injection rate (m^3/mon.)</td></tr>
<tr><td>Phase I Report 1)</td><td>Updated 2)</td></tr>
<tr><td rowspan="2">C 5737</td><td colspan="3">▪ SHELL FTSASK 1-31-55-21</td><td rowspan="2">Shell Canada Scotford Refinery</td><td>35,800
(inaccurate)</td><td>26,819</td></tr>
<tr><td colspan="3">▪ SHELL FTSASK 8-31-55-21</td><td>36,800</td><td>20,062</td></tr>
<tr><td rowspan="2">WW Analysis</td><td colspan="6">Main Contaminants & Level 4)</td></tr>
<tr><td>Name</td><td>Avg.</td><td>Range</td><td>Name</td><td>Avg.</td><td>Range</td></tr>
<tr><td>Phase I Report</td><td colspan="6">Up-to-date contaminants info. Required</td></tr>
<tr><td rowspan="3">Updated 3)</td><td colspan="6">Year : 1988 - 1993</td></tr>
<tr><td>Oil & Grease</td><td>14.3</td><td>7.2-26.9</td><td>TSS</td><td>521</td><td>282-1,109</td></tr>
<tr><td>TOC</td><td>57.7</td><td>10.5-188</td><td>pH</td><td>9.3</td><td>9.0-9.5</td></tr>
</table>

1) Adapted from Chen and Kindzierski (2005)

2) Adapted from EUB (2005)

3) Adapted from Shell (1993)

4) Unit: mg/l except pH

The removal of TOC is principally dependent on the properties of the compounds that contribute to the overall TOC. These could be colloidal or dissolved material that may be biodegradable or non-biodegradable. Because detailed information on TOC causing pollutants and wastewater characterization are not available at this time, part of the TOC is assumed to be removable along with TSS as particulate TOC, and part of the TOC is assumed to be associated with the oil and grease. Hence, the concentration of the remaining TOC may not be very high, and may be biodegraded by a properly acclimatized biomass. An alternative treatment could be provided by membrane separation, however, this process is generally less cost-effective than biological treatment. Adsorption or chemical oxidation may also be used to remove organic constituents in the wastewater, but may not be economical method because adsorption requires periodic regeneration of exhausted adsorbents, and chemical oxidation requires continuous dosing of reagent and may form harmful byproducts. Therefore, to remove the TOC remaining in the waste stream following DAF treatment, membrane separation or a biological method such as a MBR, a SBR, an attached growth system, or a lagoon would be preferable to adsorption or chemical oxidation.

4.4.3. Alternative Treatment Combinations

The possible treatment combinations for the removal of oil and grease, TSS and TOC are shown in Figure 4.5. The oil and suspended solids can be eliminated by flocculation and a subsequent filtration or DAF with proper equalization system prior to the coagulation process. If the wastewater is composed of only measured constituents, the remaining oil, TSS and TOC can be removed by membrane or biological processes such as MBR, SBR, attached growth or lagoon depending on biodegradability of the wastewater. Filtration or floatation alone may be sufficient to remove all three constituents. The pH may need to be neutralized before biological treatment or discharge to receiving waters because the pH of 9.3 exceeds the optimum range for effective biomass activity (6.5 to 8.5).

1)	Flocculation Oil, SS	→	Filtration Oil, SS, TOC		
2)	Flocculation Oil, SS	→	DAF Oil, SS, TOC		
3)	Flocculation Oil, SS	→	Filtration Oil, SS, TOC	→	Membrane Oil, SS, TOC
4)	Flocculation Oil, SS	→	DAF Oil, SS, TOC	→	Membrane Oil, SS, TOC
5)	Flocculation Oil, SS	→	Filtration Oil, SS, TOC	→	MBR Oil, SS, TOC
6)	Flocculation Oil, SS	→	DAF Oil, SS, TOC	→	MBR Oil, SS, TOC
7)	Flocculation Oil, SS	→	Filtration Oil, SS, TOC	→	SBR Oil, SS, TOC
8)	Flocculation Oil, SS	→	DAF Oil, SS, TOC	→	SBR Oil, SS, TOC
9)	Flocculation Oil, SS	→	Filtration Oil, SS, TOC	→	Attached Growth Oil, SS, TOC
10)	Flocculation Oil, SS	→	DAF Oil, SS, TOC	→	Attached Growth Oil, SS, TOC
11)	Flocculation Oil, SS	→	Filtration Oil, SS, TOC	→	Lagoon Oil, SS, TOC
12)	Flocculation Oil, SS	→	DAF Oil, SS, TOC	→	Lagoon Oil, SS, TOC

