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M.Sc. Thesis

Evaluation of Heavy Metals Removal in Different Municipal Sewage Works for Wastewater Treatment and Effluent Reuse

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Evaluation of Heavy Metals Removal in Different Municipal Sewage Works for Wastewater Treatment and Effluent Reuse

تقييم از الة المعادن الثقيلة في محطات الصرف الصحي البلدي المختلف لمعالجة مياه الصرف الصحي و إعادة استخدامه.

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The findings, interpretations and conclusions expressed in this study do not necessary express the views of Birzeit University, the views of individual members of the MSc committee or the views of their respective employers.

DEDICATION

I dedicate my dissertation work to my family. A special feeling of gratitude to my wife Manar and my Father and Mother, and to my sisters and all my friends

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It would not have been possible to write this master thesis without the help and support of the kind people around me, to only some of whom it is possible to give particular mention here.

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Abstract

Municipal wastewater contains about 7% of industrial water and is treated in different treatment systems. The production of industrial Plants mixed with domestic wastewater in the sewerage networks is called sewage. Some industries produce small amounts of water but may contain highly concentrated concentrations of organic or inorganic pollutants.

Among the inorganic pollutants heavy metals vary in concentration of metals and environmental impact. The presence of concentrations of some metals in untreated or treated wastewater exceeds the acceptable limit, which adversely affects the purification efficiency of treatment plants and the quality of treated water. The removal of heavy metals from different wastewater is a field of research that has been lectured by many researches with different objectives and methods of research.

Results of previous studies showed that activated sludge showed a variation in the level of removal of concentrations of heavy metals, and the quality and concentration of sludge played a role in the adhesion of some heavy metals and organic substances resulting from the metabolism.

The method of removing the heavy metals in domestic wastewater during the treatment process is still contradictory. According to the limits of our knowledge, answers to the potential operational problems caused by the presence of high concentrations of heavy metals and the degree of retardation of the biological process are still unknown. Is there a variation in the tolerance to different treatment systems under the presence of toxic heavy metals?

The lack of local knowledge about the levels and fate of heavy metals is still under development and calls for further research and studies. This research proposal explores the effectiveness of heavy metal removal in different treatment systems, including sludge systems in Beit Dajan (Nablus), Anza (Jenin) and the membrane bioreactor treatment plant in Al-Teereh (Ramallah).

The effects of various operational parameters including capacitor time, Age of Sludge, and wastewater characteristics will be evaluated.

The results will help to understand the efficiency of activated sludge systems in heavy metals removal, and provide optimized operational conditions, a sustainable wastewater treatment alternative for heavy metal removal, where effluent reuse schemes are planned. The possible impacts on soil and agricultural produce irrigated with heavy metals rich treated water are beyond the scope of this research study.

الملخص

تحتوي المياه العادمة البلدية على حوالي 7% من المياه الصناعية وتعالج في أنظمة معالجة مختلفة. ما ينتج من مياه صناعية يختلط بالمياه العادمة المنزلية في شبكات الصرف الصحي، ويدعى المزيح مياه صرف (عادمة) بلدية. بعض الصناعات تنتج كميات مياه قليلة ولكن قد تحتوي على تراكيز تلوث عضوية أو غير عضوية عالية التركيز.

من بين الملوثات غير العضوية العناصر الثقيلة متباينة في التركيز للعناصر والتأثير البيئي. وجود تراكيز بعض العناصر الثقيبلة في مياه الصرف الصحي غير المعالج او المعالج يفوق الحد المسموح به تؤثر سلبًا على فعالية التنقية لمحطات المعالجة وجودة المياه المعالج. إزالة المعادن الثقيلة من مياه الصرف المختلفة هو مجال بحث تناولته بحوث عديدة متباينة بالأهداف وطرق البحث.

نتائج الدراسات السابقة استخدمت فيها عملية الحمأة المنشطة أظهرت تباين بمستوى إزالة تراكيز للمعادن الثقيلة، ولعبت جودة وتركيز الحمأة دورًا بالتصاق بعض العناصر الثقيلة على الندف ومواد عضوية ناجمة عن عملية الأيض.

طريقة إزالة المعادن الثقيلة المختلفة في مياه الصرف الصحي المنزلي أثناء عملية المعالجة لا تزال متناقضة. وفق حدود معرفتنا، إجابات حول المشاكل التشغيلية المحتملة والتي تنجم عن وجود تراكيز مرتفعة من المعادن الثقيلة وما هي من درجة الأثباط بالعملية الحيوية لا تزال مجهولة. هل هناك تباين بدرجة التحمل لنظم معالجة مختلفة تحت وجود المعادن الثقيلة السامة؟

نقص المعرفة المحلية حول مستويات المعادن الثقيلة ومصيرها لازالت قيد التطوير وتدعو إلى مزيد من البحوث والدر اسات. يستكشف هذا المقترح البحثي فعالية إزالة المعادن الثقيلة في نظم معالجة تتبع تقنيات مختلفة وتشمل أنظمة الحمأة في بيت دجن (محافظة نابلس) و عنزة (محافظة جنين)، وأخرى محطة المعالجة بنظام الغشاء الحيوي في حي الطيرة (محافظة رام الله). سيتم تقييم آثار مختلفة المعايير التشغيلية بما في ذلك عمر الحمأة، وخصائص المياه الصرف الصحي وقياس تركيز العناصر الثقيلة في عينات التربة في مناطق خصصت لري السيب المعالج في كل من بيت دجن و عنزة. ستساعد النتائج في فهم كفاءة أنظمة الحمأة المنشطة في إزالة المعادن الثقيلة، وتوفير الظروف التشغيلية الأمثل. وتساعد في اقتراح بدائل لتقنيات معالجة أولية للمياه الصناعية بهدف تحقيق عمل محطات مستدام، يتوفر معه سيب معالج يكون آمن وبديل لمياه الشرب. الأثار المحتملة على التربة والمنتجات الزراعية. تقصي الأثار السلبية في بيئة التربة وجودة المنتج جراء ريها بمياه معالجة غنية بمعادن ثقيلة هو خارج نطاق هذه الدراسة البحثية.

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Abbreviations

As	Arsenic
В	Boron
BOD	Biochemical Oxygen Demand
BZUTL	Birzeit University Testing Laboratories
CAS	Conventional Activated Sludge
Cd	Cadmium
Cl	Chlorine
COD	Chemical Oxygen Demand
Cr	Chromium
Cu	Copper
EPA	U.S. Environmental Protection Agency
EPS	Extracellular Polymer Substance
FAO	Food and Agriculture Organization
Fe	Iron
Hg	Mercury
HMs	Heavy Metals
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometry

L	Liter
MBR	Membrane bioreactor
MCM	Million Cubic Meter
mg	Milligram
MLSS	Mixed liquor suspended solids
Мо	Molybdenum
Ni	Nickel
Pb	Lead
PCBS	Palestinian Central Bureau of Statistics
PPM	Parts per million
PS	Palestinian Standards
PWA	Palestinian Water Authority
QC	Quality Control Sample
Q septage	Amount of cesspits septage
Т	Temperature
WW	Wastewater
WWTP	Wastewater Treatment Plant
Zn	Zinc

Introduction

1.1 Background

Water is one of the renewable natural resources on earth and the most important characteristic of it, as a chemical compound, is its stability. Due to their occurrence in arid and semi-arid areas, most parts of the Arab world suffer from water scarcity, with the growth of the population; the problem is exacerbated as a logical consequence of the increasing demand for water to meet the needs of domestic, industrial and agricultural products. Not only the water problem in the Arab world rarely, but extends to the quality of water, which is low and turns into unsuitable water for use due to various reasons such as over pumping, excessive application of fertilizers and pesticides and the industrial, agricultural and domestic pollution (AWC and CEDARE 2004).

To alleviate the water crisis, serious consideration should be taken such as wastewater reclamation and reuse in many areas, including agricultural irrigation and this is considered as an adequate strategy to dispose of the effluents of conventional WWTPs.

According to the Palestinian Water Authority annual report of 2011, the available amount of ground water, which is the main source of drinking water, in the West Bank is estimated at 633-874 MCM of which the Palestinians have access to only about 15-20%. In addition to water scarcity and access limitation for the Palestinians, in recent years, a 'red line' has been crossed, as untreated or partly treated septage has begun to seep into these water sources. Alarming signals have been reported in some places of ground water pollution with high concentrations of Chloride, Sodium, Potassium and Nitrate, e.g. up to 250 mg/l, in both West Bank and Gaza Strip (Arij, 2007).

