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Wastewater Reuse for Irrigation Purposes on Soil Conditioned with Zeolite

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Wastewater Reuse for Irrigation Purposes on Soil Conditioned with Zeolite

أعادة استخدام المياه العادمة للزراعة في تربة معالجة بالزيوليت

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Abstract

Wastewater treatment and reuse projects are usually associated with many obstacles, mainly financial, social, institutional and technical; political reasons and public acceptance are considered the main factors affecting the wastewater reuse in agriculture.

New recycling techniques should be employed to make use of the discharged wastewater. It is important to emphasize the vitality of water reuse to the Palestinian water sector since recycling the wastewater will lower the burden and pressure on the water resources.

wastewater contains variety of inorganic substances from domestic and industrial sources including a number of potential toxic elements such as arsenic, cadmium, chromium, copper, mercury and zinc, which present in concentrations likely to affect human health especially when the treated water is used for agriculture purposes, so it is needed to use a technique to remove these residues from treated wastewater to be safe when it is used for agricultural purposes. There are numerous processes for removing these toxic materials, one of the alternatives with low cost material as potential absorbent for the removal of heavy metals of trace quantities is zeolite which has the lowest capital and operational cost, and it is the most effective process for wastewater treatment due to molecular sieving, electrostatic fields, and polarizability properties.

The main objective for the study is to check the performance of zeolite material to be as a technique for wastewater treatment and as a fertilizing material to improve soil properties and increase crop yield. This research was conducted in the research field of Birzeit University, in order to study the effect of using secondary TWW from Al-Bireh wastewater treatment plant (WWTP) on soil amended with zeolite as well as the impact on the physical and chemical properties of soil, especially on its content of heavy elements. Concrete docks at three rows each row with 4 docks are built inside greenhouse filled with soil mixed with zeolite with four different percentages are (0%, 0.5%, 2.5% and 5%). Sorghum was the tested plants, to achieve the objectives for reuse experiment, the municipal treated wastewater produced by Al-Bireh treatment plant was used, and freshwater was used as a control and also used to irrigate the planted seeds until it pass initial grows stages. After analyzing collected water, wastewater, soil (before planting and after harvesting), and harvested plants samples, the results show that zeolite has a significant effect on soil structure, water content, and nutrients content in the amended soil which is essential for plant growth. On the other hand zeolite has a high capacity to absorb and accumulate toxic material at root zone (heavy materials) due to its ion exchange and sieving property.

Abbreviations

Acronym	Definition
°C	Degree Centigrade
µg/L	Microgram per Liter
µS/cm	Micro-Siemens per Centimeter
APHA	American Public Health Association
BZU	Birzeit University
CEC	Cation Exchange Capacity
DO	Dissolved Oxygen
EC	Electrical Conductivity
E-coli	Escherichia coli bacteria
FAO	Food and Agriculture Organization
FEW	Friends of Environment and Water
HWE	House of Water and Environment
BZA	British Zeolite Association
UofA	University of Arkansas
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
ISO	International Organization for

	Standardization
M	Meter
mg/L	Milligram per Liter
PSI	Palestinian Standard Institute
TC	Total Coliform
TDS	Total Dissolved Salts
TKN	Total Kjeldahl Nitrogen
TSS	Total Suspended Solids
TWW	Treated Wastewater
USDA	United States Department of Agriculture
UV	Ultra-Violet
WW	Wastewater
WWTP	Wastewater Treatment Plant
Z	Zeolite

Chapter One

Introduction

1.1. Background

Wastewater treatment and reuse projects are usually associated with many obstacles, mainly political, financial, social, institutional and technical. In addition, the Palestinians have not developed an integrated vision for the reuse issues due to potential locations, awareness, marketing and tariff setting. However, political reasons and public acceptance are considered the main factors affecting the wastewater reuse in agriculture. This is why it is locally still on the pilot scale. Palestinians lack the proper experience in using this resource in a safe way. Nevertheless, wastewater in Palestine has a high reuse potential. New recycling techniques should be employed to make use of the discharged wastewater. It is important to emphasize the vitality of water reuse to the Palestinian water sector since recycling the wastewater will lower the burden and pressure on the water resources which is considered the main target for this research **(**FEW and HWE, 2007).

Presently the application of wastewater treatment is limited because of the high cost and technological complexity of conventional systems. Municipal wastewater contains variety of inorganic substances from domestic and industrial sources including a number of potential toxic elements such as arsenic, cadmium, chromium, copper, mercury and zinc. All of them are considered very toxic materials and present in concentrations likely to affect human health especially when the treated water is used for agriculture purposes,thus it is needed to use a technique to remove the residues of heavy metals from the treated wastewater to be safe when it is used for agricultural purposes. There are numerous processes for removing the dissolved heavy metals, ammonium, etc, including ion exchange, precipitation, phytoextraction, ultrafilration, reverse osmosis, and electro-dialysis. Examining one of the alternatives with low cost material as potential absorbent for the removal of heavy metals of trace quantities is the plan for this research. Zeolite has the lowest capital and operational cost, and it is the most effective process for wastewater treatment (Metes, et al., 2004).

The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. Application of natural zeolites for water and wastewater treatment has been realised and is still a promising technique in environmental cleaning processes. In recent years, utilization of natural zeolites has been focused on ammonium and heavy metal removal due to the nature of ion exchange with cations, anions and organic compounds are widely presented in wastewater (Wang, et al., 2009).

1.2 Current gap related to the study

The current status of wastewater reuse issue is not clear in Palestine, since there is no financial support, adequate material and needed skills to use advanced methods of wastewater treatment, and promote for reuse in various fields.

1.3 Objectives

The main objective for the study is to check the performance of zeolite material to adsorb heavy metals and nutrients from the treated effluent that is used for irrigation purposes.

Specific objectives include:

- To examine the capacity of zeolite materials to accumulate toxic materials such as heavy metals at soil zone and prevent its transport to different plant components.
- To provide the agriculture sector with zeoltic material as other alternative of fertilizing material to improve soil properties.
- To prepare a study that can benefit the people in the areas of the relevant ways of dealing with wastewater and uses in various fields.

1.4 Set up description

Green house with dimensions (7.5 x 21.5) m was built in order to success of Sorghum crop near Birzeit University treatment plant, 12 docks were built inside it area equals 8 m^2 for each of them, they were filled with soil which was brought from Bait-Lequia. The soil is clay soil, red to orange color and has surprisingly good drainage. Moreover, it is popular type of soil for different crop production, and the used Zeolite was brought from Turkey and mixed with soil at different percentages.

Sorghum was the tested plants due to the fact that sorghum is adapted to be grown on a wide range of soils throughout, has an extensive root system and short growing season (UofA,1992)

To achieve the objectives for reuse experiment, the municipal treated wastewater produced by Al-Bireh treatment plant was used, and freshwater was used as a control and also used to irrigate the planted seeds until it pass initial grows stages.

1.5 Structure of thesis

The basic structure of this thesis is organized in five chapters:

Chapter 1 gives an introduction along with a background information, problem definition and study objectives.

Chapter 2 summarizes the literature review related to previous studies.

Chapter 3 deals with the methodology used to achieve the objectives of the study.

Chapter 4 explains the findings, results and discussion

Chapter 5 concludes the results of the study and suggested recommendations.

Chapter Two

Literature Review

2.1 Background

Zeolite is derived from the Greek words for to boil and stone have been applied many catalytic processes. Zeolites are crystalline, micro porous materials whose composition is very similar to sand, which is mainly composed of silicon and oxygen atoms. The silicons are tetrahedrally surrounded by oxygen, and using these basic building blocks, all kinds of structures can be created with pores and cavities of varying dimensions (Schuring, 2002).

2.2 Zeolite Structure

A zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedral, each consisting of four O atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. This structure is usually occupied by H_2O molecules and extra-framework exchangeable cations. The channels are large enough to allow the passage of guest species. In the hydrated phases, dehydration occurs at temperatures mostly below about 400 °C. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedral (Coombs, 1997). Zeolites are hydrated aluminosilicate minerals of a porous structure with valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis and sorption. Basically, zeolite materials look like sponges, with a very regular structure and pore sizes. In zeolite cations, and zeolitic water. The general chemical formula of zeolites is:

$$\mathbf{M_{x/n}[\,Al_x\,Si_y\,O_{2(x+y)}\,]\cdot pH_2O}$$

Where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; $y/x = 1–6$, $p/x = 1–4$. See Table 2-1 which shows different chemical formulas and structural type for different zeolite types.

Table 2-1: Different chemical formulas for different zeolite types (Wanga and Pengb, 2009).

Zeolite	Chemical Formula
Clinoptilolite	$(K_2,Na_2,Ca)_3Al_6Si_{30}O_{72}.2H_2O$
Mordenite	$(Na_2,Ca)_4AL_6Si_{40}O_{96}.28H_2O$
Chabazite	$(Ca,Na_2,K_2)_2Al_4Si_8O_{24}.12H_2O$
Phillipsite	$K_2(Ca,Na_2)_2Al_8Si_{10}O_{32}.12H_2O$
Scolecite	$Ca_4Al_8Si_{12}O_{40}.12H2O$
Stilbite	$Na_2Ca_4Al_{10}Si_{26}O_{72}.30H_2O$
Analcime	$Na_{16}Al_{16}Si_{32}O_{96}.16H_20$

The primary building block of zeolite framework is the tetrahedron, the centre of which is occupied by a silicon or aluminum atom, with four atoms of oxygen at the vertices as shown in Figure 2-1.

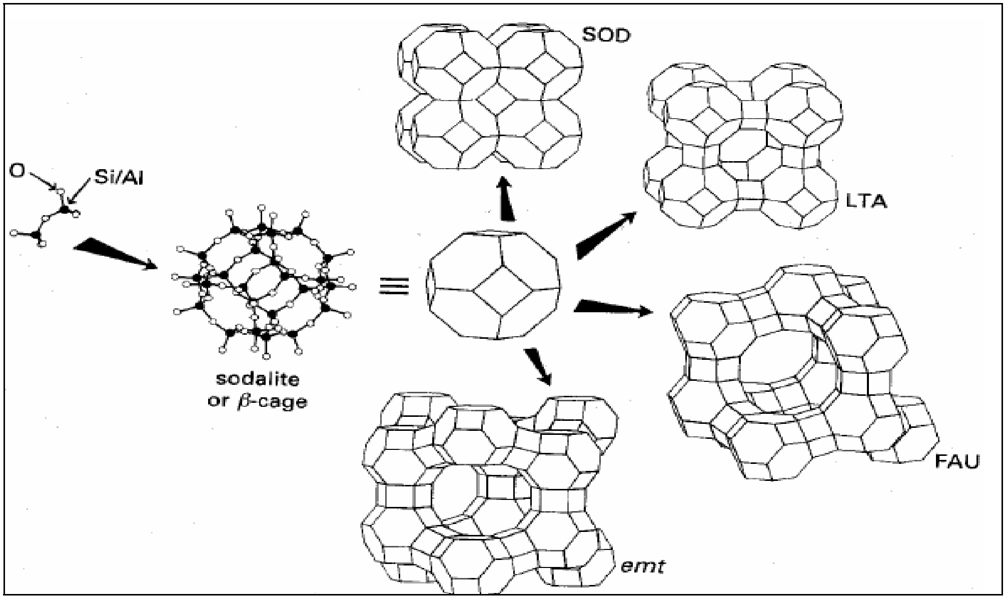


Figure 2-1: Zeolite building block (Wilkinson, 2009).

Substitution of Si4+ by Al3+ defines the negative charge of the framework, which is compensated by monovalent or divalent cations located together with water. The aluminosilicate framework is the most conserved and stable component and defines the structure type. The water molecules can be present in voids of large cavities and bonded between framework ions and exchangeable ions via aqueous bridges. The water can also serve as bridges between exchangeable cations (Wanga and Pengb, 2009).

The different zeolite types differ in pore diameter, pore shape the way these pores are interconnected. Such as Zeolite mordenite has a one-dimensional pore system consisting of channels with a diameter of about 7 A°, while the pores of silicalite-1 form a three-dimensional network of straight and zig-zag channels with a diameter of around 5.5 A° make these materials suited as a catalyst is the fact that part of the silicon atoms in the framework can be substituted by other cations like aluminum, sodium or potassium. As a result of the different valency of these cations, charges are created in the framework which has to be compensated by the addition of protons; these protons form acidic sites, which behave basically in the same way as the protons in an acidic solution (Schuring, 2002).

2.3 Types of Zeolite

More than 150 zeolite types have been synthesized and 40 naturally occurring zeolites are known. The formula of one of the better known zeolites is shown below:

$$\text{Na-A } Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5\ H_2O$$

Zeolites occur as hydrates, and all members of the family contain at least one silicon atom per aluminum atom (Abbey Newsletter, 1996).

2.3.1 Natural zeolite

Zeolites form in the nature as a result of the chemical reaction between volcanic glass and saline water. A temperature favoring the natural reaction range from 27°C to 55C ° and the pH is typically between 9 and 10. Nature requires 50 to 50,000 years to complete the reaction.

Naturally occurring zeolites are rarely phase-pure and are contaminated to varying degrees by other minerals (e.g. Fe^{++}, SO_4^-, quartz, other zeolites, and amorphous glass). For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential (Christie et al., 2002). There are many natural zeolites identified in the world, such as; clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime and laumontite are very common forms whereas offretite, paulingite, barrerite and mazzite, are much rarer. Among the zeolites, clinoptilolite is the most abundant natural zeolite and is widely used in the world (Wanga and Pengb, 2009).

2.3.2 Synthetic zeolite

Synthetic zeolites hold some key advantages over their natural analogs. The synthetics can, of course, be manufactured in a uniform, phase-pure state. It is also possible to manufacture desirable zeolite structures which do not appear in nature. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited; zeolite manufacturing processes engineered by man require significantly less time than the 50 to 50,000 years prescribed by nature (Christie et al. 2002).

2.4 Important Physical and Chemical Properties of Zeolite

Zeolites, in general, are weakly acidic in nature and sodium-form exchangers are selective for hydrogen ($R\text{–}Na^{+} H_2O \longleftrightarrow RH + Na^{+} + OH^{-}$), which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions, making metal hydroxide precipitation feasible. In natural zeolites, these metals seem to reach saturation which means that the metal had filled possible available sites and further adsorption could take place only at new surfaces (Erdem et al. 2004).

Chemically, zeolites are similar to clay minerals. In clay minerals, the molecules bond together in a fashion that creates loosely connected plates. The molecules in zeolites, however, are connected in a framework structure that is characterized by spaces or pores between the molecule groups. These “micro pores” are used for a number applications in industry and agriculture. Zeolites are colourless, white crystals, with hardness generally between 3 and 6. Many zeolites lose water fairly continuously over a temperature range of 150 to 400C without collapse of the framework structure and reabsorb it from the atmosphere at room temperature. All zeolites are molecular sieves that can selectively adsorb molecules on the basis of their size, shape, or electrical charge (Mumpton, 1998). Zeolites have other properties that are important for commercial applications, including:

1) High degree of hydration and easily dehydrated
2) Low density and large void volume when dehydrated
3) Stability of the crystal framework structure when dehydrated
4) Cation exchange properties
5) Uniform molecular-sized channels in the dehydrate crystal
6) Ability to absorb gases and vapours
7) Catalytic properties with H+exchanged forms
8) Special electrical properties.

