BIRZEIT UNIVERSITY
Faculty of Graduate Studies

Water and Environmental Engineering Master Program

An Innovative Reactor for Biological Treatment of Nitrate-Rich Groundwater Using Whey

مفاعل خلاق لمعالجة حيويه لمياه جوفيه غنيه بالنترات باستخدام شرش اللبن

Prepared By:
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March, 2016

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This thesis was submitted in partial fulfillment of the requirements for the Master's Degree in Water and Environmental Engineering from the Faculty of Graduate Studies, at Birzeit University, Palestine.

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The findings, interpretations and conclusions expressed in this study do not necessarily express the views of Birzeit University, the views of the individual members of the M.Sc. Committee or views of their respective employers.

Date of Defense: 11/4/2016

Dedication

To my beloved parents for their guidance and unconditional giving of their lives for our success,
To my dearest wife, for her endless love and encouragement,
To Ghassan whom I'll be always struggling to make future a better place for him,
To My friends for their support,
To Dr. Rashed Al-Sae'd for his guidance and continuous support,
To all who taught me, to IWES team,
And finally to the Palestinian great martyrs and prisoners, the symbol of sacrifice.

I DEDICATE THIS RESEARCH.

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Last but not the least, I would like to thank my family: my parents, for their love at the first place and supporting me throughout my life.

Abstract

Groundwater is considered as the main source of water supply for drinking, irrigation and municipal uses in Palestine. Recent publications revealed that most of groundwater wells in the Gaza Strip are contaminated with high nitrate concentrations, and unfit for potable and agricultural uses.

The nitrate in groundwater with high concentrations is mainly resulted from point sources such as sewage disposal systems and livestock facilities, and from nonpoint sources such as fertilized lands, and gardens, or from naturally occurring sources of nitrogen. Groundwater contamination by excessive nitrate poses significant public health problems and have caused those shutdown of ground wells as a main water sources.

The objective of this study is to evaluate and examine the feasibility of biological denitrification process to treat or reduce the nitrate-rich in groundwater using whey as an external carbon sources. Whey, a dairy waste product, will be added to the bioreactor to provide an external carbon source for heterotrophic denitrifiers.

To achieve the main objective, a lab-scale bioreactor was designed, assembled and run in both batch and continuous modes. Operational results using batch tests revealed an optimum COD/NO_3^--N ratio of 7.2 with a maximum specific denitrification rate of 14.61 (mg NO_3^--N/gMLSS.hr). This C/N ratio was used to evaluate the performance of the system in continuous mode to obtain all the required operational parameters. Different influent nitrate-nitrogen concentrations were used in the study with different nitrate-nitrogen loading to study the effect of hydraulic retention time (HRT), nitrate loading, mixed liquor suspended solids effects on the nitrate removal efficiency in additional to the reactor removal capacity. Physical, chemical and biological parameters were determined according to the American Public Health Standards Association (APHA).

The maximum denitrification efficiency was achieved and became constant at 5 hours HRT for different nitrate influent concentrations.

Further treatment for the effluent is needed to reduce turbidity, bacterial numbers, and to increase the dissolved oxygen concentration in the effluent to comply with local drinking water quality standards.

الملخص

تعتبر المياه الجوفية المصدر الرئيسي لمياه الشرب والزراعة واستخدام البلديات في فلسطين. المنشورات والدراسات الحديثة أظهرت ان معظم الابار الجوفية في قطاع غزة المحتل ملوثة بتراكيز عالية غير مقبولة من النترات وغير صالحة للشرب او للري.

التركيز العالي للنترات في الابار الجوفية ناتج عن المصادر الثابتة مثل أنظمة التخلص من مياه الصرف الصحي , ومزارع الماشية، من المصادر غير المحددة مثل الأراضي المخصبة، والحدائق، أو من مصادر النيتروجين التي تحدث بشكل طبيعي. تلوث المياه الجوفية بالنترات بتركيز عال يشكل مشكلة صحية عامة كبيرة وتسببت زيادة تركيز النترات في المياه الجوفية اغلاق العديد من الآبار باعتبارها مصادر المياه الرئيسية.

الهدف من هذه الدراسة هو تقييم جدوى عملية نزع النتروجين من خلال بكتيرية عضوية التغذية لمعالجة المياه الجوفية الغنية بالنترات باستخدام مصل اللبن باعتبارها مصدر خارجي للكربون الخارجية. مصل اللبن، يعتبر من مخلفات مصانع الألبان والأجبان والناتجة من عملية التصنيع، ستضاف إلى المفاعل لتوفير مصدر الكربون الخارجي للبكتيريا عضوية التغذية.

في هذه الدراسة، تم اختيار تم تصميم وبناء وتشغيل مفاعل بيولوجي والذي تم تفعيل العمل به بطريقتين، التغذية دفعة واحدة والتغذية بوضع مستمر. وقد تم الانتهاء من الدراسات المختبرية لهذه العمليات البيولوجية. تم تقييم جدوى النظام في ظل ظروف نقص الأكسجين وقد وجد ان قيمة COD/NO_3^-N باستخدام التغذية دفعة واحدة دفعة 7.2 وقد كان معدل نزع النترات الأعلى عن تلك النقطة 14.61 (mg NO_3^-N/gMLSS.hr) . هذه النتيجة تم استخدامها في التغذية المستمرة لفحص المتغيرات المطلوبة.

استخدمت تراكيز مختلفة لنترات النيتروجين في هذه الدراسة من اجل دراسة تأثير وقت الإحتفاظ الهيدروليكي، واثر تحميل النترات، واثار اختلاف تركيز المواد الصلبة المعلقة على كفاءة عمل المفاعل لإزالة النترات من المياه الملوثة. المعايير الفيزيائية والبيولوجية المختلفة تم احتسابها بالإعتماد على معايير جمعية معايير الصحة العامة الأمريكية.

اعلى كفائة لإزالة النترات تم تحقيقها عند HRT 5 ساعات لتراكيز مختلفة من النترات للمياه الداخلة.

هناك حاجة إلى معالجة لاحقة للملوثات في السيب المعالج للحد من درجة العكورة، وعدد البكتيريا، ومن اجل زيادة تركيز الأكسيجين الذائب في المياه المعالجة لتتوافق مع مواصفات منظمة الصحة العالمية لمياه الشرب. من العلاج للنفايات السائلة للحد من التعكر، وأرقام البكتيرية، وزيادة تركيز الأكسجين الذائب في مياه الصرف الامتثال لجودة مياه الشرب.

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List of Abbreviations

APHA	American Public Health Association
BCR	Benefit- Cost Ratio
BZU	Birzeit University
C:N	Carbon to Nitrogen Ratio
CFU	Colony Forming Unit
COD	Chemical Oxygen Demand
CR	Chemical Reduction
CSTR	Completely Stirred Tank Reactor
DO	Dissolved Oxygen
ED	Electrodialysis
EDR	Electrodialysis Reversal
HRT	Hydraulic Retention Time
IX	Ion Exchange
MLSS	Mixed Liqueur Suspended Solids
MLVS	Mixed Liqueur Volatile Solids
NO_3^-	Nitrate
NO_3^--N	Nitrate-Nitrogen
OLR	Organic Loading Rate
PCBS	Palestinian Central Bureau of Statistics
PSI	Palestinian Standard Institution
PWA	Palestinian Water Authority
RO	Reverse Osmoses
TAB	Total Annual Benefits
TKN	Total Kjeldahl Nitrogen
TS	Total Solids
TSS	Total Suspended Solids
TVS	Total Volatile Solids
WHO	World Health Organization

1. CHAPTER ONE INTRODUCTION

1.1 OVERVIEW

Groundwater is considered as the main source of water supply for drinking, irrigation and municipal uses in Palestine. Similar to the West Bank, there are hundreds of municipal and private wells in the Gaza Strip that supply groundwater to major cities and refugee camps. However, groundwater aquifers in the Gaza Strip are highly vulnerable to natural (salt intrusion) and man-made (wastewater), induced environmental pollution due to sand and gravel soil types (Shomar, 2006). One of the most critical chemical pollutants in drinking water is nitrate (NO_3^-). High concentration of nitrate in groundwater resulted from point sources such as sewage disposal systems and livestock facilities, from nonpoint sources such as fertilized lands, and gardens, or from naturally occurring sources of nitrogen (Alawneh and Al-Sa'ed, 1997).

During 2001-2007, Shomar *et al.* (2008) examined the levels and sources of nitrate in groundwater wells of Gaza Strip, they discovered that almost 90% of groundwater wells exceeded the acceptable nitrate concentration limit 11.3 mg NO_3^--N/L (nitrate-nitrogen) for drinking water set by the WHO (WHO, 2011). The local confirmation suggested that wastewater infiltration from domestic cesspits, agricultural practices, raw and partially treated wastewater are the major sources of the NO_3^- in groundwater (Shomar *et al.,* 2008).

According to WHO (2006), if nitrite is absorbed in the blood, then, the hemoglobin is converted to methemoglobin which does not carry oxygen efficiently. This results in a reduced oxygen supply to vital tissues such as the brain. Methemoglobin in new babies' blood cannot return back to hemoglobin in contrary to adults. Severe methemoglobinemia can result in brain damage and death.

$$\underset{\text{(Can Combine with oxygen)}}{\text{Hemoglobin } (Fe^{2+})} \xrightarrow{NO_3^-} \underset{\text{(Cannot Combine with oxygen)}}{\text{Methemoglobin}}$$

Though the latest WHO guidelines for drinking water set a maximum limit for nitrate, 50mg/l as nitrate (WHO, 2011).

Ion exchange, reverse osmosis and biological denitrification are the main processes now in use for the removal of nitrate from nitrate laden water and wastewater (Matejuet *et al.*, 1992). There is no specific nitrate removal system in operation neither in the Gaza Strip nor in the West Bank as a part of municipal drinking water treatment (PWA, 2015). In the past, only one project proposal on nitrate removal from domestic wells in Gaza strip has been identified (Al-Sa`ed, *et al.*, 2000). However, due to non-technical reasons it was not performed. Biological denitrification process has not yet been introduced to the water treatment field in Palestine. Therefore, water treatment technologies that are cost effective, sustainable, ease of operation, maintenance and repair with locally available materials are required.

Since nitrate contaminated groundwater in Gaza Strip has relatively low organic carbon contents as most of the groundwater in the world, in situ heterotrophic denitrification is not effective (Della Rocca et al., 2007). Therefore, the availability of low-cost organic carbon sources is a limiting factor for effective remediation systems using the biological denitrification process. Researchers have studied the biological denitrification process as the most promising and versatile approach for nitrate removal from water and wastewater. Biological denitrification is highly selective for nitrate removal. In recent years, heterotrophic denitrification of drinking water has been applied using numerous liquid and solid organic substrates including ethanol, acetic acid, methane, sugars, straw and cotton (Ghafari et al., 2008). On the other hand, autotrophic denitrification (Soares, 2000) has been investigated using variable ratios of sulfate and limestone at lab-scale system with moderate success. Since groundwater has low carbon source, an external source should be provided to the heterotrophic denitrifiers in order to proceed uninhibited. Whey, a semisolid waste product in the dairy industry, has been successfully used as a substrate for generation of bioelectricity in microbial fuel cell (Nasirahmadi and Safekordi, 2011). Soares, *et al.,* (2004) developed an innovative and low cost bio-treatment technology for nitrate

polluted groundwater, however, this has never been achieved as of political and financial issues. Also, higher biomass content in the treated water with possible disinfectant by-products has been reported.

Therefore it is proposed to investigate the performance of a biological denitrification system to treat high-nitrate waters and compare its performance with well- established systems such as reverse osmosis. Different whey/nitrate ratios will be investigated using an experimental study at lab-scale level to define the optimal C:N ratio for the nitrate removal.

The donor countries are interested much more in exporting high-tech instrumentation including desalination systems, rather supporting local efforts in remediating nitrate contaminated water resources. Thus, whey will be used in this research study as low-cost external carbon source for the denitrifying bacteria in the bioreactor to reduce nitrate content in groundwater.

Whey is a liquid waste remains after the production of cheese, labneh, cottage, and other dairy products, and its categorized into; sweet whey which is produced from manufacturing the cheese curd, cheddar and mozzarella, while the other type is the acid whey which is produced during the production of labneh, fresh cheese, cottage and other products (Mustafa et al., 2014).

The used whey in this study is the acid whey from Al-Pinar dairy factory after the production of the labneh.

1.2 RESEARCH QUESTIONS AND MAIN GOAL

The main questions of the study are as follows:

- What is the impact of process design parameters [HRT, loading rates] on the effectiveness of nitrate removal from groundwater?
- Can the developed bioreactor be applied for domestic and agricultural wells?

- What are the types of post-treatment units needed for biologically safe and potable water quality?
- What are the estimated capital and operational costs of nitrate removal considering post treatment units (filtration and disinfection units)?

Finally, the cost analysis will include a comparative financial analysis pertinent to other advanced water treatment technologies as desalination process [RO] and Ion Exchange.

1.3 SPECIFIC OBJECTIVES

This research study aims at bioremediation of nitrate-rich groundwater to increase the availability and improve water quality of available water resources in Palestine. The specific objectives to evaluate the feasibility of heterotrophic denitrification process to remediate nitrate-rich groundwater using whey as an external carbon sources by answering the research questions. *Whey, a dairy waste product, will be added to reactors to provide an external carbon source for heterotrophic denitrifiers.*

1.4 EXPECTED RESULTS

Expected outputs from this applied research include provision of a low-cost biological treatment of nitrate while using whey as a carbon source. Results can be used by the water utilities and industrial sector to trial full-scale denitrification systems as a local low-cost technology. Full-scale systems shall aim at ensuring feasible nitrate removal from groundwater with treated water complying with drinking water standards or suitable for agricultural irrigation.

1.5 RESEARCH APPROACH

Denitrification experiments in a slurry bioreactor (batch and continuous flow modes) using nitrate and whey were performed to determine optimum design and operational conditions for the bioremediation of amended nitrate-rich groundwater.

To achieve this objective, the following research methodology is planned:

- Design of the reactor

The research study entails building a bench-scale bioreactor, as follows:

- Fabrication from an acrylic plastic reactor with working volumes of 12 L.
- Variable Speed mixer will be installed to provide mixing, and to keep all the culture inside the reactor in suspended mode and to achieve a dissolved oxygen concentration of zero during anoxic period, also nitrogen will be provided by a nitrogen tank with a regulator from time to time;
- Use of peristaltic pumps with digital regulator to control the hydraulic retention time and organic loading rates for feeding for feeding to the bioreactor.

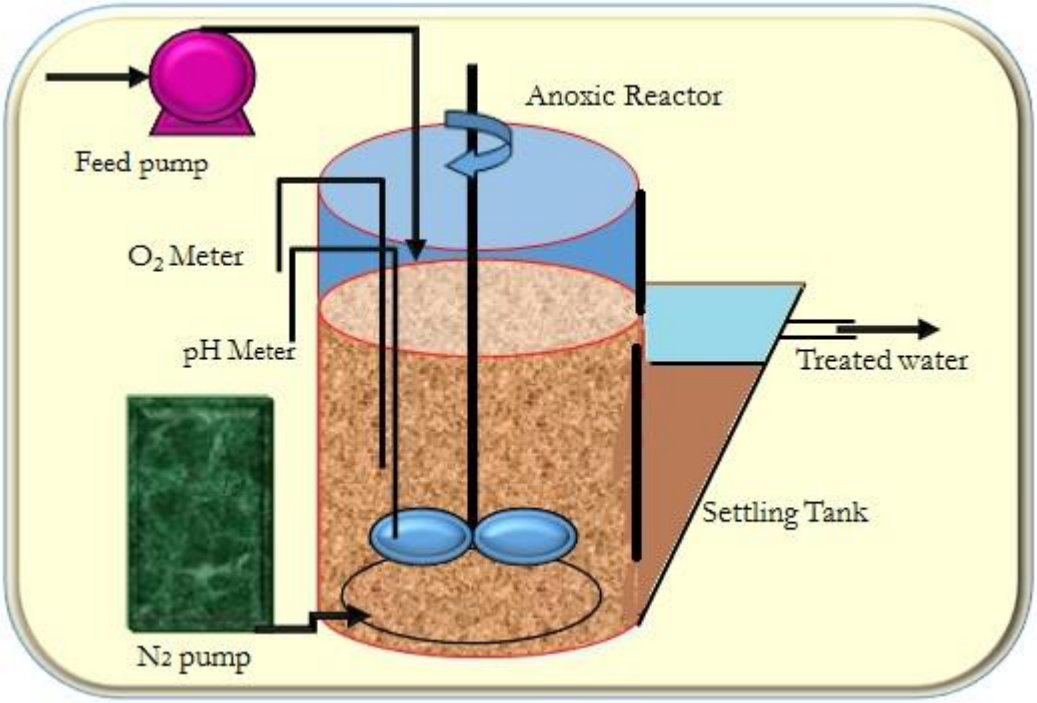

Figure 1.1: Schematic diagram of the bench-scale denitrification reactor

- Operation and process monitoring

  - Run the denitrification reactors using variable nitrate and carbon concentrations at ambient temperature (20-25 ^{o}C), this will give different volumetric and sludge loading rates. The denitrification reactors will be seeded with activated sludge from anoxic zone of Al-Teereh MBR system, a large scale advanced wastewater treatment plant.
  - A bench-scale anoxic reactor with working volume of 12 Liters will be used. Mixing will be maintained in the anoxic reactor by using variable speed mixer and by supplying nitrogen gas from time to time. Controlled concentration of nitrate will be added to the influent water. The study will deal with several nitrate concentrations (20, 50,100, and 200 mg/l $NO3^{-}$-N) with COD/$NO3^{-}$-N ratio of 1, 2, 3, 5, 7, 10.
  - Research results including nitrate concentration, carbon concentration, pH, DO (i.e., to examine the anoxic conditions), nitrite, nitrate, colony forming units (CFU), and total suspended solids (TSS) will be analyzed and documented.
  - The results will be collected, analyzed and discussed in the final thesis report.

1.4 THESIS OUTLINE

1. Chapter One introduces the problem and the major goals and research questions, also it shows the specific objectives, research approach and expected results from the study.
2. Chapter Two discusses briefly the literature review; Nitrate Removal in general and in Groundwater in particular, different types of treatment plants, Biological Denitrification, Attached and Suspended growth of Bacteria in Biological Denitrification.
3. Chapter Three illustrates the materials and methodology applied and used in the thesis.
4. Through chapter Four results will be discussed and analyzed.
5. Chapter Five gives an example for a financial analysis for a proposed large scale nitrate removal treatment plant.
6. Finally Chapter Six will show the conclusions, recommendations, and future work.

2. CHAPTER TWO
LITERATURE REVIEW

This chapter reviews the literature on Nitrate Removal from Groundwater including different types of treatment technologies, biological Denitrification, growth of bacteria in biological denitrification and other technologies.

2.1 Introduction

Nitrate contamination in groundwater resources originates mainly from uncontrolled land discharges of treated and untreated wastewater and the excessive use of fertilizers. This can cause potential health hazards to infants and pregnant women (Cynthia et al. 2002), thus limiting the direct use of the groundwater resources for the human consumption in many places of the world.

The World Health Organization has set a limit of 11.3 mg/l $NO3^-$-N for human consumption and 100 mg/l $NO3^-$-N for animals (WHO, 2011).

The contamination of groundwater with nitrate can occur if the added concentrations of nitrate into soil exceeds denitrification and the plants consumption , and so, it will infiltrate into the groundwater (McClain et al. 1994).

Groundwater denitrification is the process of removing or reducing the nitrate concentration in the groundwater using several methods and technologies, and it could be applied in situ or ex situ (Della Rocca et al. 2007).

Wide range of biological processes with different carbon sources and several applied technologies and process, in addition to the biological treatment a physical and chemical processes were also applied, such as the reverse osmosis (RO), ion exchange (IX), and chemical reduction denitrification processes, are being developed for the nitrate removal from drinking water all over the world (Tabash, 2013).

