An-Najah National University
Faculty of Graduate Studies

Kinetics Of Groundwater Nitrate (NO_3^{-1}) In Soil Leachate In Tulkarem City Using Soil Columns

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Dedication

To my mother, soul of my father God bless him, wife, children and to all my family and to everyone who helped and supported me in my research.

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إقرار

إنا الموقع أدناه مقدم الرسالة التي تحمل عنوان:

Kinetics Of Groundwater Nitrate (NO_3^{-1}) In Soil Leachate In Tulkarem City Using Soil Columns

دراسة حركة النترات باستخدام أعمدة التربة في مياه الآبار الجوفية لمدينة طولكرم

اقر بان ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص ، باستثناء ما تمت الإشارة إليه حيثما ورد، وان هذه الرسالة ككل من أو جزء منها لم يقدم من قبل لنيل أية درجة علمية أو بحث علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Dedication

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has been submitted elsewhere for any other degree or qualification.

Student's name: .... سم الطالب:

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Abstract

As we know nitrate ions are considered to be global pollutant that pollute water sources which include surface and ground water. This pollution results mainly from nitrogen fertilizers in agricultural areas, wastewaters and animals manure. World Health Organization (WHO) standards of the nitrate ions concentration is put at 45 mg/l, hence any source of water exceeding this value consider as contaminant and put in focus for treatment. The method of vertical columns that are filled with different types of soil taken from Tulkarem City is to study the effects of soil on the groundwater if contaminated water with nitrate leaches through the soil and its relationship with elevation of nitrate in these areas.

Three soil samples of different concentrations of nitrate will be collected from near Tulkarm Municipality wells no (1, 3 and 5). These samples will be put in nine vertical plastic tubes (PVC), then these tubes will be divided into three parts designated as zero-short-long-term of concentrations (0 year, 1 years, 25 years) for each soil sample. Three different concentrations of nitrate-contaminated water will be added as time-term of concentrations to nine columns daily.

For the columns, blank and short-term of time concentration (1 year), the high concentrations of nitrate ions concentrated in the bottom of the columns while the lower concentration concentrated in the upper of the column. For the columns long-term of time of concentration (25 year) high concentrations of nitrate ions concentrated in the upper of the columns while the lower concentration concentrated in the bottom of the columns.

The results indicate that the texture of the soil is sandy to sandy loam and contain high percentage of organic matter ranging from 3.71 % to 4.25 %. It is found that the average concentration of nitrate ions in the content of the soil samples (1, 3 and 5) is equal to 263.3 mg/L, 216.7 mg/L and 799 mg/L respectively.

Kinetic studies (Freundlich adsorption isotherm) is applied to study the adsorption of nitrate ions to the soil particles in the wells no. (1, 3 and 5). The results of adsorption study of wells 1, 3, and 5 are found to be 0.611, 0.779 and 0.821 respectively. These results are satisfactory where the optimum time for adsorption of nitrate ions was after 24 hours.

CHAPTER ONE

Introduction:

1.1 General Background

Pollution nowadays is the most important subject for many countries because pollution has major effects on all aspects of life and threatens human health, animals, plants, and environment [1].

There are three major types of pollution: water pollution, air pollution and soil pollution.

Water pollution is defined as anything done by humans to cause harmful effects to the water bodies. This can include pollution of ground water, lakes, rivers, and oceans pollution. Different manufacturing plants such as factories are the major causes of water pollution, that they use seas waters, rivers and oceans to carry away their wastes which may contain nitrates, lead, phosphates, mercury and other harmful and toxic substances. Waste chemicals and detergents poured into water, wastes of small boats and large ships, oil spills into seas and oceans, and dropping untreated poisoning and harmful sewage into these water are all considered pollutants. These pollutants are carried away by waves or to other parts of oceans and seas [2].

The water resources that are available to Palestinians are groundwater, springs and rainwater. The Jordan River, is not a water resource for the Palestinians in the West Bank because it is used by Jordanians and Israelis only. The West Bank lies over two main aquifers, the mountain aquifer and the coastal aquifer, which are shared with Israel.

The mountain aquifer is divided into the eastern aquifer, northern-eastern aquifer, and western aquifer. Part of the northern-eastern aquifer and eastern aquifer flow east towards the Jordan River. The western aquifer, coastal aquifer and part of the northern-eastern aquifer all flow west towards the Mediterranean Sea [3].

In the West Bank there are forty municipal wells that are used partially or wholly by Palestinians and their annual yield is about 30 million m^3 [4].

This is insufficient amount of water to meet water demand so the deficiency is supplied mainly through springs or through Mekorot (the Israeli Water Company) and by some agricultural wells. In the West Bank there are more than 300 springs the total average annual yield of the springs is about 60 million m^3, where more than 100 spring are considered to have substantial yields. Although springs are secondary water source in Palestine, however, they are for important source of drinking water and for some agricultural needs. Rainfall cisterns are also another source of water that collects about 6.6 million m^3 /year from rooftops [5].

The average consumption of water per capita is about 70 liters per day. About 88 % of the total West Bank population and 55 % of towns and villages in the West Bank have access to piped water supply systems [6].

Leachate from industrial and municipal wastes that entering an aquifer is a major source of organic and inorganic pollution. Organic pollution of groundwater in large scale is rarely, because organic wastes usually cannot be easily introduced to the subsurface. The problem is different with inorganic solutions (e.g. nitrate and chloride), since the inorganic anions move easily through the soil. Once groundwater contaminated then it is difficult and costly to treat [7].

High concentrations of nitrate ions are found throughout the West Bank, these contamination of groundwater with nitrate is caused mainly by percolating of fertilizers and raw sewage. A detailed study done on samples for drinking water collected from wells in the Jordan Valley, Nablus, Jenin , and Tulkarm district, found that the nitrate levels were above the World Health Organization standard guideline values for drinking water which is greater than 50 mg/L. These is found up to one-third of samples collected[8].

There is a major concern of microbiological pollution in the groundwater in the West Bank, since there are frequent outbreaks of diarrhea among the Palestinian population. According to the data published by Ministry of Health in 2001 showed that 600 of 2,721 samples including water from both wells and tanks, failed to meet WHO bacteriological standards for drinking water [9].

There is no developed treatment method of water in the West Bank except using chlorine to disinfect municipal wells and some springs. This is done by addition of sodium hypochlorite to the stream water, just before its distribution from reservoirs. For springs and many private (domestic) wells, disinfecting is not carried out in a regular way. In some municipal wells, chlorination process was not always carried out in the acceptable levels 0.1 mg/L to 0.5 mg/L [10].

1.2 Research Objectives:

The goals of this work is the followings:

1- Determination of nitrate (NO_3^{-1}) in drinking water of Tulkarm wells due to tests that done by Palestinian Water Authority (PWA) and ministry of health that shows high levels of nitrate in drinking water above WHO standards.

2- Determination of nitrate (NO_3^{-1}) in different soils that are collected from nearby different wells and other parameters such as acidity of soil (pH), humidity, nitrogen (N), fertilizers that contain nitrogen, total organic carbon (TOC), salinity, phosphorus, and adsorption isotherm .

3- To improve our understanding, quantitatively and qualitatively, to the issue of groundwater contamination.

4- To study the kinetics behavior of nitrate leachate to the ground water through soil.

1.3 Problem Identification:

This research is done according to the reports released by PWA and ministry of health that shows high concentration of nitrate in the Tulkarem wells especially the wells belonging to the municipality. It noticed that the nitrate concentration is high near Wadi Zaimer, located in the middle of Tulkarem City, and near agricultural lands that use manure and chemical fertilizers.

1.4 Research Methodology:

Three soil samples of different concentration of nitrate will be collected from near Tulkarm Municipality wells numbered 1, 3 and 5. These samples will be put in nine vertical plastic tubes (PVC), then these tubes will be divided into three parts designated as zero-short-long-term of concentrations (0 year, 1years, 25 years) for each soil sample. Three different concentrations of nitrate-contaminated water will be added as time-term of concentrations to nine columns daily. The concentration of nitrate will be detected for resulting water and soil and kinetic studies will be done for each column.

CHAPTER TWO

Literature Review:

2.1 Definition of Nitrate:

Nitrate ion is odorless, tasteless, and colorless anion [11], and consist of a polyatomic ion with the molecular formula (NO_3^{-1}) and a molecular weight of 62.0049. It is consisting of one nitrogen as central atom surrounded by three identical oxygen atoms in a trigonal planar arrangement. The formal charge for the nitrate ion is negative one, where each oxygen atom carries a −2/3 charge while the nitrogen carries a +1 charge. It has three canonical (resonance) structures of the nitrate ion are illustrated in Figure (2.1) below:

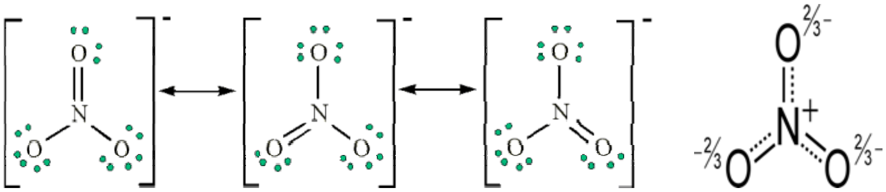


Figure (2.1): The three canonical structures of nitrate ion and its hybrid structure,(Source: Michael Blaber, 1996).

The bonds between nitrogen and oxygen are intermediate in length and strength between a single bond and a double bond as illustrated in the hyprid structure in the figure above.

Almost inorganic salts that contain nitrate are water soluble at standard temperature and pressure. When nitrate is a functional group in organic chemistry it has general chemical formula $RONO_2$ where R is any organic part. Nitrate ions are the esters by following nitroxylation reaction by reacting of nitric acid and alcohols, i.e., methyl nitrate is formed by reacting methanol with nitric acid [12, 13].

$CH_3\text{-}OH + HNO_3 \xrightarrow{H_2SO_4} CH_3\text{-}ONO_2$ (equation 2.1) [14]

In ultraviolet radiation the nitrate ions and little dissolved organic matter were absorbed at 220 nm and enable rapid determination of nitrate ions, and nitrate does not at 275 nm. When the nitrate absorbs at 220 nm it follows Beer's law with linear behavior to 11 mg/L nitrogen solution[15,16].

2.2 Concentration of Nitrate:

Nitrate concentrations in groundwater are less than 3 mg/L in most naturally environments, the denitrification helps to maintain low concentrations of nitrate in ground and surface waters. National standards for nitrate in drinking water is 10 mg/L nitrate-nitrogen [17, 18].

To provide a higher margin of health safety this standard applies to all public supply systems. South Africa and Germany have decrease their nitrate-nitrogen drinking water standards to 4.4 mg/L [19], but Thailand has poured drinking water bottle with standard of nitrate at 4.0 mg/L [20].

2.3 Two Ways of Reporting Nitrate Concentrations:

The report that comes from the lab after the water tested for nitrate, these is either as nitrate-nitrogen (NO_3-N) or as nitrate (NO_3^{-1}). If the lab reports the concentration as nitrate-nitrogen, then the drinking water standard is 10 mg/L. If the lab reports the concentration as nitrate, then the drinking water standard is 45 mg/L [21].

2.4 Sources of Nitrate in Drinking Water

The higher concentrations of nitrate in groundwater that is higher than 10 mg/L are attributed to the sources listed below.

2.4.1 Human and Animal Wastes

Humans and animals waste are major sources of nitrate in any area that has high populations of humans or animals. For human waste, nitrate originates mostly from individual septic tanks or from municipal wastewater treatment plants. For septic tanks the effluent has 30 mg/L to 60 mg/L total nitrogen with ammonia making up the majority of the nitrogen. The nitrogen content of this effluent varies widely depending upon the condition of the individual septic tanks and the type of waste being introduced in each one.

The majority of the population in the big cities is served by municipal wastewater treatment systems, that is connecting all houses, factories, schools, shops, and others to the sewerage network and these will take wastewater for treatment in the wastewater treatment plant. Nitrogen content of effluent from municipal systems will vary according to the nature of the incoming waste stream and the type and condition of the system. After treatment with activated sludge the total nitrogen in the effluent is about 15 mg/L to 35 mg/L, in more advanced systems the total nitrogen in the effluent is reduce to about 2 mg/L to 10 mg/L.

The effluent from wastewater treatment plants in western Australia is currently disposed in ocean, although there are moves to use the effluent in land-based applications, which has implications for groundwater quality.

Waste from open feedlots, dairies, confined feeding operations, stockyards and other facilities for raising animals is also a potential source of nitrate and other forms of nitrogen. The public concern in animal waste includes such issues as flies, odor, and surface water impacts, these facilities represent a massive source of nitrogen and other nutrient inputs to groundwater. In 1998 the university of Nebraska Cooperative Extension estimates that waste that are resulted from animal stock contains from about 100 g to 400 g of nitrogen/kilogram of animal weight, so the total nitrogen concentrations of dairy wastewater range from 150 mg/L to 500 mg/L.

2.4.2 Fertilizers:

The major component of fertilizer is nitrogen that use for agricultural and in gardening. Normally two forms of nitrogen fertilize are present:

- Inorganic fertilizer.
- Animal waste.

In the last half of the twentieth century the inorganic fertilizer used in Australia has become common with the presence of anhydrous ammonia, urea, liquid nitrogen, and similar formulations of nitrogen that have greatly increased crop yields.

In some conditions nitrogen fertilizer has been supplied in large quantity to the soil, either out of ignorance of its impacts on the environment, or for its relative inexpensive fertilizer.