In general, all types of zeolites have their value to one or more of three properties: adsorption, ion exchange, and catalysis.

2.4.1 Adsorption

The most fundamental consideration regarding the adsorption of chemical species by zeolites is molecular sieving. Species with a kinetic diameter which makes them too large to pass through a zeolite pore are effectively "sieved". This "sieve" effect can be utilized to produce sharp separations of molecules by size and shape.

The particular affinity a species has for an internal zeolite cavity depends on electronic considerations. The strong electrostatic field within a zeolite cavity results in very strong interaction with polar molecules such as water. Non-polar molecules are also strongly adsorbed due to the polarizing power of these electric fields.

Adsorption based on molecular sieving, electrostatic fields, and polarizability. This allows the zeolite to be reused many times, cycling between adsorption and desorption. This accounts for the considerable economic value of zeolite in adsorptive applications (BZA, 2001).

At different particle size of zeolite at specific ionic strength. Figure 2-2 shows that the removal of Cd, Cu, Pb and Zn ions as a factor of particle size of zeolite, From the figure we can observe that as the particle size of zeolite decreases a slight increasing in the removal of these metal ions. This can be explained in terms of active surface area of the adsorbent and the probability of solid solution interaction (Baker et al., 2009).

A zeolite is a crystalline, hydrated aluminosilicate of alkali and alkaline earth cations having an infinite, open, and three dimensional structures. It is further able to lose and gain water reversibly and to exchange extra framework cations, both without change of crystal structure. The large structural cavities and the entry channels leading into them contain water molecules, which form hydration spheres around exchangeable cations. On removal of water by heating at 350–400°C, small molecules can pass through entry channels, but larger molecules are excluded—the so called ‘‘molecular sieve’’ property of crystalline zeolites. The uniform size and shape of the rings of oxygen in zeolites contrasts with the relatively wide range of pore sizes in silica gel, activated alumina, and activated carbon, and the Langmuir shape of their adsorption isotherms allows zeolites to remove the last trace of a particular gas from a system (e.g., H2O from refrigerator Freon lines). Furthermore, zeolites adsorb polar molecules with high selectivity (Mumpton, 1999).

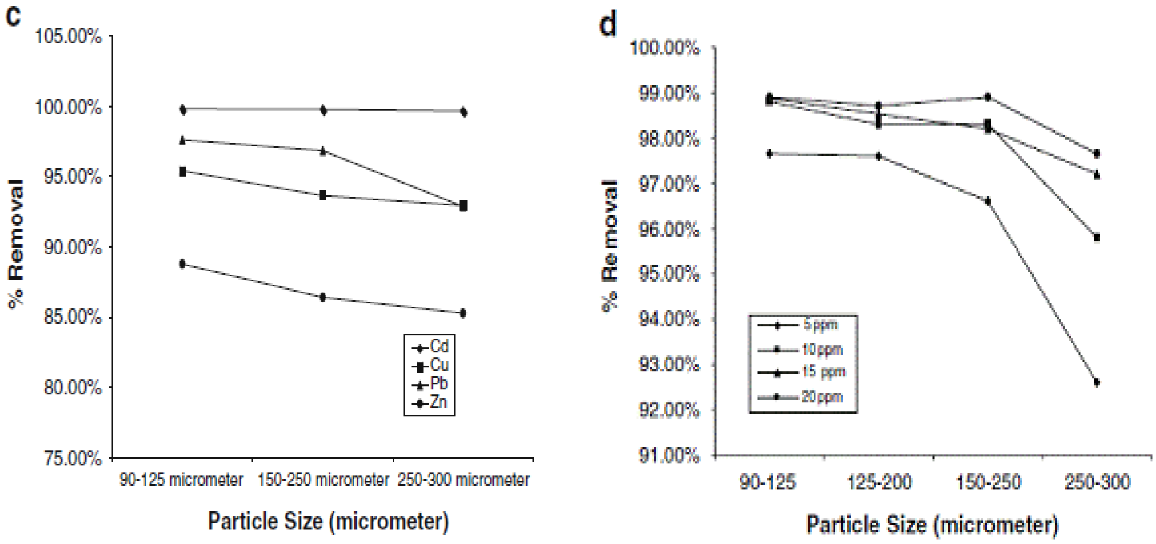


Figure 2-2: Zeolite particle size effect on adsorbent (Baker et al. 2009).

2.4.2 Ion Exchange

Because cations are free to migrate in and out of zeolite structures, zeolites are often used to exchange their cations for those of surrounding fluids. The preference of a given zeolite among available cations can be due to ion sieving or due to a competition between the zeolite phase and aqueous phase for the cations that are present(Abbey Newsletter,1996).

Zeolite with a negative charge provides an ideal trap for positive cations such as sodium, potassium, barium and calcium and positively charged groups such as water and ammonia. Both carbonate and nitrate ions are attracted by the negative charge within zeolites (Polat et al., 2004). Therefore, alkali and soil alkali metallic cations are attracted in the same way and water can be absorbed by zeolites. Absorbed cations are relatively mobile due to their weak attraction, and can be replaced using the standard ion (Mumpton, 1999).

2.4.3 Catalysis

Zeolites make extremely active catalysts. Steric "shape selective catalysis" is a very important phenomenon in zeolite catalysis, selective reactions can be made to occur over zeolites when certain products, reactants or transition states are kept from forming within the pores because of size or shape as shown in Figure 2-3.

The catalytic properties of zeolites are due to their large surface areas (internal and external) and their Si-Al frameworks. The Si _ Al + H+ exchange is widely used for catalysis, because the Al-tetrahedra can function as proton donors or acceptors (Bish and Guthrie, 1993).

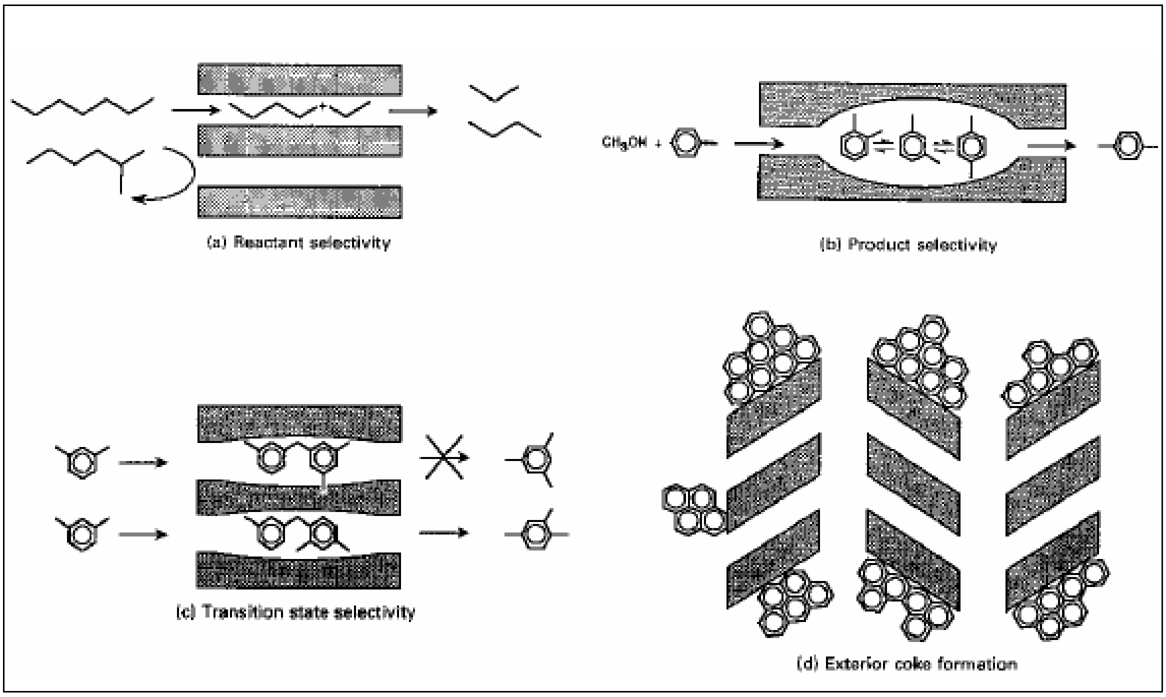


Figure 2-3: Shape selectivity property for zeolite (Wilkinson, 2009).

2.5 Zeolite used for wastewater treatment

The improvement of sewage treatment technologies is of both ecological and economical importance to obtain increased removal of ammonium, phosphorus, and organic floating material (suspended solids). Chemical methods have usually been applied. Suspended solids are flocculated by adding aluminum salts or synthetic polyelectrolytes; phosphorus is precipitated as phosphate with aluminum or iron salts or with lime; and ammonium is generally removed by biological nitrification. Similarly, organic contaminants are biologically oxidized. The problem of the disposal of the sludge that is produced has not been satisfactorily solved, mainly because of accumulated heavy metals, which are easily released from it into the soil. In addition, the above-mentioned chemicals are rather expensive and often result in undesired emissions (Ming, 1995). The use of relatively low-priced natural zeolites as ion-exchangers and/or adsorbents has been found to remove heavy metals, ammonium and phosphorous as illustrate in the following sections.

2.5.1 Heavy metal Removal

Many toxic heavy metals and organic pollutants have been discharged into the environment as industrial wastes that cause serious soil and water pollution. Therefore people were needed for advanced treatment facilities to remove these pollutants, such as adsorption and ion exchange (AL-Degs et al. 2003). The toxic metals, probably existing in high concentrations (even up to 500 mg/1), must be effectively removed from the wastewaters. If the wastewater was discharged directly into natural water, it will constitute a great risk for the environmental ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment (Hui et al. 2005).

The toxicity of heavy metal ions depends on the chemical form of the element that is upon its speciation. For example, the toxicity of Pb as the ion Pb+2, and the Pb in the form of covalent molecule differ substantially.

Zeolite exchangeable ions are relatively innocuous (sodium, calcium, and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters where the structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra; the aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium). These cations are exchangeable with certain cations in solutions such as lead, cadmium, zinc, and manganese. Clinoptilolite is the most abundant natural zeolite which is formed by open channels of 8- to 10-membered rings which improves ion-exchange capacity for inorganic cations (Erdem et al. 2004), where the selectivity series of clinoptilolite in the sodium form was determined by Roić et al. (2000) as follows: $Pb^{2+} > Cd^{2+} > Cs^{+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$.

2.5.2 Zeolite used for nutrients removal

Development of high capacity and more effective processes alternative to the conventional biological processes is of great importance for nutrient removal and recycling operations. The application of zeolite as an ion exchange for ammonium removal is one of the most effective technologies that have received considerable attention in recent years. For phosphorus, there are a number of technologies, both established and under development, which can be used to remove/recover phosphorus from wastewaters. Amongst them, chemical precipitation, biological phosphorus removal and crystallization are the most commonly known processes, with chemical precipitation being the leading technology today. However, biological phosphorus removal has become firmly established; crystallization technology has also completed its progress towards commercialization and technologies extending chemical precipitation to assist nutrient removal which beyond the pilot stage. In the phosphate removal studies based on crystallization, several materials including calcite, sand, and a variety of Ca-phosphate crystals have been used as seeding material to initiate and enhance phosphate precipitation and recycling (Karapinar, 2009).

The most widely used methods for removing ammonia from wastewater are air stripping, ion exchange, breakpoint chlorination and biological nitrification denitrification (Metcalf and Eddy, 2003). The capacity of zeolites to remove NH_4+ from wastewater has been found to vary, depending on the type of zeolite used (e.g., mordenite, clinoptilolite, erionite, chabazite, and phillipsite), zeolite particle size, and wastewater anion-cation composition, and the extent of aluminum (Al_3+) substitution for silicon (Si^{4+}) in the zeolite framework. Each Si^{4+} substitution by Al^{3+} generates a negative charge. The greater substitution means higher negative charge, and hence the greater the number of cations required for balancing the negative charge (Nguyen et al. 1998).

In the aqueous solution, ammonia may exist in either the non-ionized form (NH_3) or ionized form (NH_4^+) depending on the pH and temperature. The ion exchange process can remove only the ionized one. The equilibrium exchange capacity remains constantly up to pH 7. During the ion-exchange process, the Na^+ ion is replaced by the NH_4^+ ion, and hence the Na^+ ion concentration increases in the liquid phase during the ion-exchange processes as shown in the following equation:

$$Z\text{-}Na^+ + NH_4^+ \longleftrightarrow Z\text{-}NH_4^+ + Na^+$$

However, the ammonia ion-exchange capacity by using Zeolite varies depending on the presence of other cations in the aqueous phase and initial ammonia concentration (Rahmani et al. 2004).

2.5.3 Zeolite versus activated carbon as a wastewater treatment process

Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals at trace quantities and organic pollutants. However, the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon (Ali and El-Bishtawi, 1997). The high cost of this adsorption material, new researches focused on non-conventional adsorption materials, such as carbonized coconut shell, wood, coal, straw, organic clays, and zeolite.

Zeolites are hydrated aluminosilicate materials that having cage-like structures with internal and external surface areas of up to several hundred square meters per gram and cation exchange capacities of up to several milli-equivalents per kilogram. The expansion of industrial activities, including metal-based industries, requires the availability of low-cost technology and materials for wastewater treatment (Baker et al. 2009).

There are many methods available to reduce heavy metal concentration from wastewater; the most common ones are chemical precipitation, ion-exchange and adsorption and reverse osmosis. Most of these methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Ion-exchange is feasible when an exchange has a high selectively for the metal to be removed and the concentrations of competing ions are low. The metal may then be recovered by incinerating the metal-saturated resin and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view. This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals (Hui et al., 2005).

2.6 Zeolite used for soil amendment

The zeolite in natural condition is combined with cations such as Na^+, K^+, Ca^{2+} and etc. In general Zeolite has three distinguished properties: one is great high cation exchange capacity (CEC; ten times more than that of soil); the other is large amount of free water in the structural channels; and the third is high ability of adsorption (with surface area of about 1150.5 m^2/g) (Sand and Mumpton, 1978).

The zeolite does not only have large capacity of water storage, but also can improve the ability of water storage of the soil. In addition, it can reduce overland flow (surface runoff) and protect soil from erosion. Furthermore, it can regulate water supply for crops, for the fertility of loess soil depends on water availability as illustrated in Figure 2-4. Therefore, zeolite has special properties that can be potentially applied to water efficient use in agriculture (Xiubin and Zhanbin, 2001).