Access to fresh water resources is considered one of the main pillars that enhance the development of human civilization. In the Middle East area, groundwater is considered the main fresh potable water. In this region, the main fresh water sources come from the shallow Plio-plesocene and the deep Cenomounous (Eastern Mountain) aquifers.

In order for groundwater to meet its intended uses, it should achieve the assigned quality requirements. In the West Bank aquifers, the quality of ground water is considered good, in spite of the high salinity values in some areas mainly in the eastern part of West Bank. For example, in Jericho area, Chloride (Cl) was detected in very high concentrations. The reason behind that may be due to anthropogenic sources of pollution, or deep brine water and salt dissolution from the Lisan layers or due to agricultural back flow. However, considering the karstic nature of these aquifers, any pollution sources will eventually lead to extensive pollution in them (Aliewi et. al., 2005).

The effects of industrial development, urbanization and enormous human activities on the environment and natural resources are still the main issue in most of the environmental studies all over the world. High concentrations of pollutants such as nitrate and dissolved organics in drinking water can cause environmental and health problems. In rural areas, high levels of nitrogen and organic pollutants are usually detected in water resources due to live stocks and animal manure. Moreover, discharging raw wastewater to wadies and water streams and infiltration of wastewater from cesspits cause higher risk to ground water resources.

In Palestine about 59.8 % of the West Bank households have cesspit sanitation system where almost 3% are left without any sanitation systems (PCBS, 2011). The cesspits are left without lining, so septage seeps into the soil layers and eventually reach groundwater. Consequently, cesspits themselves pose increasing environmental pollution problems (Amous, 2014).

During infiltration process through soil and rocks layers, characteristics of fresh water in terms of dissolved materials change dramatically, the water-soil-rock interaction and/or mixing with saline formation water trapped in sedimentary rocks affect the solute inventory. Therefore, groundwater composition does not necessary matches that of infiltrated water. The change in composition depends to a large extent on recharge process itself where rate of interaction between infiltrated water and the surrounding interaction and the hydrochemical compositions of groundwater (Shalash, 2007). In semi-arid and arid areas where there is variation in their seasonal rainfalls, the amount and mechanism of recharge of aquifers control the quality of groundwater (Khayat, 2005).

Pollutants such as heavy metals pose a major threat to groundwater resources. They can contaminate groundwater through bioaccumulation, mobilization and migration for long distances from the source of input, leading to the contamination of groundwater supplies. Furthermore, heavy metals can also contaminate drinking water resources when transfer and react with other natural or additive elements leading to formation of side hazardous products. On the other hand, the impact of heavy metal on groundwater quality can be reduced or even eliminated by adopting best management practices for wastewater and agriculture disposal system.

In many areas, ground and surface water are now contaminated with an assortment of pollutants like heavy metals, persistent organic pollutants (POPs), nutrients and microorganisms that have an adverse effect on health. The effects of water pollution are not only devastating to people but also to natural resources and biodiversity (Strategic Environmental Research and Development Program-SERDP 2012).

1.1.1 Heavy Metals in Biosolids

Some heavy metals that commonly found in sewage sludge are micro- nutrients which considered to be essential for plant growth (e.g., copper, and zinc) and then beneficial to crops. However, like most elements, excess concentrations would have negative effect for plant growth. Other heavy metals are not considered to be essential for plant or animal nutrition, they are known to be toxic at defined concentrations to plants, animals and humans also (e.g., arsenic, cadmium, lead, and mercury).

Heavy metals are also somewhat immovable in soil, so they accumulate in the below layer of the soil and remain there to unknown period.

When determining the toxicity of a heavy metal, the route by which the smallest amount of an element can cause harm is used as the limiting concentration. For most heavy metals, this limiting route of exposure falls into one of three categories: plant growth, animal health, or human health (Table 1.1).

Element	Essential for	
	plant growth	Toxic
В	No	*P, **A, *** H
Cd	No	P, A, H
Cu	Yes	Р
Pb	No	A, H
Мо	Yes	Р, А, Н
Cr	Yes	P , A
Fe	No	P, A, H

Table1.1 : Heavy metal effects. (Brady and Weil, 1996).

*P = plants; **A = animals; ***H = humans. Bold designates the limiting route of exposure.

The sources of heavy metals in bio-solids are summarized to be as industrial, commercial businesses, internal everyday waste (from feces, cleaners, paints, utensils and equipment), eroding pipes, and excess from roads and roofs. However through the past few decades the heavy metal content of bio-solids has decreased as a result of the pre-treatment of industrial waste. But still existing in bio-solids in certain concentration.

The Environmental defense Agency in the United States stated in its rules of bio-solids proceeding (40 CFR Part 503), the hazardous indicators of HMs in bio-solids founded on many practices and removal activities as shown in table 1.2.

Table1.2: Environmental profiles/hazards indices of heavy metals in Biosolids (EPA, 40 CFR PARTS 257, 403 and 503):

Pollutants	Land Application	Landfill	Incineration
В	Х	Х	Х
Cd	Х	X	Х
Cr	Х	X	Х
Cu	Х	X	Х
Pb	Х	X	Х
Мо	Х	X	
Fe	Х		

Agreeing to (Sorme et al 2003), the quantities of different HMs that can arrive the central sewage system up to the treatment plant from altered incomes liable on several issues. (Sorme et al 2003) considered the sources of B, Cd, Cr, Cu, Pb, Mo, and Fe that came in to one of the largest WW Plants in Sweden.

Table1.3 : Main goods and activities that produce heavy metals to the combined sewage system up to the treatment plant (Sorme et al, 2003).

Heavy metal	Potential sources		
Cd	 Artists paint Atmospheric deposition Car washes Drainage water 	 Food Galvanized materials Large enterprises Powdered laundry detergent 	
Cu	 Brake lining Car washes Drainage water Food Large enterprises 	 Pipes and taps in the tap water system (including drinking water) Roofs 	
Hg	 Amalgam in teeth Amalgam from dentists Food 	Pipe sedimentsPowdered Laundry detergents	
Ni	 Chemicals added during wastewater treatment Car washes Atmospheric deposition 	 Drainage water Drinking water Food Large enterprises 	
Рb	 Asphalt Brake lining Car washes Atmospheric deposition 	Drainage waterLarge enterprisesPipe sediments	

		Galvanized materials
	• Car washes	• Large enterprises
Zn	• Drainage water	• Pipes and taps in the tap water
	Chemicals	system (including drinking
	• Food	water)
		• Tires

1.2 Study Objectives and Significance

In Palestine, the responsibility for the cost-effective of using wastewater treatment products is at present one of the most priorities at both levels formal and public, despite the fact that many sectors of wastewater treatment still having poor strategy and inadequate process and maintenance of the treatment plants, and where only low sanitization efficiency could be achieved, there are enormous plans for establishment of well-organized wastewater collection and treatment services in Palestine (Samara, N., 2009).

Planned plants which are under the donors significances are generally located in the bigger cities and urban areas (such as Jerusalem, Hebron, Ramallah, and Nablus). Moreover the effort of existing planned projects in the wastewater sector is more remarkable treatment facilities (e.g. German funding for WWTP in Al-Bireh). The planned and recently established urban sewage works were supporter determined and initiated (PWA, 2011).

The reuse of reclaimed wastewater in Palestine is a first concern rooted in the Palestinian Water Policy accepted by the PWA and the Ministry of Agriculture. Farming use of treated effluents was firstly projected in Jabaliah and Gaza City. On the other hand, the operation failed because of the absence of funds and refusal by local farmers as there is no social and cultural recognition. Reuse of treated effluent could become true only if productive treatment systems are fixed that provide effluents that fulfil with flooding principles. This gives the impression not to operate with any of the existing treatment plants in Palestine (EMWATER Project, 2004).

The goal of this study is to investigate the performance for using influent, effluent, oxic, anoxic, MBR effluent and dewatering machines produced in Al-Teereh MBR WWTP, and comparing it with influent, effluent, oxic and anoxic zones in Anza and Beit Dajan WWTPs.

In this study, effluent strategies and limitations were examined and compared with quality standards standings for HMs consolidation limits and appropriateness for additional application.