For generations, animal waste has been applied to cropland, both as a means of waste disposal or as fertilization.

Due to the high nitrate solubility and low sorptivity excess nitrate ions or excess watering may allow nitrates to pass to groundwater unabsorbed by plants. As a result, the groundwater would have high concentration of nitrates in the heavily farmed areas.

Nowadays, they are focusing on reducing nitrates contamination of groundwater by reducing the amounts of fertilizer used or by proper timing of its application and irrigating.

2.4.3 Industrial Uses of Nitrate:

In industrial settings, nitrogen-containing compounds are used extensively. Some of these compounds are: nitric acid, ammonium nitrate, urea, and anhydrous ammonia.

World industry uses nitrates as raw material in the textile industry, or as manufacturing of plastic, or in metal processing, or in paper and rubber production, and household cleaners.

Contamination of nitrate may occur from bad handling and disposal of these compounds in critical places that contain either surface or groundwater so levels of contamination will depend on the source.

2.4.4 Naturally Occurring Nitrates

It is unusual for groundwater to accumulate more than 3 mg/L nitrate. Some naturally processes may cause nitrate contamination in groundwater.

During storm, lightning converts atmospheric nitrogen in the presence of oxygen to nitrate which falls as rain, and this nitrate concentration may be transported to the shallow aquifer where nitrate concentrations can reach up to 60 mg/L.

The higher concentrations of nitrate $\geq$10 mg/L in groundwater may be also caused by geologic formations. Sedimentary deposits with high organic matter may release nitrogen [22].

2.5 Nitrates in Soil:

Nitrate is naturally occurring in water and soil. The primary source of nitrogen for plants is nitrate (NO_3^{-1}) which is essential nutrient for plants. cannot live without it and also can increase crop production. Plants could not survive without nitrogen supplement. Nitrogen as food is necessary for increasing crop production.

If more fertilizers containing nitrogen is added to the soil than the plants can use, then the excess nitrate, cannot taken up by plant, will be leached into groundwater and contaminate wells [23].

2.6 Nitrates in Food:

Vegetables account for more than 70 % of the nitrates in human diet, and it is seldom source of acute toxicity. Collard green, spinach, broccoli, cauliflower and root vegetables like carrot have naturally greater nitrate content than other plant food do.

The reminder of the nitrate in our diet comes from drinking water which is about 21 % and about 6 % from meat and meat products in which sodium nitrite is used as preservatives [24].

2.7 Nitrates in Water:

Rural domestic wells that are shallow in depth are likely to be contaminated with nitrates especially in the agricultural areas where fertilizers that contain nitrogen are widespread used [25]. Contamination with nitrate occurs when there is excess nitrate in the soil than plants can use and when water can consume easily through the soil and underlying rock.

The excess nitrate is taken through the soil into groundwater supplies by rainwater, irrigation, and snowmelt. The leachate of nitrate to groundwater occurs particularly where the soil is sandy, gravelly or shallow over porous limestone bedrock.

Excess nitrate can accumulate in the soil in different ways:

- Applying fertilizer that contain nitrate to the soil more than a crop can consume will increase levels of nitrate to higher level.
- Sewage and manure contain both ammonia and organic forms of nitrogen. Organic nitrogen may be converted to ammonia in the soil then ammonia is converted to nitrate by soil bacteria in a process called nitrification.
- Some plants like soybeans and alfalfa can take nitrogen from the air and put it into the ground through their root nodules and this process

is called nitrogen fixation. Finally small amounts of nitrate also entering the soil with the help of rain during electrical storms into soil and groundwater [23].

In the united states about 13 million households use private wells to supply their drinking water. In agricultural areas fertilizers that contain nitrogen are a major source of contamination with nitrate for shallow wells that provide drinking water [26, 27]. According to recent geological survey study showed that more than 8200 wells in all united states were contaminated with nitrate levels above the standards which equal to 10 mg/L drinking. According to estimation done by Environment Protection Agency (EPA) about 1.2 % of public wells and 2.4 % of private wells exceed the nitrate standards[28, 29].

2.8 Effects of Nitrate Ions:

2.8.1 Effects of The Nitrate Ions in The Blood:

Pregnant or nursing women and infants are especially vulnerable to health problems from drinking water with levels of nitrate above 10 mg/L. Figure (2.2) shows infant less than 4 months old infected with methemoglobinemia.

Figure (2.2): infant less than 4 months old infected with methemoglobinemia. (Source: www. Nitrate Poisoning in Ruminants).

Infants may be vulnerable if they are fed with formula mixed with well water that has a high concentration of nitrate. Nitrate conflict with the ability of the blood to carry oxygen to tissues of the body in infants of six months old or younger so that the disease called methemoglobinemia, or blue baby syndrome [30].

The metabolic way for nitrate is the conversion to nitrite and then to ammonia . About 5 %-10 % of the total nitrate intake is converted to nitrite by bacteria in stomach, small intestine, and saliva. This reaction is pH dependant, no nitrate reduction occurring below pH 4 or above pH 9, and that what makes infants to be more susceptible to nitrite toxicity from elevated nitrate ingestion [24].

After the nitrate is converted to nitrite, then it will be absorbed into the blood stream and causes hemoglobin to be converted to methemoglobin, which is unable to transport oxygen. Thus, when human dies from nitrate poisoning, it is due to the lack of oxygen.

Methemoglobin is hemoglobin that oxidized from the ferrous (Fe^{+2}) to the ferric (Fe^{+3}) state, thus hemoglobin unable to bind oxygen due to the oxidation of iron. Nicotinamide ademine dinucleotide hydrogen (NADH) methemoglobin reductase enzyme, presents in adults, reduces methemoglobin to hemoglobin as illustrated in Figure (2.3).

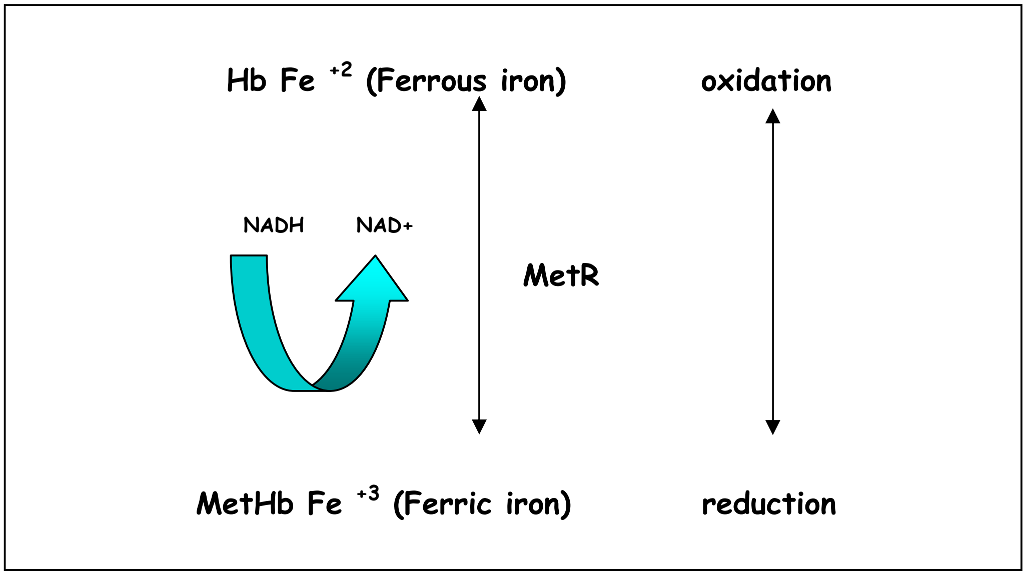


Figure (2.3): Reduction of methemoglobin to hemoglobin by reductase enzyme (NADH). (Source: www. Nitrate Poisoning in Ruminants).

Methemoglobinemia results from either too much methemoglobin production or inadequate enzyme activity [31].

Older than six month, the level of hydrochloric acid will increasing in baby's stomach which kills most of the bacteria that convert nitrate to nitrite. By the age of six of six month, the digestive system is fully developed and the risk of nitrate–nitrite methemoglobina is reduced sharply because the digestive system naturally absorb and excrete the nitrate [32].

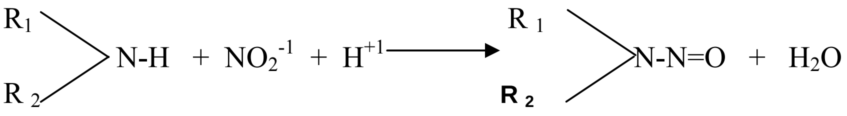
Consuming drinking water with nitrate levels near the drinking water standard does not normally increase the methemoglobin level of humans.

Drinking water that contain nitrate begin its effect on the health of the general populace at levels in the range of 100 mg/L to 200 mg/L, so that the effect on any given person depends on many factors including other sources of nitrate and nitrite in the diet [33].

2.8.2 Stomach Cancer & Nitrate:

Stomach cancer is the second largest number of deaths, lung cancer kills more men and only breast cancer kills more women.

Stomach cancer is a painful and slow way to die, and the link to nitrate in water that has been suggested is a serious matter. There are good theoretical reasons for proposing such a link. Nitrite produced from nitrate could react in the stomach with a secondary amine that result from the decomposition of meat or other protein to produce an N-nitroso compound.



$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!N\text{-}H + NO_2^{-1} + H^{+1} \longrightarrow \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!N\text{-}N{=}O + H_2O$$

(equation 2.10)

The N-nitroso compounds are carcinogenic material, hence, excess nitrogen may will be the primary cause of stomach cancer due to the formation of the nitroso-containing compounds [34].

2.9 Nitrate Standards in Drinking Water:

The concentration of nitrate up to 3 mg/L for well-drinking water is generally believed to be occurring naturally and safe for drinking. The U.S. Environmental Protection Agency puts standards for the concentration of nitrate in drinking water (for public water supplies) 10 mg/L as nitrate-N, or 45 mg/L as (NO_3^{-1}), so higher concentration of nitrate is put as dangerous to people and animals, and for private wells there is no standards.

2.10 Time and Testing Nitrate:

For the drinking water that comes from a public water like municipalities, the drinking water must meet standards for nitrate so that water must be tested every year and quarterly if the results go above 5 mg/L. The public supplier is required to send an annual report to all water users about the tests that done by the Utah Department of Environmental Quality, Division of Drinking Water illustrating the concentration of nitrate and other contaminants found in these water. If water comes from a private well like agricultural (domestic) wells, testing for nitrate is required every five years. The following Table (2.1) showing the nitrate levels and its interpreting of how using water.

Table (2.1): The nitrate levels in drinking water and its interpret of using water.

NITRATE LEVEL (NO_3^{-1})	**INTERPRETATION**
0-10	Safe for humans and livestock. However, concentrations of more than 4 mg/L are an indicator of possible pollution sources and could cause environmental problems.
11-20	Generally safe for human adults and livestock. Not safe for infants because their digestive systems cannot absorb and excrete nitrate.
21-40	Should not be used as a drinking water source but short-term use acceptable for adults and all livestock unless food sources are very high in nitrates.
41-100	Risky for adults and young livestock. Probably acceptable for mature livestock if feed is low in nitrates.
Over 100	Should not be used.

If the concentration of the nitrate is higher than standards in a well, this indicates that the groundwater drawn from shallow depth, and vulnerable to the types of contaminants moving through the soil, like wastewater, fertilizers and animal manure [30].

2.11 Removal or Reduction of Nitrate From Water:

Nitrate is a very water soluble ion hence it is easy to dissolve in water and difficult to remove from drinking water. The best solution for these problem is either finding an alternative drinking water supply or trying to reduce or remove nitrate contamination. Treatment of nitrates are very complicated and expensive. There are four methods of reducing or removing nitrate:

(1) Demineralization by distillation.

(2) Reverse osmosis.

(3) Ion exchange.

(4) Blending [21].

2.11.1 Demineralization

Demineralization technique removes nitrate and all minerals found in the water. Distillation method is the oldest and most effective types of demineralization. The distilling has only three steps:

(1) Boiling the water first .

(2) The steam that are resulting from boiling is caught.

(3) The steam is condensed on a cold surface.

The nitrate and other minerals remain concentrated in the boiling tank and this illustrate in Figure (2.4) [35]:

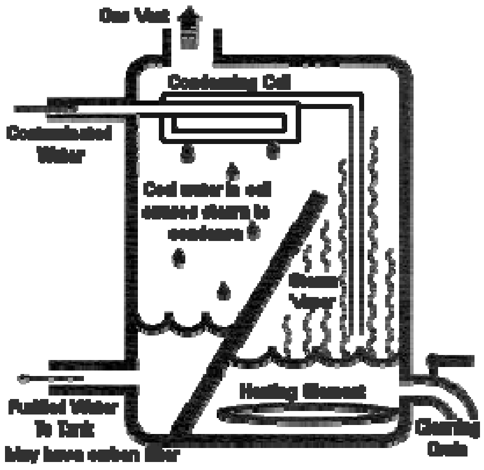


Figure (2.4): Schematic diagram of distillator and how it works. (Source: Randy Johnson, 2005).

Volatile organic compound is a contaminant that will evaporate and condense with the water vapor. The resulting vapor must filtrated by carbon filter in the distiller to ensure the more complete removal of contaminants [36].

2.11.2 Reverse Osmosis:

Reverse osmosis is another treatment method . Figure (2.5) shows the reverse osmosis process. As water enters the unit under pressure, it pushes against semipermeable membrane of plastic sheet or cellulose, so the membrane acts like a sieve leaving ions like nitrates on one side and allowing water that is free from ions to pass through the membrane.