2.2 Contaminated groundwater in Gaza Strip-Palestine

The Gaza Strip is a narrow area lying along the southwestern portion of the Palestinian coastal plains; its area is about 365 km^2. The density of the population in the Gaza Strip is considered to be the highest in the world, with a population of 1.6 million people and a

growth rate of 3.5% annually (PCBS, 2010). The annual precipitation ranges from 230 mm in the south to 410 mm in the north (Aish et al. 2008).

The Gaza Strip aquifer is an extension of the Mediterranean coastal aquifer, and it extends from Askalan in the north to Rafah in the south, and from the seashore to 10 km inland (Fink, 1970). The aquifer is composed of different layers of dune sandstone, silt clays and loams appearing as lenses, which begin at the coast and feather out to about 5 km from the sea, separating the aquifer into major upper and deep sub-aquifers. The aquifer is built upon the marine marly clay (Saqiye group) from the Neocene (Fink, 1970).

Groundwater is considered as the only valuable resources of drinking water for the people In the Gaza Strip (Shomar, 2006), where more than four thousands wells are exploited from the aquifer (Shomar et al., 2010). As a result of its intensive exploitation, the aquifer has been experiencing seawater intrusion in many locations in the Gaza Strip mainly in Rafah Area, Khan Younis, North area, middle area and Gaza city (Shomar et al., 2008). In addition to the un even distribution of fresh in Gaza, the over-abstraction of the groundwater causes the intrusion of seawater and increases the salinity (Shomar, 2006).

The profile of the soil of Gaza which contains sands and gravel is considered high permeable which leads to groundwater aquifer contamination from the ground surface (Shomar et al., 2005).

Some studies have reported the high levels of nitrate in GAZA groundwater as one of the important worries among the decision makers (Shomar et al., 2008), while no scientific evaluation of the nitrate sources was included in a scientific evaluation nor their effects on the health of the people in Gaza (Maila et al. 2004).

The results of the groundwater depth and nitrate concentrations, after seven years of studying and monitoring, are given according to Shomar et al. (2008) and presented in Table 2.1, where the tabulated results ranged between 30 to 450 mg /l as nitrate, and it was found that about 90% of the wells that were sampled had high levels of nitrate exceeds the WHO guidelines while the rest are at the point of below the guidelines limit.

Table 2-1: Nitrate Concentration in Gaza Wells. (Shomar et al. 2008)

No.	Area	Well ID	Purpose	Depth (m)	NO_3^- (mg/l)
1	North area	A/185	Municipal	90	96
2		D/2	Municipal	54	255
3		E/10	Municipal	90	155
4		E/11b	Municipal	93	26
5		A-19	Private	95	130
6	Gaza area	E-142	Municipal	55	101
7		E/4	Municipal	60	85
8		R/162w	Municipal	100	218
9		R/162c	Municipal	110	147
10		Q/68	Municipal	55	47
11		R/162h	Municipal	100	215
12		R/162ha	Municipal	95	177
13		R/254	Municipal	72	56
14		R/75	Municipal	80	130
15		F/203	Municipal	52	43
16	Middle area	FI/85	Private	50	146
17		FI/87	Private	65	136
18	Khan Younis area	L/87	Municipal	90	358
19		Unknown	Municipal	90	55
20		L/43	Municipal	90	428
21		L/41	Municipal	105	212
22		L/179 a	Municipal	110	92
23		L/127	Municipal	120	397
24		Unknown	Municipal	75	104
25		L/190	Municipal	95	112
26		Unknown	Municipal	78	134
27		M/11	Municipal	70	82
28		L/181	Municipal	67	60
29		P/146	Municipal	90	59
30		Unknown	Private	95	245
31		Unknown	Private	85	201
32		Unknown	Private	100	59
33		Unknown	Private	90	429
34		LI/12	Municipal	80	422
35		L/159a	Municipal	72	380
36		L/127	Municipal	83	434
37		L/43	Municipal	89	445
38		L/87	Municipal	90	370
39	Rafah area	P/10	Municipal	100	147
40		P/145	Municipal	90	258
41		P/138	Municipal	85	127
42		P/15	Municipal	82	201
43		P/148	Municipal	90	110
44		P/147	Municipal	90	35
Unknown: new or private well with no official number.					

Because of the potential for nitrate in groundwater to cause methemoglobinemia in babies younger than six months of age, they should not drink that water or any formula made by it and exceeds the WHO nitrate limits (Cynthia, *et al.*, 2002).

A descriptive study of the Gaza Strip, was carried out for 3 years in 2002, to determine the factors related with high methaemoglobin levels in infants and the relationship with nitrate concentration in drinking water wells, and it was found that drinking water sources were likely to be the main factor for high levels of methaemoglobin (Abu Naser et al., 2007) .

According to the annual report by the ministry of health in 2011, out of 338 infants attending for vaccination, having supplemental feeding, use of boiled water and age 3-6 months were associated with high methaemoglobin levels, where the highest mean methaemoglobin level was in Khan-Younis area, where the highest mean nitrate concentration was recorded in drinking water (Ministry of Health, 2001).

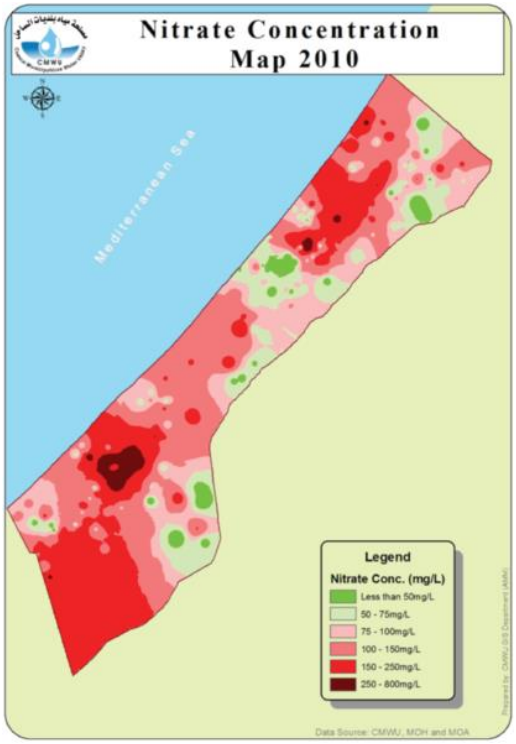

Figure 2.1: GIS Map for the Nitrate Concentrations in the groundwater of the Gaza Strip (Shomar et al., 2010)

Al-Khatib and Arafat (2009) studied the chemical and microbiological quality of desalinated water, groundwater and rain-fed cisterns in the Gaza strip, Palestine, through this study they aimed to evaluate the physiochemical and microbiological quality of the

domestic water through one-year long surveillance in Gaza Strip, where high percentage of water samples from all sources exceeded the limits of the Palestinian Standard Institution (PSI) and the World Health Organization (WHO) for nitrate.

Several sources are suspected of causing water pollution in the Gaza Strip, Palestine. These primarily include wastewater, overuse of fertilizers and agricultural pesticides, and solid waste that might produce toxic substance, like nitrate (Almasri, 2008).

In Identification of nitrate sources in groundwater and potential impact on drinking water in Goczałkowice reservoir, Poland, it was found that nitrogen compounds are the main threat to groundwater quality, and the main sources of NO_3^- are manure/septic waste and agriculture. Also, it was concluded that NO_3^- contaminated groundwater does not impact on surface water quality (Czekaj et al., 2015).

The changes in groundwater salinity and nitrate concentrations due to aquifer recharge by treated wastewater taking Korba as a case study was analyzed and monitored by Ayni et al. (2013), The monitoring of water quality progress of the Korba aquifer during 3 years of recharging operations using infiltration basins since its establishment in 2008 until 2011 showed the effectiveness of the project to cure high salinity levels.

2.3 Drinking water Treatment Options

Several nitrate removal technologies have been used in water treatment, either physical or biological, for example ion exchange, reverse osmosis, adsorption and chemical and biological methods (Bhatnagar and Sillanpää, 2011).

Five major types of nitrate treatment technologies were categorized in this section; some of these technologies are physical which removes nitrate, like the Ion exchange (IX), reverse osmosis (RO), and electrodialysis/electrodialysis reversal (ED/EDR), those technologies have some concerns like the management cost of the waste and the pretreatment requirements to avoid scaling and foaming of the used membranes mainly in reverse osmosis , and the other category uses the and chemical reduction denitrification (CD) and biological nitrate removal which reduce nitrate to nitrogen gas and other species (Jensen et al., 2012).

Choosing the suitable treatment technology depends on several factors and criteria, like the site topography and nature, operational and maintenance cost, the size and capacity of the required system, and many other key factors (Jensen et al., 2012). Table 2.2 gives a brief

comparison for the advantages and disadvantages of the above mentioned treatment options which does not be considered as a comprehensive criteria for the selection and design of the treatment options (Jensen et al., 2012).

Table 2-2: Advantages and Disadvantages of the major treatment options for nitrate removal. *(Jensen et al., 2012)

	Advantages	Disadvantages
Ion Exchange	• Years of industry experience, • Multiple contaminant removal, • Selective nitrate removal, • Financial feasibility, • Use in small and large systems, and • The ability to automate.	• waste brine disposal, • The potential for nitrate dumping specifically for non-selective resin use for high sulfate waters, • The need to address resin susceptibility to hardness, iron, manganese, suspended solids, organic matter, and chlorine, and • The possible role of resin residuals in DBP formation.
Reverse Osmosis	• High quality product water, • Multiple contaminant removal, • Desalination (TDS removal), • Feasible automation, • Small footprint, and • Application for small and POU applications.	• The disposal of concentrated waste, • High investment and O&M costs, • The need to address membrane susceptibility to hardness, iron, manganese, suspended solids, silica, organic matter, and chlorine, • High energy requirements, • Poor control over complete demineralization.
Electrodialysis/ Electrodialysis Reversal	• Limited to no chemical usage, • Long lasting membranes, • Selective removal of target species, • Removal rate flexibility by controlling the voltage, • Good water recovery leads to lower volume of waste, • Feasible automation, and • Multiple contaminant removal.	• The disposal of concentrated waste, • The need to address membrane susceptibility to hardness, iron, manganese, and suspended solids, • High maintenance requirements, • Higher Costs with comparison of the RO • Gaseous byproducts venting need, • The potential for precipitation with high recovery, • Complex system, • Conductivity dependent.
Biological Denitrification	• High water recovery, • No brine stream • Low sludge waste, • Less expensive operation, • Limited chemical input, • Increased sustainability, and • Multiple contaminant removal.	• The need for substrate and nutrient addition, • High monitoring needs, • The requirements of post treatment, • High investment costs, • Sometimes the system is sensitive to the environmental conditions, • Partial denitrification is possible sometimes, • Permitting and piloting requirements, and • Initial start-up need higher time than other technologies.
Chemical Denitrification	• No brine stream • The potential for more sustainable treatment, • good water recovery, and • Can remove other contaminant than nitrate.	• The potential reduction of nitrate beyond nitrogen gas to ammonia, • Partial denitrification is possible sometimes, • The performance denpendent on pH and temperature, • The need of iron removal sometimes,

2.3.1 Biological Denitrification

Biological nitrate removal is the well-known and mostly used in wastewater treatment, and it's also used and applied in the denitrification of drinkable and other uses of nitrate contaminated water (Brown, 2008). Biological nitrate removal for drinkable water treatment was implemented and tested in several locations in Europe since 1804 (Lenntech, 2009), and it was applied as a full scale systems in many countries like France, and Germany (Dördelmann, 2009; Meyer et al., 2010).

Biological nitrate removal depends on different types of bacterial culture based on the type of denitrification (Autotrophic/heterotopic) in which it transforms nitrate into nitrogen gas through reduction, where some key factors should be considered like the nutrients requirements in some cases in addition to the need of the post treatment (Aslan and Türkman, 2003).

As an advantage for the biological treatment for the reduction of nitrate to nitrogen gas over the other physical treatment, is that there is no brine waste stream, which is considered as an important problem to face in all aspects (site disposal and economic issues) when using physical process like RO (Jensen et al., 2012).

Biological denitrification systems can be categorized into heterotrophic process, where the carbon and energy sources are served by organic compounds, and the second type of biological denitrification is the autotrophic process, and here the energy source is served by an inorganic compound and also supplied for the cell synthesis as a carbon source, where both types could be adapted and reformed to drinking water treatment technologies (Kumar and Doble, 2005).

The heterotrophic bacteria that is used in the denitrification process for the nitrate removal of groundwater requires an external organic carbon source for respiration and growth, where different carbon sources such as methanol, ethanol, glucose and acetic acid have been used, with a variety of industrial wastes including molasses, such as sulfite waste liquor have also been used. However, the most common chemicals used for drinking water treatment are methanol, ethanol and acetic acid (Koeve and Kähler, 2010).

Biological denitrification for removing nitrate in groundwater can occur in either attached or suspended growth systems. In attached growth systems, the biomass is attached

physically to a solid materials like rotating biological contactors, and other technologies, while in suspended growth systems, the bacterial culture is continuously mixed with the reactor content to keep all the culture in suspended mode (Dabi, 2015).

Heterotrophic nitrate removal is a used process in biological treatment and advanced treatment of wastewaters, where carbonaceous substrate are added, and the bacteria will grow using the oxygen bond for respiration by reduction the nitrate as an elector acceptor into nitrogen gas which is considered harmless (Kumar and Doble, 2005).

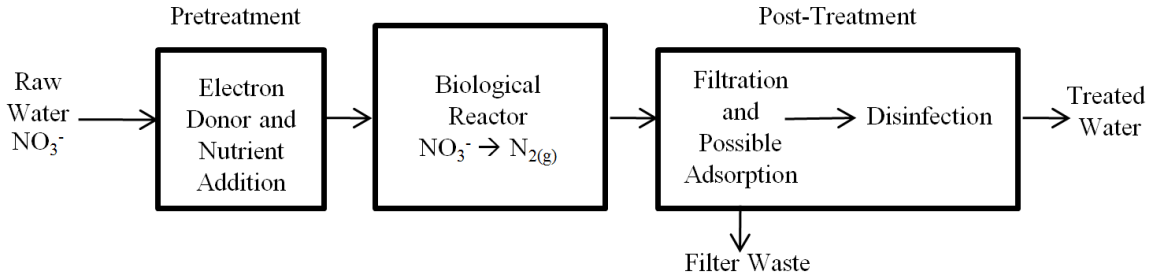

Figure 2.2: Biological Denitrification process schematic (Jensen et al., 2012)

2.3.2 Ion-exchange [IX]

The ion exchange (IX) is one of the most common and used technology in nitrate treatment and removal from water, in this process, the contaminated water enters the IX plant and the synthetic resin removes the nitrate anions and exchange them for chloride with equivalent amount (Samatya et al. 2006).

As a result from the removal process, is the production of concentrated brine waste with a volume depends on the quantity and quality of the influent water, which requires disposal to a proper site, and this considered as one of the drawbacks of this technology since it affect the management and running cost for the disposal (Jensen et al., 2012).

Other drawbacks and factors in using the ion exchange include the requirement of pretreatment in order to avoid the fouling of the resin, and the requirements of the post treatment to meet the required treated water, and so the use of IX may not be a good choice and it will not be feasible when the influent is highly concentrated with nitrate due to high quantities of salt use and the volume of the waste (Jensen et al., 2012).

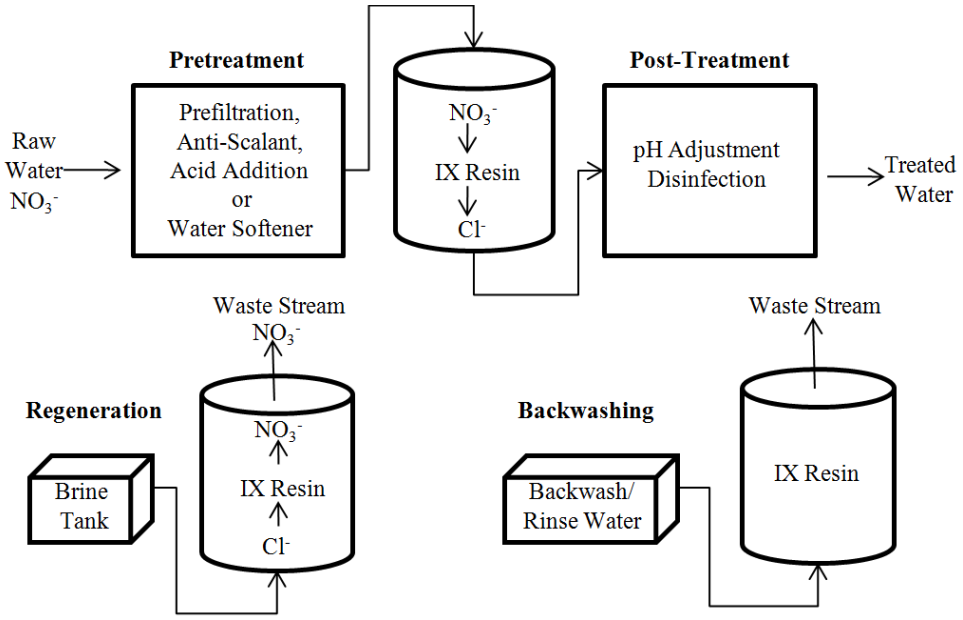

Figure 2.3: Conventional Ion Exchange process schematic (Jensen et al., 2012)

2.3.3 Reverse Osmosis [RO]

Another well-known and used physical technology for the removal of nitrate from water is the reverse osmosis (RO), which can be feasible for several applications and it can be used for desalination and nitrate removal (Cevaal et al. 1995).

As the IX, the RO treatment plant required pretreatment in order to avoid the sacaling and fouling of the membrane modules, in this process, after entering the pretreatment the water permeated from the membranes using permeable pumps, and so the water will pass through the membranes, while the contaminant are impeded on it (Jensen et al., 2012).

Other obstacles and key factors in choosing the RO technology in addition to the required pretreatment, are the resulted waste management and cost which is higher than IX (Jensen et al., 2012).

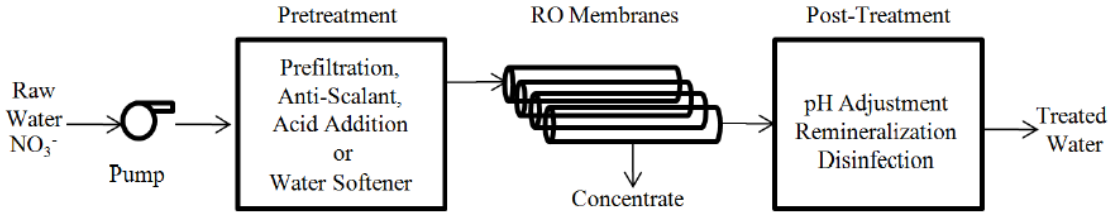

Figure 2.4: Reverse Osmosis process schematic (Jensen et al., 2012)

Epsztein et al. (2015) studied the nitrate removal from groundwater, for the production of low salinity waste brine that can be simply discharged to sewerage systems and high recovery of the produced water using two filtration scheme, they found that high total recoveries of 91.6 and 94.3% was achieved for the single and double NF scheme, respectively.

2.3.4 Electrodialysis

Electrodialysis (ED) is another option used for nitrate removal from water, and its considered as a membrane process driven by a difference in electrical potential over a membrane stack, in which charged compounds are removed from a feed solution (Van der Bruggen, 2015).

Two kinds of membranes are used in electrodialysis: anion exchange and cation exchange, where the two membrane types are alternated in a membrane stack so that a repeating unit is obtained consisting of a compartment with an anion exchange membrane on the left side and a cation exchange membrane on the right, followed by another compartment with an anion exchange membrane on the right side and a cation exchange membrane on the left, to minimize fouling and thus the need for chemical addition, the polarity of the system can be reversed with electrodialysis reversal (Hell et al., 1998).