The study also tried to clarify the conception of any suggested strategies that may be established to regulate effluents application proceedings in Palestine.

1.3 Water in Palestine: supply and demand

The most important water sources in Palestine are rain, runoff, groundwater, and springs. As part of the Arab world, Palestine suffers from an additional problem, in addition to the arid and semi-arid climate conditions and rainfall variability, Palestinian territory suffers from a high population density and a lack of natural resources. The population density in the Palestinian territory reached 663 person/km² in 2009 (439 person/km² in the West Bank and 4,140 person/km² in the Gaza Strip), compared to 350 person/km² in 'Israel' (PCBS 2010). More than 177 thousands persons in the Palestinian territory (22.9% of West Bank localities) are not served by water services, About 454 thousand persons (12.1% of the total population in Palestine) obtain their water through the 'Israeli' company (Mekorot); 110 of these localities are Moreover, Palestine suffers from abnormal political situation. Since the beginning of the occupation of historic Palestine in 1948, 'Israel' has turned to control the water sources in the Palestinian.

territories and adopted several resolutions providing for the ownership of water in Palestine, and followed these decisions several measures on the ground to identify areas along the Jordan River, building of 'Israeli' settlements on Palestinian water resources, confiscation of Palestinian wells for the benefit of 'Israeli' settlements, impounding the waters of the valleys, as in eastern Gaza Strip, and not to give license to Palestinians to dig new wells. This is clear from the World Bank report (World Bank 2009). The report showed that the amount of water consumed by one 'Israeli' settler is four times the amount consumed by a Palestinian. 'Israeli' settlements control water resources and waste a lot of fresh water quantities, producing a lot of water which is disposed on the Palestinian areas contaminating the soil and the limited Palestinian water resources (Al-Tamimi, A; Rabi, A; Abu-Rahma, A 2007). About 142.7 million liters of water drained daily.

By settlers in the West Bank 'Israeli'settlements. Furthermore the establishment, expansion and annexation of the separation wall led to a large loss of western basin water; Palestinians lost 23 wells And 51 spring which produce about 7 million cubic meters of (PCBS 2009a). Currently water demand exceeds water supply. Groundwater is the major source of fresh water in Palestine and provides about 70% of drinking and domestic water needs. The main source of groundwater in the West Bank is in the Mountain Aquifer System (Figure 1.1), which is divided into three subsurface drainage basins: Northeastern; Western and Eastern (Qannam 1997). The Palestinian territories depend on two main sources of water: groundwater from wells and springs and the water purchased from the 'Israeli' water company (Mekorot). According to water statistics in the Palestinian territory annual report. (PCBS 2009b) groundwater is the largest source of water and it represents about 73.1% of the total water, followed by water purchased from Mekorot Company and springs water, which accounted for 18.7% and 8.2% respectively (Figure 1.2).

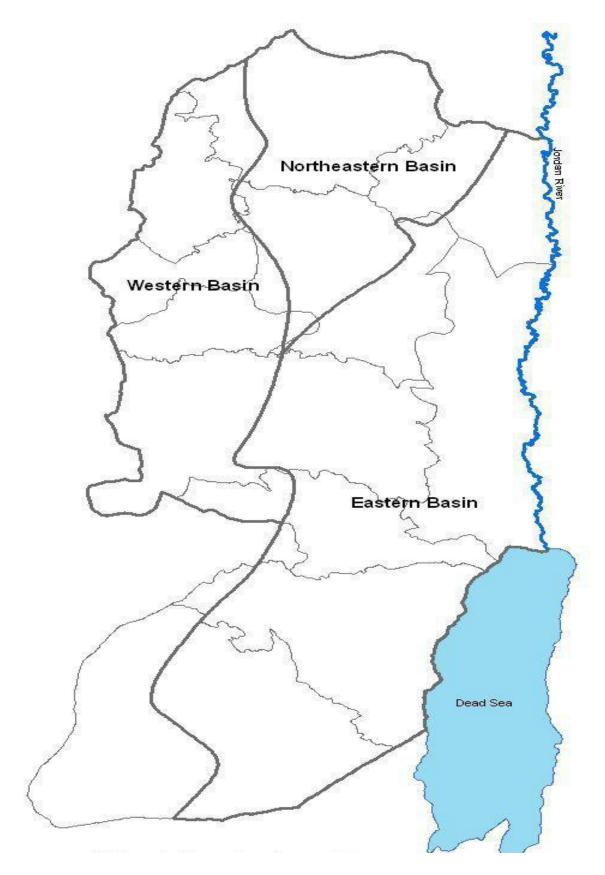


Figure (1.1) Mountain aquifer system in Palestine (ARIJ, 2007).

Literature Review

2.1 Background

In recent times controversial issues have been raised about the contamination of the environment with heavy metals. The discharges of industrial wastes that contain heavy metals drive a potential risk to an aquatic environment (Gautam, 2004). The removal of these heavy metals contaminants can be accomplished by applying different established techniques, including methodologies that either reduce or precipitate these HMs, ion exchange, electrochemical methods and reverse osmosis. However, all these could be still unsuccessful, especially for solutions with 1 to 100 (mg/l) of metal concentrations (Wang Q, 2011). HMs has been demonstrated to be toxic to microorganisms when they exceed acceptable concentration limits. Heavy metals forms an ill-defined group of inorganic chemical hazards, and the most commonly found at contaminated sites are: lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni). Soils can also be contaminated by the accumulation of heavy metals and metalloids in the course of the expanding industrial areas, disposal of high metal wastes, leaded gasoline and paints, fertilizing, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues. (S.Khan, et al, 2008). Heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering at levels that are regarded as trace (<1000 mg/kg) and rarely toxic, most soils of rural and urban environments may accumulate one or more of the heavy metals above defined limitations values, as a result can cause risks to human health, plants, animals. (Amore, et al, 2005).

2.2 Forms of Heavy Metal Occurrence in Sewage and Sewage Sludge

The level of pollution with HMs is determined by the amount of metal ions dissolved in sewage and sludge liquid phase, floating in suspension and precipitated with the sludge.

Ions of HMs can be naturally bound in them through (Alloway, 1995):

- Cation exchange and adsorption binding on the surface of fine particles (e.g. iron and organic substances).

- Organic binding – especially with humicacids, which are insoluble in water and which are characterized by a high ability to exchange cations. They cause the formation of chelates, from which HM ions do not return to the solution.

- Inorganic binding, which is a main means of binding HM ions.

- Co-precipitation with oxides or hydroxides of iron and manganese, which allows HM ions binding with the sludge.

- In sewage sludge, HMs can occur in mobile forms that migrate from the sludge to the fertilized soil, and also in immobile forms that do not produce any toxicological effect under given environmental conditions.

2.3 Removal Techniques (MBR, CAS)

2.3.1 Wastewater Treatment Processes

The principle of wastewater treatment is changing raw wastewater into clean water effluent and solid effluent (sludge) through a series of physical, chemical and biological processes. Therefore, wastewater treatment aims at converting raw wastewater influent into environmentally and hygienically safe effluents that can be reused safely in agricultural or industrial activities or even to be discharged into the receiving environment. New treatment techniques now a day such as membrane filtering process can even produce potable water, while the produced sludge can be used as bio-fertilizer which is more supportable than chemical fertilizers.

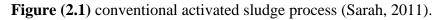
From the generation source until it is discharged as treated effluent, wastewater goes through many stages. The conventional wastewater treatment process is made up from a series of physical, chemical and biological unit operations according to which treatment systems can be classified as primary, secondary, and tertiary or advanced treatment. All these process aims at removing organic, inorganic constituents including nutrients and microbiological contaminants (Amirossadat, 2014).