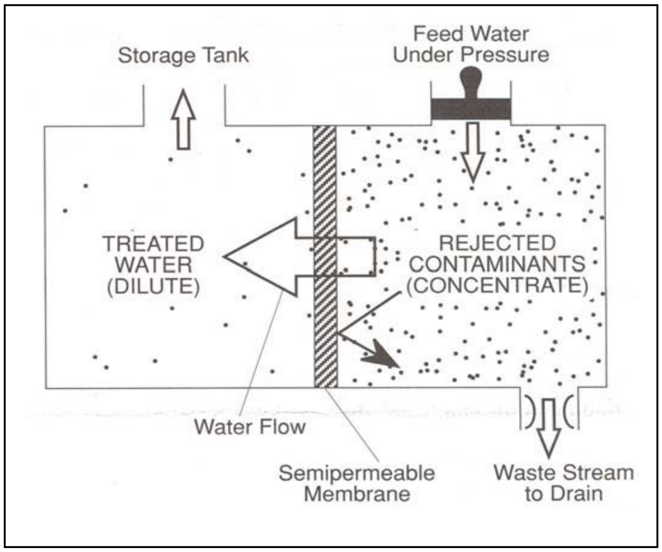


Figure (2.5): A schematic of the reverse osmosis process.
(Source: Barbra Kneen et al., 1995).

About 83 % to 92 % of the incoming nitrate is removed by the membrane. Reverse osmosis requires a membrane, a sediment filter, storage tanks and an activated carbon filter. Many factors like water pressure and temperature, membrane selection, and proper maintenance influence performance.

The disadvantages of reverse osmosis the is that equipment is expensive, initial costs ranging from 300 $ to 900 $, the high energy costs for operation and slow inefficient process, sometimes producing only a few gallons a day of purified water while wasting up to 90 percent of the incoming water[37, 38].

2.11.3 Ion Exchange:

Ion exchange is the third method of water treatment for nitrate contamination which based on nitrates trading places with other substances such as chlorides, hence chloride ions exchange for nitrate ions. The ion exchange unit is a tank filled with special resin beads that are charged with chloride. As water-containing nitrate flows through the tank with the resin, the resin takes up nitrate and exchanged the nitrate with chloride. The resin can then be recharged by backwashing with sodium chloride and reused.

The advantage of ion exchange system can treat large volumes of water and they are more appropriate than demineralization for treatment of livestock water supplies. There are few setbacks of ion exchange systems includes:

- The resin beads also take sulfate from the water in addition to nitrate and exchange them with chloride so that the capacity of the resin to take nitrate is reduced if the drinking water contain sulfate with nitrate.
- The resin may also make the water corrosive so for this reason the water must go through a neutralizing system after going through the ion exchange unit.

2.11.4 Blending:

The fourth and most common method in reducing nitrates level in the water is blending. Blending is to dilute the water that contain high level of nitrate with water from another source that has low nitrate concentrations. Therefore, blending the two waters produces water that is low in nitrate concentration. Blended water is not safe for infants, but is frequently used for livestock [35].

2.12 Protection Water Supply From Nitrate Contamination:

In selecting a new well position for drinking water, put in your mind the possible sources of contamination and also the suitable depth that prevent most pollutants to reach groundwater. So the longer time the water move through soil, the safer it becomes as contaminants are diluted or filtered in the soil. Nitrate is an exception of these contaminants. It is not filtered out of water by the soil, so in choosing a new well location it must be totally isolated from nitrate leaching to prevent contamination.

New and existing wells also need to be protected from surface drainage by making properly cased and head cover from concreter to prevent entering the pollutants to the groundwater and pollute it. If the well is unprotected the contaminants can drain directly into the groundwater and cause serious contamination.

Sinkholes are a direct route to the groundwater, and have them miles far away from wells is the best way of preventing nitrate contamination. Sinkholes can contribute to groundwater contamination by throwing in it dead animals, garbage, chemical containers, leftover chemicals or other forms of waste should never be thrown into a sinkhole or stored where water might drain into a sinkhole.

2.13 Management of Nitrogen:

The only way to ensure a safe water supply from contamination of nitrate and other contaminants, is to control the application of nitrogen to the surface of the ground especially of manures or fertilizers. Hence the key to good nitrogen management is to match the nitrogen application to the needs of the crop by making tests for the soil to know the concentration of nitrate, nitrite and nitrogen.

Manure application to the soil can also affect the leaching of nitrate into the groundwater. For example, if the manure is applied before the plant absorption, a large portion of the nitrate can be lost by leaching to the groundwater [23].

2.14 Definition of Soil:

Soil is a natural body that consist of many layers of minerals of variable thicknesses, which differ from the parent materials in their physical, chemical, morphological and mineralogical characteristics. Soil is composed of particles of broken rocks that have been changed by environmental and chemical processes that include weathering and erosion. Soil differs from its parent rocks due to interactions between the hydrosphere, atmosphere, lithosphere and the biosphere. It is a mixture of minerals and organics components that are in gaseous, solid, and aqueous states. Soil particles are loosely packed, forming a soil structure that filled with pore and spaces. These pores contain air (gas) and solution (liquid) and these illustrate in Figure (2.6). Most soils have a density between 1 and 2 g/cm³ [39, 40, 41].

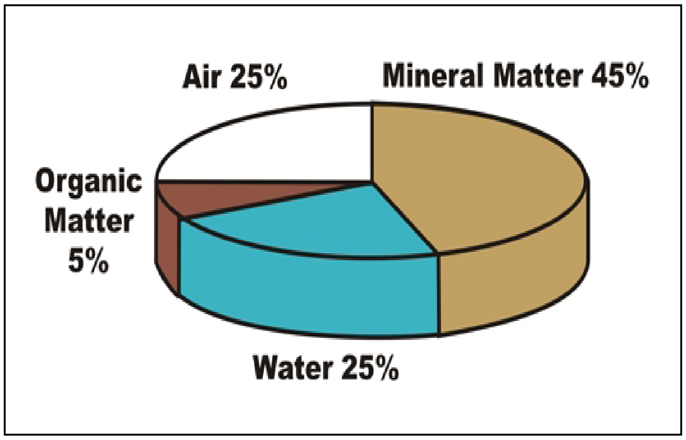


Figure (2.6): The component of soil.
(Source: Sam Kinchloe. Soil Defined, Efficient Fertilizer Use Manual).

2.15 Soil Characteristics

2.15.1 Depth

The groundwater depth is important because it determines the volume of soil through which a contaminant move in the soil before reaching an aquifer. The depth is also important because it determines the contact time between the soil and contaminant. If the soil is deep the following processes sorption, biodegradation, filtration and volatilization operate effectively. Conversely if the soil is shallow it can absorb limited amount of pollutants and pollution potential increases in these shallow (thin) soil and the underlying bedrock is permeable and where the water table is near the surface.

2.15.2 Texture

The different proportions of clay, silt, and sand in a soil determines its texture and in otherworld its coarseness or fineness. The texture influences the movement of water and other pollutants through the soil by effects of particles size and pores and total surface area for each type of soil. Sandy soil has large pores and spaces between the particles and low surface areas, which allows water to percolate through the soil rapidly. The sand hills region is characterized by soils of sandy texture.

Clay soil has a large surface area on which sorption can take place. As a result, leaching through the soil is less in clay soil. Most of the piedmont region is characterized by soils with clay sub soils [42].

2.15.3 Organic Matter Content & Activity

Mineral particles is not originate in soil, it is modified, influenced, and supplemented by living organisms. Animals and plants enrich the soil with organic matters. These organic matters decomposed by the aid of fungi and bacteria into a semi-soluble chemical called humus. Humus, then vertically redistribute within the mineral matter found beneath the surface of a soil by the effect of larger soil organisms like earthworms, beetles, and termites. Humus makes the upper layers of the soil become dark so it is colored dark brown to black. Humus benefits the soil in many ways:

- It enhances soil's ability to hold and store moisture.
- It is the primary source of carbon and nitrogen required by plants for their nutrition.
- It improves soil structure which is necessary for plant growth.
- It reduces the eluviations of soluble nutrients from the soil profile[43].

- Well humified organic matter has a very large adsorptive capacity for both inorganic and organic compounds including most pollutants. For most soils organic matter is concentrated in the top soil and these enhances the soil's capacity to serve as a filter [42].

2.16 Soil Types

One basic way to classify soil is by the size of the soil particles. There are three major types of soil particles, sand, silt, and clay.

Most soil consists of a combinations of these three types. The soil that contains all three types of particles in equal amounts is called loam. There are many simple tests used to determine soil type such as, for instance texture tests, suspension tests, and compaction test..

2.16.1 Sand

- Particle size: 0.5 mm to 2 mm.
- Texture: Gritty.
- Suspension: Sand particles generally settle first, when the soil is suspended in water.
- Compaction: Low.

Sand particles are large and heavy and also has larger spaces among particles as a result then have has small surface area, hence they are less compact than silt or clay. Sandy soil is porous and usually holds less water for plants than other soil types. Soil with large amounts of sand is not as useful for growing most plants because of the property of dryness. The particles of the sand tend to be weakly bonded together, so sandy soils are easily affected by erosion.

2.16.2 Silt

- Particle size: 0.02 mm to 0.5 mm.
- Texture: Smooth and slippery.
- Suspension: Silt particles will settle after sand but before clay, when soil is suspended in water.
- Compaction: Medium.

Silt particles are medium in size and weight, but they are heavier than clay particles. Silty soil more easily eroded by both wind and water because the bonds formed by the silt particles are weaker than those formed by clay particles. Silty soil can hold both nutrients and water well, which can make them good soils for to growing plants.

2.16.3 Clay

- Particle size: Less than 0.02 mm.
- Texture: Sticky.
- Suspension: Clay particles are generally the last to settle comparing to the other two type, when soil is suspended in water.
- Compaction: High.

Clay particles are small and light, and have small pores and spaces so the soil tends to bond together strongly, which is one of its characteristics that makes clay useful for manufacturing pottery. Clay soil is highly compact due to the little space among particles and large surface area. It is difficult for many plants to survive in soil containing a high level of clay, since it is harder for roots to grow and the for circulating air to reach the roots. Clay soil can also tends to hold water [44].

2.17 Soil Textural Classes

Textural classification is the determination of combined portions of sand, silt, and clay. Sand particles range in size from 0.5–2.0 mm, silt ranges from 0.02–0.5 mm, and the clay particles less than 0.02 mm. Rocks or gravel greater than 2 mm are not considered when determining texture. The percentages of silt, sand and clay of a soil are known as textural class and can be read from the textural triangle (Figure 2.7). For example, a soil with 40 % silt, 20 % clay and 40 % sand and would be classified as a loam[45, 46].

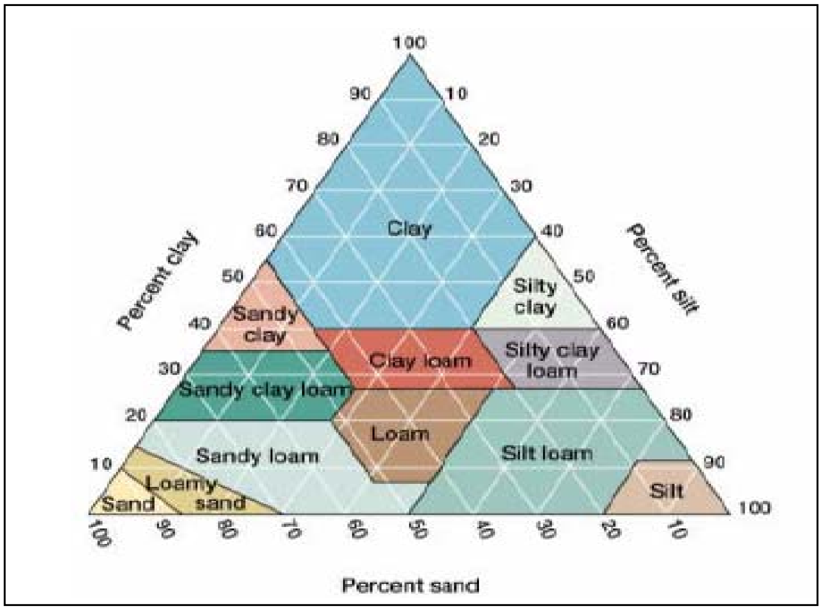


Figure (2.7): A soil textural triangle is used to determine soil textural class from the percentages of sand, silt, and clay in the soil. (Source: www.gloucesterscd.org.).

2.18 Soil pH:

pH is one of the most important physical properties that influence the reactions in a soil and the pH scale illustrated in Figure (2.8). The soil pH is controlled by the concentration of free hydrogen ions in the soil, and the soil with large concentration of hydrogen ions tends to be acidic, and the soil with low concentration of hydrogen ions tends to be alkaline. The availability of hydrogen ions in the soil matrix is caused by chemical weathering reactions and by dissociation of water by the action of plant roots.

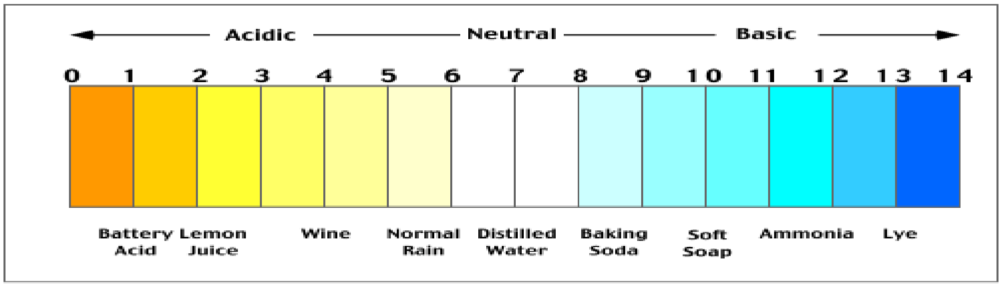


Figure (2.8): The pH scale, (Source: Michael Pidwirny, 2006).