According to Hell et al. (1998), there are some factors that should be considered when choosing the electrodialysis mainly the requirement of pretreatment, the waste management and cost, and the complex operation of the system.

Electrodialysis reversal (EDR) is used for desalination and it can be used also for nitrate treatment like the RO, and it's also similar to RO cost (Hell et al., 1998). As an advantage

over the RO, in electrodlialysis treatment the contaminants are not filtered in the treatment stream, but it's transferred outside and trapped by other membranes which will minimize the fouling of the membranes and reduce the requirement of the pretreatment (Cheikh et al., 2013).

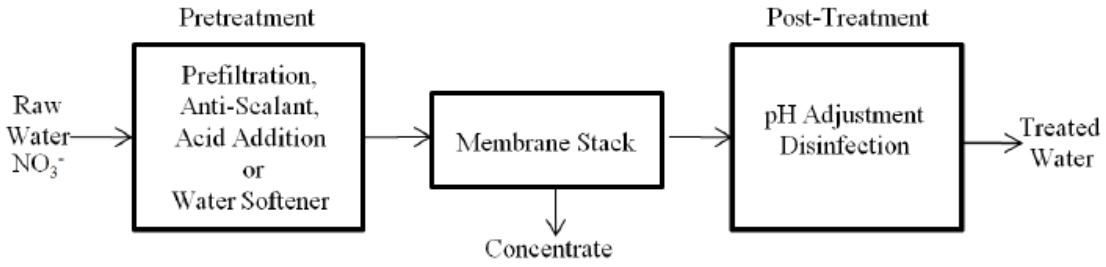

Figure 2.5: Electodialysis process schematic (Jensen et al., 2012)

2.3.5 Chemical reduction [CR]

Chemical nitrate reduction transforms the nitrate into other nitrogen species using metals and other compounds mainly hydrogen (Pintar and Batista, 1999), other metals have been investigated including aluminum and iron (Hou et al., 2015), other metals like copper, are used as reagents in nitrate chemical reduction (Shrimali and Singh, 2001).

Some key factors and obstacles in the chemical reduction process are the production of ammonia that need post treatment (Luk and Au-Yeung, 2002), and the highly affecting of the system with the temperature and pH (Jensen et al., 2012).

2.4 Denitrification Process

Denitrification is a microbially facilitated process of nitrate reduction that occur in anoxic conditions, and performed by a heterotrophic facultative bacteria, that may ultimately produce nitrogen (N_2) through a series of gaseous nitrogen oxide products (Kumar and Doble, 2005).

Denitrification generally proceeds through some combination of the following intermediate forms:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_{2(g)}$$

Heterotrophic denitrification is a well-known process in advanced biological treatment of wastewaters. By adding a carbonaceous substrate, bacteria will grow using the oxygen bond in nitrate for their respiration. Under these conditions, the bacteria utilize nitrates as a terminal electron acceptor and the resultant nitrates are reduced to harmless nitrogen gas. Autotrophic bacteria can reduce nitrate to nitrogen gas, where the energy source of autotrophic microorganisms is resulting from oxidation reduction reactions by using hydrogen or sulfur as the electron donor, and it utilizes the inorganic carbon compounds (such as CO_2, HCO_3^-) as their carbon source (Kumar and Doble, 2005). The autotrophic denitrification processes is divided into 'hydrogen' and 'sulfur' autotrophic denitrification (Kumar and Doble, 2005).

2.4.1 Parameters affecting Denitrification

2.4.1.1 pH effect

It has been established that in the wastewater treatment there is a maximum denitrification rate when pH values ranges between 7-8.5, whereas obvious decrease in the nitrate removal in the denitrification activity was found for pH values below 6 and larger than 8.5, a low pH value less than 6 is not good and will not achieve proper denitrification (van Haandel and van der Lubbe, 2007) . In order to maintain the pH in the optimal range of $7 < pH < 8$, a minimum influent alkalinity of $CaCO_3$ is required.

Removal of nitrate from drinking water using nano SiO_2–FeOOH–Fe core shell was tested and the results showed that nitrate removal increases with decrease of pH values, The achieved results in the study was 99.84% nitrate removal at optimum pH value of 3 (Ensie and Samad, 2014).

2.4.1.2 Temperature effect

Concerning the effect of temperature on the denitrification activity, it was established that nitrate removal rate increases with temperature up to optimum temperature of 40˚C, while higher temperatures reduces the denitrification activity very quickly (van Haandel and van der Lubbe, 2007).

The effect of temperature on the denitrification rate can be seen from the following relationship. In this relationship, the growth rate at 20°C is used as the baseline.

$$P = 0.25\ T^2$$

Where;

P = percent of denitrification growth rate at 20°C

T = wastewater temperature, °C

The effects of HRT and water temperature on nitrogen removal in autotrophic gravel filter was tested by Xu et al. (2016) and they achieved 91% removal efficiency at HRT of 12 h and temperature range 15-20 °C, while they achieved 18% removal efficiency at 3-6 °C. They reported that by increasing the HRT the removal efficiency increases from 18% into 41% at 3-6 °C.

In a separate study Wang and Wang (2011) found that at HRT 2 hours and 50 mg/l influent nitrate-nitrogen concentrations, the nitrate removal efficiency at 12°C was approximately 40% while it was around 100% at 25°C.

2.4.1.3 Carbon to Nitrogen Ratio (COD/NO_3^--N)

Denitrifying bacteria require an adequate supply of carbon as they break down nitrate into oxygen and nitrogen gas. The general rule of thumb is that the wastewater to be denitrified should have a Carbon-to-nitrogen (nitrate) ratio of 3:1.

In this experiments the different COD/NO_3^--N ratios were tested in batch modes to get the optimum COD/NO_3^--N ratio for the system.

2.4.1.4 MLSS Concentration

Mixed Liquor Suspended Solids (MLSS) are the suspended solids in the mixed liquor of an aeration tank. Optimal in terms of aeration tankage and secondary clarifier sizing is 2,500 – 3,000 mg/L. Higher MLSS values can be used, but usually means very large secondary clarifier to account for higher solids loading

2.5 Groundwater Denitrification Applied Researches

Many pilot and field studies on groundwater denitrification have been conducted over the past decades. These studies are physical, and biological denitrification including autotrophic and heterotrophic biological denitrification;

Using whey as a supplemental carbon source under real time control conditions or a story of Turds and whey to enhance denititrification was studied by Brischke et al., (2010) on a full scale pilot test at the Water Reclamation Facility in Colorado Springs, and it was figured out that fermented whey provide greater and higher results to unfermented whey, and it was also concluded that the addition of acid whey to enhance denitrification for the recovery of alkalinity to increase effluent pH was successful. Also, the addition of fermented acid whey has verified that whey is an effective supplemental carbon source for enhancing N and P removal. And turning a waste product into a valuable carbon commodity has significant cost savings potential.

Denitrification efficiencies of alternative carbon sources was tested for biological wastewater treatment by Kaplan et al., (1984), some of the carbon sources that was tested were the acid whey and sweet whey, the analysis showed that acid whey and sweet whey contain 63% and 74% sugar, respectively, indicating this is a main energy source for the bacteria utilizing these wastes for denitrification. It was found that 90% and above denitrification efficiencies were achieved for acid whey for C/N values ranged between 1.5 and 3.3 while it was ranged between 1.4 and 9.6 for sweet whey.

In using electrochemical nitrate removal, Govindan et al. (2015) studied the mechanism of nitrate removal from aqueous solutions by electrochemical denitrification process (EDN) in an undivided electrolytic cell. The sacrificial (Fe and Al) electrodes and Inert (graphite (Gr) electrode are employed for evaluation of operational parameters, The experimental results reveal that nitrate-N removal efficiency of 92% for Al–Fe (anode-cathode) and 80% for Fe–Fe are achieved at a current density of 25 mAcm−2and 180 min electrolysis time in 100 ppm of NaCl when the initial nitrate-N concentration is 100 ppm. However, during

this process approximately 20 ppm of ammonia-N is also formed. Ammonia-N generated is significantly lower compared to the amount of nitrate-N removal.

The combined effects of chemical oxygen demand (COD) to total nitrogen ratio (COD/N) and nitrate recycling ratio (R) on simultaneous nitrogen, phosphorus, and COD removal were studied in a laboratory-scaled anaerobic/anoxic/aerobic (A2/O)-biological aerated filter (BAF) system by Chen et al., (2015), in anoxic conditions at the COD/N ratio of 5.5, the TN removal efficiency was 90% with recirculation ratio increasing from 100 to 600%. At the COD/N ratio of 4.0, the TN removal efficiency steadily increased was 81% when R was increased from 100% to 400%, but decreased to 70% at the highest R (600%).

Ravnjak et al. (2013) investigated the removal of nitrate from contaminated groundwater in a biofilm membrane bioreactor with two stages anoxic and oxic MBR, using the ethanol as a carbon source in the process. Their obtained results demonstrated that the biofilm MBR system in suspension growth shows a great potential for the treatment of groundwater contaminated with nitrate, without any occurrence of nitrite and ammonium ions in treated water. In comparison with suspended biomass MBR systems, much higher denitrification rates were achieved in the anoxic stage of the BMBR system.

Sulfur-based autotrophic denitrification of drinking water using a membrane bioreactor was studied. A bench-scale MBR equipped with hydrophilic flat sheet polyethersulfone (PES) membranes (0.45 lm) was used. Sulfur was externally added to the MBR considering the theoretical requirement. Almost complete denitrification efficiency was achieved when the influent nitrate concentrations were 25–50 mg NO_3^--N /L at HRT as low as 5 h corresponding to nitrate loading rates up to 0.24 g NO_3^--N /(L d) (Sahinkaya et al. 2015).

Biological nitrate removal using a food waste-derived carbon source in synthetic wastewater and real sewage was investigated and studied by Zhang et al. (2016), in this study, acidogenic liquid from food waste was used as an alternative carbon source for synthetic wastewater treatment. C/N ratios of 5 and 6 were suitable for denitrification, and the change in acidogenic liquid composition had no negative effect on denitrification. The

denitrification rates using optimal carbon-to-nitrate ratios of acidogenic liquid were more than 25 mg NO_3^--N /(gVSS.h).

Xie et al. (2012) studied the effect of carbon source and COD/NO_3^-–N ratio on anaerobic simultaneous denitrification and methanogenesis for high-strength wastewater treatment. Experimental results showed that denitrification was the main nitrate reduction pathway for all COD/ NO_3^--N ratios tested in two substrates. Simultaneous denitrification and methanogenesis occurred at COD/ NO_3^--N higher than 7 regardless of carbon sources, and incomplete denitrification was observed at COD/ NO_3^--N ratio below 7.0.

Autotrophic denitrification according to Soares, (2000) has been investigated using variable ratios of sulfate and limestone at lab-scale system with moderate success, also it was concluded that In situ treatment may be problematic in fine aquifers but may also be the only practical and affordable solution in a remote village.

Nuhoglu et al., (2002) investigated the hydraulic and biological parameters function through bench scale membrane biological reactor (MBR) for the removal of nitrate from drinking water in batch and continuous modes, their results showed excellent effluent quality with nitrate-nitrogen concentration less than 4mg/l and nitrate removal efficiency of 98.5 % at optimum C/N value of 2.2 when the influent nitrate-nitrogen concentration of 367 mg/l and influent nitrate loading rate of 0.310 kg/m^3.d, and the results also indicated that by using the membranes there is no need for additional post treatment processes for the removal of MLSS from the treated water (Nuhoglu et al., 2002).

Wang and Wang (2011) investigated the denitrification of nitrate-contaminated groundwater using biodegradable snack ware as carbon source under low-temperature condition, and they found that at HRT 2 hours and 50 mg/l influent nitrate-nitrogen concentrations, the nitrate removal efficiency at 12°C was approximately 40% while it was around 100% at 25°C.

Denitrification potential and rates of complex carbon source from dairy effluents in activated sludge system was studied by Sage et al., (2006) and it was found that

denitrification rates ranged from 0.0034 to 0.008 gN/gVSS/h in studying denitrification potential and rates of complex carbon source from dairy effluents in activated sludge system.

Hoover et al. (2015) studied the impact of temperature and HRT on nitrate removal by woodchip denitrification bioreactors and it was concluded that greater NO_3–N removal (%) was obtained when N loads entering the bioreactor were reduced, either by reducing the influent NO_3–N concentration or by decreasing the influent flow to obtain longer HRTs. The NO_3–N load reduction (g N m^{-3} d^{-1}) increased as influent NO_3^--N concentration increased above 10 mg L^{-1}, but at influent concentrations of ≥30 mg L^{-1}, the bioreactors appeared to be saturated with respect to NO_3–N. also, is was found that nitrogen removal was temperature dependent, and at 10°C, between 27 and 57% of the NO_3^--N was removed, depending on the NO_3^--N loading.

Effect of influent nutrient ratios and hydraulic retention time HRT on simultaneous phosphorus and nitrogen removal in two-sludge sequencing batch reactor was studied in lab scale and it was found that the optimum COD/TN ratio was 9.9 for achieving 91% nitrogen removal (Wang et al., 2009).

Using polycaprolactone as an organic carbon source and biofilm carrier in fixed-film denitrifying reactors was tested to study the effect of dissolved oxygen by Luo et al. (2016), the tests were categorized into three groups based on the dissolved oxygen concentrations 0.28, 2.5, and 5.63 mg/l. the results showed that the removal rates were 1.53, 1.6, and 1.42 kg/m^3 for influent nitrate-nitrogen concentration of 200 mg/l. it was also found that the removal efficiencies for the first two groups reached 90% while it decreased to 75 % in group three at higher dissolved oxygen.

The effect of COD/NO_3^- , and nitrate concentration was examined in a high-rate biological rotating-bed reactor by Jafari et al., (2015), they found that the maximum denitrification rate was 3.56 $kgNO_3^-/m^3$.d at COD/NO_3^- value of 1 and HRT of 10 hours, which also

achieved maximum nitrate removal efficiency of 99% when the influent concentration of nitrate was 500 mg/l.

In a study for evaluation of two carbon sources for inducing denitrification: Batch and column experiments was conducted by Grau-Martínez et al., (2015), The experiments demonstrate that the commercial compost enhanced nitrate reduction in both experiments (batch and column) although an initial release of nitrate was observed; also it was concluded that palm tree leaves were a good carbon source to induce denitrification.

Tong et al., (2013) tested a heterotrophic/biofilm-electrode autotrophic denitrification reactor to improve the nitrate removal efficiency and to reduce the organic carbon source consumption, they achieved a 99.9% denitrification efficiency at optimum current density of 200 mA/m^2.

The Behavior of solid carbon sources of wheat straw, sawdust and biodegradable plastic (BP) for biological denitrification in groundwater remediation, was investigated by Zhang et al., (2012), biodegradable plastic in batch experiments achieved higher removal efficiencies of nitrate than wheat straw and sawdust, while they achieved complete nitrate removal in column experiment using biodegradable plastic as a carbon source at different influent concentrations of nitrate.

Huang et al., (2012) studied the remediation of nitrate-nitrogen contaminated Groundwater by a heterotrophic-autotrophic denitrification approach in an aerobic environment using methanol as a carbon source, it was found that C/N ratio of 3.75/1 was the optimum value for complete denitrification.

Combining heterotrophic and autotrophic denitrification using an intensified biofilm–electrode reactor was developed for treatment of nitrate contaminated groundwater, and the results of the experiment demonstrate that high nitrate removal efficiency 100% was achieved at C/N = 1, and HRT = 8 h , for nitrate-nitrogen 60 mg/l in the influent (Zhao et al., 2011).

Enhanced denitrification in groundwater and sediments from a nitrate contaminated aquifer after addition of pyrite was tested in laboratory experiments the extent to which the addition of pyrite to groundwater and sediments from a nitrate-contaminated aquifer could stimulate denitrification by indigenous bacteria (Torrentó et al., 2011), complete nitrate removal initiated in the early stages of the experiments (less than 24 days) and lasted for the 180-day experimental period. This demonstrates the rapid response of the indigenous bacterial community to adapt to the new conditions and efficiently reduce nitrate.

Jang et al., (2011) studied the denitrification of simulated nitrate-rich wastewater using sulfamic acid and zinc scrap In a batch and column tests with initial nitrate concentration of 500 mg/l NO_3^--N, and approximately 98.8 % of nitrate anions were removed. Based on these experimental results, it was concluded that chemical nitrate denitrification using sulfamic acid and zinc scrap is an effective alternative treatment protocol for nitrate-rich wastewater.

Different organic carbon sources for the nitrate removal of wastewater containing 2500mg/l nitrates was tested and studied by Fernandez-Nava *et al.*, (2010) in a sequence batch reactor (SBR), they tested three carbon sources; from a dairy plant, soft drink factory, and wastewater from sweet factory, they achieved a maximum specific denitrification rates of between 42 and 48mg NO_3^--N /g VSS h, where complete nitrate removal and low COD concentration were obtained in 4–6 h reaction time, and the found that he optimum COD/N ratios varied between 4.6 and 6.5 for the three tested sources.

Lin et al., (2008) studied the performance of free water surface and subsurface flow constructed wetlands based on the effect of hydraulic loading rate, and they resulted that when hydraulic loading rate is not exceeding 40 l/d the effluent nitrate concentrations meets the drinking water standards with nitrate removal efficiencies exceeds 85%.

Several organic substrates as potential carbon source for use in a denitrification permeable reactive barrier were studied in order to select the organic substrate with high performance

(Gibert et al., 2008), seven organic substrates were tested in a batch tests, where most of the substrates assessed in batch tests developed conditions that favored denitrification, attaining nitrate removals generally >95%. The top performing substrate in terms of denitrification efficiency was Softwood, showing a nitrate removal through denitrification >98% and a denitrification rate of 0.067 mg NO_3^--N dm^{-3} d^{-1} g^{-1}_{sub}.

Denitrification of drinking water was studied using various natural organic solid substrates such as poplar, hornbeam, pine shavings and wheat straw as a carbon source in a batch unit, and it was found that highest nitrate removal efficiency was observed using the wheat straw, (Aslan and Türkman 2003), the wheat straw was tested in column continuous study and showed a good results where effluent nitrate concentration were below 50mg/l.

A membrane biological reactor was investigated for nitrate removal, and achieved over 99% of nitrate removal when the influent concentration was 200 mg/l nitrate-nitrogen, and the results also showed low turbidity values for the effluent (Ergas and Rheinheimer, 2004).

Nabi Bidhendi et al., (2006) studied and examined the application of biological method for eliminating nitrate from the water using a fixed bed bioreactor, they used the acetic acid as source of carbon due to its lower price and easier to storage comparing with methanol, and they achieved 77% nitrate removal efficiency at HRT 2 hours and COD/N value of 2.

Foglar and Briški, (2003) investigated nitrate removal from SW in a batch denitrifying reactor and in a continuous-flow stirred reactor by the mixed bacterial culture. In the culture with the dominant Paracoccus sp. and Pseudomonas stutzeri, a high denitrification rate was achieved. Complete denitrification (200 mg NO_3^--N/l) was found during approximately 6 h for the MeOH/ NO_3^--N ratio above 2.5 in SW. In the continuous denitrification process during 45days specific denitrification rates increased to 250 mgNO_3^--N/gVSS h, while HRT decreased from 62 to 28 h.