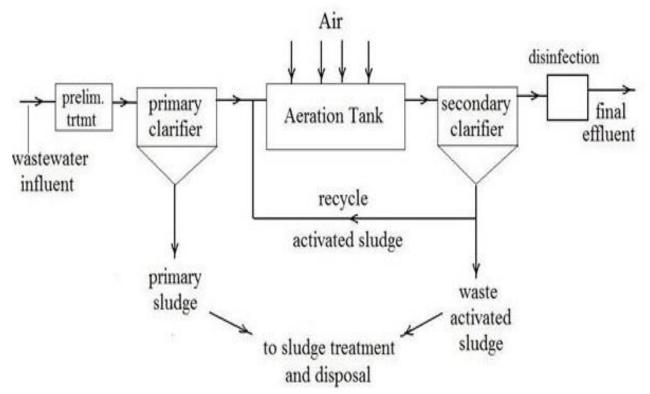
2.3.2 Conventional Activated Sludge Process (CAS)

Activated sludge-process was developed in England in the early 1900s but became widely used only after commenced in U.S. until 1940s. Now is the most widely used biological wastewater treatment in the world. This technique is the practical application of the theory of

suspended growth process in which microorganisms that are responsible for treating wastewater are maintained in the liquid suspension by some suitable mechanical means. Basically, these processes utilize the produced activated mass of microorganisms (MLSS or MLVSS) under aerobic conditions to stabilize the organic contents of wastewater. It is very effective process for the removal of soluble contaminants such as BOD₅ and ammonia.

During activated sludge, flocculation process occurs where flocs of particles ranging from 50 to 200 μ m are formed and then removed by gravity settling in the clarifier. The efficiency of treatment depends on the temperature and solid retention time (SRT) which is the time available for the flocculation and settling process. Basically, 3 to 5 days is usually recommended for BOD₅ removal at 18 to 25°C, while nitrification for example needs 1 day or less (Metcalf & Eddy, 2003).





Activated Sludge Wastewater Treatment Flow Diagram

2.3.2.1 Activated sludge process description

Basic mechanisms of activated sludge process:

- Aerated Reactor: To preserve microorganisms responding to biological treatment in the suspension as MLSS or MLVSS.
- Aeration Mechanism: Supply mixture with oxygen.
- Clarifier: Separate solids from liquid in the activated sludge effluent. This include mechanism for collecting settled solids to be either recycled as returned activated sludge (RAS) or eliminated from treatment process as waste activated sludge (WAS).

In activated sludge process, wastewater containing organic matters is supplied with oxygen by means of aerators in order to enable the microorganism to metabolize the suspended and soluble organics. During this process, some of the organics are converted into new cells (biomass), while other is oxidized into CO2 and water to obtain energy. In order to create a suitable environment for microorganism and increase the efficiency of the process, the pH and temperature should be maintained between 6.5 to 7.5, and15°C to 40°C respectively, while DO concentration should be kept above 2 mg/L (SUSTARSIC, 2009).

After definite time, bacterial lifecycle stops, the new formed biomass are then removed from water stream by settling in the clarifier. Part of the settled biomass (about 30-40%) is returned to the aeration tank to enhance the organic biodegrading process, the remaining part is removed from the process as wasted sludge and send to sludge digestion unit where it is treated to produce biogas and bio-fertilizer (Pipeline, 2003).

2.3.3 Membrane Bioreactors (MBRs)

2.3.3.1 Definition, applications and historical developments

Membrane bioreactors (MBRs) consist of two processes, the membrane-based filtrations processes such as MF or UF systems and the suspended growth biological reactors. MBRs can significantly change the bio solids separation role of secondary clarifiers in conventional activated sludge systems.

Membranes by themselves are not an efficient process for filtering raw wastewater directly. However, a combination of membrane with biological process can be more efficient in

treating raw wastewater containing dissolved organic matter and suspended biomass (Hai et al., 2014). Recently, MBRs are most common adopted processes to achieve a good quality of

treated wastewater through a combine operation of oxidation of organic matter, suspended solids and nutrient removal and microbial decontamination (Marti et al., 2011).

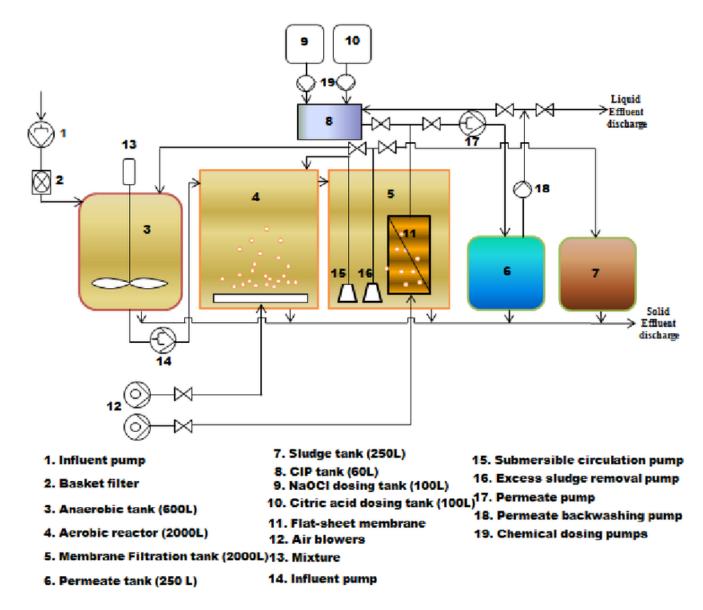
MBR systems have been developed since 1960, and it was a milestone in the history of wastewater treatment process. Between 1960s and 1980s, MBRs was at its golden age of membrane science. The cross-flow membrane filtration looped side stream was the first application of MBRs that couple membrane system with activated sludge bioreactor (Smith et al., 1969).

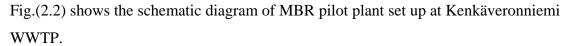
One of the disadvantages that face the early MBRs was the high cost and high energy consumptions. In 1989, MBR technology witnessed a new era by the introduction of the first submerged or immersed membranes. This new technology is considered more cost effective when talking about large scale plants and lower organic loading rates, while the side stream MBRs (sMBR) remains more effective for smaller scale and higher organic loading rates (Hai et al., 2014). Accordingly, aerobic and anaerobic MBRs started to be used commercially with small footprint over conventional processes (Brindle, Stephnson, 1995).

2.3.3.2 Membrane Bioreactor (MBR) pilot plant set up and process descriptions

In an MBR pilot plant developed by Kubota Corporation, a membrane module consisting of a submerged Membrane Unit (SMU) and MF process has been used for solid-liquid separation in biologically active mixed liquor. Solid particles having larger diameter than the membrane pores get trapped outside the membrane surface, therefore, organics, inorganic, pathogens and micro pollutants are screened from liquid passes through membrane pores.

Figure (2.2): Schematic diagram of MBR pilot plant set up (Khum, 2016).





In the MBR pilot plant (Fig 2.2); a water pump at the starting point (1) controlled by automatic valve feeds the MBR system with wastewater. Wastewater fed by the pump is firstly filtered by a basket type filter (2). The filtered wastewater is then sent to anaerobic tank (3) equipped with mechanical mixing equipment (13) placed in the beginning of the system. In the anaerobic tank, the incoming flow is agitated continuously to achieve

anaerobic digestion. After that, wastewater in the anaerobic tank is pumped (pump 14) to an aerobic reactor (4). Wastewater is then sent to by gravity the membrane tank (5) consisting of flat-sheet membrane cartridges (11). In order to supply the aerobic tank a membrane tank

with air, two air blowers (12) with air diffusers are used. Pumps (15 and 16) in the membrane tank are used to circulate and waste the excess of the mixed liquor from the tank respectively. Waste sludge is either pumped to the sludge tank (7) or recycled back to the anaerobic tank.

Liquid extracted through membranes are collected in the permeate tank (6) by means of negative pressure created by permeate pump (17). The collected permeate is then discharged as treated effluent, part of which is used for backwashing and chemical treatment of membranes to get rid of fouling using pump (18). The membrane washing chemicals are stored in two different tanks, tank (9) for sodium hypochlorite (NaOCl) and tank (10) for citric acid. In the chemical cleaning process, liquid NaOCl and Citric acid are pumped to the Clean-in-Place (CIP) tank (8) along with permeate water and the ready diluted solution is injected to the membranes by gravity flow.

2.3.4 Comparison between MBR and CAS

MBRs generate high quality effluent since they can remove nearly 100% of suspended solids and almost 90% of COD (Abeynayaka, 2009). They appear to have many advantages over the CAS processes among which: cheap footprint, better effluent quality, and low sludge generation (DeCarolis et al., 2007). On the other hand, membrane fouling, high cost investments are still considered the major disadvantages. A comparison between conventional activated sludge process and emerging MBR technology are summarized in Table (2.1).

Table 2.1: Comparing between conventional activated sludge processes and emerging MBRtechnology (Samarah, 2009).