The pH influences the fertility of the soil by solubility of many nutrients, in pH lower than 5.5 many nutrients become soluble and are readily leached from the soil to the groundwater, in contrast at higher pH nutrients become insoluble and plants cannot readily extract them. Maximum soil fertility occurs in the range 6.0 to 7.2 [43].

2.19 Movement of The Chemicals Through Soil

The major processes that move substances (chemicals) through soil are diffusion, convection, and hydrodynamic dispersion.

2.19.1 Diffusion:

Diffusion is the movement of substances or molecules from the regions of high concentration to the regions of low concentration, so diffusion occurs due to the random movement of chemical molecules [47].

2.19.2 Convection:

Convection is heat transfer in which the fluid motion caused by external forces like gravity and other electrostatic forces [48]. Movement of water and chemicals in soil occurs due to differences in the gravity and attractive forces associated with small pores between soil particles.

2.19.3 Hydrodynamic Dispersion

When the water molecule moves in the soil, it travels around soil particles and rocks, making paths like a bundle of capillary tubes of different lengths. Water and chemicals following these ways and paths in the soil making a phenomena called hydrodynamic dispersion.

When applying chemical to the soil its concentration first is high as it moves in the soil, its concentration will be less than the concentration at which the chemical was first applied and this is because of dilution.

Movement of water in real soil is not so ideal, because soil is not uniform in structure or texture or in the distribution of their organic matter. Movement of water in soil may be slow or fast, these is because of presence of spaces between soil particles may be blocked, slowing water and chemical movement. Animal burrows, large cracks, and former root channels may exist which allow rapid movement of water and dissolved chemicals [49].

2.20 Interactions:

Chemical properties of the soil like solubility, sorption and density influence the ability of substances to be transported within the soil. Chemicals that are more soluble at the soil's pH tend to move more easily with water than chemicals that are less water soluble, and chemicals with lower water solubility will tend to attach to clay particles and organic matter near the soil surface. Some of these will form chemical precipitates.

Chemicals that are only slightly water soluble can still reach surface or groundwater and their movement will tend to be slowed through interactions with soil particles.

Adsorption process is the attraction of molecules to the surface of soil particles. When molecular layers form on a soil particle surface true adsorption occurs .

The driving force for adsorption resulted from a specific affinity of the solute to the solid, where the atoms at the solids surface are subject to unbalanced forces of attraction [49, 50, 51].

There are two types of adsorption: Physical adsorption and chemical adsorption. Physical adsorption does not include transferring or sharing of electrons and maintains the individuality of interacting species like Van der Waals attraction. Physical adsorption is fully reversible reaction where adsorption occurs at the same temperature and the process may be slow because of diffusion effects. Molecules in the physical adsorption are free to undergo translation movement within the interface. Chemical adsorption includes transferring or sharing of electrons, as a result there is chemical bonding and chemical adsorption is irreversible. Molecules in the chemical adsorption are not considered to be free to move on the surface where they are attached to active centers [52].

Chemical interaction between adsorbent and adsorbate is favored by high temperature while the heat of physical adsorption is low [53].

Desorption is the process in which molecules are detached or separated from the surface of soil particles. Desorption and Adsorption usually occur simultaneously. Absorption process is mixing molecules with another substance. Most soils absorb water and chemicals, although in amounts much less than those adsorbed.

Positively charged chemicals (cations) such as phosphorus are strongly sorbed to soil particles near the surface of the soil and tend to contaminate surface water if erosion happens. Negatively charged chemicals (anions) such as nitrate ions are more water soluble and less strongly sorbed to soil particles, will tend to contaminate ground water if irrigation or rainfall exceeds plant water use.

Cation exchange is the movement of cations between clay or organic particles and the surrounding soil water, and these can seen in Figure (2.9) and it is an important process [49].

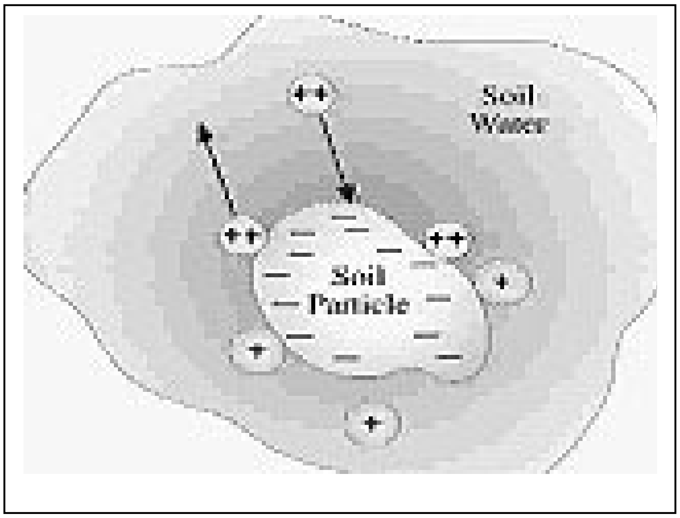


Figure (2.9): The cationic exchange between clay or organic particle and soil. (Source: Jack Watson et al., 1998).

2.21 Adsorption Equilibrium Isotherms:

Adsorption equilibrium is a physic-chemical aspect which determines the adsorption capacity , as the adsorption process continue, the solute that is adsorbed tends to desorbs so equal amount of solutes are absorbed and desorbed simultaneously, hence there is no net change in the solute concentration so the system reach equilibrium [53].

Adsorption isotherm is the amount of solute adsorbed per unit of adsorbent as a function of the equilibrium concentration of adsorbent in the bulk solution under a set of experimental conditions [54, 55].

When solute molecules adsorbed on the surface of the solids (soils), these adsorption may appear in two forms: single layer adsorption or multi molecular layers adsorption. Several types of isotherms may occur, Langmuir and Freundlich isotherms are valid for single layer, where as Brunauer Emmett and Teller (BET) isotherm represents multilayer adsorption [51].

The Langmuir equation is expressed as :

$$\frac{x}{m} = \frac{x_m\, bCe}{1 + bCe} \qquad \text{(equation 2.11)}$$

Where :

X : amount of solute adsorbed in moles (mg, mole).

m : weight of adsorbent (mg, g).

b: a constant related to the heat of adsorption, 1/unit weight .

X_m : amount of solute adsorbed per unit weight of adsorbent required for monolayer.

Ce : equilibrium concentration of the solute [56].

For linearization of equation (2.11), it can be written in the form :

$$\frac{Ce}{x/m} = \frac{1}{bx_m} + \frac{Ce}{x_m} \qquad \text{(equation 2.12)}$$

or

$$\frac{1}{x/m} = \frac{1}{x_m} + [\frac{Ce}{bx_m}] \cdot [\frac{1}{Ce}] \qquad \text{(equation 2.13)}$$

Any of these equations may be used to evaluate b & Xm from experimental data using graphic or linear least squares analysis [57].

Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems. The Freundlich equation is expressed as:

$$\frac{x}{m} = KCe^{1/n} \qquad \text{(equation 2.14)}$$

Where

X : amount of solute adsorbed in moles (mg, mole).
m : weight of adsorbent (mg, g).
Ce : equilibrium concentration of solute.
(1/n) : constant , a measure of adsorption intensity .
K: constant, a measure of adsorption capacity.

It is generally stated by Helby (1952) that values of n in the rang 2-10 represent good adsorption [58]. The constants in the equation (2.14) can be estimated by simple transformation of equation (2.14) to logarithmic form

$$\text{Log } x/m = \log k + 1/n \log Ce \qquad \text{(equation 2.15)}$$

By plotting log x/m versus log Ce a straight line is obtained with a slope of 1/n , and log k is the intercept .

For Freundlich equation, it has been found to be more adaptable to the adsorption data than the theoretically derived Langmuir equation, this is due to the majority of adsorption processes do not comply the Langmuir equation assumption of existence of monolayer of solute solution.

The Brunauer–Emmett –Teller (BET) equation is commonly written as shown in equation (2.6) :

$$\frac{x}{m} = \frac{x_m BCe}{(Cs - Ce)[1 + (B-1)Ce/Cs]} \qquad \text{(equation 2.16)}$$

Where x, m, x_m and Ce have the same meaning as Langmuir or Freundlich isotherm.

B: is a constant describing the energy of interaction between the solute and the adsorbent surface .

Cs : is the solubility of solute in water at a specified temperature .

The transformation of equation (2.16), shows that a plot of the left side against Ce/ Cs should give a straight line having slope (B-1)/x_m B and intercept 1/x_mB:

$$\frac{Ce}{X(Cs-Ce)}=\frac{1}{x_mB}+\frac{(B-1)}{x_mB}\frac{Ce}{Cs} \qquad \text{(equation 2.17)[59].}$$

2.22 Ion Selective Electrode:

Ion selective electrode is simple and inexpensive analytical equipment which referred to sensors, and the pH electrode is the simplest member of this group and can be used to illustrate the basic principles of ISEs.

In order to measure, ion selective membrane the ISE/pH electrode must be immersed together with a separate reference electrode in the test solution and the two must be connected by a mill volt measuring system. At equilibrium, the electrons added or removed from the solution by the ISE.

The relationship between the ionic concentration (activity) and the electrode potential is given by the Nernst equation:

$$E = E_0 + (2.303RT/ n F) . Log(A) \qquad \text{(equation 2.18)}$$

Where

E = the total potential energy (in mV) developed between the sensing and reference electrodes.

E_0 = is a constant which is characteristic of the particular ISE/reference pair.

T = the absolute temperature.

R = the gas constant (8.314 joules/degree/mole).

F = the Faraday constant (96,500 coulombs).

Log(A) = the logarithm of the activity of the measured ion.

n = the charge on the ion (with sign).

When plotting E versus log (A) a straight line will appear in the resulting graph, note that 2.303 RT/nF is the slope of the line from the plot and the intercept is E_0 this is an important diagnostic characteristic of the electrode [60].

2.23 Kinetic Studies:

Adsorption and desorption are very important phenomenas that happen in the environment especially in soil and water. The adsorption and desorption of the different materials in the environment can be studied kinetically by using different equations like Freundlich and Langmuir isotherms and by knowing especial conditions like pH, time, temperature, concentration and other different conditions.

Many researchers in the chemistry department at Al-Najah National University in Palestine studied the kinetics behavior of may substances in the environment.

- Attaallah (2011), the kinetic study of Glyphosate leachate in Palestinian soil at different concentrations.

Manar Attaallah focused here research on the impact of pollutant such as glyphosate pesticide on the soil and environment, and here study was to study glyphosate kinetically in soil. The amount of glyphosate in soil decreases with increasing depth of soil, and due to organic content and metal oxides founded in soil that can form stable complexes with glyphosate. Glyphosate is highly adsorbed to soil due to metal oxides founded in soil. Glyphosate fit the first order reaction, Freundlich adsorption isotherm equation is used to find the values of R, k and n which is higher than one that indicates good adsorption to soil. The adsorption isotherms for the soil is of S-type this indicating the easiness of the adsorption, mainly at higher concentrations [61].

- Awartani (2010), fate of Oxytetracycline and Doxycycline in soil and underground water.

Lama Awartani studied the adsorption behavior of two antibacterials, oxytetracycline and doxycycline as examples of pharmaceuticals that are released into the soil, also studied the effect of organic matter and magnesium chloride hepta hydrate addition on the adsorption of the two antibacterials. The results showed that increasing organic matter increases the adsorption of oxytetracycline more than doxycycline, also showed that the composition of oxytetracycline complex with magnesium ion was more stable than doxycycline complex with magnesium. The study also revealed a higher concentration of doxycycline in leachate water from the soil than those of oxytetracycline, because doxycycline has higher solubility in water. It also showed a decrease of the concentrations for both substances over time in the leachate water due to degradation [59].

- Hattab (2010), adsorption of some fluoroquinolones on selected adsorbents.

Areej Hattab studied the adsorption of some fluoroquinolones (antibiotics) such as : Gemifloxacin Mesylate and Levofloxacin Hemihydrate by using selected adsorbents such as charcoal, kaolin, silica gel and alumina.

For equilibrium studies, two adsorption isotherms were used, Freundlich and Langmuir, the later fitted most data very well. Maximum adsorption capacity for fluoroquinolones occurred into adsorbent charcoal. The amount adsorbed at equilibrium decreases as adsorbate's concentration increases and as the weight of adsorbent increases the amount of drug adsorbed increases. pH played a significant role in the adsorption process especially with silica and alumina. Thermodynamics parameters showed that adsorption process was exothermic and spontaneous as ΔG^o and ΔH^o had negative values, ΔS^o was positive [62].

- Al-Haitali (2009), sorption characteristics of nonionic surfactant Triton X-100 in soil contaminated with diesel.