Figure 4.5. Possible Treatment Combinations for the Wastewater Disposed of Under Approval No. 5737.

4.4.4. Evaluation of Potential Treatment Combinations

The evaluation of possible treatment combinations according to the criteria may not be an effective manner to distinguish more feasible alternative options from less applicable treatment methods due to the similarities of each treatment sequence proposed in Figure 4.5. In comparison to filtration, DAF is generally more efficient to remove TOC, TSS and oil simultaneously, due to the operational problems incurred by filtration such as clogging and frequent backwashing.

If DAF or filtration alone is not adequate to reduce constituent concentrations to the required levels, membrane separation or a lagoon can be applied, depending on the biodegradability of the wastewater, land availability, and further usage of treated wastewater. If the wastewater contains a considerable amount of not readily biodegradable organics (BOD:COD ratio less than 0.3), and/or reuse of the purified wastewater is required within the plant, a membrane process would be the more appropriate alternative (Metcalf & Eddy, 2003). However, if the BOD of the wastewater is high enough and if sufficient land is available, a lagoon is another possible economical and simple option. A MBR may be a suitable alternative for biological treatment if adequate space is not available to construct a lagoon system. A SBR or an attached growth system may be appropriate, but require subsequent solids separation.

4.4.4.1. Most Suitable Treatment Combination

As indicated in Figure 4.6, oil demulsification followed by DAF is the more promising of the alternatives, provided the system can achieve sufficiently low TOC and TSS concentrations. The waste stream pH may have to be adjusted either before or after the DAF process to either aid in oil demulsification or protect the receiving waters, respectively. The alternative option is flocculation and followed by filtration. If effluent polishing is required to reduce TOC and/or TSS a treatment train could be applied that includes oil demulsification, DAF treatment, followed by either a membrane separation or a lagoon. The choice between a membrane separation and a lagoon is principally based on wastewater properties and site-specific conditions.

The final selection of a suitable treatment combination should be decided following a thorough analyses of the waste stream characteristics, of plant's physical and economic status, and of the intended use of the treated water. Because the current evaluation of treatment alternatives is based on limited information, these results should be re-assessed when more detailed current information becomes available.

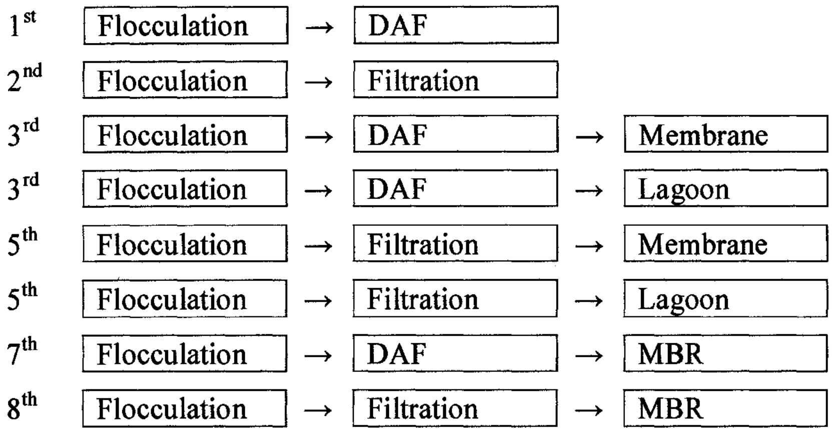


Figure 4.6. Ranked Treatment Alternatives for Wastewater Disposed of Under Approval No. 5737.