Membrane bioreactor	Conventional activated sludge
(MBR)	(CAS)
Advantages:	Disadvantages:
• High quality effluent	• Low quality effluent
• Smaller treatment plant foot print	• Large land requirement
• No need of secondary clarifier or	• Secondary clarifier is necessary for
even primary clarifier	solid and liquid separation of treated
• Relatively shorter start-up time	effluent
• Can operate with higher MLSS	• Need longer start-up period
concentrations	• Limited to MLSS concentrations

- Lower sludge production Higher sludge production ٠ • High endurance on shock loading Low endurance to shock loading Less man power needed for O/M More man power needed for O/M • Less sludge bulking and rising High sludge bulking and rising Disadvantages: Advantages: Higher risk of membrane fouling No means of fouling • Expensive membrane costs and other Low O/M cost ancillaries Relatively low energy
- High energy dissipation cost
- Shorter membrane life span
- Need of proper pretreatment •

- consumption
- Relatively longer operational life span

2.4 Basic Soil Chemistry and Potential Risks of Heavy Metals

Knowledge of the basic chemistry and associated health effects of these heavy metals is necessary in understanding their speciation, bioavailability, and remedial options. The destiny and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are absorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity (J. Shiowatana, R. G. McLaren, 2001, J. Buekers, 2007). Heavy Metals' distribution in soil controlled by several reactions such as (i) mineral precipitation and dissolution, (ii) ion exchange, absorption, and desorption, biological immobilization and mobilization. (NSC,2009).

2.4.1 Lead

Lead: is a metal with atomic number 82, atomic mass 207.2, density 11.4gcm⁻³, melting point 327.4°C, and boiling point 1725°C. Lead ranks fifth behind Fe, Cu, Al, and Zn in industrial production of metals. About half of the Pb used in the U.S. goes for the manufacture of Pb storage batteries. Ionic Lead, Pb (II), Lead oxides and hydroxides, and Lead-metal oxyanion complexes are the general forms of Pb that are released into the soil, groundwater, and surface waters. The most stable forms of lead are Pb (II) and Lead-hydroxy complexes. Lead (II) is the most common and reactive form of Pb, forming mononuclear and polynuclear oxides and hydroxides (GWRTAC, 1997).

Lead (II) compounds are predominantly ionic (e.g., $Pb^{2+} SO4^{2-)}$, whereas Pb (IV) compounds tend to be covalent (e.g., tetraethyl lead, Pb (C₂H₅)₄). Some Pb (IV) compounds, such as PbO₂, are strong oxidants. Lead forms several basic salts, such as Pb(OH)₂·2PbCO₃, which was once the most widely used white paint pigment and the source of considerable chronic lead poisoning to children who ate peeling white paint. Many compounds of Pb (II) and a few Pb (IV) compounds are useful. The two most common of these are lead dioxide and lead Sulphate, which are participants in the reversible reaction that occurs during the charge and discharge of lead storage battery.

Lead is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys (GWRTAC, 1997).

2.4.2 Chromium

Chromium is a first-row *d*-block transition metal of group VIB in the periodic table with the following properties: atomic number 24, atomic mass 52, density 7.19g cm⁻³, melting point 1875° C, and boiling point 2665° C. It is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Major sources of Cr-contamination include releases from electroplating processes and the disposal of Cr containing wastes (Smith et al., 1995). Chromium is associated with allergic dermatitis in humans.

2.4.3 Cadmium

Cadmium is a metal with atomic number 48, atomic weight 112.4, density 8.65 g cm-3, melting point 320.9°C, and boiling point 765°C. Together with Hg and Pb, Cd is one of the big three heavy metal poisons and is not known for any essential biological function.

Cadmium is produced as an inevitable byproduct of Zn and occasionally lead refining. The application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the

total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake occurs to a significant degree (Weggler et al., 2004). Cadmium is very biopersistent but has few toxicological properties and, once absorbed by an organism, remains resident for many years. Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in protein urea is the result of Cd adversely affecting enzymes responsible for re-absorption of proteins in kidney.

2.4.4. Copper

Copper is a transition metal which belongs to period 4 and group IB of the periodic table with atomic number 29, atomic weight 63.5, density 8.96 g cm⁻³, melting point 1083°C and boiling point 2595°C.

Copper is an essential micronutrient required in the growth of both plants and animals. However; in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Copper normally occurs in drinking water from Copper pipes, as well as from additives designed to control algal growth.

2.4.5. Sources of Heavy Metal in the Domestic wastewater:

The sources of heavy metals to a wastewater treatment plant was investigated. Sources can be actual goods, e.g. runoff from roofs, wear of tires, food, or activities, e.g. large enterprises, car washes. The sources were identified by knowing the metals content in various goods and the emissions from goods to sewage. Results show that it was possible to track the sources of heavy metals for some metals such as Cu and Zn (110 and 100% found, respectively) as well as Ni and Hg (70% found). Other metals sources are still poorly understood or underestimated (Cd 60%, Pb 50%, Cr 20% known). The largest sources of Cu were tap water and roofs. For Zn the largest sources were galvanized material and car washes. In the case of Ni, the largest sources were chemicals used in the WTP and drinking water itself. And finally, for Hg the most dominant emission source was the amalgam in teeth. For Pb, Cr and Cd, where sources were more poorly understood, the largest contributors for all were car washes (Sormea,2002).

Metal	Soil concentration range	Regulatory limits
	(mg/kg)	(mg/kg)
Pb	1.00–69 000	600
Cd	0.10–345	100
Cr	0.05–3 950	100
Hg	<0.01-1 800	270
Zn	150–5 000	1 500

Table2.2 : Soil concentration ranges and regulatory guidelines for some heavy metals.

Table2.3 : Target and intervention values for some metals for a standard soil.

Metal	Target value	Intervention value
	(mg/kg)	(mg/kg)
Ni	140.00	720.00
Cu	0.30	10.00
Zn	-	-
Cd	100.00	380.00
Pb	35.00	210.00
As	200.00	620.00
Cr	20.00	240.00
Hg	85.00	530.00

* <u>The intervention values</u> indicate the quality for which the functionality of soil for human, animal, and plant life are, or threatened with being seriously impaired. Concentrations in excess of the intervention values correspond to serious contamination. <u>Target values</u> indicate the soil quality required for sustainability or expressed in terms of remedial policy.

(Rosin et al., 1982) carried out research on the influence of process parameters on removal of heavy metals. They studied the behavior of six heavy metals Cadmium, Copper, Nickel, Chromium, Zinc and Nickel at normal to elevated concentrations. The maximum removal was observed for the sludge age of 12 days. The shock loads does not have very significant effect on the removal efficiency. The soluble metals, i.e. Nickel, Cadmium and Copper exhibited less removal efficiency than other three metals. Overall activated sludge found to be satisfactory bio-absorbent for removal of majority of heavy metals of concern.

Ajaykumar, (2009) investigated various parameters in the bio-sorption of heavy metals on activated sludge. To understand the action of bio metals uptake, the essential role played by extracellular polymer substance (EPS) needs to be understood. They studied factors influencing the bio-sorption of the heavy metals are cleaning of the sludge, pH, initial metal ion concentration, weight of the adsorbent, mixing index, time and temperature. As the sludge mass increases the number of binding sites for the ions also increases with initial metal ion concentration the removal efficiency decreased. The reason may be agglomeration

and aggregation of adsorbent particles at higher concentration, leading to decrease in surface area available. Mixing speed was found to increase the removal efficiency. With temperature the loading capacity of adsorbent decreases.

Liu et al. (2001) investigated the heavy metals removal in a fixed activated sludge system (FAS) from industrial wastewater containing Cr, Ni and Pb. They achieved removal rates of 84%, 75% and 80% for chromium, lead and nickel; respectively. Other researchers (Niec et al., 2000) reported that using an anaerobic selector preceding the activated sludge system improved the heavy metals (Zinc, Cadmium, and Nickel) bio-sorption capacity on microbial flocs compared to conventional activated sludge system. (Oviedo et al., 2002) studied the toxic effects of the metals Cadmium, Zinc and Copper on the microbial activity in the activated sludge process and concluded that Cadmium is the most highly toxic metal for the microbial communities present in the activated sludge process, followed by Copper, and lastly Zinc. Other studies (Wu et al., 2004) investigated the immobilization of heavy metals (Zn, Cu & Cr) on activated sludge using Calcium alginate beads to immobilize the sludge flocs. They found that heavy metals adsorption rate of pretreated activated sludge was much greater than the immobilized sludge.