Mahmoud Al-Haitali studied the adsorption of the surfactant on solid surfaces which can lower the concentration of free surfactant in aqueous solution. If the degree of adsorption is high, surfactant concentration could drop below the critical micelle concentration, rendering the surfactant solution with no ability to solubilize. In this study, diesel was used as an organic contaminant to study sorption characteristics of non ionic surfactant, Triton X-100. The results indicated that when the concentration of surfactant was lower than the critical micelle concentration, the amount of surfactant sorbed on soil increased with increasing the surfactant concentration, the amount of desorbed diesel was relatively low compared with the original amount added to soil, but amount of diesel desorbed from soil at surfactant concentration above the critical micelle concentration was relatively high. Other factors such as temperature, pH, and ionic strength were also studied to examine whether they improve or inhibit diesel desorption from soil. The study has shown that high pH, low pH, high temperature, and ionic strength decreases the capacity of surfactant in desorption of diesel from soil [63].

- Jaradat (2009), adsorption and desorption characteristics of Endosulfan pesticide in three soils in Palestine.

Karbalaa Jaradat studied the adsorption and desorption of the pollutant (endosulfan) in three soil samples (red soil, chalk soil, and sandy soil). Adsorption and desorption rates were calculated on soil samples by using kinetic studies and the values varied based on the type of soil. By using Langmuir model, maximum specific adsorption capacities were measured also. Maximum adsorption was measured in red soil followed by chalk soil, but it was the least for the sandy soil. Also organic matter played a major role in both processes adsorption and desorption on the soil samples. A significant reduction in the process of the adsorption occurred in the soil samples compared with the decline in pH, desorption was higher at both acidic and alkaline pH ranges compared to neutral pH. The increase in temperature and the concentration of pollutant increase the adsorption and desorption in all soil samples [64].

Also the kinetic of many substances studied in many countries in the world Many such as USA, India, Malaysia and Egypt.

- Taha et. ale (2010), assessment removal of heavy metals ions from wastewater by Cement Kiln Dust (CKD).

Taha and his team in Egypt studied the removal of heavy metal (HM) ions Al (III), Cd (II), Zn (II), and Co (II) from aqueous wastes by using adsorption technique using Cement Kiln Dust (CKD) which are both wastes and are pollutants. Batch adsorption was conducted to evaluate the removal of Al (III), Cd (II), Co (II) and Zn (II) onto CKD waste over a wide range of operating conditions of sorbat concentration, pH, contact time, sorbent dose.

The removal efficiency of (HM) ions showed that Al (III) required a shortest contact time, for Zn (II) and Cd (II), binding to the (CKD) was rapid and occurred within 20 to 40 min and completed for Co (II) within 4 hrs.

The equilibrium data for heavy metal ions fitted both Langmuir and Freundlich models. The adsorption isotherm studies showed that the adsorptive behavior of (HM) ions on (CKD) satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy [65].

- N. Kannan and S. Murugavel (2007), comparative study on the removal of acid violet by adsorption on various low cost adsorbents.

N. Kannan and S. Murugavel in department chemistry in Indian Institute of Tropical Meteorology studied the kinetic of the removal of Acid Violet - 17 (AV) which is a dye that contaminates the environment by adsorption on various adsorbents such as iron chromium oxide (ICO), fly ash (FA), kapok fruit shell carbon (KC), lignite coal (LC) and cashew nut shell carbon (CC). These adsorbents used as low cost adsorbents as alternative materials to (CAC) for the removal of (AV) and the results compared with the commercial activated carbon (CAC). The removal of (AV) increases with decrease in the initial concentration of (AV), initial pH and particle size of adsorbent and increases with increase in the contact time and dose of adsorbent. Freundlich and Langmuir adsorption isotherms were used for modulation of the given data at 30± and the reaction is first order kinetic with intra particle diffusion as one of the rate determining steps [66].

- S. Yean et. al. (2005), effect of magnetite particle size on adsorption and desorption of arsenite and arsenate.

S. Yean and his team in Rice university, Houston in Texas in USA made their study to evaluate the effect of magnetite particle size on the adsorption and desorption behavior of arsenite and arsenate, and to investigate the competitive adsorption between natural organic matter and arsenic. Increases in adsorption maximum capacities for arsenite and arsenate were observed with decreasing magnetite particle size. Arsenic desorption is hysteretic, more so with the smaller nanoparticles. Such desorption hysteresis might result from a higher arsenic affinity for magnetite nanoparticles. In the presence of natural organic matter, substantial decrease in arsenic sorption to magnetite nanoparticles was observed [67].

- Ghafar (2004), adsorption studies of aromatic compounds in aqueous solution onto activated carbon.

Faridah Bt Ghafar in Sains Malaysia University focus here research on the removal of aromatic compounds like toluene, o-xylene and benzene from aqueous solutions by adsorption on commercial activated carbons, Calgon Filtrasorb 300 (F 300) and Norit GAC 1240 (N 1240) .

The adsorption capacity of all adsorbate - adsorbent increased with increasing initial concentrations but decreased with temperatures. The equilibrium time was in the following benzene > toluene > o-xylene. Adsorption isotherm studied by using the Freundlich and Langmuir isotherm models indicate that the adsorption isotherms of toluene ,benzene and o-xylene on both adsorbents F 300 and N 1240 can be described by both isotherm models. The N 1240 adsorbent has higher adsorption capacity than F 300 adsorbent for all adsorbates due to its higher surface area and porosity. The adsorption kinetic of all adsorbate-adsorbent systems was pseudo second order kinetic model. The thermodynamic studies showed that the adsorption process was physical adsorption, spontaneous and exothermic in nature for all adsorbate-adsorbent systems.

In the continuous system, the adsorption capacity of both adsorbates for all adsorbates increased with increasing initial concentration, flow rate and amount of adsorbent.

Adam - Bohart and Yoon-Nelson kinetic models were suitable to measured the adsorption data well for all adsorbate-adsorbent systems. It was found that the adsorption capacities of both adsorbents in continuous system were higher than those in the batch system [68].

2.24 Study Area:

2.24.1 Location:

Tulkarem city lies on a hill. It is bounded by Nablus and Jenin cities in the east and north, Qalquilia and Tiba cities in the south and by 1948 cease- fire line in the west as illustrate in Figure (2.10) [69].

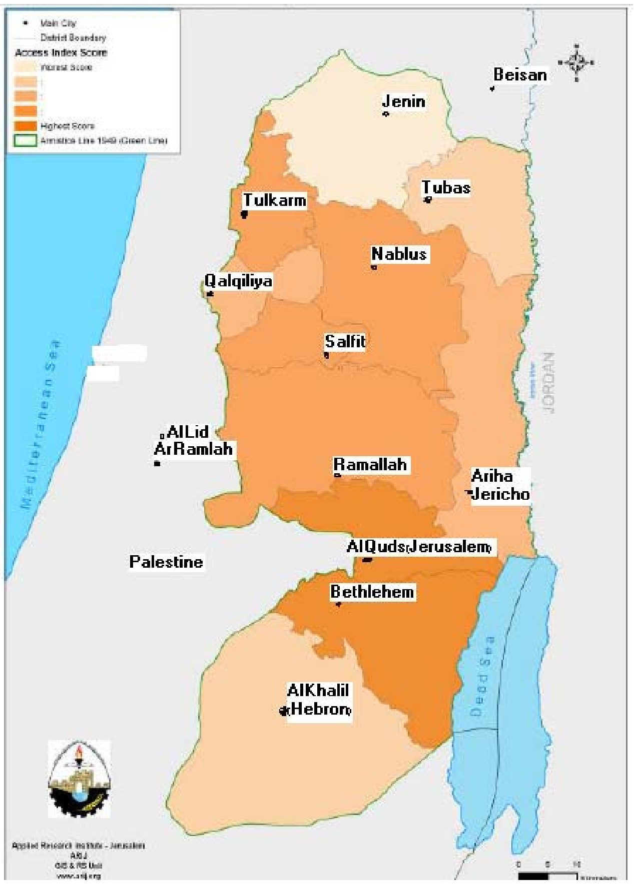


Figure (2.10): The boundary of Tulkarem city. (Source: Hilal, j. et al. Domestic Water Vulnerability Mapping in The West Bank. Applied Research Institute-Jerusalem (ARIJ).

2.24.2 Area & Agriculture:

Tulkarem City is an agricultural city and its area about 253,450 dunum from the total area of Tulkarem district that is about 334,530 dunum, the arable area in Tulkarem City is 209,064 dunum, but the actually cultivated area is 138,368 dunum. These areas are mainly cultivated with fruit trees, vegetables and field crops [70, 71].

2.24.3 Climate:

Climate of the study area is a Mediterranean type with hot summers and warm winters.

Precipitation the rainy season starts in October and continues through May. Almost 70 % of the annual rainfall occurs in December and January. The mean annual rainfall in Tulkarem City is 612.3 mm for the period from 1952 to 2009.

Humidity in Tulkarem district reaches high values with an annual average of 69.6 %, which rises in winter to 75.9 % in February, while it reaches its lowest value of 62.4 % in May.

Temperature in Tulkarem district, the mean annual maximum temperature is 22.3 C.

Winds the wind direction in Tulkarem mainly lies between the southwest and northwest with mean annual wind speed of 3.4 km/hr. Khamaseen winds blow over the area in the spring full with sand and dust, causing rising temperature and drop in humidity. The main daily wind speed from April to June is 7 Km/hr. Table (2.2) shows different parameter that is related to weather of Tulkarem City for the year 2008-2009 [72].

Table (2.2): The average climatic parameters for Tulkarem City for the year 2008- 2009.

MONTH	MAX. TEMP(C)	MIN. TEMP(C)	AVERAG TEMP(C)	HUMIDIT (%)	WIND SPEED (KM/HR	RAINFAL (MM) 2008-2009
Jan.	20	11.6	17	52	04	26.7
Feb.	20	11	19.9	59	05	229.8
Mar.	19	10.6	16.2	65	05	50
Apr.	25.8	14.9	22.6	56	06	6.7
May	27.8	17.8	24.7	52	08	-
June	31.8	21.8	28.8	56	07	-
July	32.5	24.1	30.5	55	07	-
Aug.	31.6	24.3	30	60	07.6	-
Sep.	30.3	22.6	28.6	60	07	10.5
Oct.	30.8	21.8	28.6	50	05	18.3
Nov.	23.9	15.4	21.5	57	06	32.7
Dec.	20.5	13.5	18.3	62	06	151
Average	30.1	17.5	23.9	57		-
Total						525.7

(Source: Palestinian Meteorological Department).

2.24.4 Topography:

The Tulkarem district (city) lies on the western slope of the West Bank, with plain areas to the west and mountainous terrain to the east. The height of the city from the sea ranges between 50 m above sea level (a.s.l). near Tulkarem Municipality and 450 m a.s.l. near Bal'a Municipality as shown in Figure (2.11). The valley of the Wadi Zeimar stretches from the green line to Anabta Town from the west to east and from Anabta onwards in southeastern direction, so the bottom of the valley elevated between 50 m a.s.l. and 200 m a.s.l.

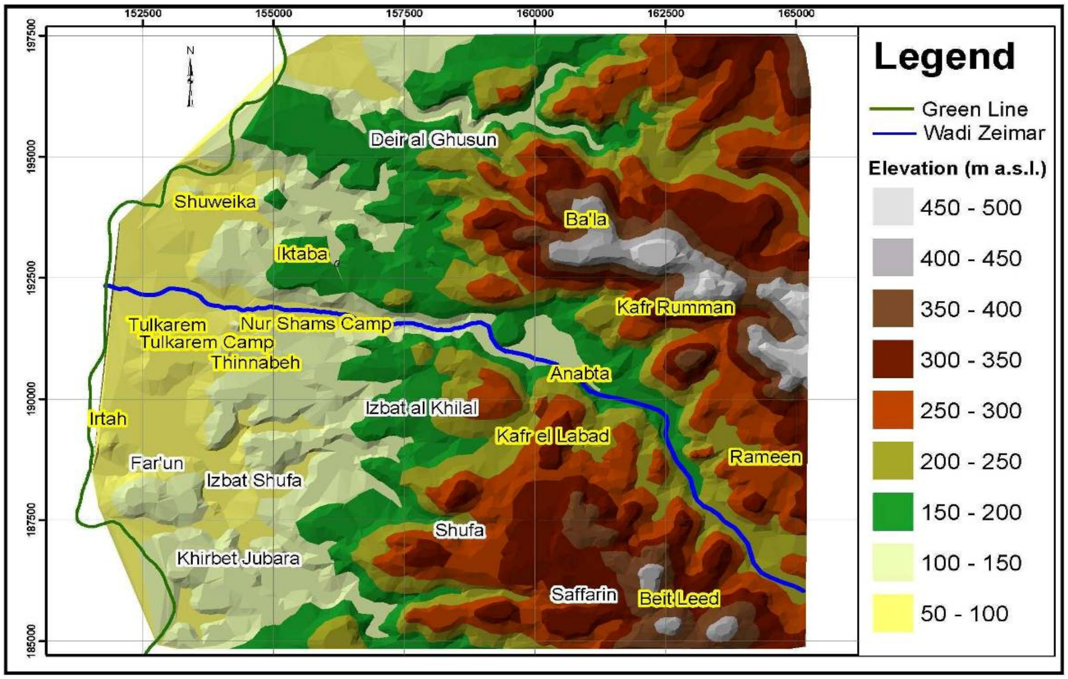


Figure (2.11): Topography of the study area,

(Source: JV DAHLEM .IGIP, (2008). Regional Wastewater Disposal Tulkarem).

2.24.5 Geology:

The formation of the rock in the Tulkarem region range in age from upper cretaceous to recent and cretaceous and tertiary rock formation are characterized by marine carbonate sediments such as chalks, limestones, marls, dolomites and chert nodules. The geological features and folding process, fractures, as well as tensional and compressional faults, are well developed in the region, and this development increases the groundwater potential and hydraulic conductivity of the existing aquifers.