4.5. Wastewater Injected Under Approval No. 7842

4.5.1. Wastewater Characteristics

Only one well has been used for the injection of the wastewater produced at AT Plastics Inc. under Approval No. 7842. The well, named AT PLASTICS CHEM IN 14-36-52-24, was classified as category F in the Phase I report. This categorization indicated that disposal volume had to be obtained in order to determine whether a treatability evaluation was required, since the injection records could not be found among the documents used in Phase I project. Updated injection volumes reported in EUB (2005) indicated an average injection rate of 13,490 m^3/mon. This disposal rate was identified as sufficient to warrant evaluation of alternative wastewater treatment methods to retain the water within the active hydrological cycle (Chen and Kindzierski, 2005).

Contaminants including TSS, TDS, BOD, TOC, and various metals, were reported in the injected waste stream in the Phase I report as shown in Table 4.41, even though the date of measurement was not reported. However, updated information indicates that the wastewater is relatively dilute and contains lower levels of constituents than originally reported, as shown in Table 4.42. Nevertheless some parameters measured previously were not included in the most recent report. These include TDS, TOC, Cobalt, Selenium, and Vanadium. According to Stantec (1999) and AT Plastics (2002) the sources of the wastewater injected into the deep well were mainly from treated domestic wastewater, steam condensates, filter backwash, cooling water blowdown, API clean side backwash, process water from polymer equipment, and city water used for once-through cooling.

Table 4.41. Wastewater Injected Under Approval No. 7842.

<table>
<tr><th rowspan="2">Category & Well Approval #</th><th colspan="3" rowspan="2">Well Name or ID</th><th rowspan="2">WW Source</th><th colspan="2">Injection rate (m^3/mon)</th></tr>
<tr><th>Phase I Report1)</th><th>Updated2)</th></tr>
<tr><td>F 7842</td><td colspan="3">AT PLASTICS CHEM IN 14-36-52-24</td><td>AT Plastics Inc.</td><td>-</td><td>13,490</td></tr>
<tr><td rowspan="2">WW Analysis</td><td colspan="6">Main Contaminants & Level4)</td></tr>
<tr><td>Name</td><td>Avg.</td><td>Range</td><td>Name</td><td>Avg.</td><td>Range</td></tr>
<tr><td rowspan="10">Phase I Report</td><td colspan="6">Year : not specified (3 different sampling points)</td></tr>
<tr><td>pH</td><td>7.1</td><td>7.0-7.2</td><td>Chromium</td><td>1.03</td><td>0.72-1.19</td></tr>
<tr><td>TSS</td><td>70</td><td>63-81</td><td>Lead</td><td>0.01</td><td>0.01</td></tr>
<tr><td>TDS</td><td>2636</td><td>2,430-2,838</td><td>Mercury</td><td>0.0001</td><td>0.0001</td></tr>
<tr><td>BOD</td><td>108</td><td>97-126</td><td>Molybdenum</td><td>0.06</td><td>0.018-0.148</td></tr>
<tr><td>TOC</td><td>137</td><td>107-163</td><td>Nickel</td><td>0.01</td><td>0.004-0.017</td></tr>
<tr><td>Total Sulfides</td><td>6</td><td>2.2-11.3</td><td>Selenium</td><td>0.0003</td><td>0.0002-0.0004</td></tr>
<tr><td>Arsenic</td><td>0.0017</td><td>0.0014-0.0019</td><td>Vanadium</td><td>0.022</td><td>0.021-0.023</td></tr>
<tr><td>Cobalt</td><td>0.017</td><td>0.015-0.02</td><td>Zinc</td><td>0.529</td><td>0.424-0.616</td></tr>
<tr><td>Copper</td><td>0.01</td><td>0.01-0.02</td><td></td><td></td><td></td></tr>
<tr><td>Updated 3)</td><td colspan="6">Year : 1999 (Refer to Table 4.42)</td></tr>
</table>

1) Adapted from Chen and Kindzierski (2005)

2) Adapted from EUB (2005)