The presence of heavy metals in domestic wastewater, though of low content, has been explored because of their known toxic effects on the receiving environment and also on the performance of biological wastewater treatment systems (You et al., 2009; Vaiopoulou et al., 2012; Dhokpande et al., 2014). Heavy metals limits exceeding those nationally prescribed in rules and guidelines for the recycling of treated effluent in agricultural irrigation may cause health and environmental hazards public, irrigated produce and soil environment.

Chapter Three

Research Design and Applied Methodologies

3.1 Introduction

Three WWTPS operating in Anza, Beit Dajan and Alteereh were investigated for heavy metals removals, the reclaimed water is will be used for agricultural purposes. Anza and Beit Dajan WWTPs, using extended aeration process and serving 3500 and 4500 capita, are located in Jenin and Nablus districts respectively. Alteereh WWTP, an advanced membrane bioreactor (MBR) is serving Alteereh suburb with about 25.000 capita in Ramallah city. The activated sludge systems in Anza and Beit Dajan WWTPs treating domestic wastewater from Anza and Beit Dajan villages are designed for biological nutrient removal with separate aerobic sludge digestion. Whereas Alteereh MBR facility presents an advanced WWTP using ultra filtration membranes instead of secondary settling tanks as implemented in both Anza and Beit Dajan sewage works. Farmers in both Anza and B. Dajan are using the treated wastewater (350 and 450 m³/d, respectively) in agricultural irrigation while the reclaimed water (1600 m³/d) from Alteereh MBR facility is discharged into nearby seasonal wadi, hence unplanned aquifer recharge is practiced.

3.2 Brief Description

This study reflected mainly laboratory work for measuring the HMs in wastewater samples obtained from specific plants from different regions (Ramallah, Nablus and Jenin), in order to compare the removal Efficiency, and evaluate the concentrations of HMs in the soil.

It has been collected 72 samples from influent, oxic, anoxic and effluent samples from three selected wastewater treatment plants per month at particular time intervals around. The aim of these analyses was to have clear indicators about types of HMs inflowing the activated sludge and MBR sinks through the coming flow of raw wastewater. Moreover, it was also important to evaluate quantities of different examined o HMs which could be in turn accumulated in soil.

The HMs that had been examined are (Cu, Cr, Fe, Mo, Pb, Cd and B) are generally recognized to contaminate wastewater and have toxicity effects on crops grown in contaminated soils.

3.3 Heavy metals determination and assessment for WWTP

The methodology of the experiment consisted of four main steps:

I. Samples collection: This step include the gathering of requested samples (wastewater and soil) from the aimed sources (Alteereh, Beit Dajan and Anza WWTP), applying a recommended sampling and preservation techniques. Collected samples of wastewater from influent, oxic, anoxic and effluent have been handled in order to prepare them the performance of the planned analysis. This preparation involved samples drying, digestion, dilution and preservation. These samples were tested to determine the HMs concentrations.

II. Laboratory analysis of heavy metals concentrations:

Inductively Coupled Plasma – Atomic Emission Spectrophotometer ICP-AES was used to examine the collected samples at Testing Laboratories Center in Birzeit University, in order to measure the concentrations of listed HMs: Pb, Zn, Cu, Ni, Cr, Cd, As, and B.



Photo 3.1: ICP-AES instrument used for heavy metals analysis

3.3.1 Sampling procedure

In each single sampling round, six kinds of samples were collected. These samples as mentioned before; were collected from the raw WW Influent, WW oxic, WW anoxic and treated WW effluent; however, the soils samples were collected from the site around Anza plant.

The procedure of sampling was applying according to the (APHA 2005).

3.3.1.1 Wastewater sampling

The WW samples were taken over six months (August 2015- January 2016). A total of six samples has been gathered and analyzed to determine the concentration of HMs. Aimed at each sampling round, four samples were collected, the sample from the raw WW coming in to the plant (influent sample), oxic sample, anoxic sample and also the sample from the treated WW coming out of the treatment plant (effluent sample).



Photo 3.2: Alteera Wastwater treatment plant



Photo 3.3: Alteera oxic and anoxic zone



Photo 3.4: Anza oxic and anoxic zone



Photo 3.5: Water treatment line for irrigation in Anza

Sampling tools

- Clean polyethylene bottles were used to collect the samples.
- From each type of samples A 1 liter samples had been collected.
- Samples were collected through 15 minutes of continuous flow.
- Finally; the collected samples had been sent to the test center within 1 hour.

Chapter Four

Results and Discussion

4.1 Results:

Detailed samples and analyze results is attached in annexes as following:

- Results of Data Collection include:
 - o Influent and effluent concentrations in each wastewater treatment plant
 - Influent and effluent concentrations in each wastewater treatment plant for oxic and anoxic zone

Recommended values for irrigation

Table4.1 : Recommended maximum concentrations of trace elements in irrigation water according to Palestinian standards (Yassin et al, 2008)

	Alteereh	Beit Dajan	Anza	Palestinian limit
Element	effluent	effluent	effluent	values
	(mg/l)	(mg/l)	(mg/l)	(mg/l)
В	0.37	0.21	0.185	0.700
Cd	0.006	ND	ND	0.010
Cr	0.016	0.067	0.042	0.100
Cu	0.268	0.08	0.044	0.200
Мо	0.005	0.016	0.063	0.01
Fe	0.167	1.909	0.394	5.000
Pb	ND	ND	ND	0.100

• ND : Not Detected

4.2 Wastewater influent and effluent analysis Alteera

The results shown below in figure (4.1) that the Boron concentration was 0.37 mg/l, Cadmium 0.0063 mg/l, Molybdenum 0.005 mg/l, Chromium 0.016 mg/l, Copper 0.268 mg/l, Iron 0.167 mg/l, Lead was below detection limit in influent and effluent for the treatment plant.

In comparison with the recommended maximum concentrations of trace elements in irrigation water according to Palestinian standards mention in Table (4.1), all elements did not exceed the allowable limit for irrigation. Except Copper exceeded the allowable limit of 0.20 mg/l

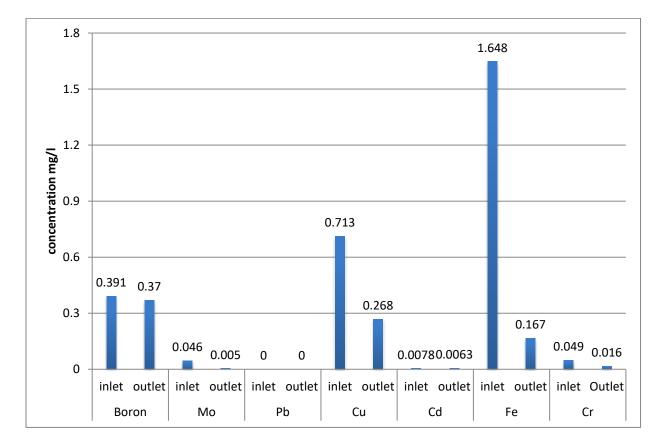


Figure 4.1 Concentration influent and effluent for heavy metals in Alteera WWTP

4.3 Wastewater influent and effluent analysis Beit Dajan

The results shown below in figure (4.2), that the Boron concentration was 0.21 mg/l, Molybdenum 0.016 mg/l, Chromium 0.067 mg/l, Copper 0.08 mg/l, Iron 1.909 mg/l, Lead and Cadmium were below detection limit in effluent and Cadmium was below detection limit in influent for the treatment plant.

In comparison with the recommended maximum concentrations of trace elements in irrigation water according to Palestinian standards mention in Table (4.1), all elements did not exceed the allowable limit for irrigation. Except Molybdenum exceeded the allowable limit of 0.01 mg/l.