2.24.6 Hydrogeology:

In the West Bank the main source of domestic water is abstracted from shallow and deep water bearing formations of the mountain aquifer. The mountain aquifer was divided into three main groundwater basins based on the direction of the hydraulic drainage, namely the western, north-eastern and eastern basin and illustrate in Figure (2.12) [73, 74].

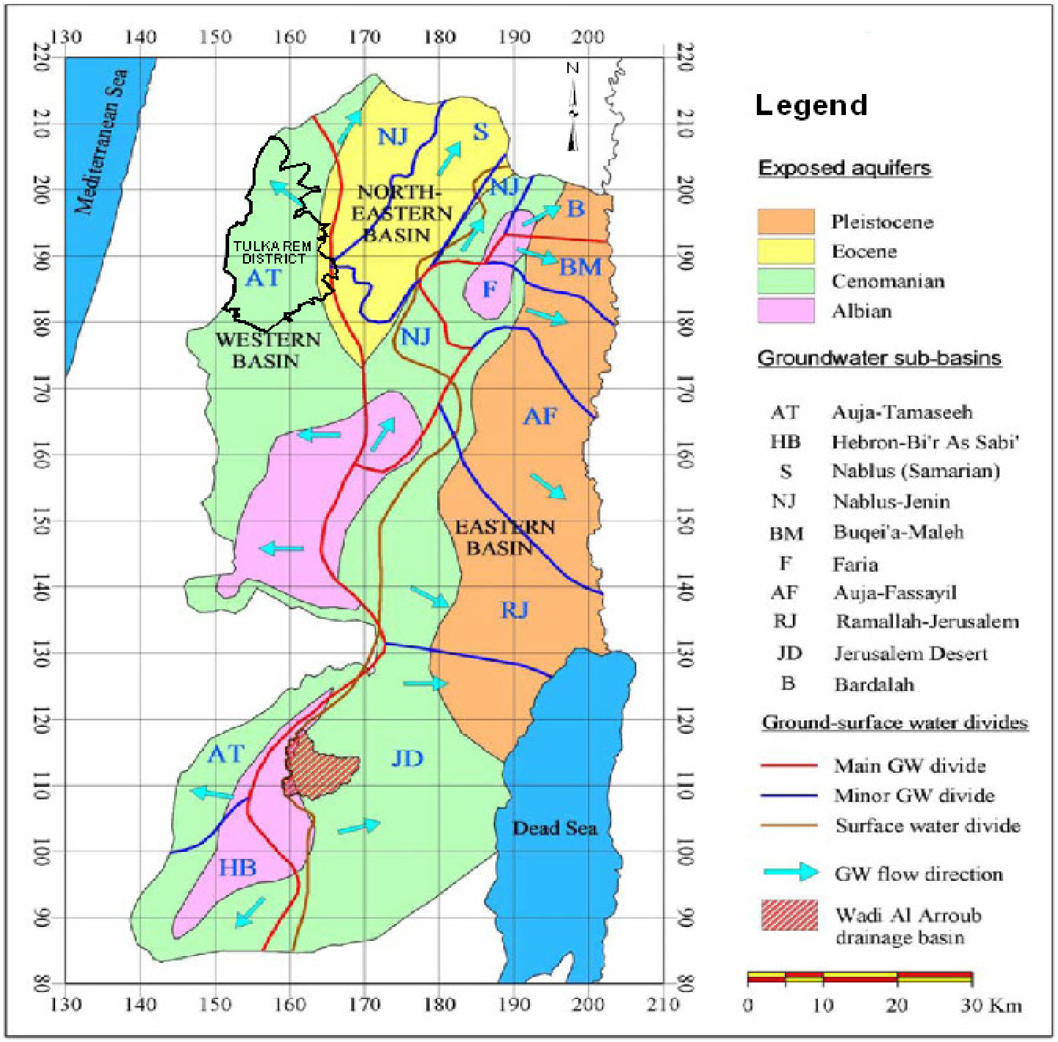


Figure (2.12): Groundwater basins in the West Bank.

(Source: Ziad Qannam, 2002. Hydrological, hydro-chemical and environmental study in Wadi Al Arroub drainage basin, south West Bank Palestine).

The Tulkarem district lies entirely on the western aquifer basin, that is the largest of all groundwater basins in historical Palestine. Geologically it is located in the western part of the West Bank mountains and stretches to the coastal areas, and from central mountains area in the north to the Hebron mountain in the south. Two main aquifers are present in this basin:

the upper and the lower aquifers. The average thickness of these aquifers ranges between 600-900 meters.

The average annual natural recharge of water for the western aquifer is around 400-440 Mcm/yr. The annual abstraction of water from the basin reaches to 338 Mcm/yr, and most of these waters 317 Mcm/yr is being pumped from the Israeli wells that are situated along the West Bank border.

Palestinians have very low share in groundwater in pumping from this basin and there are 151 wells run at low pumping rate and their average pumping 20.9 Mcm/yr. Where, Israel has more than 500 wells just inside and along its borders with the West Bank [75].

In Tulkarem there are three major aquifers, the cenomanian aquifer (lower aquifer), upper cenomanian turonian (upper aquifer) and the eocene complexes. The latter is not of great importance because of its limited capability to store groundwater. The lower aquifer is deep with high capacity and productivity of water, this is due to the great thickness of up to 400 m of dolomitic limestone. In Tulkarem the lower aquifer has not been explored yet as the high yielding wells in the upper aquifer can satisfy the required amount of water.

The water quality of the upper aquifer is generally good, though the aquifer is exposed to pollution caused by sewage disposal in the wadis, leaking landfills, leaking cesspits, and the infiltration of chemicals released on the surface. Analyses show high levels of nitrate in most of the wells in the area and these high nitrate levels are attributed to the leachate of sewage into the groundwater and as a result of exceeding the standards of the WHO many times and this has already led to the closure of several wells in the area. The following Figure (2.13) illustrates that all municipalities and villages in the area lie in areas exposed to high or medium groundwater vulnerability.

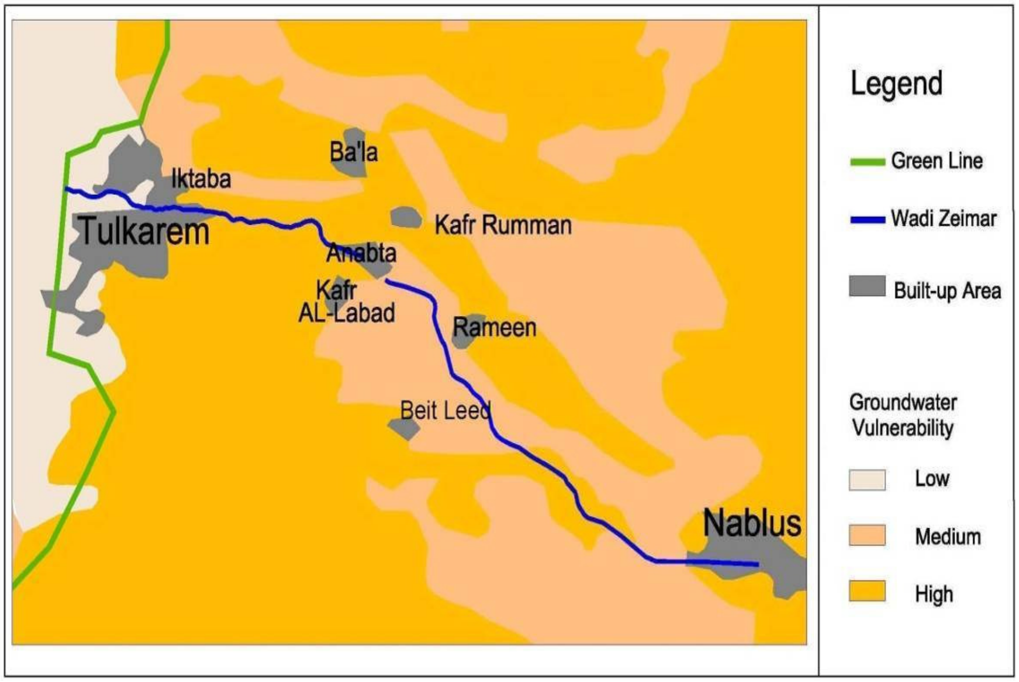


Figure (2.13): Groundwater vulnerability in the study area.
(Source: UNEP-WCMC and UNDP/GRID Geneva 2002; modified).

2.24.7 Limnology:

The major valley in the study area is the Wadi Zeimar and it is about 44 km long as shown in Figure (2.20) above. Its area stretches from Nablus to the west passing Anabta towards Tulkarem. At the green line the water from the Wadi Zeimar is transported to Emek Hefer Settlement Wastewater Treatment Plant where it is pretreated and after that either used for irrigation or discharged to the Alexander River in side the Green Line where this river drains into the Mediterranean Sea .

The main tributary for Wadi Zeimar is Wadi Deir Sharaf that confluence with the Wadi Zeimar near the Rameen Village. The border of the Wadi Zeimar is Wadi Massin which is in the north, and Wadi Sajour and Wadi el Tin which is in the south.

The wadis have a typical temporary runoff pattern with surface runoff only during the winter season from November to March. However, Wadi Zeimar shows a permanent runoff throughout the year, waste waters from Nablus, Sabastya, in the upper catchment area and from Anabta and Tulkarem in the lower catchment area during the dry season is discharged into Wadi Zeimer [73]. It contains wastewater from industries, stone sawmills, solid wastes, leather factories, garages and more.

Ten months out of every year the color of the water is white, due to the stone powder spread along the stream, the other two months of the year, October and December, the color water is black due to the organic matter from the olive waste that is released into the stream from about 26 olive mills that are spread in the area [75].

2.24.8 Groundwater Quality:

The groundwater pollution that caused by infiltration of wastewater can be evaluated by measuring the standard parameters of sulphate, chloride, phosphorus nitrate and coliform bacteria. These standard parameters and their sources are indicated in the following Table (2.3):

Table (2.3): Standard parameters and their sources.

STANDARD PARAMETERS	SOURCE
Ammonium/Nitrate/Nitrite	Fertilizer, feedlots (livestock), sewage.
Chloride	Saltwater intrusion, mineral dissolution, industrial or domestic waste & wastewater.
Coliform Bacteria	Domestic sewage, animal waste, plant or soil material.
Phosphorus	Fertilizer, domestic wastewater, detergent.
Sulphate	Saltwater intrusion, mineral dissolution, domestic or industrial waste & wastewater.

The concentration of the above parameters in the groundwater is related to the physical rainfall and anthropogenic factors like agricultural activities, industrial and domestic pollution and the geological formation of high permeability of the rocks making the groundwater vulnerable to anthropogenic factors. Land used around the wells mainly varies from agricultural, including olive groves, to urban. All wells are drawing their water from the upper aquifer.

Names of some selected wells located in the study area are given in the following Table (2.4), also indicating the land use pattern of adjacent areas and whether the well is located in the Wadi Zeimar area or not.

Table (2.4): Some wells in the study area.

WELL NAME	URBAN AREA	AGRICULTURAL AREA	OLIVE GROVE	WADI ZEIMAR
TulkaremMunicipality wells1, 2, 3, 4, 5, 6.	√	√	-	√
Hafedh Alhamdallah	√	√	-	√
Rafeeq Hamdallah	√	√	-	√
Rafat Al Qubbaj	√	√	-	√
Hasan Mahmud Khaleel	-	√	-	-
Bala Village Council	-	-	√	-
Anabta 1, 2	√	√	-	√

Nitrate is the main indicator for the pollution of groundwater by sewage, so that investigations focused on this parameter. The nitrate values of 10 wells are presented in Figure (2.14) for the period 2003-2006 and these wells have been examined in detail.

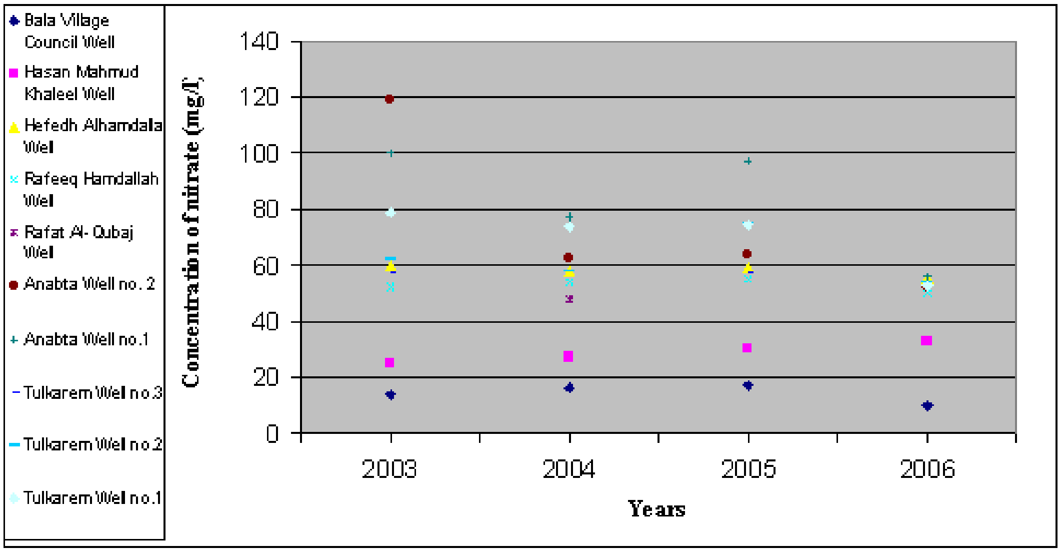


Figure (2.14): Nitrate level in selected wells in the study area.