The denitrification of rinse wastewater generated from the stainless steel manufacturing process in a (SBR) was studied using the methanol as a carbon source, and the results

showed 98% nitrate removal efficiency in HRT of 7 hours and optimum COD/N value of 3.4 while the maximum denitrification rate was 30.4 mg NO_3^--N /g VSS.h. (Fernandez-Nava et al., 2008)

The effect of pH variation, on an activated sludge nitrate removal of wastewater with 2700 mg/l nitrate-nitrogen was tested in a bench-scale sequence batch reactor by Glass and Silverstein, (1998), they found that pH has affected the nitrate removal of synthetic wastewater, were at influent nitrate concentrations of 1350 mg/l nitrate-nitrogen and pH $\leq$ 7.0, a completely nitrate removal was inhibited, and they also found that at higher pH values the accumulation of nitrite increased significantly, and so they concluded that pH is a strong indicator of the denitrification progress.

3. CHAPTER THREE
MATERIALS AND METHODOLOGY

This chapter covers the materials and methods that was used in the reactor design, construction and operation in addition to the site selection and the factors affecting the plant design and operation. By going through this chapter, the master candidate has covered the methods that was used in the Lab analysis including the COD/ NO_3^--N ratio, Nitrate feeding, effluent concentrations and the retention time.

3.1 Experimental Methods.

This study starts from the mid of June and run until the mid of September 2015. Daily routine monitoring was held; like influent flow rate, pH, temperature, dissolved oxygen. While the nitrate effluent concentrations was monitored every couple of days and sometimes daily, or hourly to detect any deviation or improper state. The wasted Whey from Al-Pinar dairy factory was used as a carbon source for the bacteria in the system. The system was run at the Lab room real temperature.

3.2 Site Selection.

The denitrification reactor was installed in the Water and Environmental studies Lab at Birzeit University, where all the materials were available, while it was hard to get some controllers and automations for accurate nitrate and COD feeding.

3.3 Experimental system

Figure 3.1 shows the experimental system used in the nitrate removal tests. The used components in the system are completely stirred bench scale reactor, consisting of;

- Main denitrification reactor (Anoxic compartment)
- secondary sedimentation tank
- Feed solution tank
- Feeding peristaltic pump.

- Temperature, DO and pH Monitoring devices, and rubber based tubes for liquid flows.

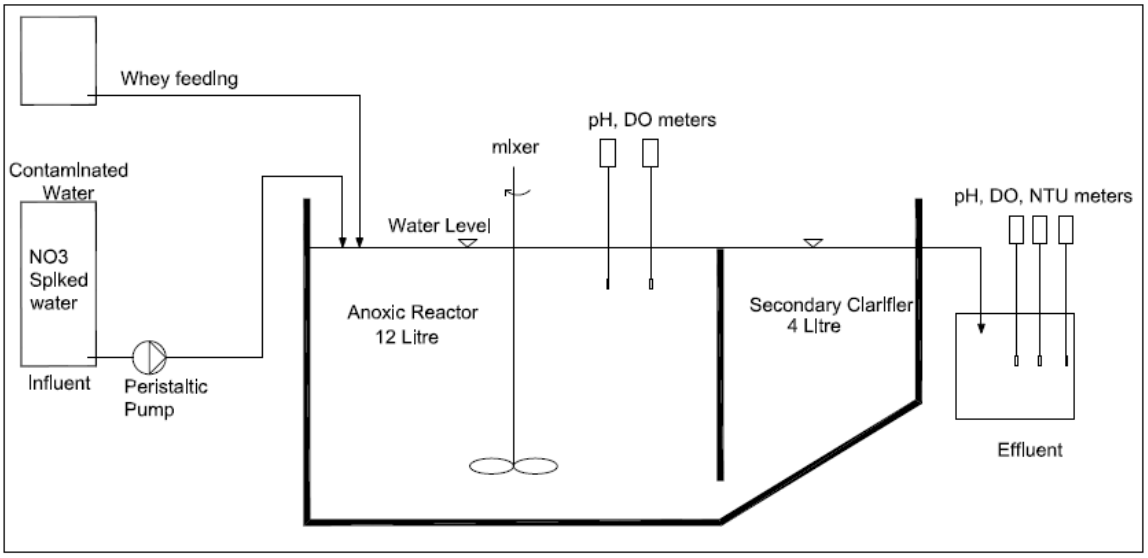

Figure 3.1: Process Flow Diagram (PFD) for nitrate removal reactor

A biological reactor with 20L total volume was manufactured from acrylic Plastic material with a working volume of 12 L was throughout the study. The free volume was kept to control the foaming and to prevent the washout of the bacteria. A variable speed mixer, pH, DO, and temperature meter were fitted to the reactor.

The contaminated water was prepared from tab water by spiking Potassium nitrate (KNO_3) as the contaminant. Whey was used as carbon source and it was feed to the reactor with controlled concentrations based on the nitrate concentrations in the influent flow, in-order to get the required COD/NO_3-N in order to measure the optimum COD/ NO_3^--N and to get the proper value for testing the required parameters .

Due to the limited availability of the control devices, it was impossible to get constant COD/ NO_3^--N during the test, but it was always near the required value.

3.4 Reactor Design

The reactor design is the initial step in the development and construction of the denitrification process. It includes the technology used, equipment, Volume determination, and retention time calculation.

The objective of the design is to build a full process, that will work to reduce the nitrate pollution from a groundwater to the WHO allowed concentration of drinking water.

The treatment plant consists of two main Steps; feeding Zone, biological reactor. These steps and units are discussed below.

3.4.1 Feeding Zone.

The feeding zone consists of a 50 L feeding tank, where the contaminated water is stored and supplied into the reactor through peristaltic pump, where the hydraulic retention time (HRT) and nitrate loading is controlled.

Figure 3.2: Feeding tank with capacity 50L

In the initial starting phase of the process, a 1000 L feeding tank was used, where all the solution was mixed using controlled speed mixer, the content of the feeding tank consisted of the contaminated water that was prepared by adding the KNO_3 with a specified mass of whey. Due to mixing and long time running the denitrification process has taken place inside the feeding tank which affected the final results. And so, instead of the 1000 L tank a 50 L tank was used for easy monitoring and controlling.

Figure 3.3: The 1000 L feeding tank with mixer

3.4.2 Biological Reactor

This step is the core of the treatment plant, it consists of two compacted units; the anoxic denitrification zone with 12 litre available working volume, and the secondary settling tank with available volume of 4 litre. In the anoxic zone a variable speed mixer was installed in-order to keep the solution (water, bacteria, and carbon source) homogenous and in a suspended state.

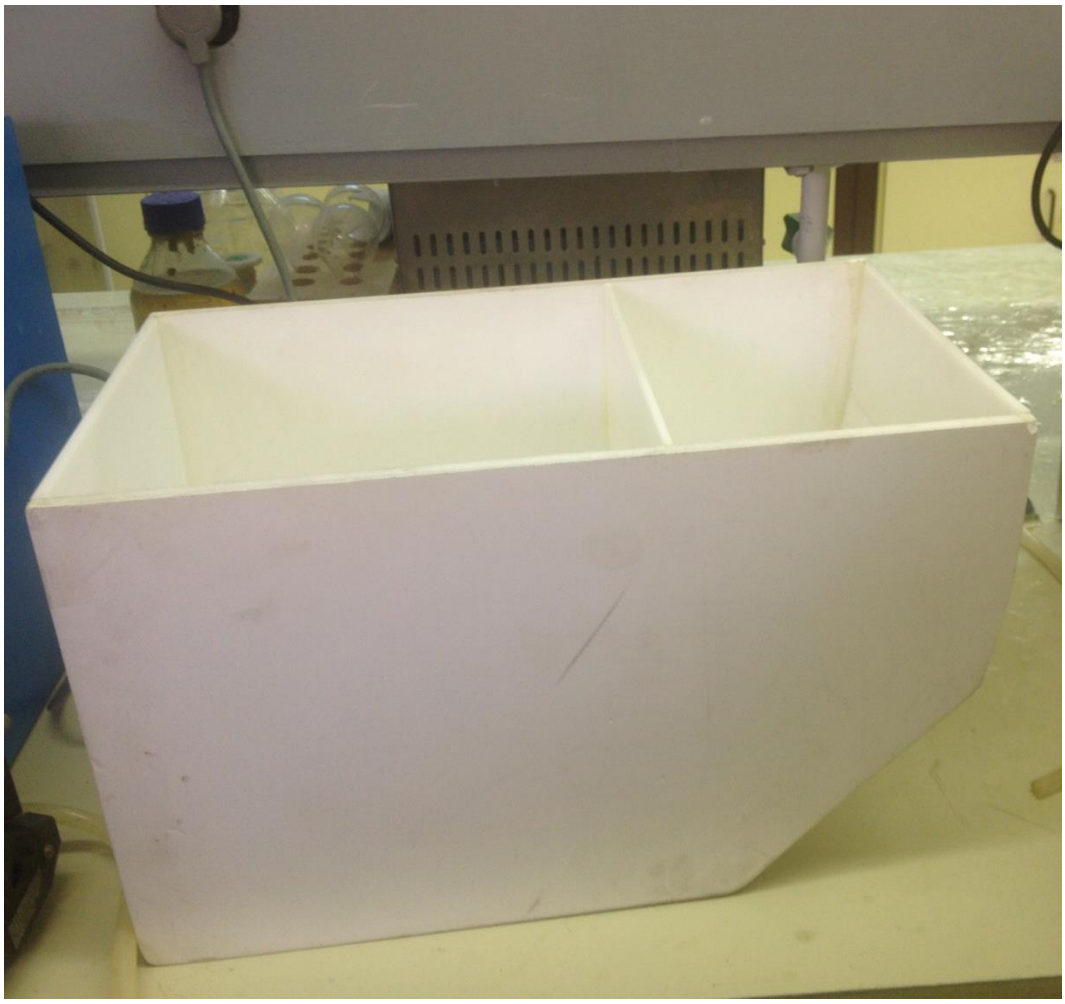

Figure 3.4: Biological Reactor

The volume of the reactor was 15 liter, while the available working volume was kept 12 liter, the remained volume was remained to prevent the washout of the bacteria and the foam during the run of the tests.

Figure 3.5: Variable speed mixer

3.5 Groundwater sources

In consideration of avoiding quality change in the actual groundwater, synthetic groundwater was used in this study. It was prepared by spiking tap water with KNO_3 to create a NO_3^-–N in different concentration depending on the test procedure.

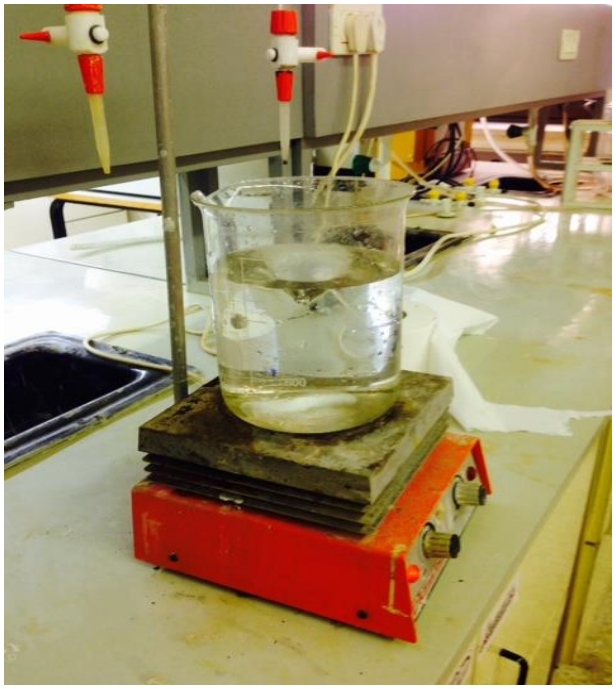

Figure 3.6: Mixing the KNO_3 with tap water

3.6 Seed sludge

Seed sludge was obtained from the first anoxic zone of Al-Teereh MBR wastewater treatment plant, and it was filled in the reactor and kept for few days for acclimatization under soft mixing before starting the test.

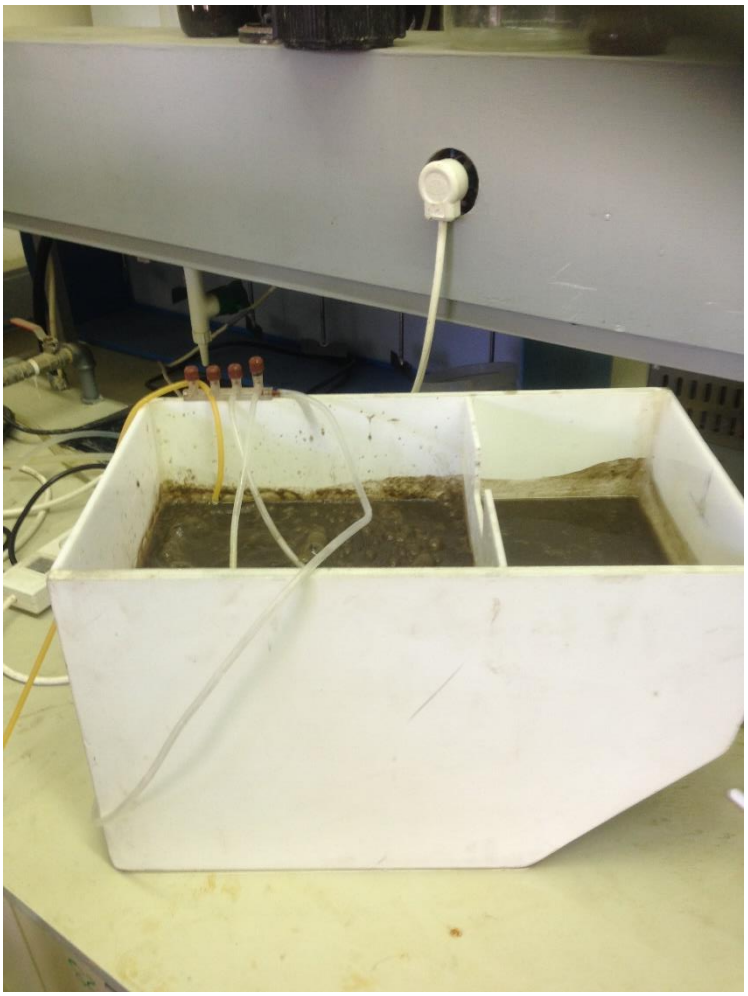

Figure 3.7: Sludge seeding in the Bench reactor from Al-Teereh MBR WWTP

3.7 Experimental procedures

The culture that was used for denitrification, was collected from Alteereh MBR WWTP, and it was kept for few days for adaptation in an anoxic conditions before starting the experiments.

The contaminated solution was kept in a 50 Litre feeding tank and it was connected using rubber tubes with the peristaltic pump for the feeding. A high rate feeding flow rates ranges between 2 and 12 L per hour was controlled and adjusted by using the variable speed peristaltic pump. Variable speed mixer was attached and used for the mixing in the reactor, where the mixer provides soft mixing to the solution and keep the culture in suspended mode with all the solution.

The anoxic condition in the reactor was obtained by mixing and by compressing nitrogen gas (N_2) through the reactor from time to time.

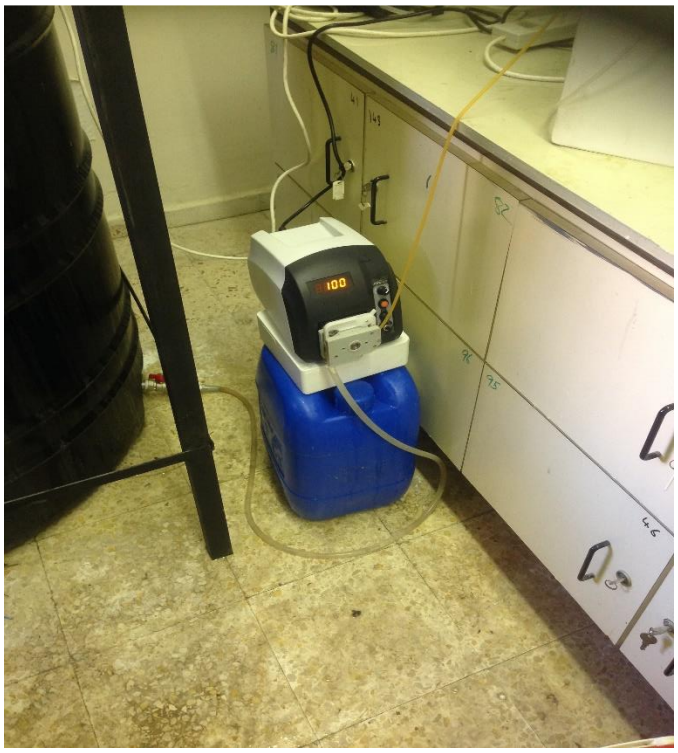

Figure 3.8: The Peristaltic pump that was used during the test

The dissolved oxygen was monitored by a DO meter, and the reading was always below 0.5mg/l. A pH meter was used to monitor the pH values during the tests.

The mixed liquor suspended solids (MLSS) and the mixed volatile suspended solids (MLVSS) were measured and monitored weekly.

The influent total nitrogen (TN), Nitrite (NO_2), Ammonia (NH_3) and Nitrate (NO_3^-) concentrations were tested at the start of each run to figure out the concentration and percentage of nitrate in the effluent contaminated water.

In addition to the above mentioned tests, the COD concentration was tested and the COD/NO_3^--N was calculated.

Effluent nitrate, nitrite and COD was tested for the treated effluent water to figure out the amount of COD consumed in during the reaction.

As an initial startup and to get a starting point for the tested parameters, a batch mode feeding was run to measure the optimum COD/ NO_3^--N, which was used in the continuous feeding mode.

After getting the optimum COD/ NO_3^--N value, it was used to test the all the other parameters like the HRT, nitrate loading rate, MLSS concentrations and its effect on the nitrate removal efficiency.

The data and results were tabulated and illustrated in figures for discussion, conclusion and recommendations for future work.

Figure 3.9: Treated effluent

3.8 Laboratory analysis

All experimental analysis of this thesis was generated in the laboratory at BZU, the sample and analysis was according to Standard Methods for the examination of water and wastewater applied at BZU lab (APHA and AWWA, 1992), in order to attain finest results

and right sampling methodology. In this section explain the procedure, instrument, and materials that used for this experimental analysis.

3.8.1 Sampling procedure

Details on sampling of the contaminated and treated water in this study were according to the standard methods. The samples of the influent contaminated water were collected from the feeding tank after well mixing, while the samplers of the treated effluent were collected from the effluent tank. The samples were placed in a labeled plastic bottle, these bottles were kept in the laboratory at 2°C refrigerator until analysis, which was at the same day of sampling and sometimes after few days. The MLSS samples was analyzed after collecting from the mixed reactor.