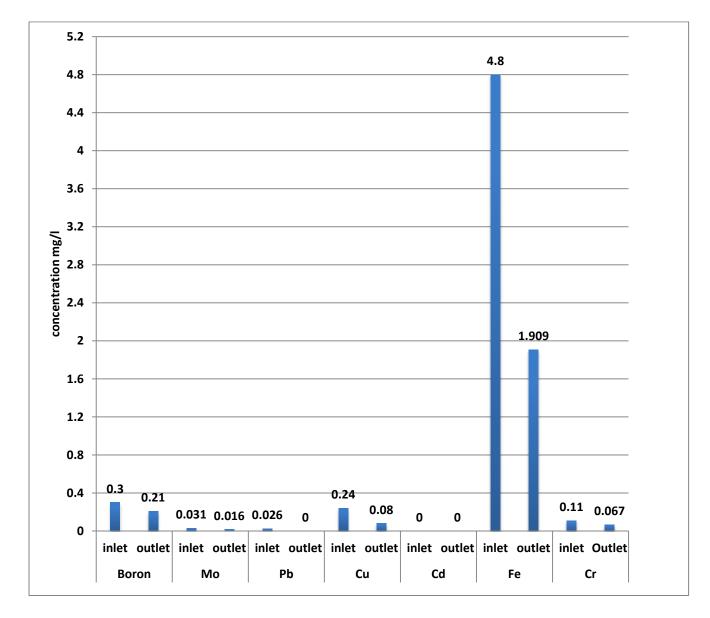


Figure 4.2 Concentration influent and effluent for heavy metals in Beit Dajan WWTP

4.4 Wastewater influent and effluent analysis Anza

The results shown below in figure (4.3), that the Boron concentration was 0.185 mg/l, Molybdenum 0.063 mg/l, Chromium 0.042 mg/l, Copper 0.044 mg/l, Iron 0.394 mg/l, Lead and Cadmium were below detection limit in effluent in treatment plant.

In comparison with the recommended maximum concentrations of trace elements in irrigation water according to Palestinian standards mention in Table (4.1), all elements did not exceed the allowable limit for irrigation. Except Molybdenum exceeded the allowable limit of 0.01 mg/l.

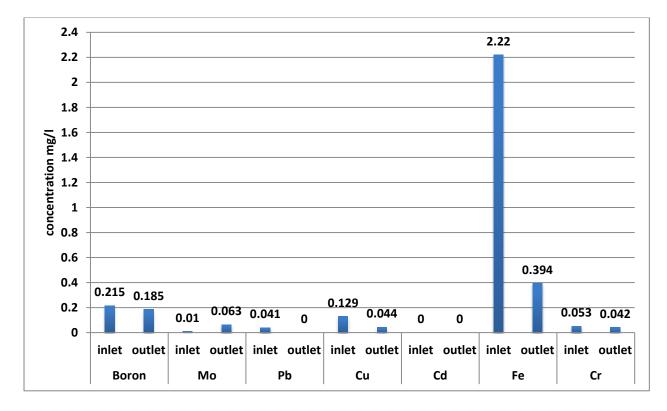


Figure 4. 3 Concentration influent and effluent for heavy metals in Anza WWTP

4.5 Compare removal efficiency between Alteereh (MBR), Anza and Beit Dajan (CAS)

The results shown below in figure (4.4), the removal efficiency was higher in MBR than CAS for all of analyzed heavy metal.

The removal efficiency for boron, Molybdenum, Copper, Cadmium, Iron and Chromium was 21%, 89.1% ,62.40%, 90% and 74% respectively in (MBR), according to analyze samples there was BDL for Lead in effluent and influent in Alteereh WWTP (MBR).

The removal efficiency for Boron, Molybdenum, Copper, Iron and Chromium was 14%, 70% ,56%, 82% and 37% respectively in (AS), according to analyze samples there were BDL for Lead and Cadmium in effluent and influent in Anza and Beit Dajan WWTP (CAS).

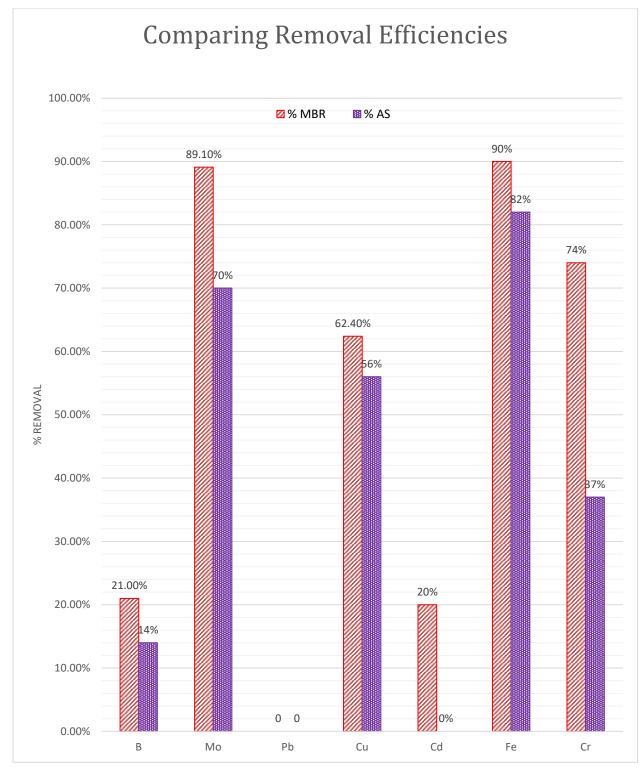


Figure 4.4 Comparing Removal Efficiencies MBR vs CAS

4.6 Heavy metal accumulation in oxic and anoxic zones in MBR and CAS

This study shows that the accumulation was higher in MBR than CAS, which is according to the higher removal efficiency for heavy metal in MBR. As shown in figure (4.5) and figure (4.6) accumulation occur in both oxic and anoxic zones.

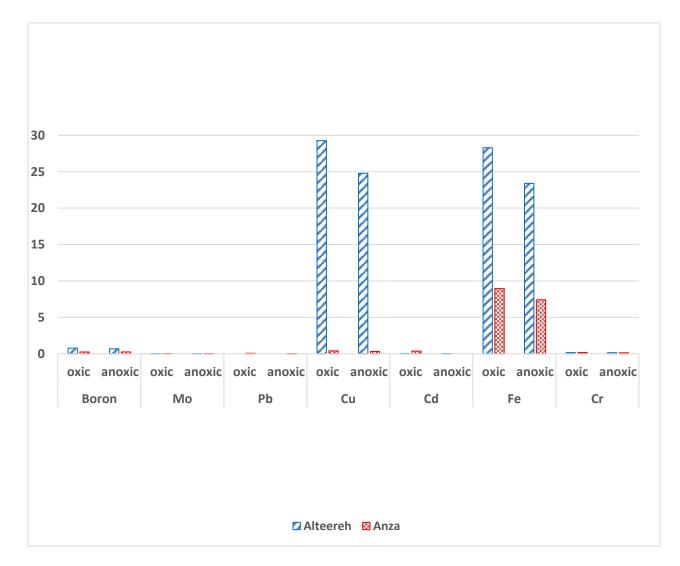


Figure 4.5 Comparing concentration oxic and anoxic Alteereh vs Anza

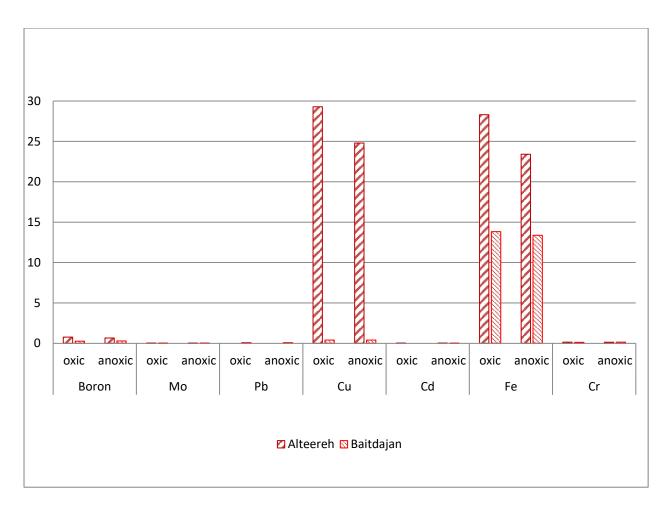


Figure 4.6 Comparing concentration oxic and anoxic Alteereh vs Bitdajan

Chapter Five

Conclusion and Recommendation

5.1 Conclusion

- According to the findings of this study, treated wastewater by the Anza, BeitDajan and Alteereh WWTPs is suitable for agricultural utilization. The maximum heavy metals concentration limits are lower than the permissible Palestinian limits of treated wastewater standards.
- Alteereh MBR facility should better removal of HMs compared to conventional activated sludge systems. There for Opportunity of reusing reclaimed wastewater is higher in the MBR than AS.
- The low concentration of HMs in soil indicates that there will be no major impact of reusing the treated wastewater for agricultural purposes. On the other hand sludge contains a higher concentration of HMs.