3) Adapted from Stantec (1999)

4) Unit: mg/l except pH

Table 4.42. Updated Wastewater Characteristics (Approval No. 7842) and the Discharge Limits Regulated by City Sewers Use Bylaw

Parameters1)	WW from API Separator		WW from Sanitary Sewer		City Sewers Use Guidelines (Stantec, 1999)		City Sewers Use Bylaw (City of Edmonton, 2003)	
	Average	Range	Average	Range	Storm Sewer Limits	Sanitary and Combined Sewer Limits	Storm Sewer Limits	Sanitary and Combined Sewer Limits
pH	7.4	7.3-7.6	6.8	6.7-6.9				
TOC	29.7	16-56	7.7	7-8				
BOD5	42	10-96	<2		20	10,000	50	10,000
COD	117	80-190	25	10-40	60	20,000	100	20,000
Oil & Grease	2	1-3	1.3	1-2	15	800	15	800
TSS	11.7	9-15	11	9-12	20	5,000	-	5,000
TKN	1.5	1.2-1.8	3.9	3.7-4.0	-	-	-	500
Chlorine (free)	0		2	1.9-2.1	0.2	5	0.005	5
Cyanide	0.003	0.002-0.004	0.004	0.003-0.004	0.05	2	0.05	2
Fluoride	2.16	2.15-2.17	0.8	0.79-0.86	1.5	10	-	-
Sulfate	149		50.9	49.7-53.0	-	1,500	-	-
Sulfide	1.18	1.1-1.22	0.021	0.011-0.046	-	1	-	3
TP	1.28	1.13-1.55	0.48	0.44-0.54	0.5	200	1	200
Aluminum	0.43	0.38-0.51	0.53	0.26-0.75	-	50	-	-
Arsenic	<0.2		<0.2		0.5	1	0.05	1
Boron	0.06	0.05-0.08	<0.05		-	30	-	-
Cadmium	<0.001		<0.001		0.013	0.1	0.0005	0.1
Chromium	0.01	0.005-0.019	0.031	0.01-0.08	0.02	4	0.089	4
Copper	0.1	0.06-0.18	0.015	0.007-0.025	0.03	1	0.16	1

Parameters[1]	WW from API Separator		WW from Sanitary Sewer		City Sewers Use Guidelines (Stantec, 1999)		City Sewers Use Bylaw (City of Edmonton, 2003)	
	Average	Range	Average	Range	Storm Sewer Limits	Sanitary and Combined Sewer Limits	Storm Sewer Limits	Sanitary and Combined Sewer Limits
Lead	0.006	0.005-0.008	<0.005		0.04	1	0.02	1
Molybdenum	<0.005		<0.005		-	5	-	5
Nickel	0.004	0.002-0.006	0.005	0.003-0.009	-	4	-	4
Silver	<0.005		<0.005		0.001	5	0.001	5
Thallium	<0.05		<0.05		0.01	0.5	0.008	1
Zinc	1.02	0.97-1.05	0.065	0.03-0.099	0.3	2	0.3	2
Mercury	0.0005	0.0002-0.0011	<0.0002		0.001	0.1	0.00013	0.1
Benzene (in ppb)	<0.05		0.9	0.6-1.3	20 (BTEX)	1000 (BTEX)	0.37	50mg/l (HC)
Toluene (in ppb)	<0.5						0.002	-
Ethylbenzene (in ppb)	<0.5		<0.5				0.09	-
Xylene (in ppb)	0.7	0.5-1.0	<0.5				0.5	-
Carbon Tetrachloride (in ppb)	<1		<1		20	200	0.0133	-
Chloroform (in ppb)	<1		5		20	200	0.0018	-
Pentachlorophenols (in ppb)	1.0	0.1-2.9	<0.1		-	200	-	-
Phenols	0.008	0.007-0.009	0.06	0.02-0.13	0.01	1	0.0005	1
Total Volatiles (in ppb)	<100		<100		-	-	-	-
Total Extractables (in ppb)	143	110-180	203	130-270	-	50,000	-	-