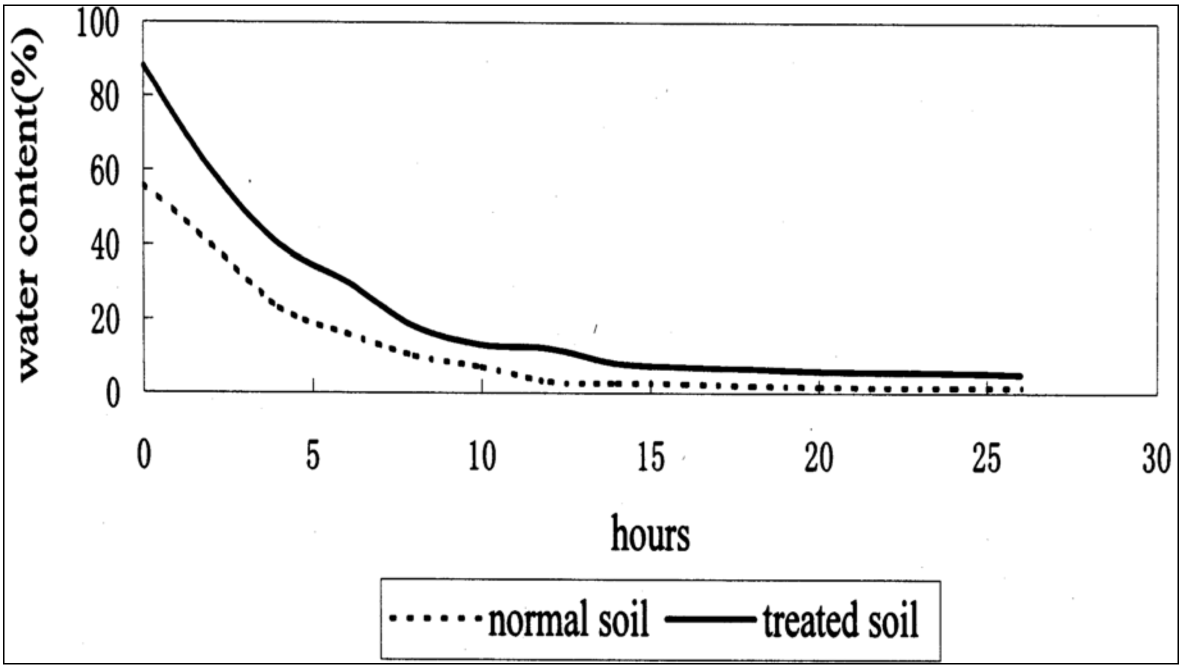


Figure 2-4: Zeolite water storage capacity (Xiubin and Zhanbin, 2001).

Natural zeolites as cilnoptilolite have special physical and chemical properties that could improve the soil properties. Generally zeolite has been used to release fertilizers enriched with ammonia as well as to affect the buffer capacity of soil.

On the other hand pore size makes zeolite ideal for sorption what is beneficially used e.g. in gas purification saturated material can be regenerated or utilized. Zeolite into agricultural soil considered as a source of nitrogen for plants fertilization (Karapınar, 2009).

Zeolites are one of the greatest cationic interchangers and their cationic interchange capacity is two to three times greater than other types of minerals found in soils. The application of zeolites to soils increases their

E.C, and as a result, it increases nutrient retention capacity. Furthermore, the addition of zeolites usually increases pH levels.

Huang and Petrovic (1994) studied the possible advantages of applying zeolites to soils; they proposed the application of these minerals in order to reduce the leaching of nitrates in golf courses located on sandy soils. The researches confirmed that zeolite mixed with manure increases the effectiveness of organic fertilizers on meadowland soils. Subsequently, it was demonstrated that zeolite is an important resource in agriculture, owing to its water and ammonium retention capacity, because it helps to reduce nitrogen loss. Furthermore, it has been verified that, when mixed with nitrogen, phosphorous and potassium compounds, zeolite enhances the action of such compounds as slow release fertilizers, both in horticultural and extensive crops. Hence, zeolite acts as a slow release fertilizer, giving the plant access to water and nutrients for longer, which results in a significant saving in water resources and reducing the amount of fertilizer to be applied, thus helping to decrease the amount of water used per crop and the contamination of aquifers resulting from the overuse of fertilizers (Caballero and Benitez, 2008).

However, use of poor quality water for irrigation may lead to soil salinity and its associated problems. Accumulation of salts in the root zone affects plant performance through creation of water deficit and disruption of ion homeostasis which in turn cause metabolic dysfunctions (Munns, 2002). These stresses change hormonal status and impair basic metabolic processes resulting in growth inhibition and reduction in yield (Mass, 1993). Soil permeability problems may be prevented or corrected by using soil or water amendments. Synthetic zeolite produced from coal ash is a beneficial soil amendment because it enhanced the absorption and retention of plant nutrients and water and supplemented micronutrients. Concentrations of elements in soil were definitely related to their relative concentrations in the irrigation water. Treatment with zeolite increased cation concentrations in the upper soil layer and decreased concentrations down the profile. The lower salt accumulation in the subsurface soil or root zone may offer a reduced salt stress on plants. Thus, an application of higher doses of zeolite may filter harmful salts from the root zone, thereby creating a favorable environment for plant growth (Al-Busaidi et al., 2008). The most common type of zeolite for agricultural applications is clinoptilolite since it has high absorption, cation exchange, catalysis and dehydration capacities (Polat, 2004).

Chapter Three

Methodology

3.1 Site preparation

There is an important consideration and local conditions must be taken in to account during site preparation

3.1.1 Soil transport and application

The soil that was used in the project was provided by Mashtal Abu- Shusheh at Ramallah city-West Bank. Soil was obtained from area, in which sorghum can produce commercially, where the source of soil from Bait-Lequia. The soil texture was analyzed and identified according to grain size based on international definitions.

3.1.2 Major features of sorghum seeds used on the project

The sorghum seeds were obtained from locally source which is classified as good quality seeds, where the seeds was grounded to be analyzed later at Birzeit University labs.

3.1.3 Green house features

Building a green house with dimensions (7.5 x 21.5) m in order to success of the crop which was chosen for the test, Figure 3-1 that shows the activities of green house building which start at 23, November, 2010, and finished at the beginning of January, 2012.

Figure 3-1: Activities of green house buildings.

3.1.4 Works of agriculture docks

The docks (12 pots) were built by using concrete blocks on the surface of land near Birzeit University treatment plant, each of them with area equals 8 m^2 with dimensions (5 X1.6 X 0.8) m and their arrangement are shown in following figure (Figure 3-2).

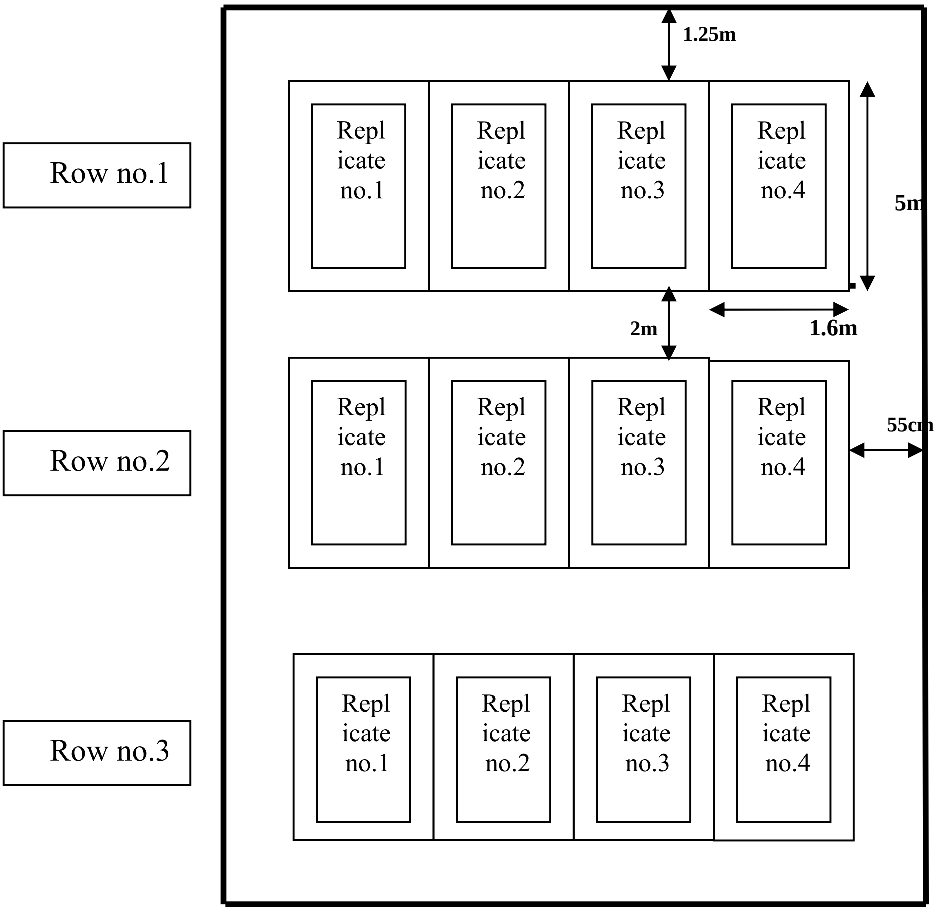


Figure 3-2: The arrangement of docks at the site of the experiment.

The works of docks building including building of docks and plastering the command walls between docks to prevent leakage as shown in Figure 3-3.

Figure 3-3: Agricultural docks building works.

3.1.5 Mixing process

Providing the required quantity of soil which was brought from Bait-Lequia and equivalent to 60 m^3 for all docks (5 cubic meters per basin), and the used Zeolite was brought from Turkey. Mixing percentages of Zeolite material are described in Figure 3-4. After mixing 4 composite samples (see Table 3-1) were taken from agricultural docks before plantation to determine its texture, physical and chemical characteristics.

Table 3-1: Soil samples coding after mixing

Sample No.	Zeolite (%)
1	Z1 (0%)
2	Z1 (0.5%)
3	Z1 (2.5%)
4	Z1 (5%)

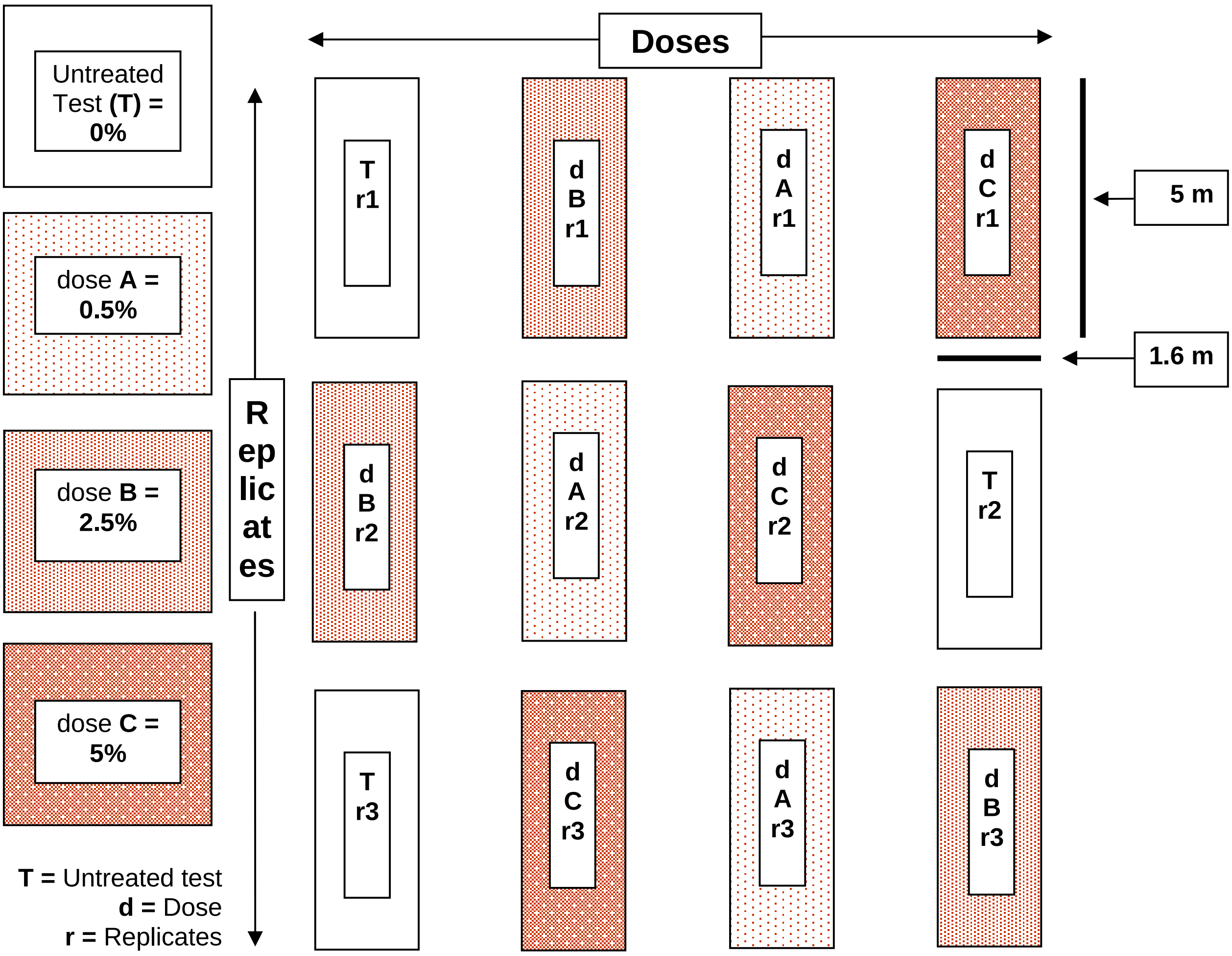


Figure 3-4: Zeolite mixing percentage.

3.2 Setup of reuse project

3.2.1 Major features of sorghum seeds used on the project

Therefore, certified seeds which were used was obtained from certified nurseries, and planted in docks filled with soil mixed with zeolite. The seeds were bought from the local markets, and they were commonly planted and used. Sorghum seeds were planted in pots and subjected to the standard cultivation procedures in respect to best management.

3.2.2 Fresh water and treated wastewater

As proposed, freshwater is the tap water of Birzeit University. It has been used for irrigation. On the other hand treated wastewater was obtained from Al Bireh Wastewater Treatment Plant transported and stored in barrels with enough capacity (1 m^3) every 10 days as shown in Figure 3-5.

Figure 3-5: Treated wastewater transporting and storing.

3.3 Experiment

3.3.1 Site description

The area of the study site is about 165 m^2 on the campus of Birzeit University (BZU) near the treatment unit as shown in Figure 3-6.

Figure 3-6: Experiment site

3.3.2 Treatments and experimental units

To achieve the objectives for reuse experiment, the municipal treated wastewater produced by Al-Bireh treatment plant was given the priority and as a control case, freshwater was used only to irrigate the planted seeds until it pass initial grows stages. Seeds were planted in 4 January 2011, 5 seeds near each eye of punctuation, and irrigated with fresh water until they are grown. There were 12 experimental units (docks). Samples were taken before planting and after harvesting. The samples are taken from soil and plants then prepared (dried and grinded) to be analyzed later at Birzeit University labs.

Water samples were collected from the water source at Birzeit University. The samples were collected and several physical parameters (pH, EC, TDS and DO) were taken during the sampling action. The samples were collected in clean bottles and treated according to the Standard methods (APHA, 2005). After collection and filtration via membranes < 45 μm pore size to be analyzed and determine its characteristics.

Effluent wastewater samples were taken from storage tank at the experimental site. At the sampling site, the physical parameters were determined. The effluent samples were transported directly to the laboratories of BZU where they were filtered via membranes < 45 μm to determine its characteristics.

3.3.3 Growth process and field measurements

During the growth process, a daily monitoring system were conducted and followed according to international rules and protocols.