5.2 Recommendations

- It is important to mention the long-term impact of wastewater reuse agricultural land, should be subjected to a further investigation. This investigation has to address the long term impact on heavy metals accumulation in soil and plant tissues.
- It is recommended to use membrane bioreactor system when constructing new wastewater treatment plants.
- Land application of bio solids as soil amendment might couse long-term hazardous impacts on soil and agricultural product, due to HMs accumulation.

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ANNEXS

Annex (1): Influent and Effluent Metal Concentrations- Alteereh

Alteereh	Bo	ron	Ν	Мо		Pb	(Cu	(Cd	F	ſe	(Cr
	pI	ppm		ppm		ppm		ppm		ppm		ррт		pm
	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	Outlet
Sample 1	0.409	0.557	BDL	BDL	BDL	BDL	1.016	0.431	BDL	0.001	2.614	0.145	0.033	0.006
Sample 2	0.484	0.318	BDL	0.005	BDL	BDL	0.969	0.143	BDL	0.002	1.242	0.138	0.034	0.013
Sample 3	0.316	0.317	0.046	BDL	BDL	BDL	0.663	0.022	BDL	BDL	1.606	0.058	0.014	BDL
Sample 4	0.384	0.309	BDL	BDL	BDL	BDL	0.359	0.397	0.0078	0.016	1.107	0.263	0.032	0.021
Sample 5	0.361	0.35	BDL	BDL	BDL	BDL	0.56	0.346	BDL	BDL	1.673	0.232	0.134	0.025
Avg.	0.391	0.370	0.046	0.005	BDL	BDL	0.713	0.268	0.0078	0.0063	1.648	0.167	0.049	0.016

Beit Dajan	Boron ppm		Мо		P	Pb		Cu	0	Cd	F	le le	(Cr
			ppm		ppm		ррт		ppm		ppm		ppm	
	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet	inlet	outlet
Sample 1	BDL	0.098	BDL	BDL	BDL	BDL	0.148	0.052	BDL	BDL	11.23	0.903	BDL	BDL
Sample 2	0.327	0.268	0.019	BDL	BDL	BDL	0.123	0.03	BDL	BDL	2.528	0.481	0.018	0.011
Sample 3	0.154	0.206	0.026	BDL	BDL	BDL	0.755	0.249	BDL	BDL	6.44	8.6	0.164	0.1
Sample 4	0.142	0.076	BDL	BDL	BDL	BDL	0.089	0.019	BDL	BDL	1.736	0.358	0.033	BDL
Sample 5	0.676	0.469	0.048	0.016	BDL	BDL	0.218	0.067	BDL	BDL	4.02	0.843	0.3	0.089
Sample 6	0.212	0.121	BDL	BDL	0.026	BDL	0.097	0.068	BDL	BDL	2.852	0.269	0.035	BDL
Avg.	0.30	0.21	0.031	0.016	0.026	BDL	0.24	0.080	BDL	BDL	4.80	1.909	0.11	0.067

Annex (2): Influent and Effluent Metal Concentrations- Beit Dajan

Annex (3): Influent and Effluent Metal Concentrations- Anza

Anza	Во	ron	Мо]	Pb	0	Cu		Cd	F	Fe	(Cr
11124	pi	om	ppm		ррт		ppm		ppm		ppm		ppm	
	inlet	outlet												
Sample 1	BDL	BDL	BDL	BDL	BDL	BDL	0.092	0.022	BDL	BDL	1.02	0.058	BDL	BDL
Sample 2	0.275	0.254	BDL	BDL	BDL	BDL	0.064	0.021	BDL	BDL	1.135	0.282	0.013	0.009
Sample 3	0.269	0.12	0.01	BDL	BDL	BDL	0.2	0.106	BDL	BDL	1.737	0.549	0.058	0.069
Sample 4	BDL	BDL	BDL	BDL	0.041	BDL	0.292	0.057	BDL	BDL	7.133	0.407	0.101	0.016
Sample 5	0.26	0.238	BDL	0.063	BDL	BDL	0.088	0.029	BDL	BDL	1.551	1.033	0.05	0.072
Sample 6	0.054	0.128	BDL	BDL	BDL	BDL	0.036	0.027	BDL	BDL	0.755	0.037	0.042	BDL
Avg.	0.215	0.185	0.01	0.063	0.041	BDL	0.129	0.044	BDL	BDL	2.22	0.394	0.053	0.042

Alteereh	Alteereh		Soron Mo]	Pb		u	Cd		Fe		Cr	
	p	pm	ppm		ppm		ppm		ppm		ppm		ppm	
	oxic	anoxic	oxic	anoxic	oxic	anoxic	oxic	anoxic	oxic	anoxic	oxic	anoxic	oxic	anoxic
Sample 1	0.896	0.921	0.023	0.033	0.08	0.107	8.804	10.85	0.015	0.022	16.2	17.76	0.083	0.13
Sample 2	0.938	0.724	0.056	0.023	0.205	0.083	59.85	22.98	0.075	0.03	58.52	25.12	0.244	0.103
Sample 3	0.914	0.622	0.024	0.027	0.077	0.092	41.13	41.46	0.04	0.041	24.68	24.92	0.115	0.116
Sample 4	0.59	0.485	0.025	0.026	BDL	0.061	10.81	12.44	0.015	0.019	15.94	18.03	0.111	0.134
Sample 5	0.499	0.559	0.032	0.044	0.097	0.127	25.8	36.23	0.028	0.041	26.15	31.21	0.196	0.216
Avg.	0.767	0.662	0.027	0.03	BDL	BDL	29.279	24.792	0.035	0.031	28.298	23.408	0.149	0.139

Beit	Bo	oron	Мо]	Pb		Cu		Cd	I	Fe		Cr
Dajan	ppm		ppm		ррт		ррт		ppm		ppm		ррт	
	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
Sample 1	0.302	0.268	0.01	0.011	BDL	BDL	0.131	0.143	BDL	BDL	4.496	4.565	0.024	0.026
Sample 2	0.278	0.128	0.015	0.016	BDL	BDL	0.301	0.313	BDL	0.004	8.45	8.203	0.105	0.099
Sample 3	0.144	BDL	0.017	BDL	0.034	0.043	0.273	0.235	BDL	BDL	8.875	8.094	0.152	0.171
Sample 4	0.368	0.505	0.025	0.046	0.079	0.09	0.479	0.527	BDL	BDL	16.62	16.4	0.184	0.309
Sample 5	0.202	0.275	0.03	0.033	0.142	0.131	0.838	0.792	BDL	BDL	30.7	29.61	0.152	0.114
Avg.	0.259	0.294	0.019	0.027	0.085	0.088	0.404	0.402	BDL	0.004	13.828	13.374	0.123	0.144

Annex (5): Oxic and Anoxic Metal Concentrations- Beit Dajan

Annex (6): Oxic and Anoxic Metal Concentrations- Anza

Anza	Boron		Мо]	Pb	(Cu		Cd	Fe			Cr
	р	pm	ppm		ppm		ppm		ppm		ррт		ррт	
	oxic	anoxic												
Sample 1	0.199	0.191	0.014	0.019	BDL	BDL	0.331	0.324	BDL	BDL	8.22	8.8	0.056	0.098
Sample 2	0.194	0.246	BDL	0.024	BDL	0.024	0.369	0.346	BDL	BDL	5.593	7.515	0.093	0.177
Sample 3	BDL	BDL	BDL	0.014	0.057	0.031	0.378	0.297	BDL	BDL	10.08	7.887	0.072	0.174
Sample 4	0.22	0.389	0.063	0.023	0.051	0.034	0.4	0.339	BDL	BDL	11.12	8.43	0.548	0.16
Sample 5	0.341	0.191	0.012	BDL	0.063	BDL	0.46	0.21	BDL	BDL	9.742	4.38	0.067	0.032
Avg.	0.24	0.25	0.03	0.02	0.057	0.03	0.388	0.303	0.345	BDL	8.95	7.402	0.167	0.128