[1] Units are mg/l except pH (No Unit) and as specified

4.5.2. Applicable Treatment Alternatives

The approval holder (AT Plastics) has carried out an analysis of the main sources of wastewater disposed of to the deep well in accordance with the terms of the facility's operating approval. The terms principally included efforts for reducing the disposal volume and increasing water reuse within the facility (AT Plastics, 2002). The two major sources of the wastewater directed to the deep well are the process wastewater from the API separator and treated sanitary wastewater. The analytical results for each source, which were determined in 1999, are given in Table 4.42. Because the company has evaluated the feasibility of discharging its wastewater to the municipal sewer system for off-site treatment, the storm sewer limits, and sanitary and combined sewer limits regulated by City of Edmonton's Sewers Use Bylaw (City of Edmonton, 2003) are also presented in the Table 4.42.

Several constituents including BOD_5, COD, fluoride, sulfide, total phosphorous, copper, zinc in the API separator effluent, and free chlorine, total phosphorous, and phenols in treated sanitary wastewater exceed storm sewer discharge limits. However, among the various parameters measured, only the sulfide concentration in the wastewater from API separator, 1.1 to 1.22 mg/l (average 1.18 mg/l), exceeded the City of Edmonton's Sanitary and Combined Sewer Limits in 1999. In the current City of Edmonton' Sewer Use Bylaw (as revised in March, 2003), the storm sewer limits have become more strict while sanitary and combined sewer limits have been relaxed, as shown in Table 4.42. None of the parameter values indicated in Table 4.42 exceeds the sanitary and combined sewer limits. Therefore, the discharge of the wastewater to the municipal sewer system for off-site treatment is an attractive alternative to deep well injection.

The other possible options can be advanced treatments to polish the effluent from API separator and treated sanitary sewer, and eventually to reuse the water. Several treatment technologies can be used for improving final effluent quality such as membrane, adsorption, depth filtration, and evaporation with thorough consideration of economical and site-specific conditions. The company has apparently already conducted a study on applicable treatment options because AT Plastics (2002) stated that amongst the technologies, evaporation was considered to be a feasible option to further purify current wastewater effluent, but the system would increase site energy use and solids disposal problems.

4.5.2.1. Most Suitable Treatment Option

The most effective alternative to deep well disposal of the waste stream in question is to discharge it to the municipal sewer system for treatment at the Gold Bar WWTP, as suggested in the company's water management proposal (AT Plastics, 2002). A follow-up report to the company's water management proposal will be submitted to Alberta Environment by June 30, 2006 (AT Plastics, 2002). This document will be a good source of information regarding alternatives to deep well injection because the company has been continuously evaluating economically and environmentally viable means to decrease deep well disposal volume.

5. RECOMMENDATIONS

5.1. Wells Operated Under Approval Numbers 3924, 8185 and 8926

The volumes of wastes disposed under Approval numbers 3924, 8185, and 8926 are below the minimum 10,000m^3/mon volume established in Phase I as warranting an evaluation of alternative treatment options. The average injection rates from latest available data were 5,981 m^3/mon (Approval number 3924), 4,139 m^3/mon (Approval number 8185), and 22 m^3/mon (Approval number 8926). Additionally, the wastewaters injected under Approval numbers 8185 and 8926 are too highly contaminated to be treated cost-effectively. Thus, the wastewaters injected into these wells are not deemed feasible for treatment.

5.2. Wells Operated Under Approval Numbers 8713 and 9699

No information regarding the wastewater characteristics could be obtained for wells operated under Approval numbers 8713 and 9699. Therefore, the provision of updated information regarding these injected waste streams, shown in Table 5.1, is required to evaluate the suitability of these streams for treatment.

5.3. Wells Operated Under Approval Number 8784

The wastewater characteristics and injection volumes available for the wells operated under approval number 8784 are outdated (1984-1985). No recent data could be obtained during the current project. Therefore, recent data are required (as shown in Table 5.1) before a treatability evaluation conduct can be carried out.