Several parameters related to plant morphology were obtained especially the ones related to plant high, growth rate, number of leaves, number of fruits, etc. See Figure 3-7.

Figure 3-7: Growth process for the planted Sorghum.

3.4 Harvesting

All plants were harvested in 20, May 2011. Samples were taken from roots, stems, leaves and fruits for analysis. Soil samples were also taken from each pot for analysis. After harvesting, the samples were collected and prepared according to the method and parameter to be analyzed. For the samples to be analyzed at Birzeit University, the samples were dried below 45 ^{o}C, ground manually into powder.

3.5 Laboratory analysis

Analyses of all parameters are illustrated in Table 3-2 were carried out at the Birzeit University Testing Laboratories, Birzeit, Palestine.

Table 3-2: Parameters were analyzed and methods of analysis

Parameters	**Instruments**	**Method**	**Reference**
(1) Water and Wastewater			
Turbidity	Turbid- meter	Direct in the field	APHA 2130
pH	pH-meter	Direct in the field	APHA
Conductivity (EC)	EC meter	Direct in the field	APHA
TS, TSS	Evaporation, Filtration	2540-B, C, D	APHA
NO_3, SO_4, HCO_3	Titration, UV, Turb., Titration		APHA
K^+	ICP-OES and Flame P.M	3120-B & 3500	APHA
NH_4	Ion meter-3340	4500-NH_3	APHA
Heavy metals	ICP-OES	3120B	APHA
COD	Hach COD reactor	5210-B	APHA
BOD_5	DO meter – Oxi 197	5220-D	APHA
DOC	Multi N/C 2000	5310	APHA
Total Coliforms		9222-B	APHA
Fecal Coliforms		9221-E	APHA
(2) Soil			
Texture	Mastersizer 2000 MALVERN	Grain size ratio	
Hydraulic properties			
Total N		Total Kjeldhal	
Exchangeable K		Extraction	
Available P		Olsen method	
Heavy metals(Fe,Pb&Zn)	ICP-OES	3120B	APHA
(2) Plant samples			
Sorghum Seed Total N		Total Kjeldhal	
Sorghum Seed Total K		Extraction	
Sorghum Seed Total P		Olsen method	
Heavy metals(Fe,Pb&Zn)	ICP-OES	3120B	APHA
Plant high	Meter		
Number of leaves	Manual		

Chapter Four

Results and discussion

4.1 Characteristics of irrigation water

The suitability and compliance of the two sources of irrigation water used were evaluated according to the guidelines of Palestinian standard institute. Detailed standards listed at Appendix A.

4.1.1 Tap water

Water samples were collected from the water source at Birzeit University which is coming from rainfall harvesting. The samples were analyzed to determine the main quality parameters of water. Several physical parameters (pH, EC, and DO) were taken during the sampling action. The samples were collected in clean bottles and treated according to the Standard methods (APHA, 2005). Water samples were collected and filtrated via membranes < 45 μm pore size, to be analyzed at Birzeit University. For quality control, several parameters were determined before use it for agriculture purposes.

Table 4-1: Results of water samples used for irrigation.

Parameter	Unit	Sample 1	Sample 2	Sample 3	Mean value
pH		8	7.6	8.03	7.88
EC	µS/Cm	640	637	629	635
TDS	mg/L	307	324	290	307
DO	mgO_2/L	5.02	5.5	5.11	5.21
Salinity	(g/Kg)	0.3	0.3	0.2	0.3
Turbidity	(NTU)	4.74	4.01	4.34	4.36
Cl	mg/L	242	246	257	248
F	mg/L	0.61	0.69	0.7	0.67
NO_3	mg/L	6.8	6.14	6.63	6.52
SO_4	mg/L	NM	NM	NM	NM
HCO_3	mg/L	252	255	204	237
PO_4	mg/L	<0.1	<0.1	<0.1	<0.1
Ca	mg/L	62.63	66.88	67.18	65.56
Na	mg/L	78.7	83.46	83.67	81.94
K	mg/L	3.99	4.17	4.21	4.12
NH_4	mg/L	<0.5	<0.5	<0.5	<0.5
NO_3	mg/L	4.8	4.9	4.8	4.8
SO_4	mg/L	40	40	40	40
PO_3	mg/L	ND	ND	ND	ND
Fe	µg/L	13.6	34.4	76.4	41.5
Na	mg/L	61.4	61.9	60	61.1
Pb	µg/L	3.07	1.14	2.45	2.22
Zn	µg/L	482	578	94.7	385

Table 4-1 shows the results of water analysis at Birzeit University. Most physical measurements were found in the range of standard ranges such as, pH values were found at the allowable range of standard (6-9), and the avg.TDS value is 307 mg/l less than maximum allowable value (1000mg/l).

According to the heavy metals measures for Pb its avg. value 2.22µg/l which less than maximum allowable limit (0.01 mg/l), and so on for Zn (385 µg/l < 5mg/l).

4.1.2 Treated wastewater

Treated wastewater was obtained from Al Biereh Wastewater Treatment Plant transported and stored in barrels at experiment site. Composite wastewater samples were collected. At the sampling site, the physical parameters were determined. The effluent samples were transported directly in clean bottles to be analyzed at BZU laboratories, where they were filtered via membranes < 45 μm pore size for determination of cations, anions and heavy metals.

Table 4-2 shows the main quality control parameters that were analyzed at BZU laboratories. For example, mean values of pH, PO_4, NO_3 and K are (7.9, 6.2 mg/l, 5.81mg/l and 30.51mg/l) respectively within the range of PSI standards (see Appendix A).

The average concentrations of heavy metals and all other chemical parameters were considerably lower than the maximum allowable values for the unrestricted irrigation according to the PSI guidelines. It is well known that heavy metals are toxic to plants at high concentrations, and they represent a limiting factor for wastewater to be used in irrigation (FAO 2003).

Table 4-2: Results of wastewater samples used for irrigation

Parameter	Unit	Sample 1	Sample 2	Sample 3	Mean value
pH		8.3	7.7	7.7	7.9
EC	µS/Cm	1285	1388	1356	1343
TDS	mg/L	629	677	663	656
TS	mg/L	NM	NM	NM	NM
TSS	mg/L	31.2	33.4	28.7	31.1
SS	mL/L	NM	NM	NM	NM
DO	mgO_2/L	6.2	9	6.8	7.3
Salinity	(g/Kg)	0.6	0.7	0.7	0.7
Turbidity	(NTU)	8.3	4.99	4.91	6.1
NO_3	mg/L	7.99	3.1	6.32	5.81
SO_4	mg/L	67.04	55.9	69.7	64.21
HCO_3	mg/L	275	223	278	259
PO_4	mg/L	6.6	6.2	5.8	6.2
Ca	mg/L	69.28	65.66	62.63	65.86
Na	mg/L	201.54	198.33	207.32	202.40
K	mg/L	30.41	30.34	29.69	30.15
NH_4	mg/L	<0.5	<0.5	<0.5	<0.5
Fe	$\mu g/L$	109	75.2	98.3	94.2
Pb	$\mu g/L$	1.94	2.91	1.97	2.27
Zn	$\mu g/L$	27.4	32.4	29.8	29.9

4.2 Soil analysis

After mixing process for agricultural soil with zeolite, the composite samples were collected for analysis at BZU laboratories. Absorption of heavy metals by plants depends primarily on both chemical and physical properties of soil.

4.2.1 Soil texture

The soil texture is important to know all physical, chemical and biological processes. Four samples (mixed with soil before plantation) were taken to a soil laboratory at BZU to identify the exact texture according to grain size. Sieve analysis was used to determine soil gradation then classified the soil texture grain size according to the USDA soil textural triangle (Figure 4-1), Table 4-3 shows that soil texture of the experiment was changed from clayey soil to silty loamy soil as a result of Zeolite quantity increased.

Table 4-3: Soil texture analysis

Z (0.0%)		Z (0.5%)		Z (2.5%)		Z (5%)	
Sieve (mm)	% Pass.	Sieve (mm)	% Pass.	Sieve 50	% Pass.	Sieve (mm)	% Pass.
4.750	96	4.750	95	4.750	98	4.750	99
2.000	93	2.000	94	2.000	96	2.000	98
0.850	92	0.850	92	0.850	95	0.850	96
0.425	90	0.425	90	0.425	92	0.425	90
0.250	89	0.250	88	0.250	88	0.250	86
0.106	82	0.106	80	0.106	78	0.106	79
0.075	80	0.075	78	0.075	74	0.075	77
0.072	78	0.072	73	0.072	73	0.071	76
0.054	72	0.054	68	0.052	70	0.053	71
0.041	65	0.039	66	0.039	64	0.040	65
0.030	59	0.028	63	0.029	58	0.029	61
0.022	54	0.021	60	0.022	52	0.021	56
0.016	50	0.015	54	0.016	45	0.016	51
0.012	46	0.012	47	0.012	39	0.012	46
0.009	44	0.009	41	0.009	31	0.009	41
0.006	41	0.006	36	0.007	25	0.006	37
0.004	38	0.005	31	0.005	23	0.005	32
0.003	36	0.003	28	0.003	20	0.003	29
0.002	33	0.002	24	0.002	18	0.002	27
0.002	28	0.002	21	0.002	16	0.002	24
0.001	23	0.001	19	0.001	13	0.001	22
Clay loam		Loam		Silty loam		Silty loam	

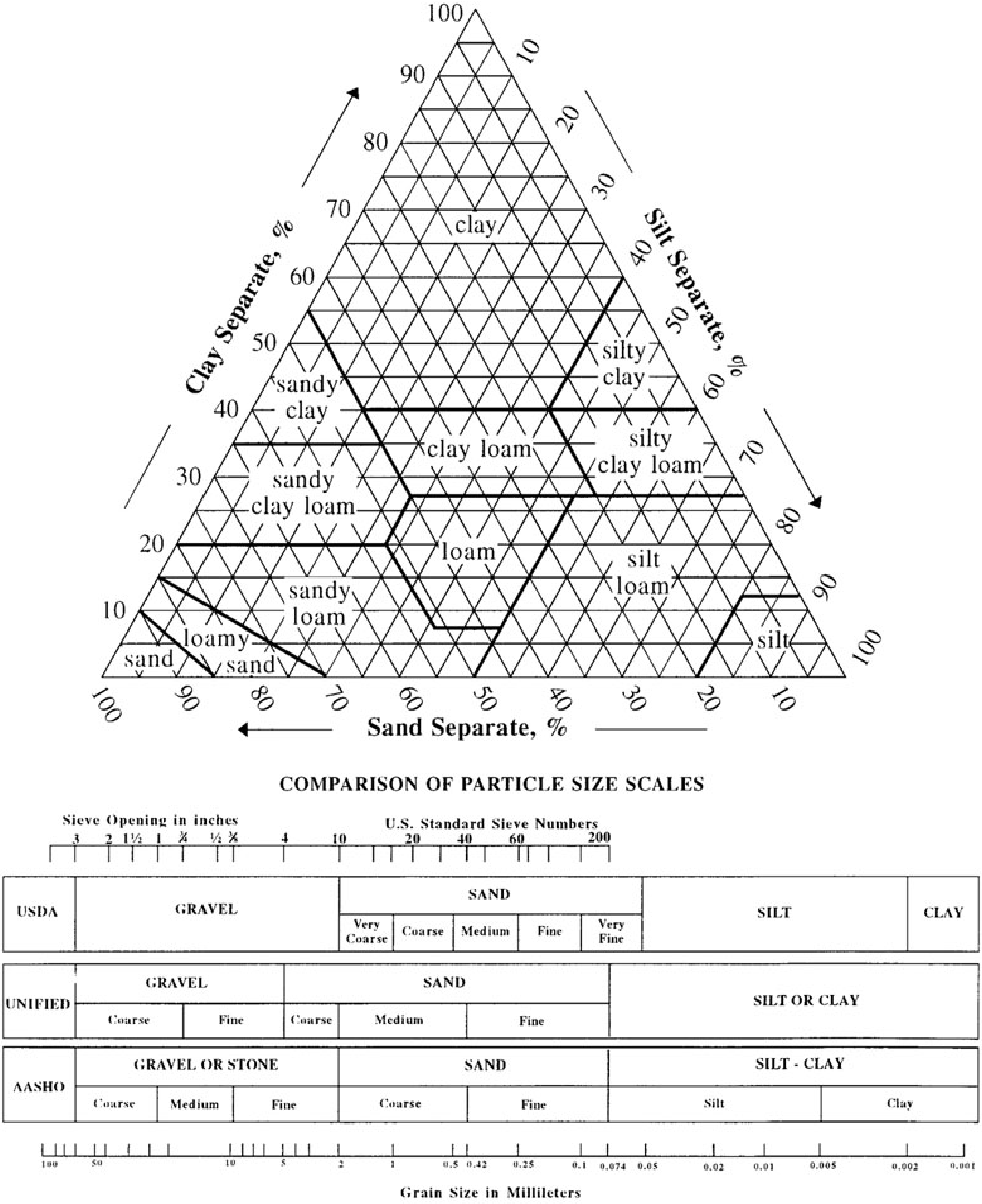


Figure 4-1: USDA soil textural triangle (USDA, 2011).

4.2.2 Soil physical parameters.

Specific gravity, hydraulic conductivity, surface area and other physical parameters effect on soil properties were analyzed as shown in Table 4-4.

Figure 4-2: Specific gravity in soil samples.

Figure 4-2 shows that increasing zeolite percentage in soil, the specific gravity (GS) was decreased. The reason is that the micro porosity for amended soil decreased with increasing of zeolite percentage as shown in Figure 4-3, where the volume of voids decreased as a result of increasing of water content.