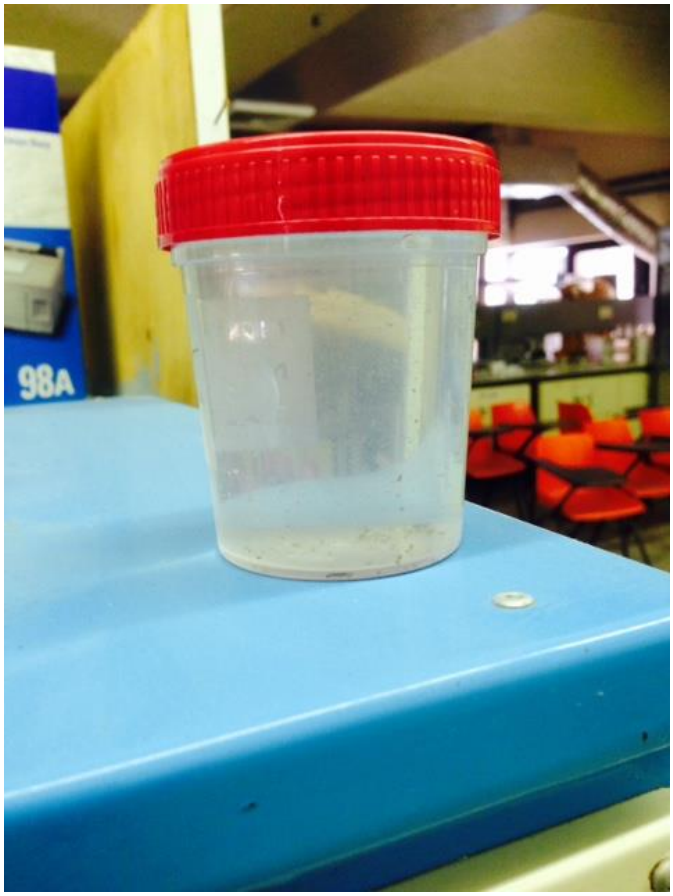

Figure 3.10: Influent contaminated water sample

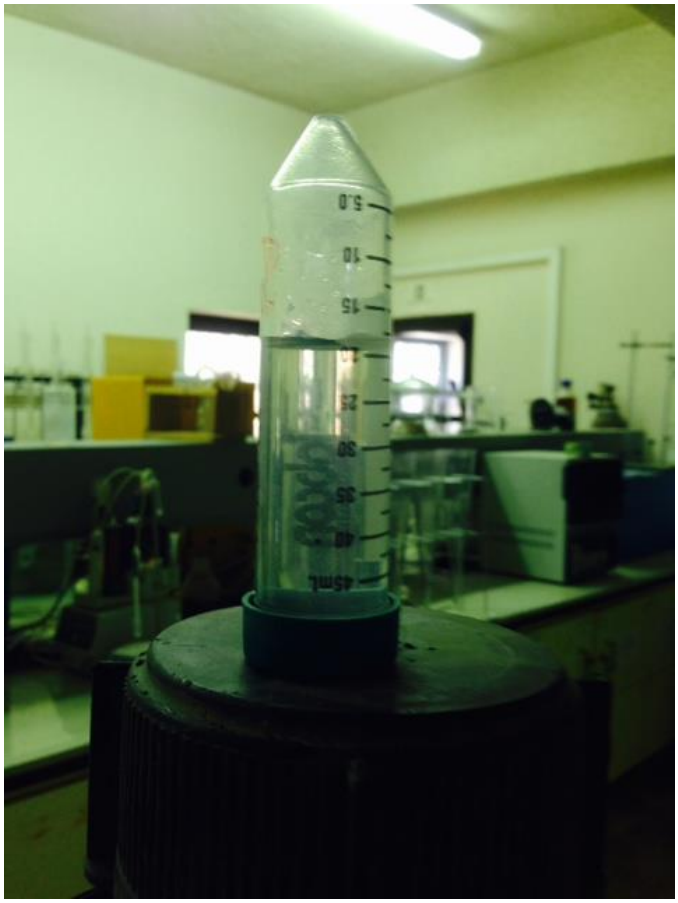

Figure 3.11: Effluent treated water sample

At the laboratory, preparation of the sample was depend on the analysis type, some sample was diluted, and the other were mixed, while some samples were dried before the analysis. More details of samples preparations for each analysis will be described in the next sections.

3.8.2 Analysis of Nitrate Treatment Plant

3.8.2.1 pH value

The pH value measures how acidic or basic a solution is. Its unit is the minus logarithm (base 10) of the concentration of hydronium ions. It is one of the most parameter that affecting the treatment process in water and wastewater treatment plants, It has been established that in the wastewater treatment there is a maximum denitrification rate when pH values ranges between 7-8.5, whereas obvious decrease in the nitrate removal in the

denitrification activity was found for pH values below 6 and larger than 8.5, a low pH value less than 6 is not good and will not achieve proper denitrification (van Haandel and van der Lubbe, 2007). In order to maintain the pH in the optimal range of 7 < pH < 8, a minimum influent alkalinity of $CaCO_3$ is required.

In this study pH value was monitored in the treatment plant with a standard potentiometric electrode. For the Process the reactor content was monitored daily.

3.8.2.2 Total suspended solid

In this analysis sample of Reactor Content of Suspended solids was dried at 105 °C oven for 5 hours according (standards EN 12880 and APHA 2540 B).

3.8.2.3 Volatile solids

Total volatile Solid determination was carried out after the TSS determination just described above. The samples were dried at 103–105 °C. Then the samples were ignited to constant weight in a furnace at 550 °C. (According to EN 12879 and APHA 2540 E standards) then samples were cooled down to room temperature and weight on balance. The volatile solids have combusted and the remaining solids are inorganic solids, triplicate samples were analyzed in order to determine VS and TS.

3.8.2.4 Chemical oxygen demand (COD)

Chemical oxygen demand is the parameter that indicates the total chemically oxidisable material in the sample and therefore indicates the energy and food content for the bacteria in the reactor (APHA and AWWA, 1992).
In this analysis 2.5 ml diluted manure sample was placed with 1.5 ml digestion solution (K2Cr2O7) and 3.5 ml sulphuric acid solution, a blank sample also prepared from distilled water. Then samples were digested for 2 hours at 150°C in HACH heating oven. The samples were colorimetric determined using HACH DR-2000 spectrophotometer

wavelength set at 600 nm. Before reading the samples, the instrument was calibrated to zero by the blank. Triplicate samples were analyzed in order to determine COD.

3.8.2.5 Nitrogen content

Determination of TN in a sample is important, primarily to evaluate the amount of nitrate in the influent water In order to add the required amount of COD to calculate the COD/NO_3-N ratio.

In this analysis, organic nitrogen was converted to ammonia nitrogen by boiling the feedstock sample in the presence of sulphuric acid and a catalyst at 380°C. After that, a base was added to make ammonia distilled from the alkaline solution to an acid solution, where ammonia was absorbed quantitatively. The amount of ammonia then was determined by potentiometric acid titration method (H2SO4 (0.02 N)) as titrant).

3.8.2.6 Financial Analysis

The basic economics that was used to analyze the total annual cost for the system is the depreciation analysis, which was used to calculate the total annual cost, and the results were used to calculate the unit cost and annual unit cost for several treatment options.

4. CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter will focus on the results from the laboratory analysis, and the reactor operation with batch and continuous feeding mode under lab temperature condition using the whey feeding as a carbon source for the heterotrophic bacteria.

4.1 Introduction

Nitrate removal from groundwater performance using a bench scale biological reactor was studied and examined as function of biological and hydraulic parameters. The reactor was a completely mixed tank and operated in a batch mode in order to get the optimum COD/NO_3^--N value in order to use this value in the continuous mode run for testing all the proposed parameters. The batch mode operation was only to get the optimum COD/NO_3^--N value that will be used to test the other parameters in the continuous mode denitrification. This chapter shows and discusses the results obtained from different parameters, including the optimum COD/NO_3^--N, the effect of Hydraulic Retention Time (HRT), nitrate loading, and the mixed liquor suspended solids (MLSS) on the nitrate removal efficiency.

The PH, temperature, and dissolved oxygen values were measured and tabulated in this chapter, and it was discussed as it have a major effect on the denitrification process and efficiency.

4.2 Optimum COD/NO3-N

In the experiments conducted with different COD/NO_3^--N ratios, nitrate concentration decreased with time at different rates. These nitrate removal tests were done in order to determine the optimum COD/NO_3^--N ratio for an initial MLSS concentration to initial NO_3^--N concentration ($[MLSS]_i/[NO_3^-N]_i$) around 18.5 by using whey as carbon source.

Where;

$[MLSS]_i$=initial concentration of mixed liquor Suspended Solids (mg/l).

$[NO_3^-N]_i$= initial nitrate concentration in the influent (mg/l).

The nitrate solution in this experiment was prepared using tap water by adding specific mass of KNO_3 to get the required concentrations of nitrate in the contaminated water. The COD/NO_3^--N ratios used were around 2.0, 3.0, 5.0, 7.0, and 9.0 in the batch test. The variation of the specific denitrification rates, with COD/NO_3^--N ratio is shown in figure 4.1, and defined as given in the following equation

$$Denitrification\ Rate\ (Dr) = \frac{[NO_3^- - N]_i - [NO_3^- - N]_O}{\overline{[MLSS]}}$$

Where;

$[NO_3^- - N]_i$= the Influent Nitrate Concentration (g/m^3)

$[NO_3^- - N]_O$= the Effluent Nitrate Concentration (g/m^3)

$\overline{[MLSS]}$= average MLSS concentration in the reactor through the denitrification process (g/m^3) =2800

Table 4-1: Batch mode Experiment Conditions and summary of the results obtained.

$[NO_3^-N]_{in}$ (g/m^3)	Flow Rate (l/hr)	COD/NO_3^--N	$[NO_3^-N]_O$ (g/m^3)	Spec. Denit. Rate (mg NO_3^-N/gMLSS/hr)	Removal Eff. (%)
150.00	4.0	2.93	77.45	8.64	48.37%
152.01	4.0	5.21	51.33	11.99	66.23%
155.28	4.0	7.82	34.11	14.43	78.03%
214.90	4.0	8.93	114.00	12.01	46.95%

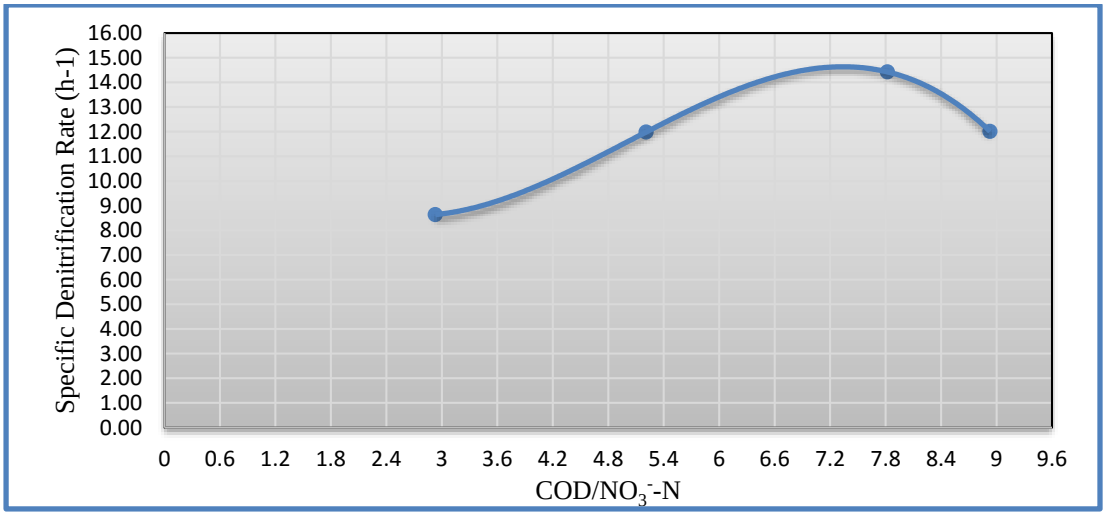

Figure 4.1: Optimum COD/ NO_3^--N Curve in batch mode

It is shown from figure 4.1 that the maximum specific denitrification rate of 14.61 (mg NO_3^--N/gMLSS/hr) is obtained for a COD/NO_3^--N ratio around 7.2. Rest of the denitrification tests stated in the next tests were all carried out at this optimum COD/NO_3^--N value. The COD from the whey (industrial waste) was measured as total COD without analyzing the biodegradable percentage and other fractions, so the real biodegradable COD consumed could be less than 7.2, and that was clear since the treated effluent water contained some COD, ranges between 20-50% of the influent COD concentration, which was not consumed in the process even at low COD influent concentrations.

Table 4.1 and figure 4.1 showed that at COD/ NO_3^--N of 2.93 the denitrification rate was 8.64 (mg NO_3^--N/gMLSS/hr), and it was 14.43 (mg NO_3^--N/gMLSS/hr) at COD/ NO_3^--N 7.82.

In separate study Sage et al., (2006) found that denitrification rates ranged from 3.4 to 8 mgN/gVSS/h in studying the denitrification potential and rates of complex carbon source from dairy effluents in activated sludge system.

A C/N value of 2.2 was found as the optimum value in batch mode tests by Nuhoglu et al. (2002) in testing drinking water denitrification using membrane bio-reactor and ethanol as a carbon source.

Another study held by Xie et al., (2012) found that excellent results and sometimes complete nitrate removal occurred at COD/NO_3^--N above 7.0, while incomplete denitrification results were found at COD/NO_3^--N ratio below 7.0 regardless of carbon sources.

The effect of different nitrate concentration, [NO_3^--N]i on continuous mode nitrate removal process was investigated for MLSS concentration of 2800 mg/l. NO_3^--N was varied in the range of 51–178 mg/l as shown in the following table and illustrated in figures 4.2 and 4.3.

Table 4-2: Continuous mode Experiment Conditions and summary of the results obtained.

$[NO_3^-N]_{in}$ (g/m^3)	Flow Rate (l/hr)	COD/NO_3^--N	$[NO_3^-N]_O$ (g/m^3)	Removal Eff. (%)
150	4.0	2.93	77.45	48.37%
51.08	4.0	5.72	31	39.31%
155.28	4.0	7.82	34.33	77.89%
177.7	4.0	9.16	38.85	78.14%
51.24	4.0	13.27	0.31	99.40%

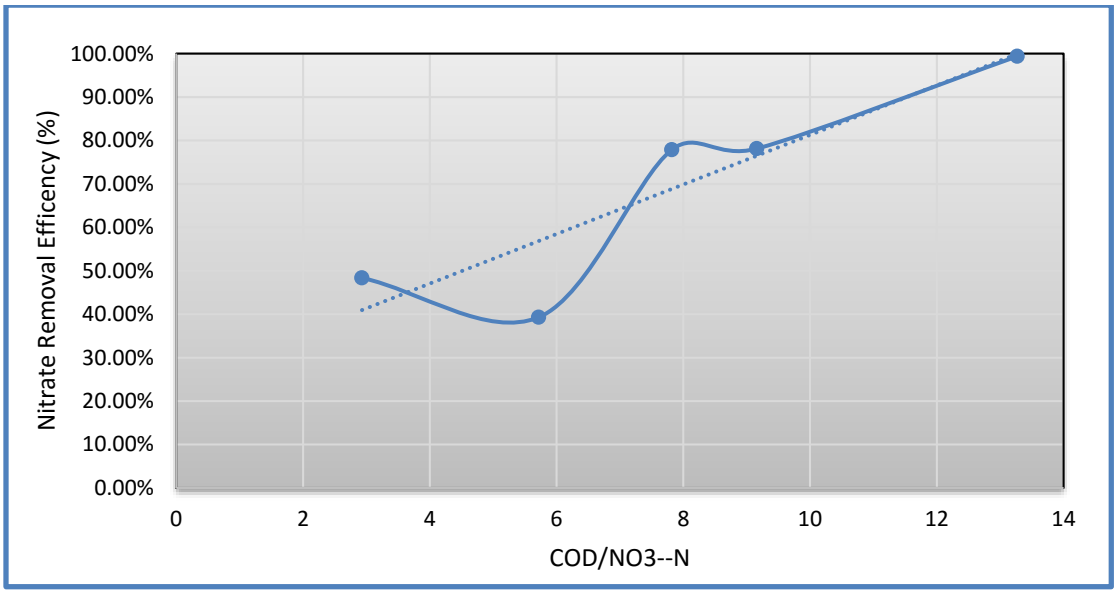

Figure 4.2: Nitrate Removal Efficiency with different COD/ NO_3^--N values

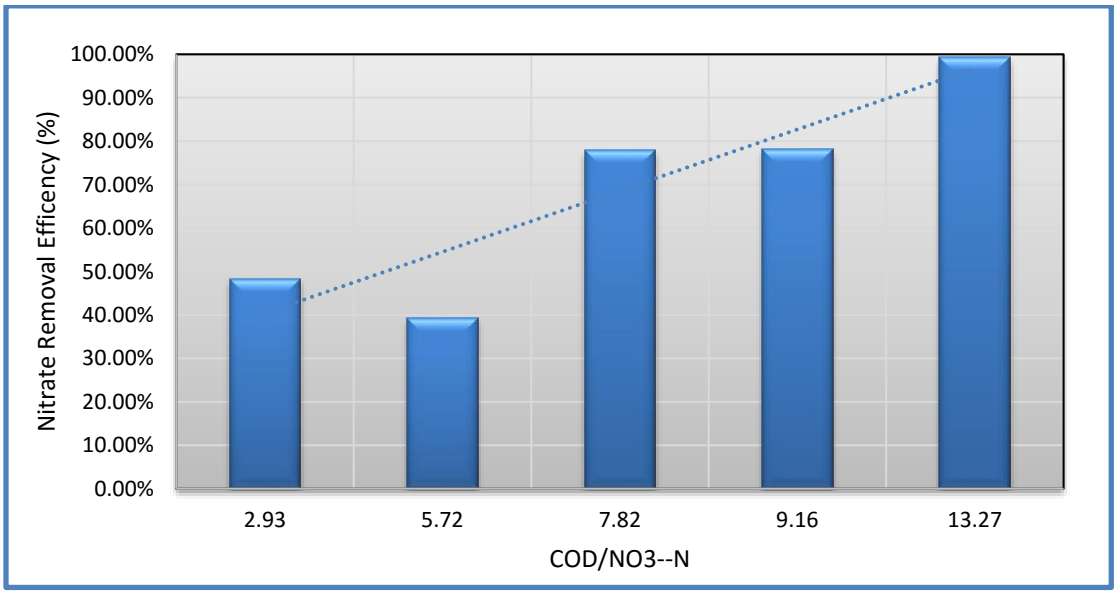

Figure 4.3: Nitrate Removal Efficiency with different COD/ NO_3^--N values

Continuous mode feeding showed that the nitrate removal efficiency in the reactor increases by increasing the COD/ NO_3^--N concentrations (table 4.2). At higher COD/ NO_3^--N values the nitrate removal efficiency was about 99%.

From Figure 4.2 and figure 4.3, it can be figured out that at COD/ NO_3^--N 2.93 the removal efficiency was about 48% while at 13.27 COD/ NO_3^--N the removal efficiency reached 99%. From the same figures it can be noticed that at 5.72 COD/ NO_3^-N and influent nitrate-nitrogen concentration of 51 mg/l the removal efficiency has decreased to about 31% and this could be due to culture adaptation at the starting of continuous mode run.

4.3 Effect of HRT on nitrate removal Efficiency

After optimizing the COD/ NO_3^--N value in a batch mode denitrification, a continuous mode denitrification was run using the same culture used in the batch mode. The tests were held to investigate the effect of the hydraulic retention time on the nitrate removal efficiency. The effect of loading Nitrate at 8 hours, at desirable HRT was investigated.

$$Flow\ Rate\ (L/hr) = \frac{V}{HRT}$$

Where;

$V = Reactor\ Volume\ (12Litre)$

$HRT = Hydraulic\ Retention\ Time\ (hr)$

$$Removal\ Efficiency(\%) = \frac{[NO_3^- - N]_i - [NO_3^- - N]_o}{[NO_3^- - N]_i} \times 100\%$$

Where;

$[NO_3^- - N]_i = Influent\ Nitrate - Nitrogen\ Cocentration(g/m^3)$

$[NO_3^- - N]_o = Effluent\ Nitrate - Nitrogen\ Cocentration(g/m^3)$

$$Reactor\ Removal\ Capacity\ (^{g}/_{m^3.h}) = D_r([NO_3^- - N]_i - [NO_3^- - N]_o)$$

Where;

$D_r = Dillution\ rate = 1/HRT\ (h^{-1})$

Table 4-3: Obtained results for different HRT values based on 50 mg/l NO_3^--N.

Flow Rate (l/hr)	HRT (hr)	$[NO_3^-N]_{in}$ (g/m^3)	$[NO_3^-N]_O$ (g/m^3)	Removal Eff. (%)	Dilution Rate (Dr) (h^{-1})	Reactor Removal Capacity ($g/m^3.h$)
12.00	1.00	50	23.60	52.80%	1.00	26.40
6.00	2.00	50	18.00	64.00%	0.50	16.00
4.00	3.00	50	14.46	71.09%	0.33	11.85
3.00	4.00	50	6.50	87.00%	0.25	10.88
2.67	5.00	50	4.00	92.00%	0.20	9.20
2.40	6.00	50	4.48	91.05%	0.17	7.59
2.00	8.00	50	4.30	91.40%	0.13	5.71

The previous table (Table 4.3) shows that the nitrate removal efficiency increases by increasing the HRT, and as illustrated in figure 4.4 below, the removal efficiency become constant after 5 hours HRT.