5.4. Wells Operated Under Approval Number 4779

The wastewaters injected into the wells operated under approval number 4779 were found to warrant further study, as a number of potential treatment technologies were identified for these waste streams. Based on the updated waste analysis data, the potentially applicable treatment technologies are given in Figure 5.1. All treatment combinations may require flow equalization at the beginning of treatment trains if the wastewater production is intermittent or fluctuated. The most promising of the alternative treatment combination is the biofilter followed by NF or RO membrane separation.

Bench-scale treatability testing is recommended for these wastewaters. It is recommended that a meeting be held between representatives of Alberta Environment, the holder of Approval No. 4779 (Agrium) and the contractor who would undertake the treatability testing, to plan the project and discuss site-specific constraints and opportunities such as existing treatment facilities, space availability, and the intended use of treated water.

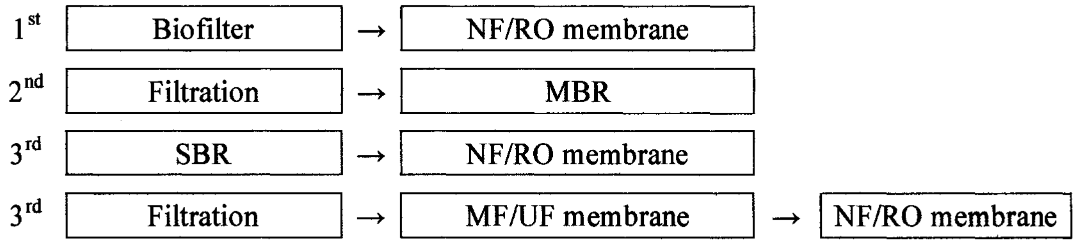


Figure 5.1. Ranked Treatment Alternatives for the Wastewater Injected Under Approval Number 4779.

5.5. Wells Operated Under Approval Number 8951

A complete characterization of the waste streams injected to the two wells (South and North wells) operated under approval number 8951 is required, as indicated in Table 5.1 to confirm or modify the recommendations of the current study. Using the most recent data available, which is more than 10 years old, the waste stream injected to the North well is not suitable for reclamation due to its high levels of contamination. The following treatment is believed to be appropriate for the wastewater injected to the South well (see Figure 5.2): equalization (if required), oil separation and solids sedimentation in an American Petroleum Institute (API) separator followed by chemical treatment to demulsify oil and subsequent removal in a dissolved air flotation (DAF) unit (if necessary) and final effluent polishing using membrane separation or a lagoon.

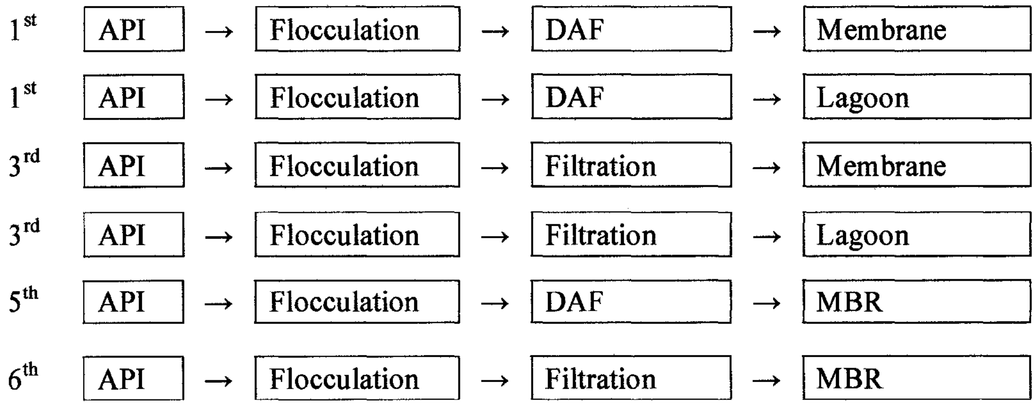
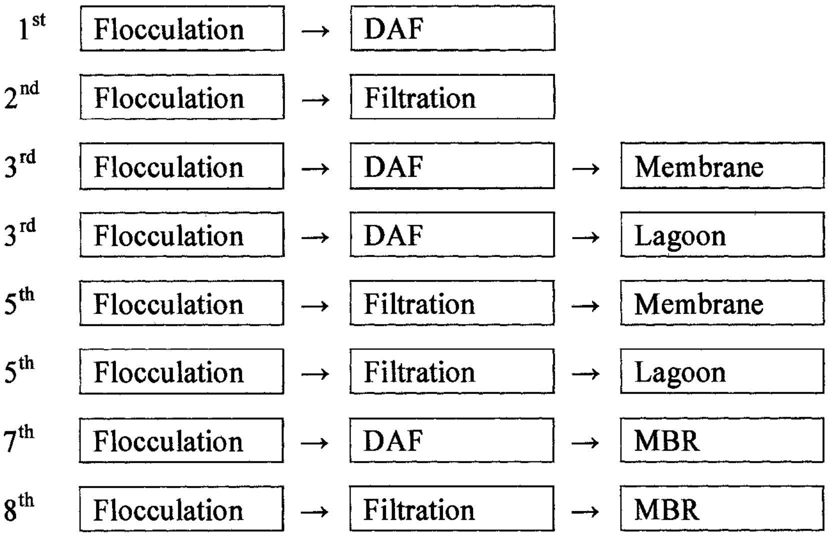