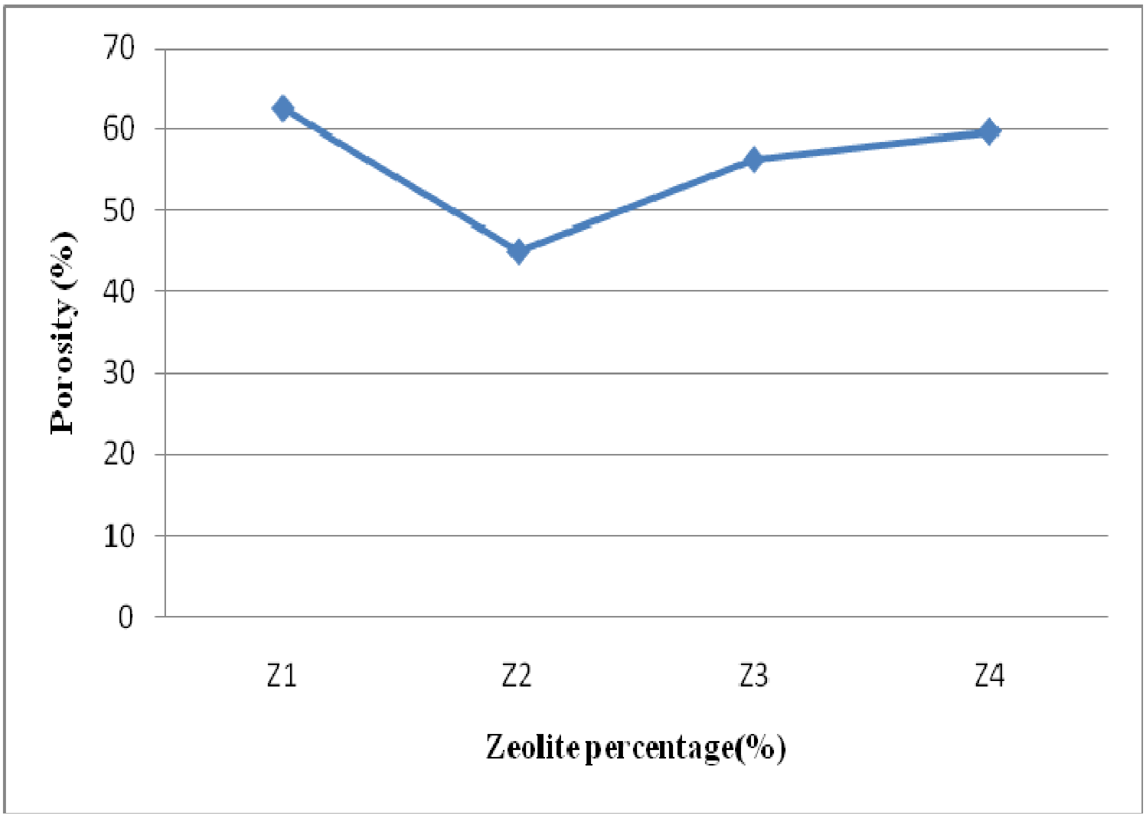


Figure 4-3: Soil samples porosity

Table 4-4: Physical parameters for soil

Soil	Type		Z(.0%)			Z(0.5%)			Z(2.5%)			Z(5%)		
	Texture	Unit	Clay loam			Loam			Silty loam			Silty loam		
PROPERTIES	Real Density	G_s	2.76	2.75	2.74	2.75	2.74	2.75	2.74	2.73	2.74	2.71	2.72	2.73
	Average		2.750			2.747			2.737			2.720		
	Wet Density	Mg/m^3	1.811	1.822	1.803	1.549	1.564	1.513	1.620	1.584	1.596	1.676	1.685	1.711
	Average		1.812			1.542			1.600			1.691		
	Moisture Con.	%	20	19	21	29	30	28	33	32	34	35	36	37
	Average		20			29			33			36		
	Bulk Density	Mg/m^3	1.509	1.531	1.490	1.198	1.203	1.182	1.217	1.200	1.191	1.245	1.239	1.249
	Average		1.510			1.194			1.203			1.244		
	Porosity	%	63	62.5	62	44	45	46	57	56	56	60	59	60
	Average		62.5			45.0			56.3			59.7		
	Surface Area	(cm^2/g)	142.6			102.2			75.4			109.8		
	Permeabilty	(cm/hour)	0.2157	0.2118	0.2172	0.0589	0.0612	0.0501	0.0300	0.0315	0.0296	0.0217	0.0238	0.0204
	Average (k)		0.215			0.0567			0.0304			0.0220		

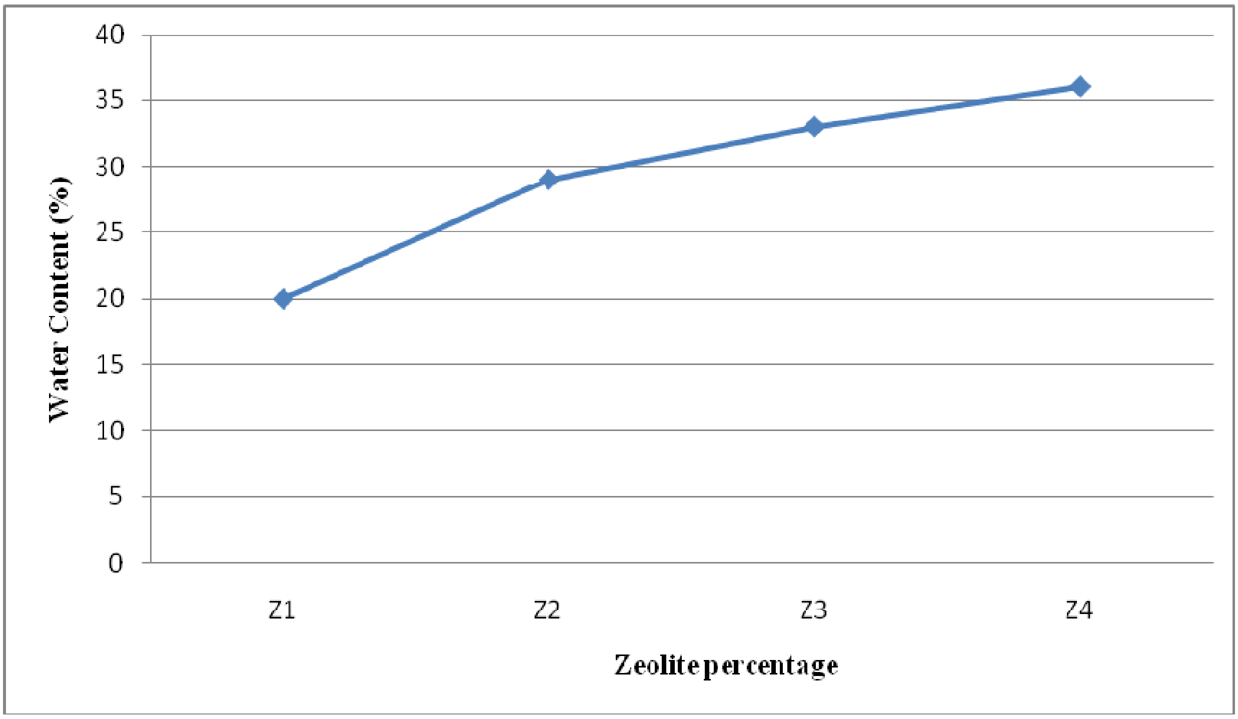


Figure 4-4: Content of water in soil samples

Figure 4-4 indicates the results of water content analysis. We can notice that water content was increased within zeolite content percentage increasing in the soil. The reason is that aluminosilicate framework which leads to increase water adsorption in the soil and minimizing soil porosity.

According to soil texture analysis the texture of soil was changed as a result of zeolite. In addition, the texture changed from clayey soil with high specific area to silty loam soil with surface area less than clayey soil.

Figure 4-5 shows that the soil with 0% of zeolite has the highest surface area in comparison with other percentages (Z2 (0.5%), Z3 (2.5%) and Z4 (5%)), due to clay particles that have small size particles.

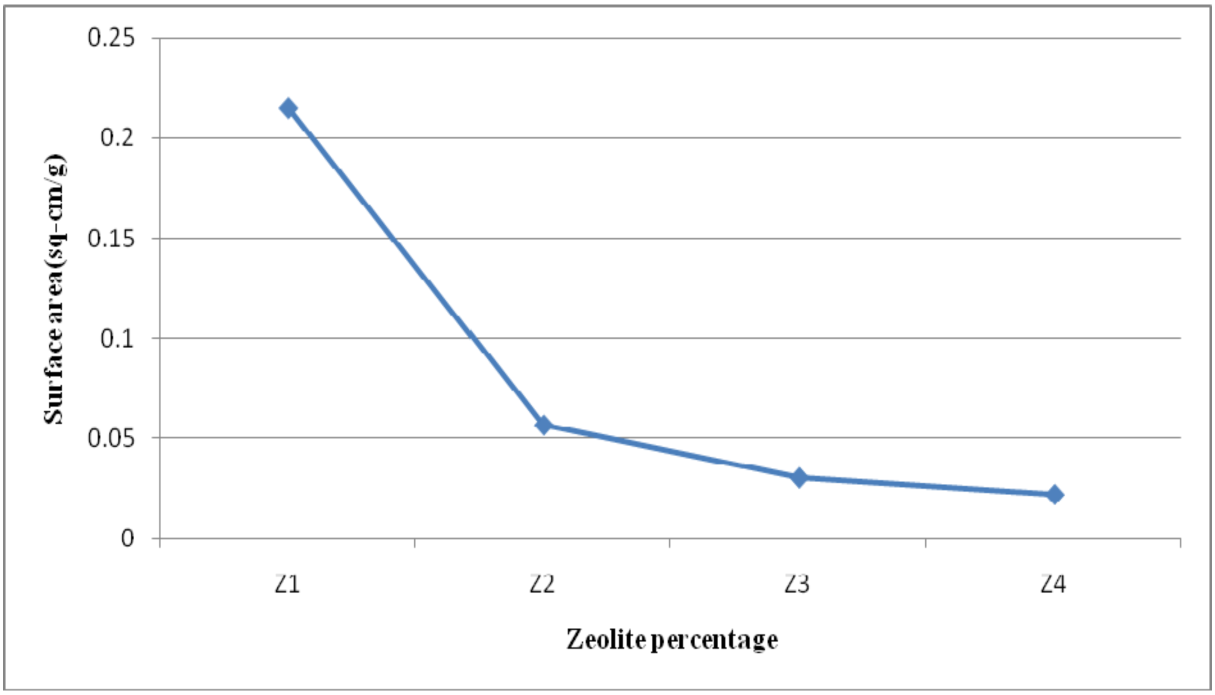


Figure 4-5: Surface area for samples

The results of hydraulic conductivity test were shown in Figure 4-6. The figure shows that hydraulic conductivity decreases with the particles diameter increases (increasing of zeolite content in agriculture soil). The reason for hydraulic conductivity decreased due to the shape selectivity and higher Si content in the amended soil.

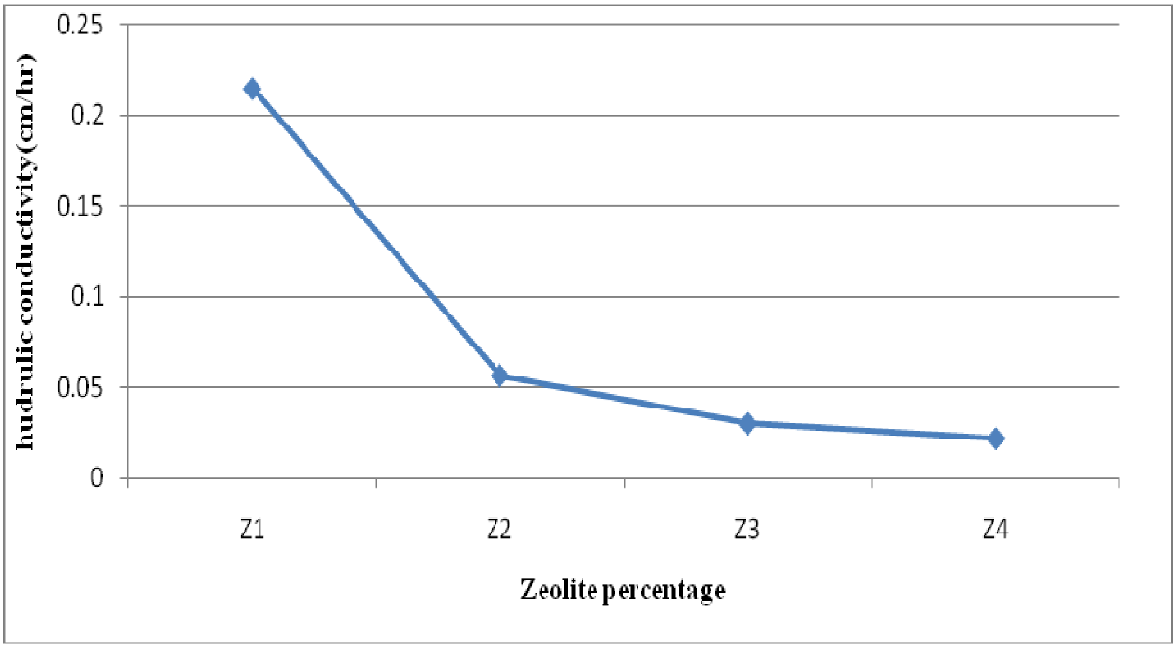


Figure 4-6: Hydraulic conductivity for samples

4.2.3. Soil heavy metals

Table 4-5 shows the results of the heavy metals in soils before planting and after harvesting. Concentration of Pb before and after cultivation wasn’t detected, which means that irrigation water and fertilizer did not significantly affect the concentration of Pb in the soil.

Table 4-5: Heavy metal concentration for soil samples before planting and after harvesting

Zeolite percentage (%)	Before			After		
	Zn (mg/Kg)	Fe(mg/Kg)	Pb(mg/Kg)	Zn(mg/Kg)	Fe(mg/Kg)	Pb(mg/Kg)
Z1 (0%)	131.5	34.9	Not detected	103	33.9	Not detected
Z2 (0.5%)	117	26.2	23.5	83.5	28.7	Not detected
Z3 (2.5%)	91.5	26.2	Not detected	117	34.35	Not detected
Z4 (5%)	87.5	22.5	23.5	100	34.8	19

In general, all types of soil contain trace levels of metals related to the parent materials of soil. Therefore, the presence of metals in soil is not an indicator of contamination. Application of TWW for irrigation purposes may represent additional loading of these metals in the tested soils.

Immobilization of metals, by adsorption and precipitation will prevent their movement, and changes in soil conditions (Shomar, Müller and Yahya, 2005).

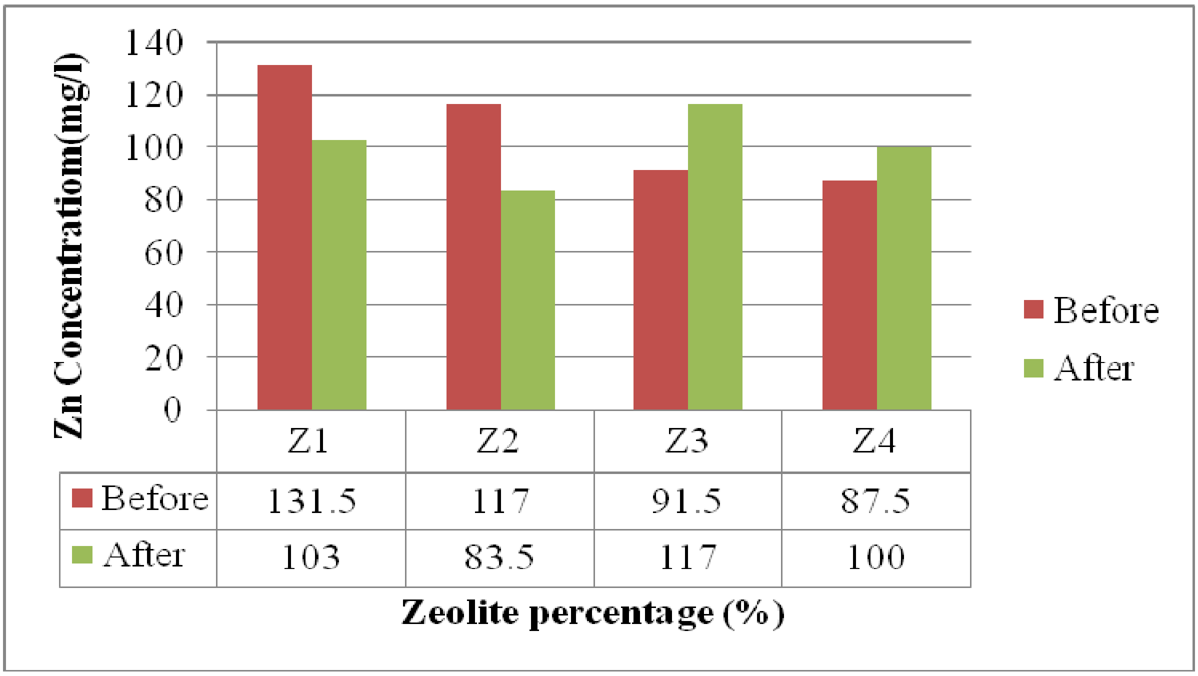


Figure 4-7: Zn concentration in soil samples before and after plantation.