In the figure above it can be seen that all samples taken from the other wells have a nitrate concentration of 50 mg/L or higher above WHO standards, with the exception of Hasan Mahmud Khaleel well and Bala Village Council well that are less than WHO standards (low). The highest value was recorded in 2003 for Anabta well 2 with a concentration of nitrate is about 119 mg/L.

For the wells in Tulkarem and Anabta, it can be noticed that a decrease of the nitrate level while for the Hefedh Alhamdallah well, Rafeeq Hamdallah well and the Bala Village council well no trends can be observed but for the Hasan Mahmud Khaleel well the concentration nitrate slightly increased.

By taking into account the land used pattern near the wells, it concluded that the nitrate level in the water of the Tulkarem wells, the Rafeeq Hamdallah well, Hefedh Alhamdallah well, and the Anabta wells are influenced by leaking sewer lines, nonsealed cesspits and agricultural activities like applying fertilizers, as well as the Wadi Zeimar for most of these [73].

2.25 Tulkarem Problem With Nitrate:

Tulkarem City depends mainly on the groundwater as a source of drinking water**,** so that the study was conducted in Tulkarem Municipality wells [number (1) located is in the middle of the city, number (3) located near Wadi Zeimar, and number (5) located in Thinaba]. There are about 31 wells for water (six of these wells owned by Tulkarem Municipality and use for drinking water and the others owned for ordinary people and used for agriculture and domestic use) and these wells shown in the following Table (2.5). Nitrate is high in the most of the municipality wells especially in wells number (1, 2, 3, 4 and 5) that is used only for drinking water and its above WHO standards [76].

Table (2.5): Name of owners of wells and concentration of nitrate in the years (1998-2009).

No	Name of the owners of wells	Concentration of (NO_3^-) (mg/L) in the years											
		98	99	00	01	02	03	04	05	06	07	08	09
1-	Ahmad Abu Shana & Partners	35	30	36	-	-	47	36	36	36	-	-	-
2-	Hasan Isa & Partners	-	-	-	-	30	33	31	31	31	-	-	-
3-	Abdallah Shraim & Partners	39	29	38	-	40	56	-	82	50	-	-	-
4-	Rasheed Hannun & Partners	48	40	27	-	46	46	49	58	-	-	-	-
5-	Muhammad Ahmad Abu Shams	61	62	-	-	66	94	57	75	-	-	-	-
6-	Khaled Saleem Hannun	36	29	-	35	-	44	42	54	-	-	-	-
7-	Iqab Fraij & Partners	52	42	49	-	52	56	56	59	51	-	-	-
8-	Ali Abu Salah	-	36	36	-	-	50	41	-	42	-	-	-

No	Name of the owners of wells	Concentration of (NO_3^-) (mg/L) in the years											
		98	99	00	01	02	03	04	05	06	07	08	09
9-	Abed Al Rahman Abu Saleh	-	40	43	-	45	-	-	-	49	-	-	-
10-	Hafedh Alhamdallah	61	69	-	-	-	69	57	63	53	-	-	-
11-	Rasheed Dhyab	40	28	-	-	-	46	-	-	-	-	-	-
12-	Abed Al Raheem Abu Baker	28	-	-	-	-	-	47	-	44	-	-	-
13-	Omar AlKarmi	30	33	-	-	-	39	45	-	44	-	-	-
14-	Tulkarem Municipality (no.1)	65	-	52	79	-	80	80	95	55	81	-	78
15-	Tulkarem Municipality (no.2)	82	76	57	81	-	73	60	95	55	78	-	76
16-	Mustafa Ahsaeed	19	19	-	-	-	21	23	27	-	-	-	-
17-	Abed Al-Qadir Quzmar	65	51	-	-	-	55	55	83	53	-	-	-
18-	Abed Al Raheem Merib	-	40	41	-	-	48	-	-	50	-	-	-
19-	Al Khaduri Agricultural School	32	35	33	-	-	-	-	-	-	-	-	-
20-	Sa'eed Jaber	-	30	-	42	-	37	33	38	38	-	-	-
21-	Shaker Samarah	46	38	42	-	-	49	51	51	51	-	-	-
22-	Tulkarem Municipality (no.3)	70	62	49	59	-	57	59	54	52	59	-	59
23-	Tulkarem Municipality (No.4)	-	-	42	45	49	54	58	55	60	57	-	62
24-	Tulkarem Municipality (no.5)	-	-	-	-	-	-	-	41	47	58	-	57
25-	Tulkarem Municipality (no.6)	-	-	-	-	-	-	-	-	43	52	-	44
26-	As'ad Taffal & Ahmad Khraishah	24	23	25	-	-	28	31	-	-	-	-	-
27-	R'afat Al Qubbaj	41	50	33	-	-	-	46	-	-	-	-	-
28-	Zubaydeh Al S'aeed	22	27	31	-	-	31	41	-	-	-	-	-
29-	Sadeeq Jamus	34	35	32	37	-	43	52	-	-	-	-	-
30-	Muhammad Omar Safareeni	23	21	24	26	-	23	28	-	-	-	-	-
31-	Rafeeq Hamdellah / Iktaba	38	46	55	-	-	53	52	-	-	-	-	-

(Source: Palestinian Water Authority).

2.26 Factors That Elevate Nitrate in Tulkarem City:

Fertilizers and manures, septic tanks are parts of contaminants that contaminate the groundwater, another source which is the main source of the contamination is Wadi Zaimer, dump site, Israeli factors and depth of wells.

2.26.1 Fertilizers and Manure:

Tulkarm City is located on agriculture lands, so that there is extensive use for chemical fertilizers and animals manure (without planning) to give nitrogen supply which is essential for plant growth, which is converted in the soil to nitrate and leachate to ground water and pollute it.

2.26.2 Septic Tanks:

Septic tanks are old way for storage wastewater that get out of houses and factories, so that if these septic tanks are not built well with concrete from inside the wastewater will leachate to groundwater and pollute it.

Parts of Tulkarm City is not connected to the public sewerage network and still using septic tanks for storage wastewater, there are about 217 septic tanks (92 is still in use which 192 are not) around wells numbers (1 & 2) only according to survey done by the department of health & department of water in Tulkarem Municipality. Sewerage network covers about (55 %-60 %) of Tulkarem, Shuweika, Irtah, Tulkarem Camp and Nur Shams Camp [77].

The sewerage system of Tulkarem City and Shuweika Village operates by Tulkarem Municipality, and the sewerage systems in Tulkarem Camp and Nur Shams Camp are operated by UNRWA.

The Tulkarem trunk system consists of several main trunks and one force main, which transport the wastewater to the existing ponds west of Tulkarem while the main trunk of Shuweika discharges the wastewater directly into the Wadi Zeimar.

2.26.3 Wadi Zaimer:

Wadi Zaimer extends from western part of Nablus city to Tulkarm City, its about 44 km long. The largest discharge of wastewater to Wadi Zaimer is comes from the western part of Nablus city at estimated rate of 7000 m^3/day, then along its path to Tulkarm area, the quantity increase according to the other discharge of wastewater from the nearby villages to reach 20000 m^3/day including industrial wastewater which is discharge directly into Wadi Zaimer [78].

2.26.4 Dump Site:

There are two dump sites in Tulkarem City, one in the eastern part of the city near Nur Shams Camp which is very close to Wadi Zaimer, used by Anabta Municipality, and other villages and the second one in the southern part of the city near Freon and Kaffa Villages, used by Tulkarem Municipality and other villages in the area and also of Israeli settlements. These dump site is close to Abu Darany, Eatar, Yousef Omar, and Hasanen wells that are used for drinking and agriculture, and as you know that there are many things that dumped in these dump sites such as animals manure, dead animals, food, fruit, vegetables and chemicals that contain nitrogen which is converted to toxic gases when its burned it pollutes the air ,and converted to nitrate and leachate to groundwater and pollute it.

2.26.5 Israeli Chemical Factories:

In the western part of the city there are about twelve Israeli chemical factories that extend from northern to southern part of the city and these factories are very dangerous on the public health. One of these factories is Gesshory Chemical Factory that manufacture many dangerous chemicals like fertilizers, pesticides, herbicides, paints and other dangerous chemicals.

2.26.6 Depth of The Wells:

Tulkarem city, Irtah, Shuweika, Tulkarem and Nur Shams Camps depend on Tulkarem Municipality wells for water drinking. Table (2.6) shows the depth of each well.

Table (2.6): Depth of Municipality wells.

	NAME OF THE WELL	DEPTH (M)
1-	Well no.(1) Al kaddeem	90
2-	Well no.(2) AlFaddlia	125
3-	Well no.(3) Shuweika	157
4-	Well no.(4) Al Mesnawi	125
5-	Well no.(5) Thenabah	186
6-	Well no.(6) Al Ezba	202

(Source: Water Department / Tulkarem Municipality).

Tulkarem City located on the western basin which is rich in groundwater, it gets its supply of water from the upper part of the aquifer that is illustrated from the depth of wells in the Table (2.6) so that the groundwater exposed to pollutants like nitrate that goes through soil to groundwater. The well's depth is not enough to prevent nitrate from leachate down, since it is found that as the well depth increase, the quality of water becomes better and less in nitrate.

CHAPTER THREE

Materials And Methods

3.1 Chemicals and Reagents:

3.1.1 Chemicals:

All chemicals used were of analytical grade.

- Sodium Nitrate [$NaNO_3$] granules.
- Ammonium Sulphate [$(NH_4)_2SO_4$] powder: MERCK.
- Potassium Dihydrogen Phosphate [KH_2PO_4] powder: Alfa Aesar.
- Concentrated acids (H_2SO_4, HNO_3, HCl).
- Concentrated NaOH.
- Ascorbic acid 90 % ($C_6H_8O_6$).
- Boric acid.
- K_2SO_4, $CuSO_4$, $AgNO_3$, NH_4SCN.

3.1.2 Reagents:

- Distilled water that is nitrate free.
- Recommended ISAB [KH_2PO_4]: Recommended ionic strength adjustment buffer [KH_2PO_4].
- Nitrate reagent of different concentrations (2000 mg/L, 78 mg/L, 1950 mg/L , 59 mg/L, 1475 mg/L, 57 mg/L, 1425 mg/L).

- Ammonium Sulphate $[(NH_4)_2SO_4]$ reagent of different concentrations (1 M, 2 M, 0.04 M) ,preparation of these reagent illustrated in appendix (1.1).

3.2 Instruments:

- Ion selective electrode meter (JENWAY) and nitrate electrode 924-300 S/N.
- Flask shaker (3F1) with max. speed 800 osc/min (Stuart).
- Analytical sieve (Cisa) BA 200N Cedacedia industry.
- Manual sieve, 2 mm .
- Oven (memmert).
- Analytical balance (Boeco/ Germany) max 210 g.
- Jenway 450 Conductimeter.
- Hanna Hi Microcomputer pH meter.
- Hermle Z 200 A, Centrifuge.
- Vulcan A 500, Furnace.
- Kjeldahl Instrument.
- Spectrophotometer.
- Analytical balance (Sartorius)) max 1200 g.
- Magnetic stirrer (Fisher scientific).
- Filter paper no. 4 MACHEREY-NAGEL , 125mm.

3.3 Column of Soil Apparatus:

To study the effect of nitrate in soil samples taken from the municipality wells (1, 3 and 5) as well as the water of these wells, a simple apparatus is designed as shown in Figure (3.1) & Figure (3.2).

The column of soil apparatus is consist of :

- PVC plastic column with 2 m long and 6 inch diameter (15.25cm) for the soil to be placed in.
- Sieve made of tin with 2 mm pores and 15.25cm diameter in order to allow nitrate to pass through these pores and to prevent soil from going out of column.
- Tin funnel (pocket) with to collect water that contain nitrate.
- Iron stand to hold the column that filled with soil and water.

This apparatus is illustrated in the Figure (3.1), Figure (3.2) bellow

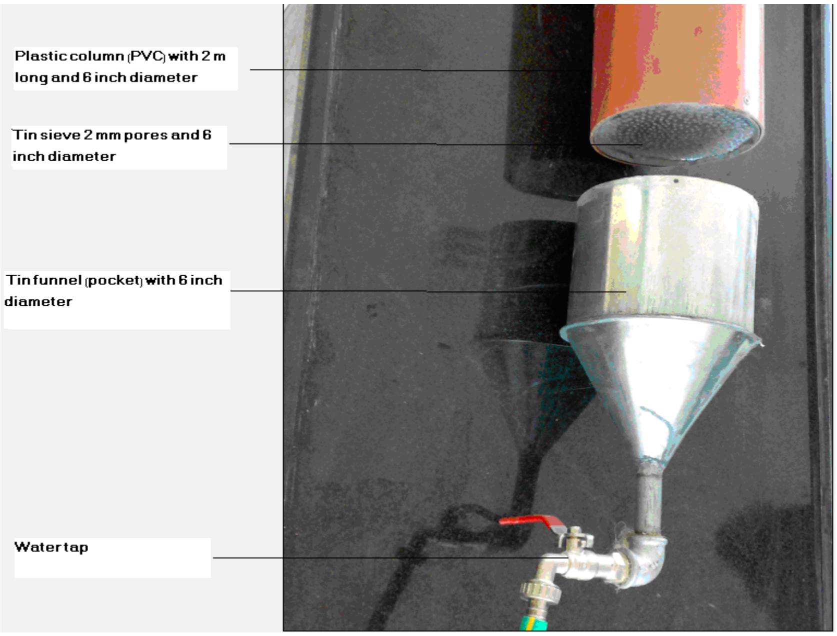


Figure (3.1): Parts of the apparatus (plastic column tiny sieve and (pocket, water tap).