Figure 5.2. Ranking of Treatment Alternatives Identified for Wastewater Disposed to the South well under Approval Number 8951.

5.6. Wells Operated Under Approval Number 5737

The information obtained during the current study for the wells operated under approval number 5737 covers the period from 1988 to 1993 and specifies only four parameters. A preliminary assessment, based on this information indicates the most feasible treatment option would be equalization (as required) chemical coagulation and flocculation of the wastewater followed by dissolved air floatation (DAF), as shown in Figure 5.3. However, because of the lack of proper updated data at this time, the recommendations should be reviewed when current and complete data (as indicated in Table 5.1) become available.



1st Flocculation → DAF
2nd Flocculation → Filtration
3rd Flocculation → DAF → Membrane
3rd Flocculation → DAF → Lagoon
5th Flocculation → Filtration → Membrane
5th Flocculation → Filtration → Lagoon
7th Flocculation → DAF → MBR
8th Flocculation → Filtration → MBR

Figure 5.3. Ranked Treatment Alternatives Identified for Wastewater Disposed Under Approval No. 5737.

5.7. Wells Operated Under Approval Number 7842

The most effective alternative to deep well disposal of the waste streams injected into the wells operated under approval number 7842 appears to be discharge to the municipal sewer system for treatment at the Gold Bar WWTP (Wastewater Treatment Plant). The concentrations of all of the contaminants in the wastewater appear to conform to the requirements of The City of Edmonton's Sewers Use Bylaw. The company will submit a follow-up report to its water management proposal to Alberta Environment in June 2006. This follow-up report will be a good reference for the alternatives to deep well disposal of wastewater from AT Plastics.

Table 5.1. Required Updated Information

Items	Description
Source of each waste stream	- Industrial process or operation
Existing wastewater treatment system	- Wastewater treatment facilities operated in the plant
Required treated wastewater quality or the usage of treated wastewater	- In case of reusing the water in the plant
Feasibility evaluation report on deep well disposed wastewater	- If already exists
Physical analysis data	- Conductivity - Total dissolved solids - Total suspended solids - Temperature
Chemical analysis data	- pH - Nitrogen parameters (NH_4^+, org N, TKN, NO_2^-, NO_3^-, TN) - Phosphorous parameters (Inorganic P, TP, Organic P) - Hardness (as $CaCO_3$) - Metals (total and dissolved) if applicable - Major ions (Cl^-, PO_4^{3-}, SO_4^{2-}) - Biochemical oxygen demand ($CBOD_5$, UBOD) - Chemical oxygen demand (COD) - Nitrogenous oxygen demand (NOD) - Total organic carbon (TOC) - Oil and grease
Biological analysis data	- Biological organisms if applicable

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