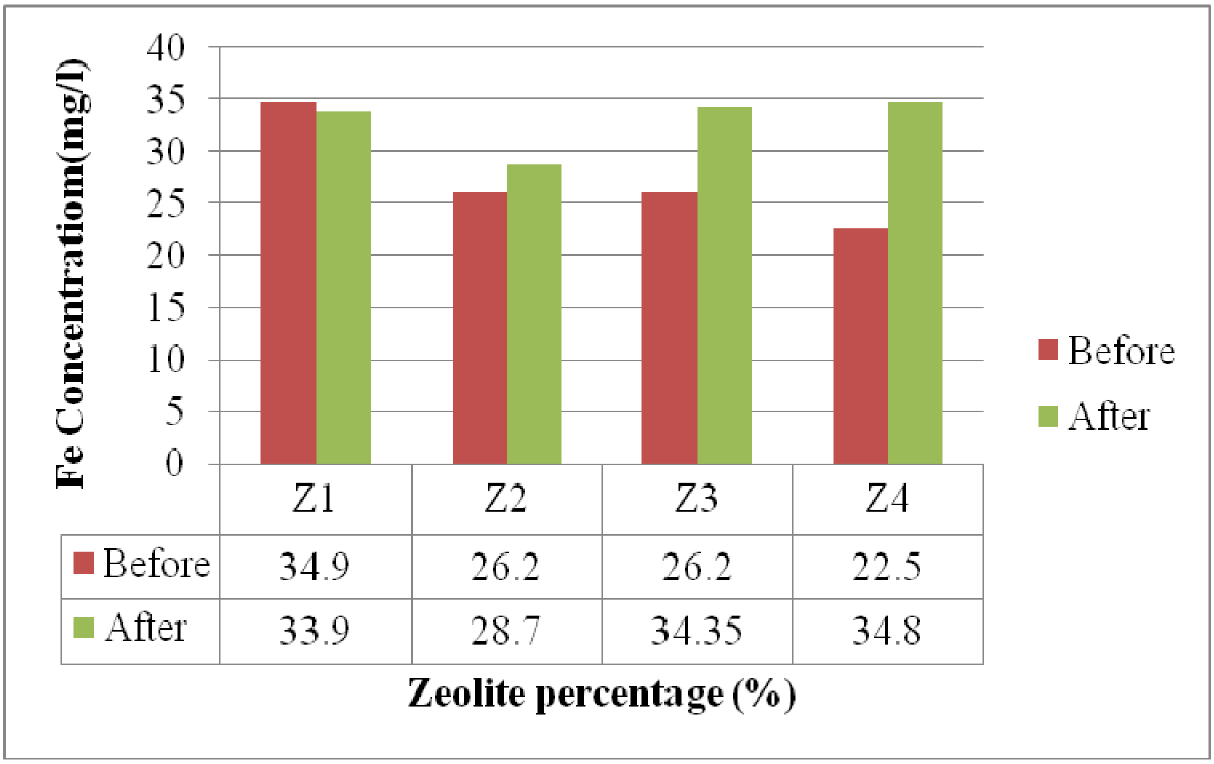


Figure 4-8: Fe concentration in soil samples before and after plantation.

Figure 4-7 and Figure 4-8 show the original concentrations of Fe and Zn in soil mixed with zeolite before wastewater application for irrigation purposes and heavy metal concentration in the soil after harvesting, the effect of differences between concentrations was shown in Table 4-3, which shows that zeolite adsorb it and minimize its transmission to different plants parts. We can observed that noticeable change in Zn and Fe concentration with zeolite percentage increasing which means that zeolite was mixed with agricultural soil able to absorb this metal and accumulate it at soil zone.

In conclusion, TWW from Al-Bireh WWTP did not cause a significance increase in the heavy metals content of soils, due to low metal concentrations a treated effluent that was used, since there is no heavy metal industrial pollution in Al-Bireh city. In addition, the short period of the experimentation might be another reason for the absence of effect.

According to Pb concentration in both cases there is no detectable quantities where the main source comes from heavy industries pollutants and we have a few of them in the West Bank.

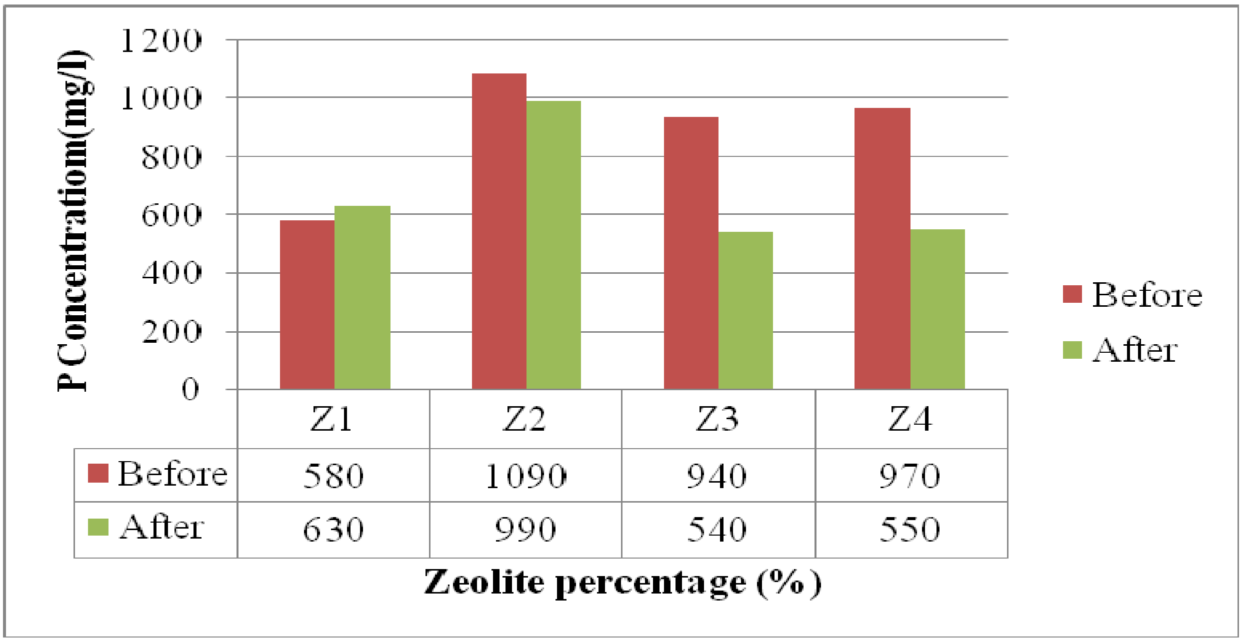
4.2.4. Soil nutrients

Table 4-6 shows the concentrations of soil nutrients (N, P and K) before planting and after harvesting.

Table 4-6: nutrients concentrations for soil samples before planting and after harvesting

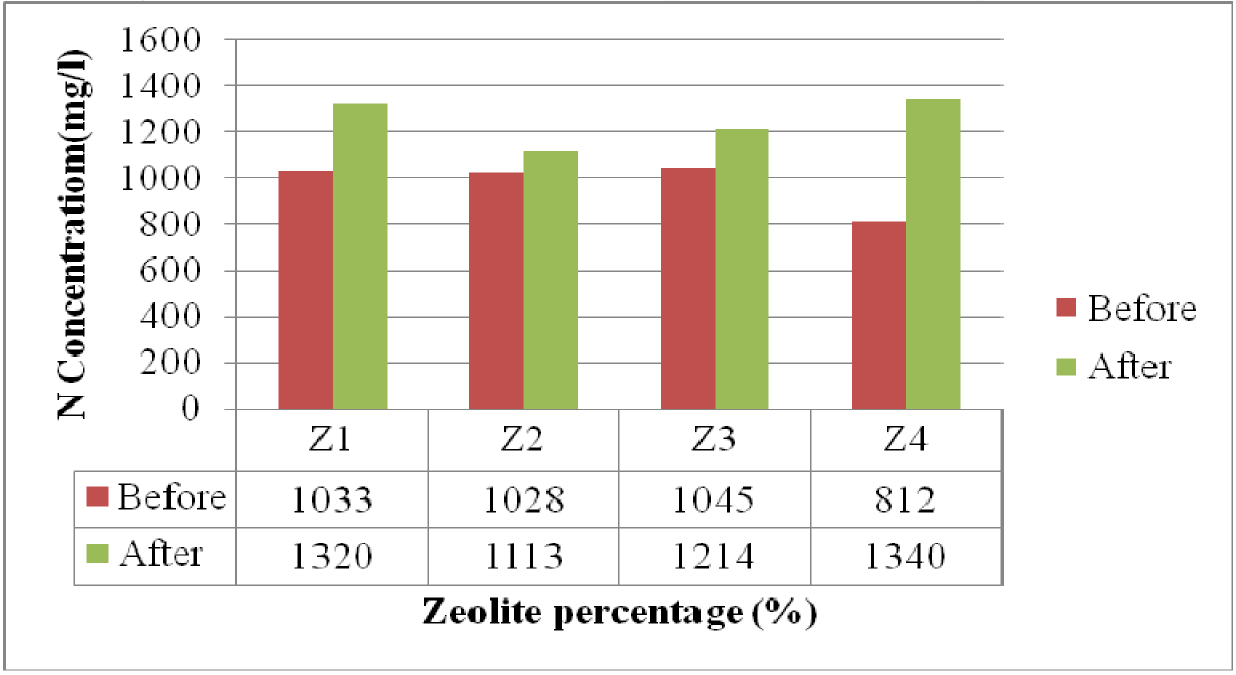
Zeolite percentage (%)	Before			After		
	K(mg/Kg)	TKN(mg/Kg)	P(mg/Kg)	K(mg/Kg)	TKN(mg/Kg)	P(mg/Kg)
Z1 (0%)	3.9	1033	580	3.62	1320	630
Z2 (0.5%)	3.83	1028	1090	3.53	1113	990
Z3 (2.5%)	4.91	1045	940	4.2	1214	540
Z4 (5%)	7.09	812	970	5.58	1340	550

N and P were increased after wastewater application with amended soil as noticed in Figure 4-9 and Figure 4-10 , where zeolite can retain these nutrients at root zone, due to its channeled structure where higher amount of Na, Ca, Fe and Al oxides in the zeolite network to be used by plants when required. Consequently this leads to the more efficient use of N and P fertilizers by reducing their rates for the same yield.



	Z1	Z2	Z3	Z4
🟥 Before	580	1090	940	970
🟩 After	630	990	540	550

Figure 4-9: P concentration in soil samples before and after plantation.



	Z1	Z2	Z3	Z4
🟥 Before	1033	1028	1045	812
🟩 After	1320	1113	1214	1340

Figure 4-10: Nitrogen concentration in soil samples before and after plantation.

According to Figure 4-11 there is no significance change in K concentration at all zeolite percentage, due to low concentration in treated effluent and consumption by plants during its growth cycle.

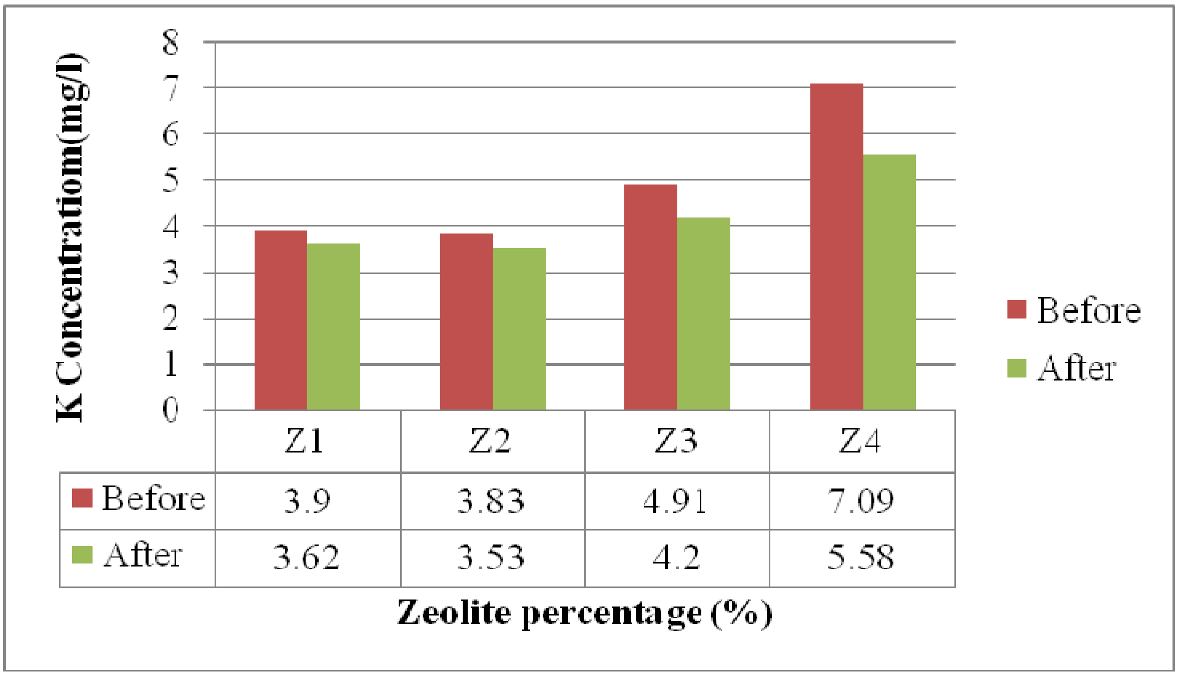


Figure 4-11: K concentration in soil samples before and after plantation.