Another studies tested Autotrophic gravel filter Xu et al., (2016) found that at HRT 12 hours the TN removal efficiency was 91% and 96% of the added nitrate nitrogen was converted to nitrogen gas.

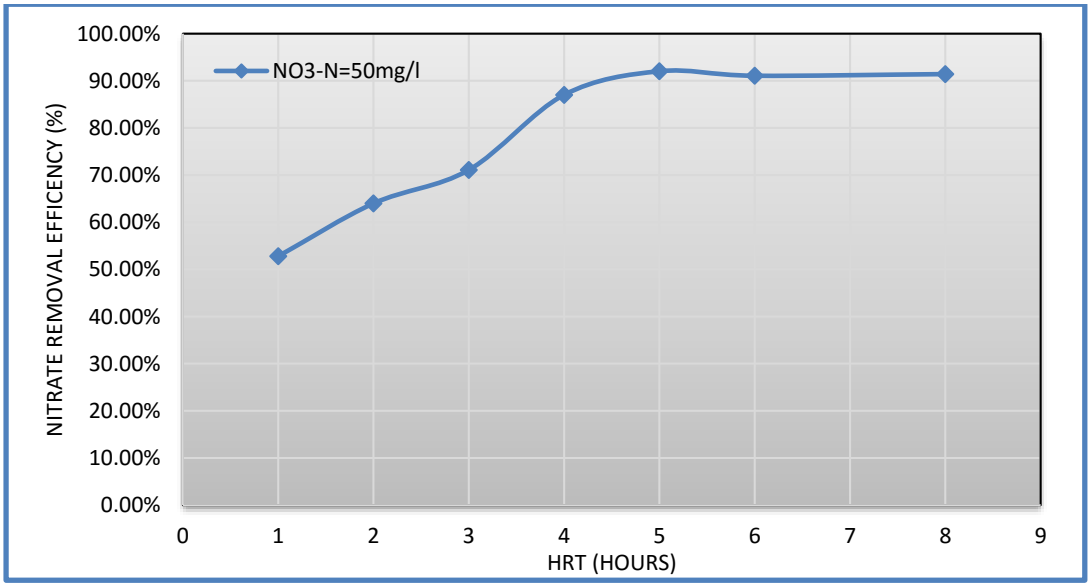

Figure 4.4: Nitrate Removal Efficiency with different HRT values based on 50mg/l NO_3^--N influent concentration

The reactor removal capacity increases with the dilution rate (1/HRT) as shown in figure4.5, and it was varied between 5.71 ($g/m^3.h$) at 8 hours HRT and 26.40 at HRT of

1 hour. At 9.20 $g/m^3.h$ a 92% removal efficiency was achieved at 5 hours HRT and 50 mg/l nitrate-nitrogen influent concentration.

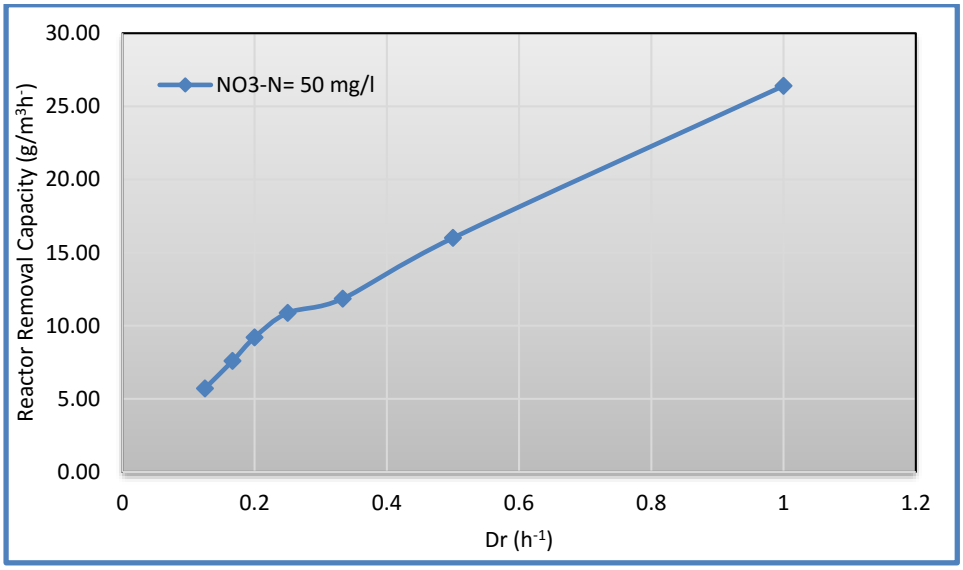

Figure 4.5: Reactor removal capacity with different dilution rate values based on 50mg/l NO_3^--N influent concentration

The previous figures (figure 4.4-figure 4.5) show the effect of different HRT ranged between 1 and 8 hours. This test was run with 50 mg/l as nitrate-nitrogen concentration. It was noticed that by increasing the HRT the nitrate removal efficiency increases until it reaches a constant denitrification efficiency 92% at 5 hours HRT.

Another results were obtained for higher influent nitrate concentrations of 100, and 152 mg/l NO_3^--N

Table 4-4: Obtained results for different HRT values based on 100 mg/l NO_3^--N.

Flow Rate (l/hr)	HRT (hr)	$[NO_3^-N]_{in}$ (g/m^3)	$[NO_3^-N]_O$ (g/m^3)	Removal Eff. (%)	Dilution Rate (Dr) (h^{-1})	Reactor Removal Capacity ($g/m^3.h$)
12.00	1.00	100	49.00	51.00%	1.00	51.00
6.00	2.00	100	45.00	55.00%	0.50	27.50
4.00	3.00	100	32.97	67.03%	0.33	22.34
3.00	4.00	100	16.91	83.09%	0.25	20.77
2.67	5.00	100	22.30	77.70%	0.20	15.54
2.40	6.00	100	8.80	91.20%	0.17	15.20
2.00	8.00	100	9.30	90.70%	0.13	11.34

Same acting to the results was obtained at higher nitrate concentrations of 100 mg/l with minimal deviation of the removal efficiencies and reactor removal capacity. The results for 100mg/l nitrate-nitrogen initial concentration tests are illustrated in figures 4.6 and 4.7 below.

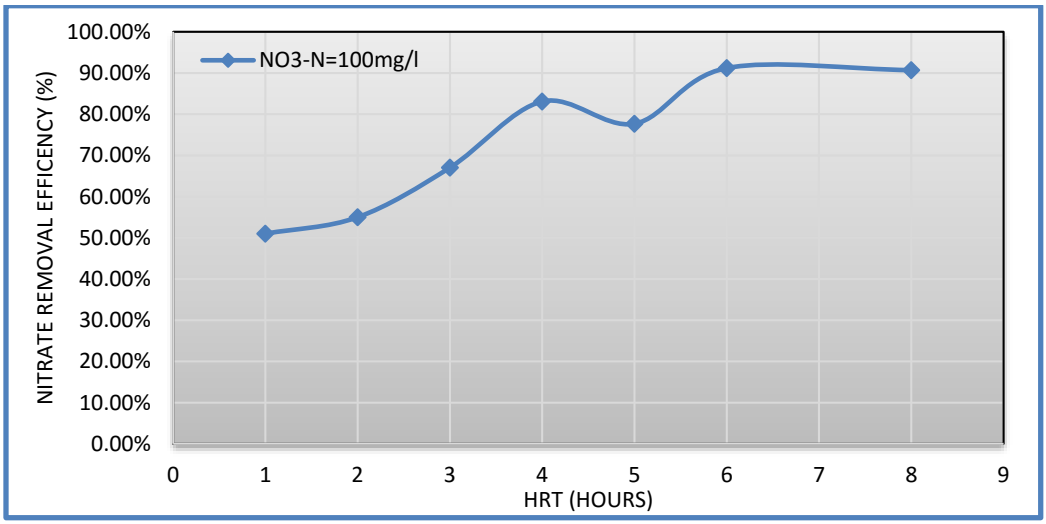

Figure 4.6: Nitrate Removal Efficiency with different HRT values based on 100mg/l NO_3^--N influent concentration

Figure 4.6 shows the effect of different HRT ranged between 1 and 8 hours at influent nitrate-nitrogen concentration of 100 mg/l. about 91% removal efficiency was achieved at 6 hours HRT and it became constant after that.

As illustrated in figure 4.7 below the reactor removal capacity varies between 11.34 and 50.00 ($g/m^3.h$), the optimum reactor removal capacity was achieved at HRT 6 hours with 15.2 ($g/m^3.h$) and denitirification efficiency of 91%.

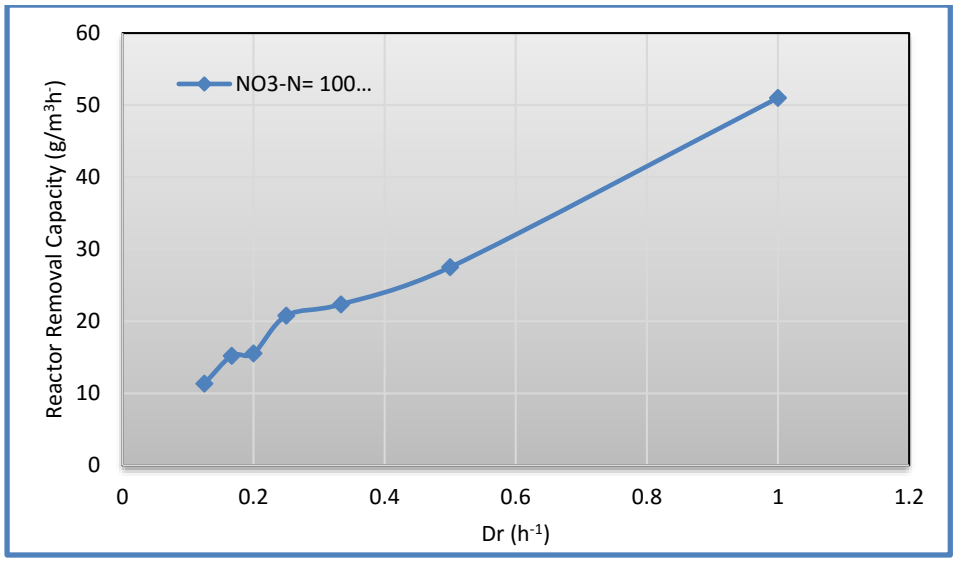

Figure 4.7: Reactor removal capacity with different dilution rate values based on 100mg/l NO_3^--N influent concentration

In Table 4.5, the obtained results for testing the effect of HRT on the nitrate removal efficiency and reactor removal capacity is shown using 152 mg/l nitrate-nitrogen influent concentration.

Table 4-5: Obtained results for different HRT values based on 152 mg/l NO_3—N.

Flow Rate (l/hr)	HRT (hr)	$[NO_3—N]_{in}$ (g/m^3)	$[NO_3—N]_O$ (g/m^3)	Removal Eff. (%)	Dilution Rate (Dr) (h^{-1})	Reactor Removal Capacity ($g/m^3.h$)
12.00	1.00	152	76.09	49.94%	1.00	75.91
6.00	2.00	152	59.72	60.71%	0.50	46.14
4.80	2.50	152	57.67	62.06%	0.40	37.73
4.00	3.00	152	53.20	65.00%	0.33	32.93
3.43	3.50	152	34.96	77.00%	0.29	33.44
3.00	4.00	152	30.40	80.00%	0.25	30.40
2.67	4.50	152	22.80	85.00%	0.22	28.71
2.40	5.00	152	16.72	89.00%	0.20	27.06
2.00	6.00	152	18.24	88.00%	0.17	22.29
1.50	8.00	152	18.24	88.00%	0.13	16.72

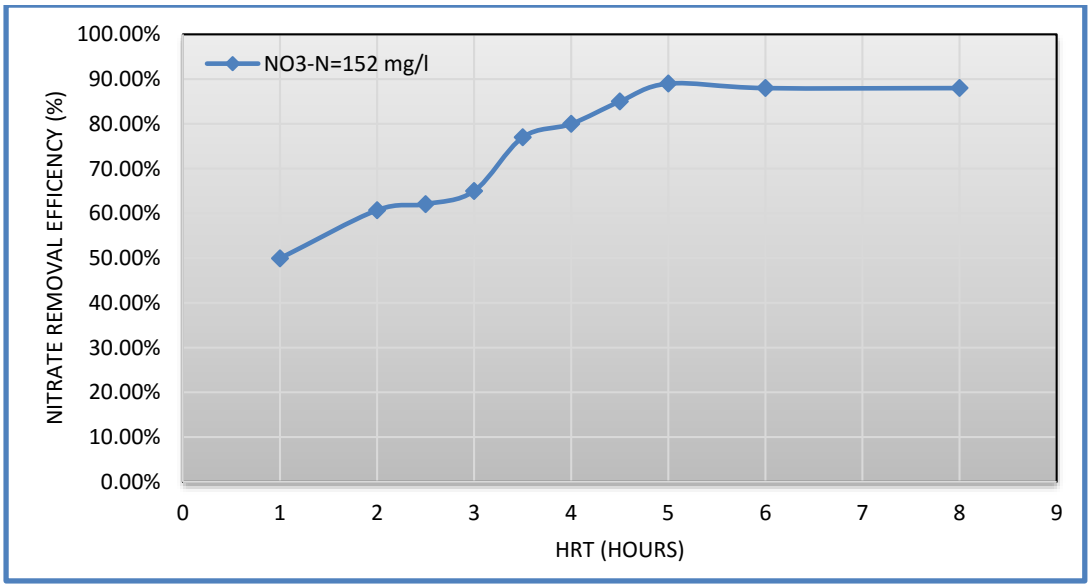

Figure 4.8: Nitrate Removal Efficiency with different HRT values based on 152mg/l NO_3^-N influent concentration

The results showed achieving 88% of nitrate removal efficiency in 5 hours HRT, and it continued constant after that as its clear in figure 4.8.

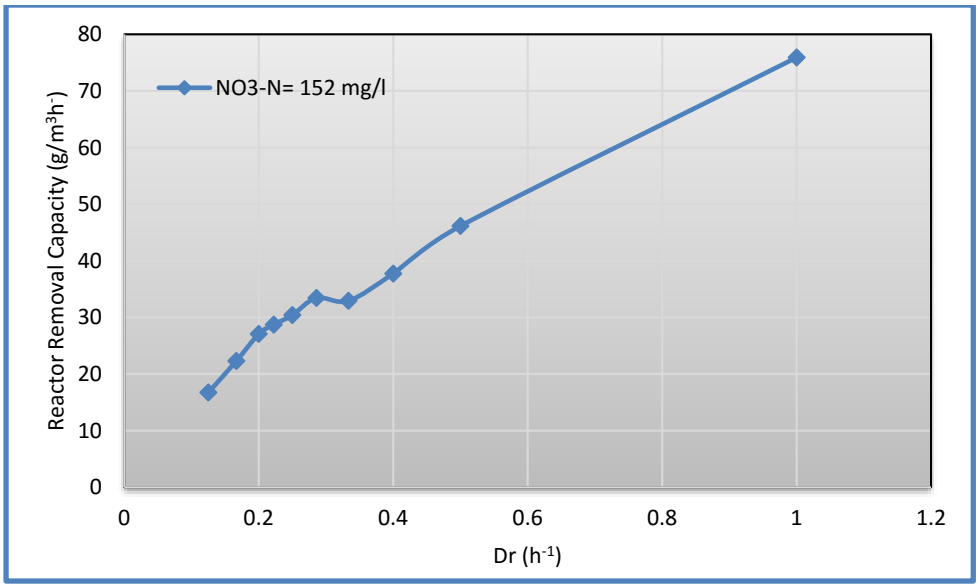

Figure 4.9: Reactor removal capacity with different dilution rate values based on 152mg/l NO_3^--N influent concentration

The reactor removal capacity results which was illustrated in figure 4.9, showed that at 5 hours HRT 88% denitrification efficiency was achieved at 27.06 ($g/m^3.h$), and it was ranged between 75.91 ($g/m^3.h$) at HRT 1hour and 16.72 at 8 hours.

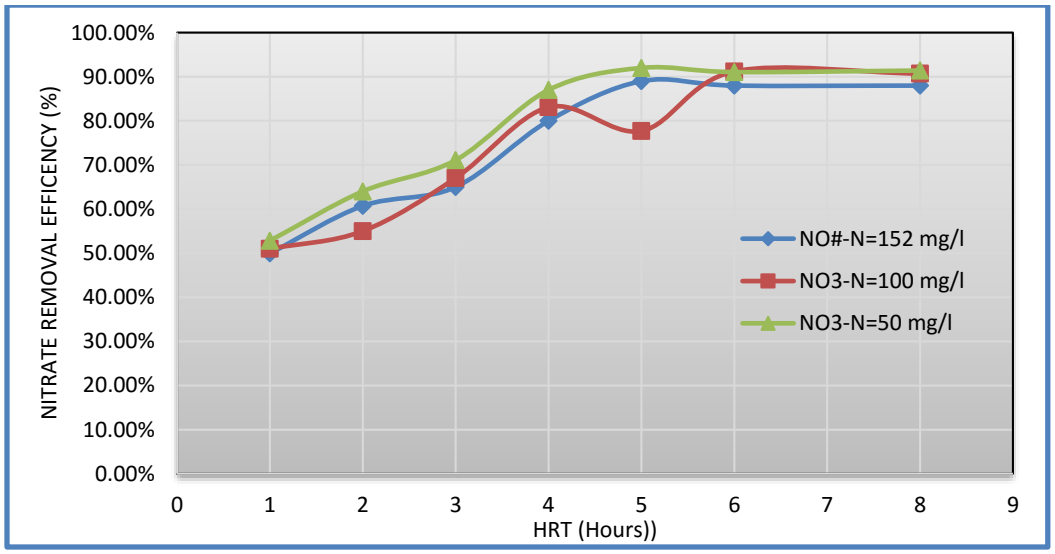

Figure 4.10: Nitrate Removal Efficiency with different HRT values and NO_3^--N influent concentrations

The results for several influent concentrations nitrate-nitrogen, was almost similar with minimal difference in the effluent quality due to higher nitrate loading (Figure 4.10). The reactor removal capacity was measured for all the tested concentrations, and it was clear that by increasing the HRT the reactor removal capacity increases proportionally. The reactor removal capacity was tested versus the dilution rate and it was plotted on the same graph (Figure 4.12).

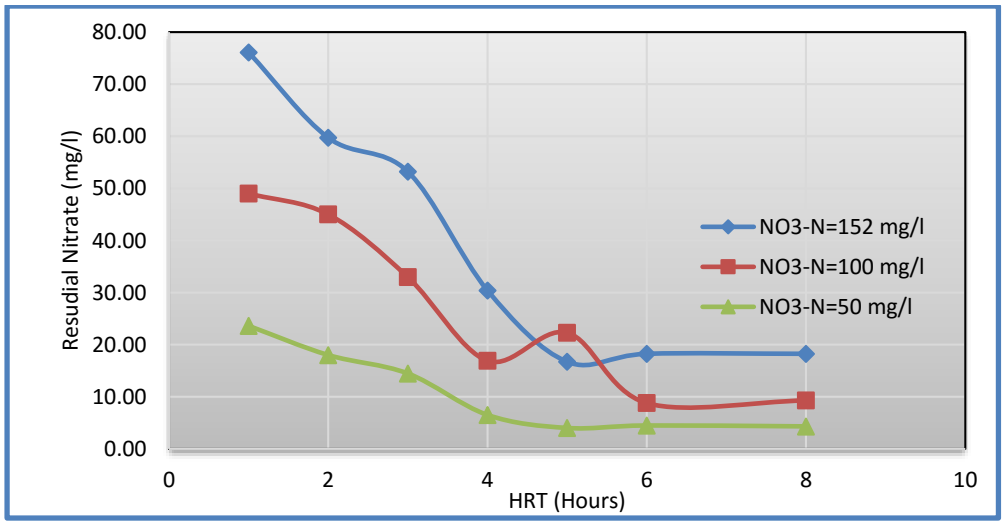

Figure 4.11: Residual nitrate effluent concentrations with different HRT values and NO_3^--N influent concentrations

The residual nitrate-nitrogen concentration for the different tested influent concentrations showed that at 100 and 50 mg/l nitrate-nitrogen, the effluent quality meets the drinking water requirements of the (WHO) after 6 hours and 5 hours HRT, as its clear in figure 4.11.