4.3. Plant analysis

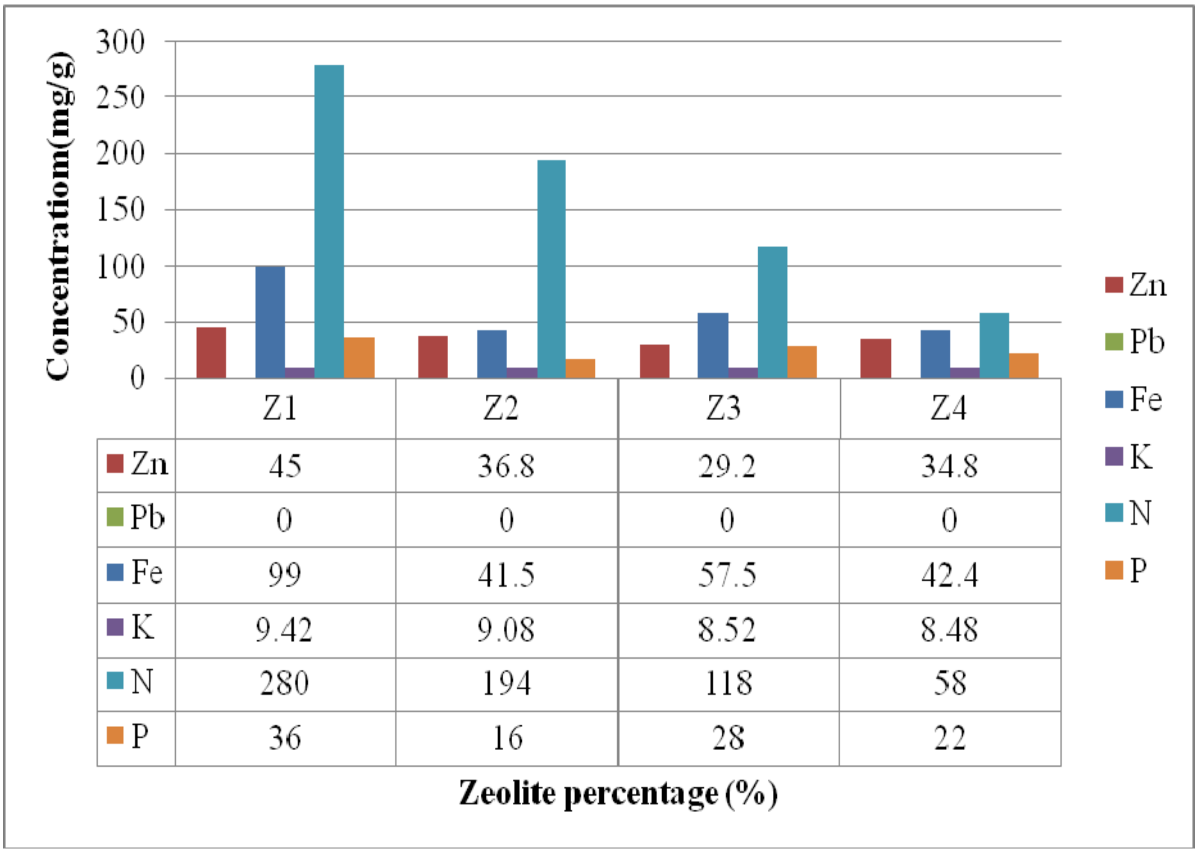
4.3.1 Chemical analysis

Before plantation 3 samples of sorghum seeds were analyzed at BZU laboratory in September 2011 as shown in Table 4-7, these results were considered as controlled for the following analysis.

Table 4-7: Results of sorghum seeds before planting

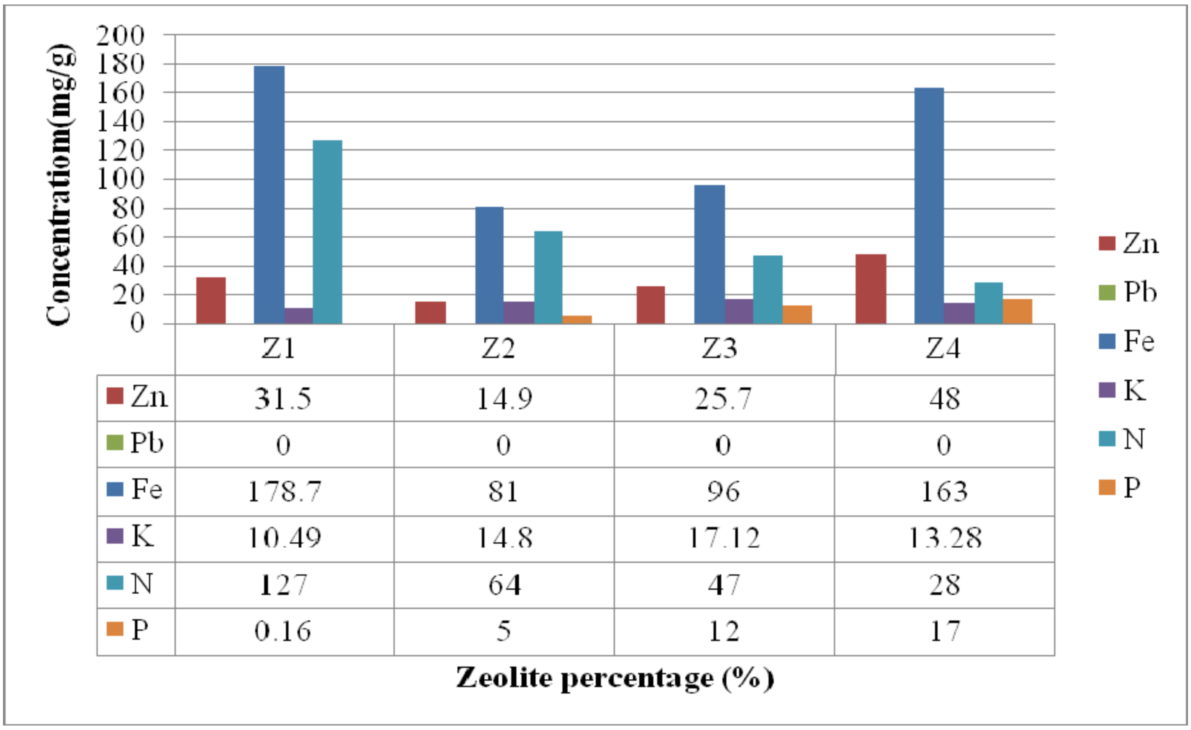
Parameter	Unit	Value
Zn	mg/kg	34
Pb	mg/kg	Not Detected
Fe	mg/kg	1435
K	mg/kg	2.99
TKN	mg/kg	880
P	mg/kg	460

Sorghum seeds grown in amended soil with different zeolite percentage and irrigated with treated wastewater showed significantly decreasing for concentrations of heavy metal (Zn and Fe) and nutrients. According to Figure 4-12 shows the accumulation of Zn, Fe and nutrients, where its concentrations decreased with zeolite percentage increasing comparing with parents seeds, which means that zeolite have high capacity to absorb the largest amount of these metals in soil structure and minimize the possibility of these cations to mobile for different parts of plant.



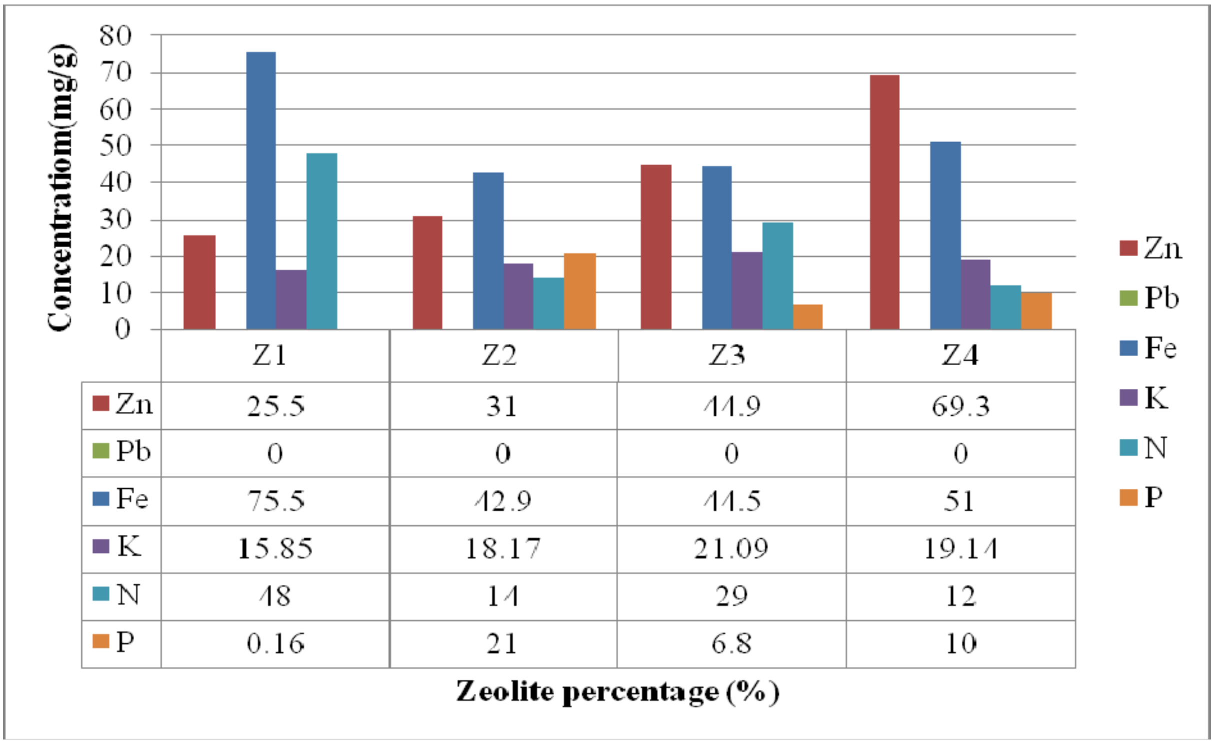
	Z1	Z2	Z3	Z4
Zn	45	36.8	29.2	34.8
Pb	0	0	0	0
Fe	99	41.5	57.5	42.4
K	9.42	9.08	8.52	8.48
N	280	194	118	58
P	36	16	28	22

Figure 4-12: Results of metal analysis for fruits



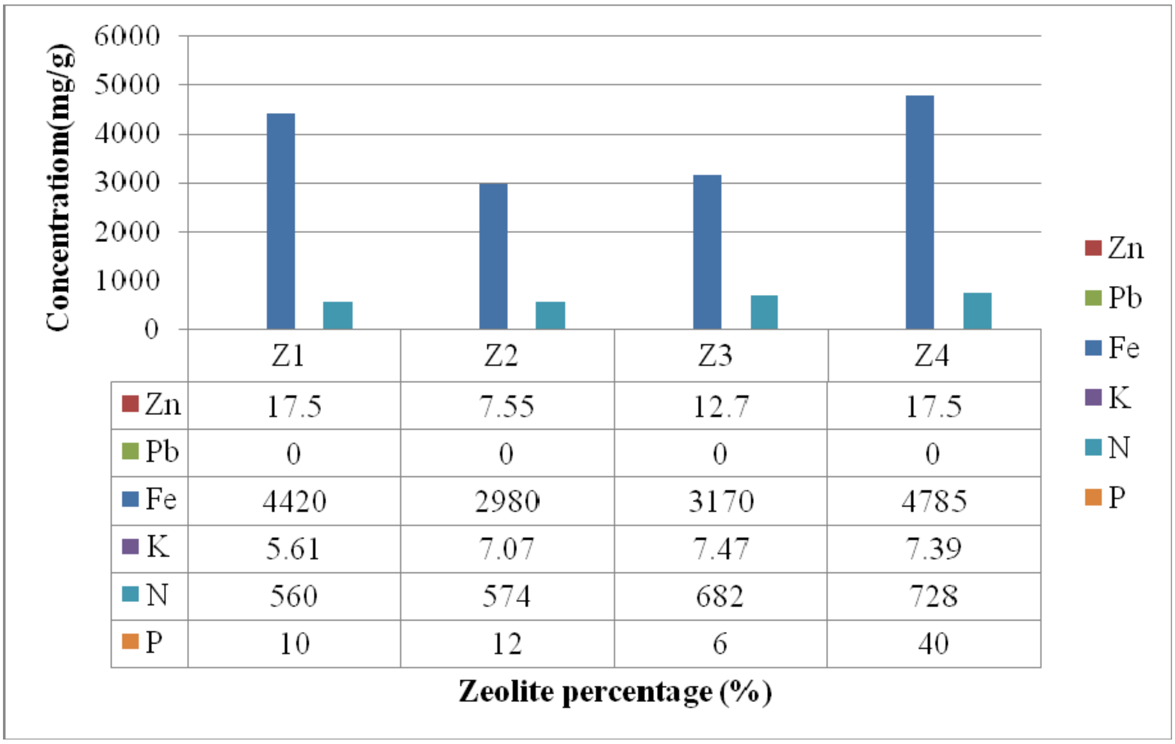
	Z1	Z2	Z3	Z4
Zn	31.5	14.9	25.7	48
Pb	0	0	0	0
Fe	178.7	81	96	163
K	10.49	14.8	17.12	13.28
N	127	64	47	28
P	0.16	5	12	17

Figure 4-13: Results of metal analysis for leaves.



	Z1	Z2	Z3	Z4
Zn	25.5	31	44.9	69.3
Pb	0	0	0	0
Fe	75.5	42.9	44.5	51
K	15.85	18.17	21.09	19.14
N	48	14	29	12
P	0.16	21	6.8	10

Figure 4-14: Results of metal analysis for steams.



	Z1	Z2	Z3	Z4
Zn	17.5	7.55	12.7	17.5
Pb	0	0	0	0
Fe	4420	2980	3170	4785
K	5.61	7.07	7.47	7.39
N	560	574	682	728
P	10	12	6	40

Figure 4-15: Results of metal analysis for roots

The concentration of heavy metals varied widely at different parts of sorghum plant with different percentage of zeolite (as shown in Figures 4-13, 4-14 and 4-15) which indicate that there is an internal transport of metals from roots toward steams, leaves and fruit. In general the lowest accumulation of Zn and Fe was at sorghum fruit which is as following (Table 4-8) for four replicates with different zeolite percentage (Z1(0%), Z2(0.5%), Z3(2.5%), Z4(5%)), and for Zn and Fe respectively (34.8,42.4)mg/g at Z4(5%).

Table 4-8: Chemical analysis for plants components

Samples codes	Parameters	Zn (mg/Kg)	Pb (mg/Kg)	Fe (mg/Kg)	K (mg/Kg)	Pathogen load *(E-Coli*	TKN (mg/Kg)	Available P (mg/Kg)
Roots	R 1 (0%)	17.5	Not Detected	4420	5.61	Nil /g	560	10
	R 1 (0.5%)	7.55	Not Detected	2980	7.07	Nil /g	574	12
	R 1 (2.5%)	12.7	Not Detected	3170	7.47	Nil /g	682	6
	R 1 (5%)	17.5	Not Detected	4785	7.39	Nil /g	728	40
Steams	S 1 (0%)	25.5	Not Detected	75.5	15.85	Nil /g	48	0.16
	S 1 (0.5%)	31	Not Detected	42.9	18.17	Nil /g	14	21
	S 1 (2.5%)	44.9	Not Detected	44.5	21.09	Nil /g	29	6.8
	S 1 (5%)	69.3	Not Detected	51	19.14	10cfu/g	12	10
Leaves	L 1 (0%)	31.5	Not Detected	178.7	10.49	Nil /g	127	0.16
	L 1 (0.5%)	14.9	Not Detected	81	14.8	Nil /g	64	5
	L1 (2.5%)	25.7	Not Detected	96	17.12	Nil /g	47	12
	L1 (5%)	48	Not Detected	163	13.28	Nil /g	28	17
Fruit	F1 (0%)	45	Not Detected	99	9.42	Nil /g	280	36
	F1 (0.5%)	36.8	Not Detected	41.5	9.08	Nil /g	194	16
	F1 (2.5%)	29.2	Not Detected	57.5	8.52	Nil /g	118	28
	F1 (5%)	34.8	Not Detected	42.4	8.48	Nil /g	58	22

The treated waste water that used for irrigation purpose relatively contain small amounts of K, because most of the K present in influent readily passes through wastewater treatment facility so its accumulation in amended soil relatively don’t vary greatly comparing with other plant components due to its uptake during plant growth cycle.

4.3.2. Plant morphology

The morphology parameters include plant high, number of leaves and dry weight. The increase of sorghum plants growth may be due to the increase in organic matter, macro-and micronutrients in the amended soil with zeolite where is the accumulated beneficial nutrients enhanced the metabolic activities and hence the vegetative growth.

i. Plant height

Figure 4-16 clearly shows the height of plants planted at amended soil increased with zeolite percentage increasing where at Z4 (5%) the plants have the heights length with mean height 263cm as noted at Table 4-9.

Table 4-9: Plant high (Cm) directly before harvesting

Zeolite %	Row No.	Plants Height(Cm)	Mean Height Plants (Cm)
0%	R1	150	190
	R2	230	
	R3	190	
0.5%	R1	240	211
	R2	163	
	R3	230	
2.5%	R1	280	233
	R2	200	
	R3	220	
5%	R1	290	263
	R2	240	
	R3	260	

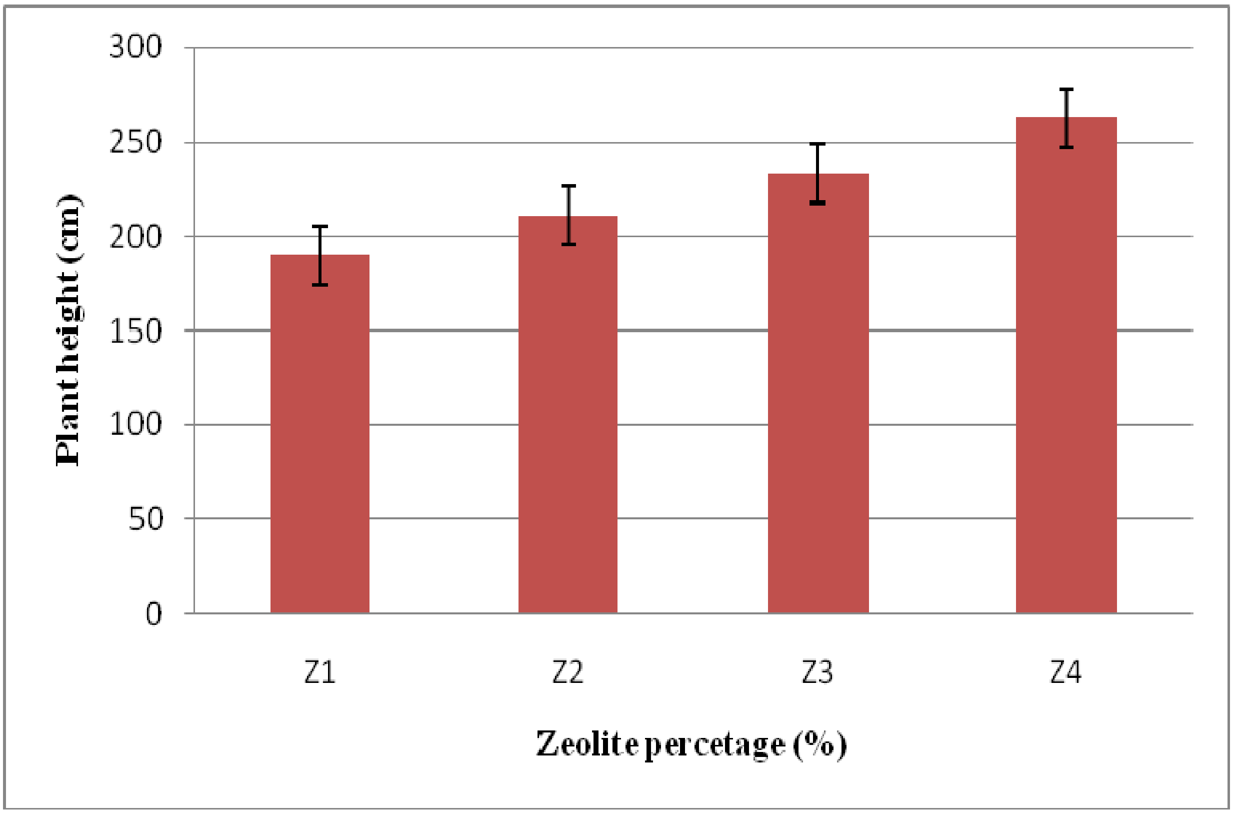


Figure 4-16: Mean of plants height.

ii. Number of leave

The number of leaves was counted directly before harvesting as shown in Table 4-10.

Table 4-10: Mean no of leaves before harvesting

Zeolite %	Replicate No.	No. of leaves	Mean No. of leaves
0%	R1	5	6.3
	R2	8	
	R3	6	
0.5%	R1	9	8.7
	R2	8	
	R3	9	
2.5%	R1	9	9
	R2	8	
	R3	10	
5%	R1	15	12
	R2	10	
	R3	11	

In general, more zeolite content and TWW irrigation significantly increased the number of leaves (Figure 4-17). Plants irrigated with TWW, with 5% of zeolite content, show significantly the highest number of leaves compared to all other agricultural pots (0%, 0.5% and 2.5%). There was no significant effecton in the number of plants leaves of different agricultural pots regardless the quantity of mixed zeolite.

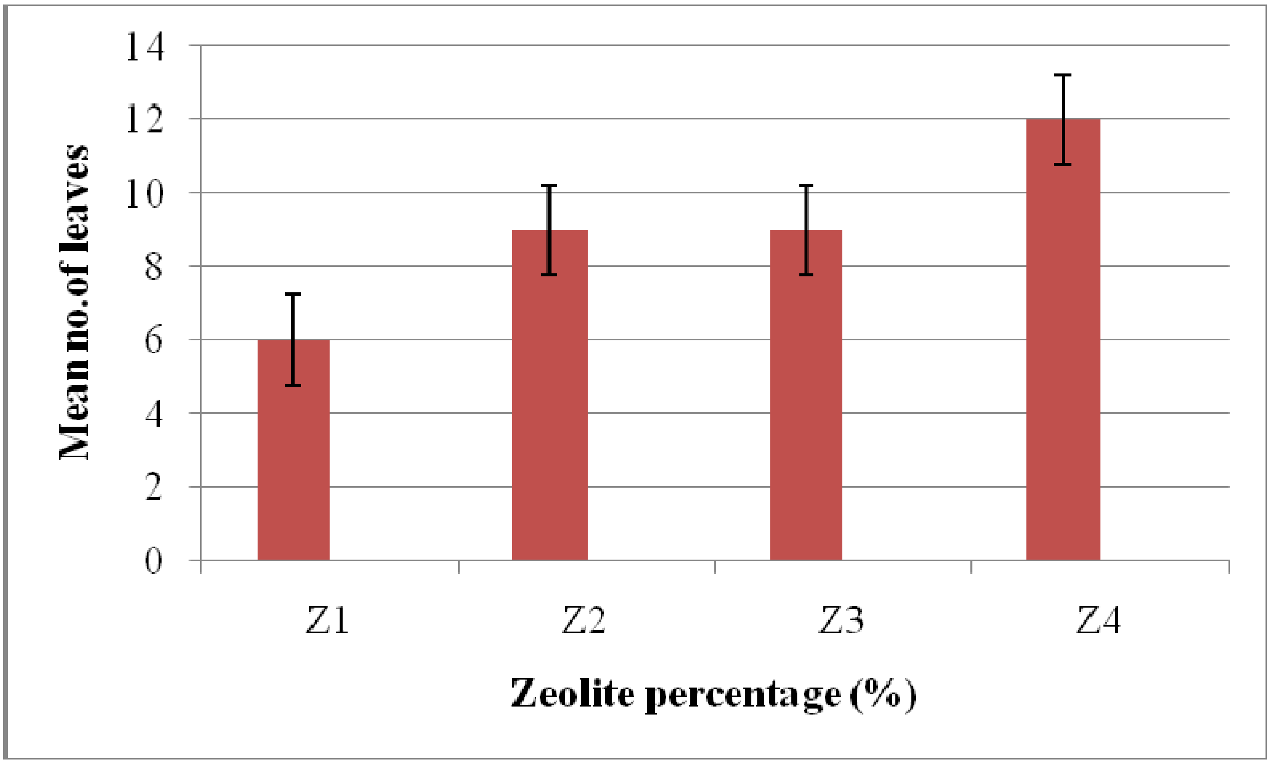


Figure 4-17: Mean no. of leaves

iii. Dry weight of fruits

Increased yield of sorghum by using wastewater on amended soil can be attributed to the presence of not only the readily available adequate amounts of N, P and K but also sufficient quantity of organic matter that improves the soil structure and other soil properties related to availability of water and nutrients which is absorbed by zeolite . It has been reported that the application of treated wastewater on amended soil with Zeolite also increases the total carbon, total nitrogen concentration along with the microbial activity in soil which leads to increase dry weight of fruit as illustrated in the following table (Table 4-11).

Table 4-11: Dry weight of harvested samples

Zeolite %	Replicate No.	Dry weight of fruit (gm)	Mean Dry weight of fruit (gm)
0%	R1	1	1
	R2	1	
	R3	1	
0.5%	R1	1	2
	R2	2	
	R3	2	
2.5%	R1	2	2
	R2	2	
	R3	3	
5%	R1	2	3
	R2	3	
	R3	3	

4.4 Pathogenic *E.coli*

The purpose of this test was to evaluate the effect of irrigation with TWW on the incidence of *E.coli* in sorghum plants and soil. Disease transmission may occur through direct contact of farmers with wastewater or through consumption of products irrigated with wastewater (FAO, 2003). Danger lies more in agricultural products, especially for products consumed raw, more severe than when cooked. The WHO standards for faecal coliform in irrigation water is less than 1000 CFU/100mL. Pathogens can accumulate in the soil and enter the food chain due to irrigation with sewage effluent. In conclusion, it was found the *E.coli* was absent in all replicates, and the treated effluents from Al-Bireh WWTP were not likely to pose a health risk in sorghum that is intended for public consumption.

Chapter 5

Conclusions and recommendations

5.1. Conclusions

In this research, the impact of zeoilte as soil amendment and irrigated with TWW from Al-Bireh WWTP has been studied on Sorghum plants

- Using zeolite as amended material for soil lead to change soil texture as illustrated in Table 5-1.

Table 5-1: Soil texture for amended soil

Zeolite percentage	Soil texture
Z1 (0%)	Clayey
Z2 (0.5%)	Loam
Z3 (2.5%)	Silty loamy
Z4 (5%)	Silty loamy

- According to the analysis of physical parameters of amended agricultural soil with zeolite, where zeolite can improve the water retaining capacity and soil structure.
- Zeolite has a high capacity to absorb and accumulate toxic material at root zone (heavy materials) due to its ion exchange and sieving property.

- Land application of treated wastewater on amended soil with zeolite provides a large part of nitrogen with adequate quantities of nitrogen and phosphorous that is essential for plant growth. Application of zeolite on agricultural soil increases sorghum grain yield, and reduce cost of production because crop in this way need less inorganic nutrients.

5.2 Recommendations for future research

- Workshops, presentations and study tours should be held to the public about the benefits of using treated wastewater in irrigation to ease people's fears and increase their awareness of the importance of the topic.
- Proposed action is recommended to reduce pathogenic contaminants in the effluent of Al-Bireh WWTP.
- It is possible to expand fodder irrigated areas to maximize the use of TWW.
- Studies should be done on the economic benefits expected from similar projects on a larger scale.
- More detailed long-term studies are necessary, to monitor the heavy metal concentrations in the soil irrigated with TWW

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Appendix A

Table A-1: Water quality standards for tap water (PSI, 2003)

Parameter	Value
Temperature(°C)	20
PH	6.5-8.5
Turbidity(NTU)	5
Color	-
TDS(mg/l)	1000
SO4(mg/l)	200
Oil and grease(mg/l)	5
Petroleum hydrocarbons(mg/l)	0.5
NO3(mg/l)	50
Fluorides(mg/l)	1.5
Aluminum(mg/l)	0.2
Mercury(mg/l)	0.001
Lead(mg/l)	0.01
Cadmium(mg/l)	0.005
Arsenic(mg/l)	0.05
Total Chromium(mg/l)	0.5
Nickel(mg/l)	0.01
Iron(mg/l)	0.3
Manganese(mg/l)	100
Zinc(mg/l)	5
Silver(mg/l)	0.01
Cobalt(mg/l)	1
Cyanides(mg/l)	0.05
Total coliform(Colony/100ml)	3

Table A-2: Water quality standards for wastewater reuse for restricted and Unrestricted irrigation (PSI, 2003)

Restricted irrigation		Unrestricted irrigation	
Parameter	Value	Parameter	Value
Temperature(°C)	25	Temperature(°C)	25
PH	6-9	PH	6-9
Turbidity(NTU)	50	Turbidity(NTU)	50
Color	-	Color	-
BOD(mg/l)	45	BOD(mg/l)	60
COD(mg/l)	150	COD(mg/l)	200
DO(mg/l)	>0.5	DO(mg/l)	>0.5
Dry residues at 150°C(mg/l)	1000	Dry residues at 150°C(mg/l)	1500
SS(mg/l)	40	SS(mg/l)	50
SO4(mg/l)	1	SO4(mg/l)	500
Oil and grease(mg/l)	5	Oil and grease(mg/l)	5
Petroleum hydrocarbons(mg/l)	0.5	Petroleum hydrocarbons(mg/l)	15
PO4(mg/l)	30	PO4(mg/l)	30
NO3(mg/l)	50	NO3(mg/l)	50
Phenol(mg/l)	0.002	Phenol(mg/l)	0.002
Fluorides(mg/l)	1.5	Fluorides(mg/l)	1.5
Boron(mg/l)	0.7	Boron(mg/l)	0.7
Aluminum(mg/l)	5	Aluminum(mg/l)	5
Ammounuim-NH4(mg/l)	-	Ammounuim-NH4(mg/l)	-
Mercury(mg/l)	0.001	Mercury(mg/l)	0.001
Lead(mg/l)	1	Lead(mg/l)	1
Cadmium(mg/l)	0.02	Cadmium(mg/l)	0.02
Arsenic(mg/l)	0.02	Arsenic(mg/l)	0.02
Total Chromium(mg/l)	0.5	Total Chromium(mg/l)	0.5
Copper(mg/l)	0.2	Copper(mg/l)	0.2
Nickel(mg/l)	0.2	Nickel(mg/l)	0.2
Iron(mg/l)	5	Iron(mg/l)	5
Manganese(mg/l)	0.2	Manganese(mg/l)	0.2
Zinc(mg/l)	2	Zinc(mg/l)	2
Silver(mg/l)	0.1	Silver(mg/l)	200
Barium(mg/l)	2	Barium(mg/l)	2
Cobalt(mg/l)	1	Cobalt(mg/l)	1
Total pesticides(mg/l)	0.2	Total pesticides(mg/l)	0.2
Cyanides(mg/l)	0.05	Cyanides(mg/l)	0.05
Total coliform(Colony/100ml)	1000	Total coliform(Colony/100ml)	1000