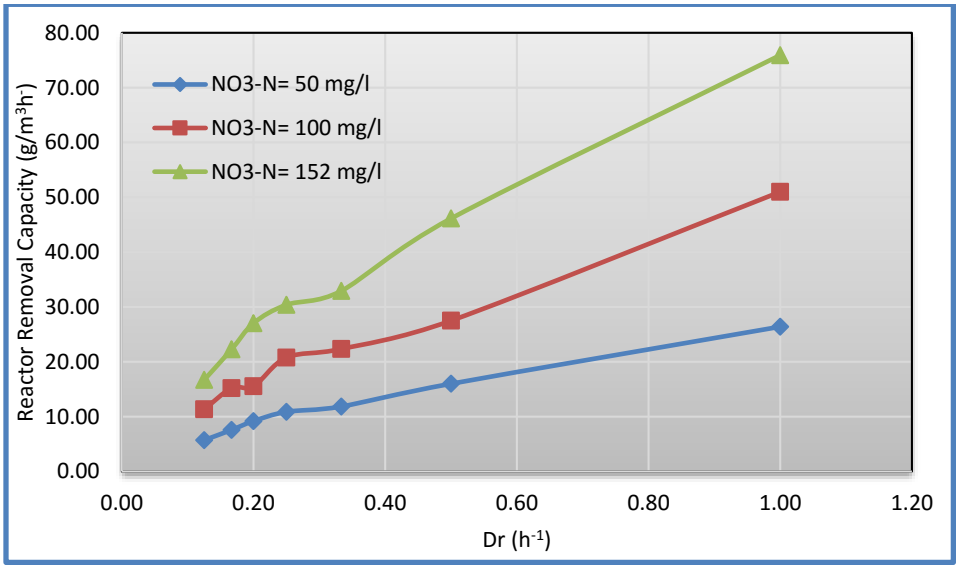

Figure 4.12: Reactor removal capacity with different dilution rate values and NO_3^--N influent concentrations

In general it can be concluded that the removal capacities are affected by the HRT and nitrate loading and drinking water quality was achieved for 100 mg/l and 50 mg/l influent nitrate-nitrogen concentrations.

Wang and Wang, (2011) during investigating the denitrification of nitrate-contaminated groundwater using biodegradable snack ware as carbon source under low-temperature condition, found that in the treated water, the nitrate concentration decreased obviously as the HRT increase, and as nitrate concentration in the influent decreases also, and they found that at HRT 2 hours and 50 mg/l influent nitrate-nitrogen concentrations, the nitrate removal efficiency at 12°C was approximately 40% while it was around 100% at 25°C.

In different study Nuhoglu et al., (2002) in testing the denitrification rate of drinking water using a membrane biological reactor, found that at dilution rate of 0.19 $d^-$the reactor removal capacity was 0.37 $g/m^3/d$, while they achieved 1.11 $g/m^3/d$ at dilution rate of 0.559 d^-, also, they found that the removal capacities for the reactor increased linearly by increasing dilution rate, and it meets the results in this study and as shown in figure 4.12.

Effect of Loading Nitrate

After figuring out that the nitrate loading affect the reactor removal capacity and denitrification efficiency, the effect of nitrate (NO_3^--N) loading concentration on the nitrate concentration was tested for influent nitrate concentrations 50, 88, 150, 185 and 225 mg/l NO_3^--N, Nitrate concentration of the effluent versus Nitrate loading is illustrated in the following figures and shown in table 4.6.

Table 4-6: Obtained results for different Nitrate loading rate.

$[NO_3^-N]_{in}$ (g/m^3)	$[NO_3^-N]_O$ (g/m^3)	Nitrate Loading (kgNO3--N/m3.d)	Nitrate Removal (kgNO3--N/m3.d)	Removal Eff. (%)
49.05	1.50	0.3924	0.38	96.94%
88.20	16.70	0.7056	0.57	81.07%
151.00	41.35	1.2080	0.88	72.62%
185.20	72.40	1.4816	0.90	60.91%
225.00	110.90	1.8000	0.91	50.71%

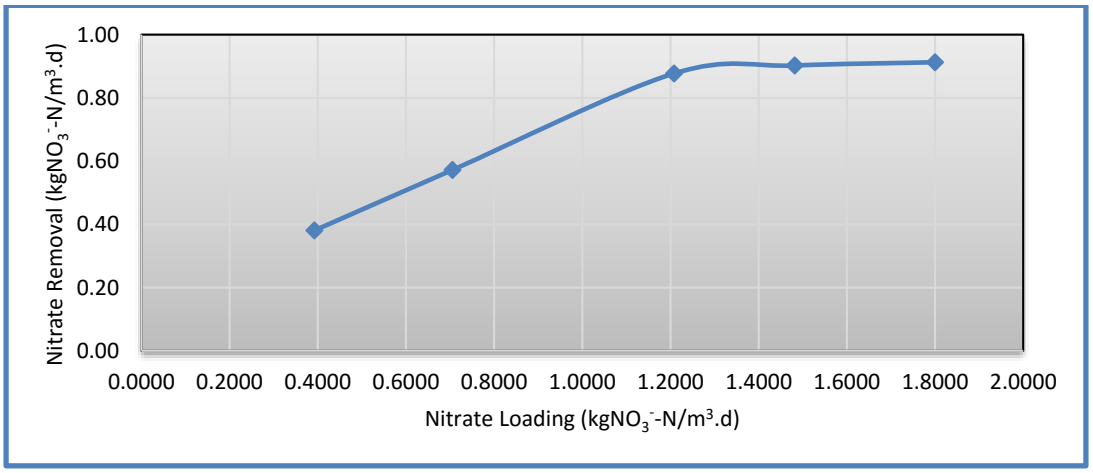

Figure 4.13: Nitrate removal loading with different NO_3^--N influent loading rates

Figure 4.13 shows that by increasing the influent nitrate loading, the nitrate removal load increases. In figure 4.14 below the residual nitrate concentration increase by increasing the influent concentration.

From the same figures and table 4.6, it was found that at nitrate volumetric loading rate of 0.394 kg/m^3.d the achieved nitrate loading rate was 0.38 kg/m^3.d, and removal efficiency

was about 97%, while by increasing the nitrate loading rate 1.2 kg/m^3.d the archived removal efficiency decreased to 72% and the nitrate removal loading rate increased to 0.88 kg/m^3.d. At higher nitrate volumetric loading rate of 1.48 and 1.8 kg/m^3.d the nitrate removal loading rate increased to 0.90 and 0.91 kg/m^3.d respectively.

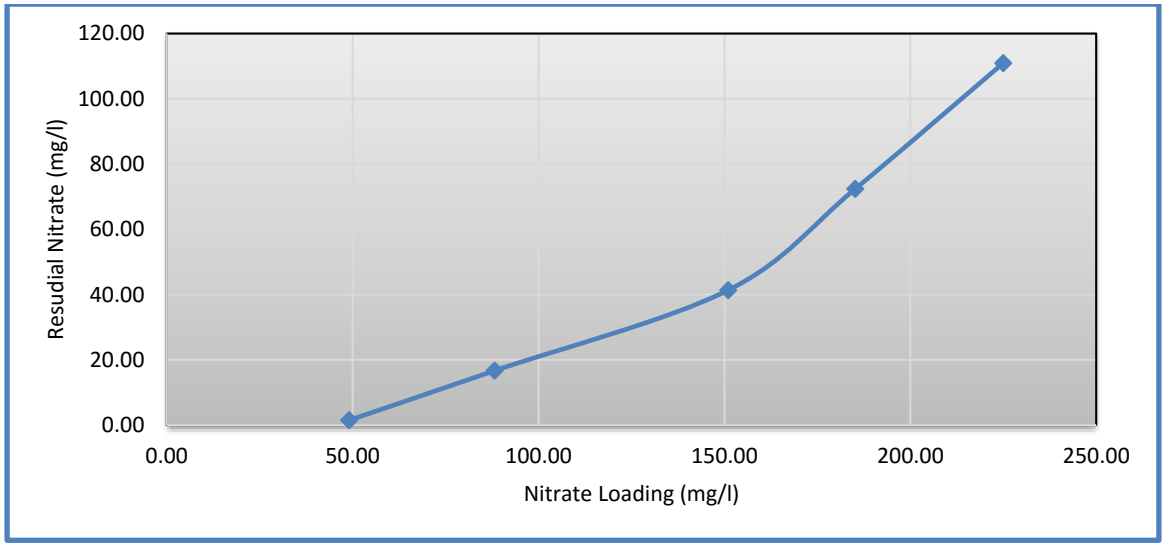

Figure 4.14: Residual effluent nitrate concentrations with different NO_3^--N influent loading rates

Nitrate removal rate significantly declined after 150 mg/l with an increase in the loading of Nitrate.

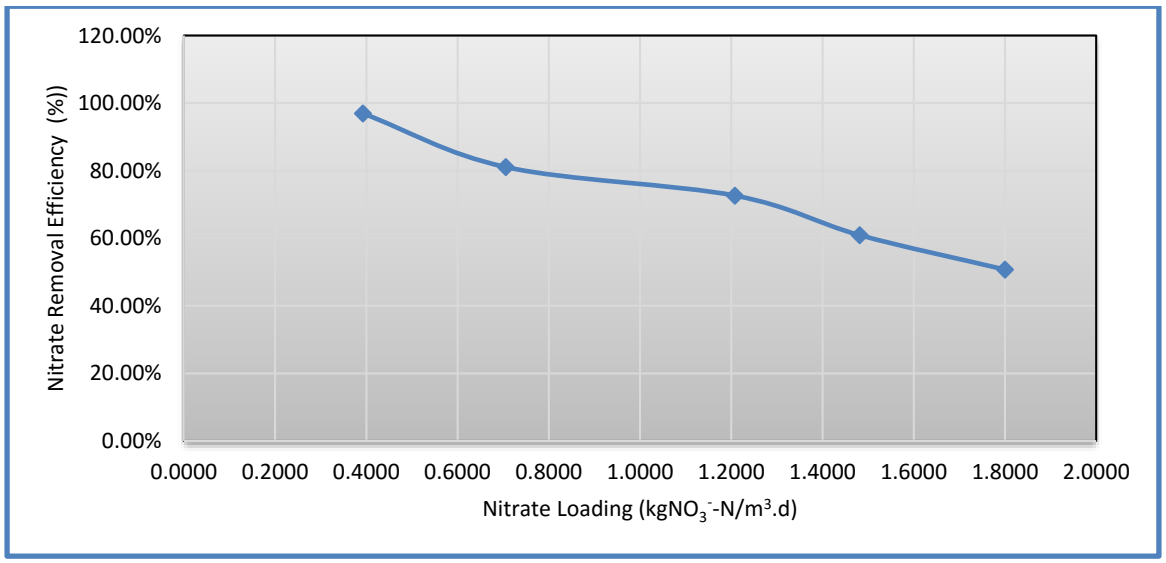

Figure 4.15: Nitrate removal efficiency with different NO_3^--N influent loading rates

By increasing the nitrate loading the nitrate removal efficiency decreases as shown in the previous figure 4.15.

Another study by Hoover et al., (2015) using woodchip nitrate removal bioreactors to examine the effect of temperature and HRT on denitrification process was held, and they found that nitrate-N removal results that under constant environmental and hydraulic conditions, NO_3^--N load reduction is increased when influent concentrations are higher. Also, it was concluded that greater NO_3^--N removal efficiency was obtained when nitrate loads entering the bioreactor were reduced, either by reducing the influent NO_3^--N concentration or by decreasing the influent flow to obtain longer HRTs.

4.4 Effect of MLSS concentration

In a continuous mode denitrification, the effect of the mixed liquor suspended solids (MLSS) concentration on the nitrate removal efficiency was tested. The test was started with 4000mg/l MLSS concentration, and it was diluted step by step to take several reading for the effluent nitrate concentration. The reactor was run with fixed COD/ NO_3^--N value around 7.0 and HRT of 5 hours.

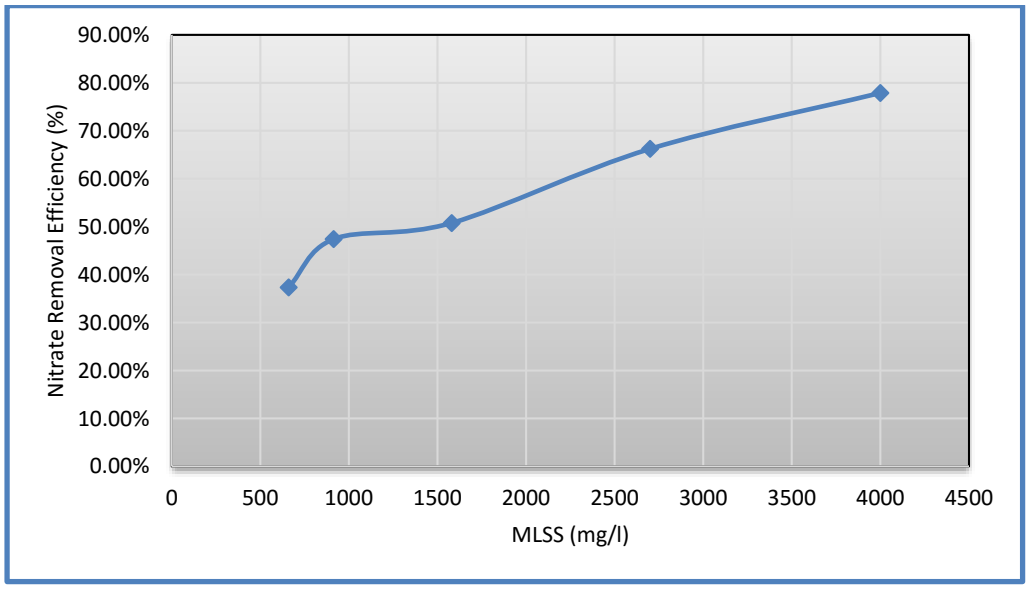

Figure 4.16: Nitrate removal efficiency with different MLSS concentrations

Figure 4.16 shows the effect of MLSS concentration on the denitrification efficiency, and it's clear that by increasing the MLSS concentration the nitrate removal efficiency increases. During the experiment, and at higher MLSS concentrations (above 2500 mg/l) a lot of foam appeared on the surface of the reactor, and affected the effluent turbidity.

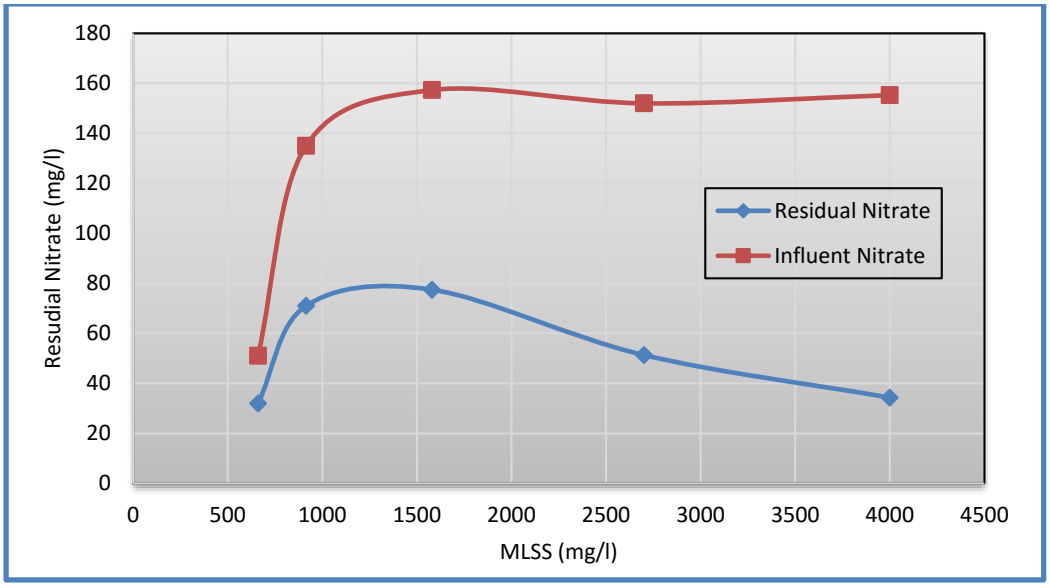

Figure 4.17: Residual nitrate concentrations with different MLSS concentrations

4.5 pH, DO, Turbidity Values

During the experiments the pH value, DO, and turbidity were monitored and tabulated and the results where illustrated in the following figures.

Table 4-7: pH values, DO concentrations, and Turbidity values during the tests.

Day	PH	Dissolved Oxygen (mg/l)	Turbidity (NTU)
1	6.8	0.60	2.12
5	6.9	0.42	1.41
10	7.2	0.35	0.4
15	6.8	0.15	0.39
20	7.7	0.21	0.14
25	6.7	0.18	0.11
30	7.4	0.30	4.66
35	7.6	0.18	6.2

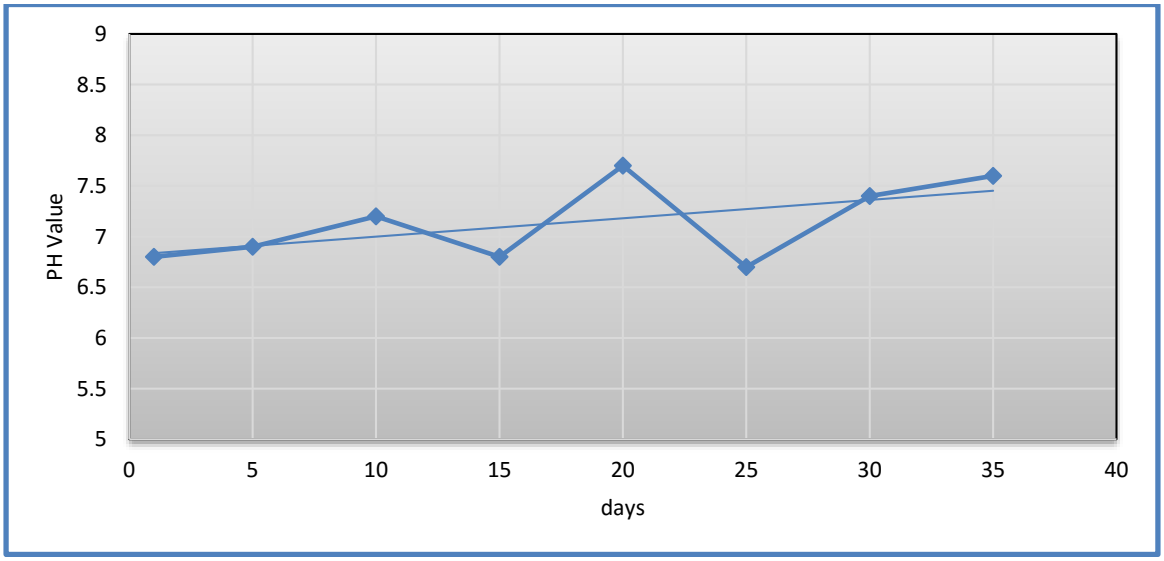

Figure 4.18: pH values during the tests

From the obtained results and figure 4.18 it's clear the pH values ranges between 6.7 and 7.6. It was expected to get high pH values above 8.5, but due to the acidity of the Whey which was used as carbon source in this experiment, it moderated the alkalinity generated during the denitrification process. And there were no need to add any solutions to get the required pH values range.

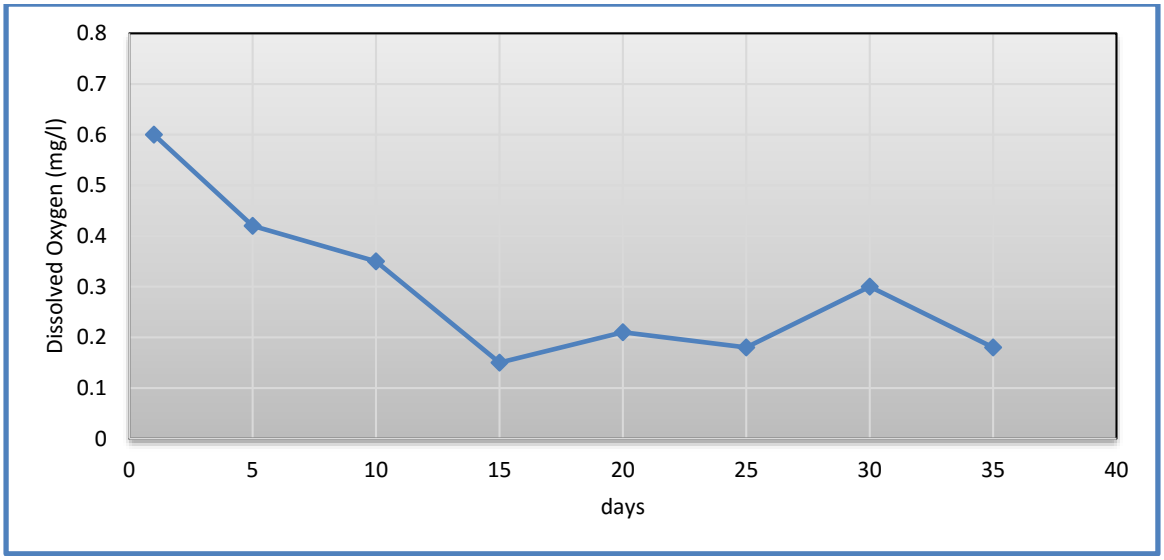

Figure 4.19: Dissolved oxygen concentrations during the tests

The previous figure shows that the denitrification process run with Dissolved oxygen concentrations below 0.5 mg/l as required and expected.

Figure 4.20: Monitoring the pH and DO values

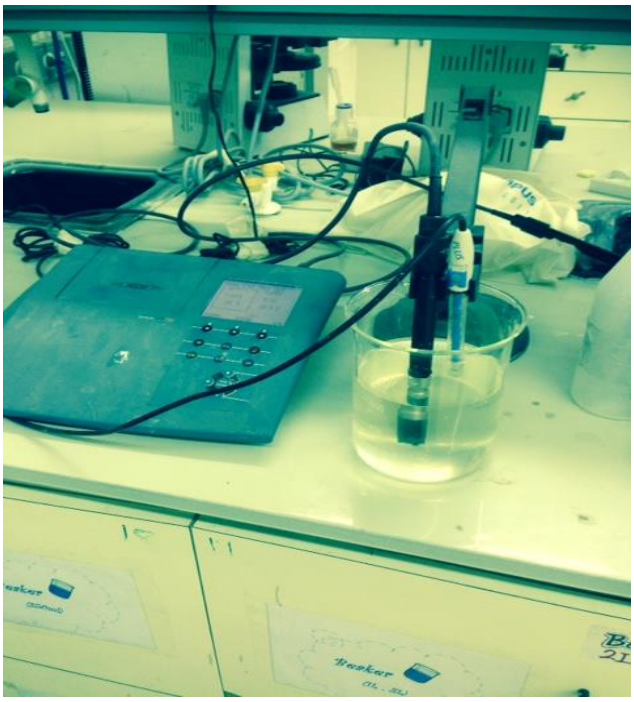

Figure 4.21: The DO and pH monitoring device

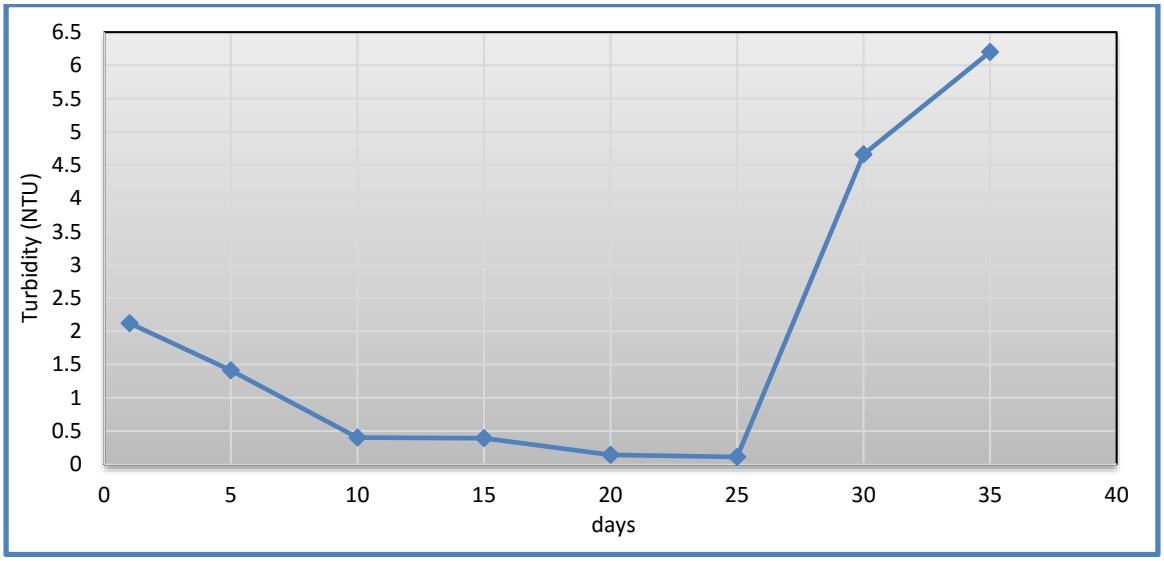

Figure 4.22: Turbidity values during the tests

Good turbidity values were obtained from the effluent. High turbid effluent was due to MLSS washout at high MLSS concentrations due to foaming.

Figure 4.23: Monitoring the Turbidity of the treated effluent

5. CHAPTER FIVE
FINANCIAL ANALYSIS

This chapter covers the capital and operational costs for a large scale biological water treatment plant for nitrate removal which simulate a real groundwater well in GAZA-Palestine. And it also covers the benefits and cost analysis.

5.1 Introduction

This thesis considers that one of the most challenges that facees the water treatment in GAZA-Palestine is to provide safe drinking water with low energy cost under the rising in the prices of fuel and electricity, at the same time reduce the amount of the nitrate contamination in groundwater. Therefore, this lead to test a design of a cost effective biological nitrate treatment plant using the whey as carbon source considering that the whey is a waste generated from the dairy production. Biological nitrate treatment can be considered as one of most options that can meet the growing energy demand in developing countries to treat groundwater sources contaminated with high nitrate levels above WHO limits.

The proposed large scale nitrate treatment plant will consists of main biological reactor, secondary sedimentation tank, sand filtration, and chlorine disinfection as shown in the following figure;

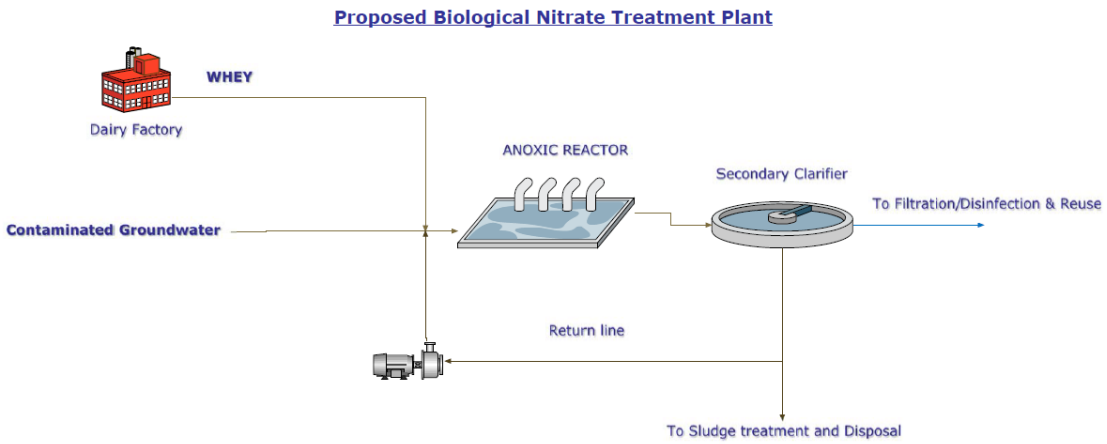

Figure 5.1: Suggested schematic diagram for the large scale nitrate removal plant

The proposed work will include;

1- Civil works; including the excavation, concrete work, backfilling, and landscaping.
2- Mechanical Work: which will include the pumps, mixers, motors, piping and valves.
3- Electrical Work; including power and control cables, instrumentation devices, PLC, MDB

The chosen well for the analysis locates in the middle area of Gaza holding the ID F1/85 according to Shomar et al.(2008). The depth of the Well is 50m and the Nitrate concentration is 146 mg/l NO3- (33 mg/l NO_3^--N) with estimated production of 90 m^3/hr. The estimated volume of the main anoxic reactor is 540 m^3, with 80m^2 surface area for the secondary sedimentation tank.

5.2 Costs of Biological Nitrate Water Treatment Plant

The cost of the biological system consists of capital cost (investment) and operational and maintenance cost

The system has been designed to reduce nitrate concentration by greater than or equal to 90%. The hydraulic retention time (HRT) adopted in the design depended on lab study; the NO3 -N, loading rate = 0.3924 kg/NO_3 -N/m^3/day and the groundwater concentration was 146 mgNO_3/l (33mg/NO_3^--N);

$$HRT\ (hr) = \frac{33\ \left[{}^{g}/_{m^3}\right]}{(0.3924 \times 1000)\left[{}^{g}/_{m^3.d}\right]} \times 24\left[{}^{hr}/_{d}\right] = 2.02$$

To be in the safe side the selected HRT is 6 hours.

Well flow rate =90 m^3/hr

$$Reactor\ working\ Volume\ [m^3] = 90\left[{}^{m^3}/_{hr}\right] \times 6[hr] = 540$$

- Based on the study results the required COD/$NO3^-$-N is 7.2
- The tested COD concentration in the Whey is 70 g/l

$$Nitrate\ Loading\ \left[{}^{kg}/_{d}\right] = 2160\left[{}^{m^3}/_{d}\right] \times 0.33\left[{}^{kg}/_{m^3}\right] = 71.28$$

$$Required\ COD\ Loading\ \left[{}^{kg}/_{d}\right] = 71.28 \times 7.2 = 513.216$$

$$Whey\ \ Required\left[{}^{m^3}/_{d}\right] = \frac{513.216}{70} = 7.33$$

5.2.1 Capital cost

Table 5.1 below lists all civil and electromechanical works needed to install large scale water treatment plant using the developed bioreactor or system considering the results obtained in this research study.

Table 5-1: Investment cost for different work types in the Treatment plant.

#	Type of Work	Application	Unit	QTY	Unit Cost (USD)	Total Cost (USD)	Design life (years)
1	Civil Work	• Whey Storage Tank • Main Anoxic Reactor • Secondary Clarifier • Aerobic tank • Sand Filtration • Chlorination • Landscaping	L.S	1	480,000	480,000	50
2	Mechanical Work	• RAS/WAS Pump • Submersible Mixers • Sand Filter Pumps • Blowers and diffusers • Chlorine Dosing Pump • Secondary Scum removal System.	L.S	1	210,000	210,000	15
3	Electrical Work	• MDB • PLC • Control and Power Cables • Isolating Switches	L.S	1	120,000	120,000	15
Total Cost (USD)						**810,000**	
Contingency (15%)						**121,500**	
Total Investment Cost (USD)						**931,500**	

The capital cost consists of all required civil, and electromechanical cost, which was estimated in table 5.1 depending on the local prices of excavation, concrete works, pumps and other electromechanical equipment and parts. The annual cost was calculated based on 8% interest rate for a project life 15 years.

5.2.2 Operation and maintenance costs

Table 5.2 shows the operation and maintenance cost estimation including the operators, guards, transportation, electrical consumption and maintenance

Table 5-2: Operation and maintenance cost for the Treatment plant.

#	Type of Work	Unit	QTY	Unit Cost (USD/year)	Total Cost (USD/year)
1	Operators	No.	2	12,000	24,000
2	Guard	No.	1	9,600	9,600
3	Transportation of Whey	No.	1	14,160	14,160
4	Maintenance	L.S	1	1,200	1,200
5	Electrical Consumption	L.S	1	35,520	35,520
	Total Cost (USD)				**84,480**
	Contingency (15%)				**12,672**
	Total O&M Cost (USD)				**97,152**

Operation and maintenance estimation cost is shown in Table 5.2 above and it was based on local cost of labors, grease, parts and electrical prices, and it presents 9% of the Capital cost.

To operate this system it was assumed that two operators are working during the day and one guard. The electrical estimated consumption was calculated based on 0.158 USD per kWh. The cost of the whey is only the cost of transportation since the whey is considered as a waste produced from the dairy factories and it was estimated as 38.8 USD per truck with capacity of 10 cubic meter per truck, and the system needs 7.33 cubic meter each day.

Table 5-3: Total Annual Cost

Type of Work	Investment Cost	Annual Cost Based of Depreciation
Investment Cost		
Civil works	480,000	9,600
Mechanical works	210,000	14,000
Electrical works	120,000	8,000
O&M		84,480
Total Cost (USD)		**116,080**
Contingency (15%)		**17,412**
Total Annual Cost (USD)		**133,492**

In finance, the depreciation is a decrease in the value of property through wear, deterioration, or obsolescence. As the technical life of a facility is limited, reservation should be made for the depreciation of facilities to recover the investment made. The users should, therefore, pay for the depreciation cost (Ross et al., 2005).

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Depreciation rate (d) = 1/n x100% (n = life period)

In order to compare the financial feasibility of the biological treatment with other well-known and applied technologies, the total annual cost and the total cost per cubic meter are calculated as follows;

$$Total\ Annual\ Cost\ (USD/year) = 133{,}492.00$$

$$Flow\ Rate\ [m^3/year] = 90\left[{}^{m^3}/_{hr}\right] \times 24\left[{}^{hr}/_{d}\right] \times 365\left[{}^{d}/_{year}\right] = 788{,}400$$

$$Total\ Unit\ Cost\ \left(\frac{USD}{m^3}\right) = \frac{133492}{788{,}400} = 0.17$$

$$Total\ Unit\ Cost\ \left(\frac{USD}{kg\ NO_3 removed}\right) = \frac{0.17}{0.33} = 0.513$$

The cost for treating one cubic meter of contaminated water with nitrate-nitrogen is about 0.17 USD and 0.513 USD per kg of nitrate-nitrogen removed. This means the municipality or the water department should add 0.17 USD for each produced cost of one cubic meter treated water.

5.3 Financial Comparison with other Technologies

The financial analysis shows that the biological system is found to be the least expensive. The reverse osmosis system is the most expensive; and the ion exchange system lies in between the reverse osmosis and the biological system in terms of overall economics as shown in table 5.4

Table 5-4: Summary for the total annual cost and unit cost for different types of nitrate removal systems.

		Biological	IX	RO
Capital Cost	USD/m^3	1725	1719	2569
Total Annual Cost	USD/m^3/year	247	325	470
Cost/m^3	USD/m^3	0.17	0.23	0.33

The Ion Exchange system consists of the Ion exchange unit, Softener and Electromechanical units and parts, for operation and maintenance it needs skilled labors, scheduled replacement of resins and salt addition.

Same as the IX system the Reverse Osmosis needs a RO unit, Softener and Electromechanical units and parts, and for the operation; in addition to the skilled labors it needs a scheduled membrane replacement and salt addition.

For reasonable and correct comparison the cost for all the compared systems was based on unit size (1000 Liter). The data for IX and RO systems were collected from a PHD thesis done in University of Regina in 2003 (Darbi, 2003). The biological unit cost in this study was the baseline for interpolation with the unit cost of the biological system in the PHD thesis in order to calculate the unit cost of the other systems (RO and IX) comparing with large treatment plant, but for sure these numbers are for study issues and could not be used directly in calculations for large scales, mainly for RO and IX.

Biological denitrification of nitrate rich brackish groundwater should be taken into consideration in future, where biological process could be examined to be coupled to renewable energy as an alternative solutions to overcome the water and energy issues in Palestine. Similar studies as Taha and Al-Sa'ed, (2014) highlighted the applicability of coupling renewable energy to desalinate brackish ground water in the Jordan Valley in order to achieve water security.

6. CHAPTER SIX
CONCLUSION AND RECOMMENDATIONS

Through this study, a bench scale of denitrification reactor with active volume 12L was designed constructed and operated under batch and continuous modes by using the Whey as a carbon source for the heterotrophic bacteria. In this study the optimum COD/NO3--N was measured through batch mode denitrification, and the effect of HRT, Nitrate Loading, MLSS concentrations on the nitrate removal efficiency and reactor removal capacity were tested. The conclusions drawn and recommendations based on results from this study are as following:

6.1 Conclusions

Biological nitrate removal of drinking water using a bench-scale reactor has been tested and studied as a function of biological and physical conditions. Several conclusions resulted from the investigation are as follows:

- The study of biological nitrate removal using Whey was a simple, reliable and cost effective treatment process for removal of nitrate that could have an application to nitrate removal from groundwater.
- Batch test results indicated that 7.2 was the COD/NO3-N best for optimal nitrate removal.
- The HRT and nitrate loading showed major impacts on the nitrate removal efficiency, and the results showed that more than 90% removal efficiency could be achieved at 5-6 hours HRT, also, increasing nitrate loading rate caused a decrease in nitrate removal.
- Whey as a carbon source for heterotrophic bacteria gives a good results on the denitrification efficiency in all the stages of the study, and it could be used as a carbon source to treat the nitrate polluted groundwater in a biological reactor.

- The results showed a good effluent quality for the other parameters (PH, Turbidity, COD, etc.) and it could be used safely for irrigation and animal drinking, while it needs post treatment if it will be used for drinking water for human consumption.
- Biological dentrification using whey could be much feasible than using other technologies like RO, especially that Whey is considered as a cheap industrial waste.
- Using whey as a carbon source is considered environmentally and economically friendly, since it will be collected from the dairy factories and there will be no free discharge for such pollutant in the environment. Also, it will encourage the dairy factory to provide their waste without the need of industrial WWTPs and this will save investment and running cost which could positively affect the dairy products cost.
- Financial results showed that Biological denitrification is the most feasible system for nitrate removal from groundwater over the RO and IX systems.

6.2 Recommendations

- Large-scale pilot studies are recommended to prove the technology of using suspended growth biological treatment for the remediation of nitrate-rich groundwater.
- Further studies are needed on effluent content (COD, Nitrite, DO, etc.).
- Further studies are needed for post treatment using filters, membranes, etc.
- Research is needed to determine the most efficient methods for post treatment.
- Several successful studies will convince the authorities for such solutions instead of expensive solutions.
- It's needed to review some parameters of the study like the HRT and nitrate loading effects using control devices and instruments.
- Applying the renewable energy in further studies for testing the denitrification of nitrate-rich groundwater.

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