Figure (3.2):Vertical column on, iron stand.

3.4 Sample Collection:

As noticed in Table (2.6) the concentration of nitrate in Tulkarem Municipality wells (1, 2, 3, 4 and 5) and other agriculture wells in the area exceeds WHO standards.

To study the elevation of nitrate in these wells, we must first study the concentration and movement of nitrate ions in the soil of these wells.

The study was done on the municipality wells :

- No.1 in the middle of Tulkarem City,
- No. 3 near Wadi Zaimer,
- No. 5 in Thenabah Village, east of Tulkarem.

Three soil samples were taken from nearby wells, 3 m distant from each well at depth of 15-20 cm.

3.5 Sample Preparation:

Soil samples that are taken from nearby wells no. (1, 3 and 5) are prepared for testing by the following :

- All of the samples are cleaned from stones, plastic and remaining parts of plants.
- The samples then sieved by manual sieve 10 mm .
- All the samples were homogenized separately by thorough mixing.
- All samples prepared were placed in their columns.

3.6 Idea of Research:

The goal of this research is to study the concentration and movement of nitrate in soil and water based on time-terms concentration which is considered as follows:

- Zero-term concentration means that distilled water (0 mg/L of NO_3^{-1}) added to three columns no. (1, 4 and 7) where these columns are considered as blank columns, remember that these columns are filled with soil collected from wells no.s (1, 3 and 5).
- Short-term concentration means that one year-term concentration, where the concentrations of nitrate ions in wells no.s (1, 3 and 5) are 78 mg/L, 59 mg/L, and 57 mg/L respectively. These three different concentration were added to other three columns no. (2, 5 and 8) in year 2009.

- Long–term concentration means that 25 years–term concentration, which is equal the concentrations of nitrate in each wells no. (1, 3 and 5) multiplied by 25, hence the following concentration of 1950 mg/L, 1475 mg/L, and 1425 mg/L were added to the other three columns no. (3, 6 and 9).Figure (3.3), and Figure (3.4) bellow illustrate the prepared 9 columns.

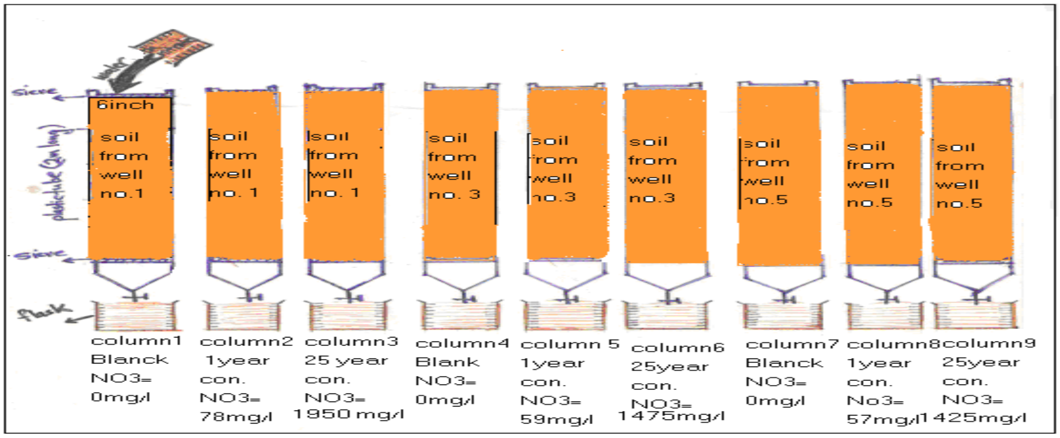


Figure (3.3): Schematic diagram of nine plastic vertical columns (PVC) filled with soil from Tulkarem municipality wells no. (1, 3 and 5) and time –term concentration.

Figure (3.4): Nine plastic vertical columns (PVC) standing on iron stands filled with soil from Tulkarem municipality wells no. (1, 3 and 5) and time –term concentration and ready for using.

3.7 Preparation The Soil Columns For Testing:

After the collection and preparation soil samples, the samples were placed in the columns in this way

- All the soil samples that put in the columns are compacted to prevent any cracks among the soil particles.
- Distilled water is added to all columns to wet the soil, to measure the concentration of nitrate ions in the soil, and to make the movements of solutions that will be added next easy and not absorbed by the soil particles.

3.8 Amount of Nitrate Solutions Added to Soil Columns:

250 mL of nine different concentration of nitrate solution (nitrate in distilled water) were prepared as follow column 1 (0.00 mg/L of nitrates, blank), column 2 (78 mg/L), column 3 (1950 mg/L), column 4 (0.00 mg/L of nitrates, blank), column 5 (59 mg/L), column 6 (1475mg/L), column 7 (0.00 mg/L of nitrates, blank), column 8 (57mg/L, column 9 (1425 mg/ L) and Appendix (1.2) illustrate the above data.

The above prepared solutions are placed once everyday for 44 days to the to the plastic columns that are filled with soil.

3.9 Measurements of Water Samples From Nitrate-Contaminated Columns:

Samples and standards were allowed to equilibrate to room temperature. After calibrating the ion selective electrode for the meter that is illustrated in appendix (1.3), the electrodes were completely rinsed with distilled water then excess water was shaken gently off and dried. Then 50.0 mL of the collected water containing nitrate and 1.00 mL of ISAB were added into a 100 ml beaker furnished with a magnetic stir bar. The beaker was placed on a magnetic stirrer plate and stirred at slow speed then the electrode tips immerse to just above the rotating stir bar. The meter reading (concentration) was recorded as soon as the reading is stable .When analyses have been completed, the electrodes were rinsed completely with distilled water and store dry after covering the electrodes with caps [79,80].

3.10 Testing Nitrate Content For Soil Samples From Nitrate Containing Columns:

By completing the addition of distilled and nitrate solutions with to all nine columns in 44 days, the excess water was eluted out of the columns completely. Now the nine columns are ready for testing according to the following procedure:

Each one of the nine column is cut using electrical disk into four-50 cm equal parts, hence there are 36. Each part was designated with specific number which is necessary to keep track of the columns part. All parts were emptied from there contents and dried. All samples were air dried by putting them on separated pieces of plastic on the floor and using ceiling fan for 3-4 days. This way dryness is done in 80 %, then complete drying was done in the oven for 1hr at 60 C°. Dryness in the oven was performed on small scales whenever needed the homogenized. The oven-dried, homogenized. The soil sample is grounded and sieved. 20 g of dried soil sample and 50 mL of extractant 0.04 M $(NH_4)_2SO_4$ were placed in a 125 mL Erlenmeyer flask. The contents were agitated a reciprocating shaker at

400 oscillations per minute. Filter The soil suspension sample was filtrated using gravity filtration. Then the filtrate sample was tested for nitrate by ion selective electrode [81].

3.11 Determination of Physical & Chemical Parameters For Soil Samples:

3.11.1 Determination of The Soil Texture (Hydrometer Test):

The soil sample was broken into particles by using a mortar and pestle . 1000 g of the sample weighted accurately. A stack of sieve made, by placing a sieve with larger opening above a sieve with a smaller opening The sieves that are used in a stack are numbers 4, 10, 20, 40, 60, 140 and 200. The sieve at the bottom should be number 200 and a pan should be placed under sieve number 200 to collect the soil that get out sieve number 200. Pour the 1000g soil sample prepared into the stack sieve from top, and put the cover on the top of the stack sieves. A sieve shaker was run for about 10 to 15 minutes. The amount of soil retained on each sieve and the pan was weighted, the amount of soil retained and pass can be calculated by the following

Percent of soil retained on nth sieve

$$\text{Soil retained on the sieve} = \frac{\text{weight retained}}{\text{total weight (w)}} \times 100 \qquad \text{(equation 3.1)}$$

Cumulative percent passing through the nth sieve

$$= \text{percent finer} = 100 - (\%\ \text{retained}) \qquad \text{(equation 3.2)}$$

Making graphs to determine soil types by plotting a graph of percent finer (passing) vs. sieve opening (diameters) as shown in the follow Figure (3.5).

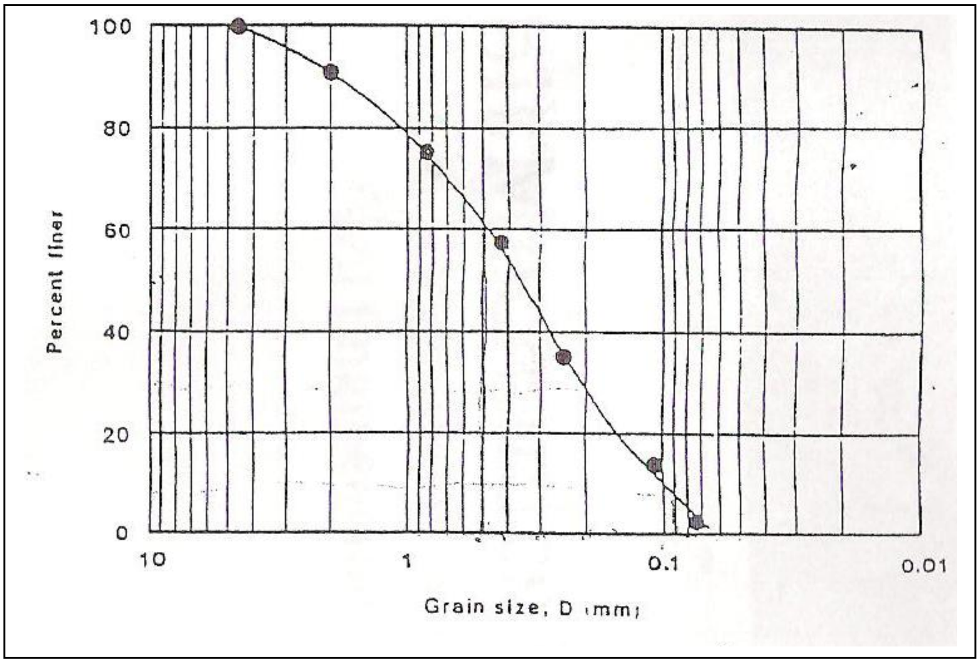


Figure (3.5): Plot of percent finer vs. grain size.

(Source: Soil Mechanics Laboratory Manual. Faculty of Engineering, Civil Engineering Department, Al-Najah National University, 2009).

If the passing soil through the sieve number 200 (0.075 mm) is 90 % the sample can be separated to clay and silt .If the passing soil through the sieve number 200 (0.075 mm) is 2 % clay and silt cant be separated and be mixed silt and clay mixture.

For determination the type (texture) of soil there is standards for these which is (American Association of State Highway and Transport Officials for the year 2010) AASHTO and these can be shown in the Table (3.1).

Table (3.1): Types (texture)of soil and there size according to AASHTO standards.

TYPE OF SOILS	SIZE (MM)
Gravel	≥ 4.75
Coarse sand	2 < Coarse Sand < 4.75
Medium sand	0.2 < Medium Sand < 2
Fine sand	2 < Fine Sand <0.2
Silt & Clay	< 0.075
Silt	0.002 < Silt < 0.075
Clay	< 0.002

For Determining gravel for example look at the value (4.75 mm) from the graph at grain size (mm) and intercept with the graph with percent finer so you can determine the percent of gravel in soil sample .

3.11.2 Determination of Moisture Content:

Empty moisture can was weighted (w_1), and certain amount of soil sample was put in the can and then weighted (w_2). The soil sample was dried in the oven at temperature between 105C°-110C° for 24 hours (w_3). The moisture content for the soil sample can be calculated by the following way

$$\text{Moisture content} = \frac{\text{Weight of water present in a given soil mass}}{\text{Weight of dry soil}} \times 100$$

$$\text{M.C (\%)} = \frac{\text{W2 - W3}}{\text{W3 - W1}} \times 100 \qquad \text{(equation 3.3)}$$

3.11.3 Determination of Specific Gravity:

Clean the volumetric flask and dry it. Carefully fill the flask with distilled water up to the 500 mL mark. Determine the weight of the flask and the water filled to the 500 mL mark (w_1). Insert the thermometer into the flask with water and determine the temperature of the water ($T= T_1C^o$).

Take approximately 100 gram of air dried soil in an evaporating dish. If the soil is cohesive, add distilled water to the soil and mix to form a smooth paste. Keep it soaked for about one–half to one hour in the evaporating dish. (This step is not necessary for granular, i.e., non-cohesive soil). Transfer the soil (if granular) or the soil paste (if cohesive) into the volumetric flask. Add distilled water to the volumetric flask containing the soil to make it about two–thirds full. Remove air from the soil–water mixture . This can be done by:

a- Gently boiling the flask with soil-water mixture for about 15 to 20 minute, accompany the boiling by continuous agitation.

b- Apply vacuum by a vacuum pump until all the entrapped air is out.

Bring the temperature of the soil–water mixture in the volumetric flask up to room temperature. Add distilled water to the volumetric flask until the bottom of the meniscus touches the 500 mL mark. Determine the weight of the bottle plus soil plus water (w_2). Check the temperature of the soil and water in the flask to see if it is $T_1C^o \pm 1$ or not. Pour the soil and the water into an evaporating dish. Using a plastic squeezing bottle, wash the inside of the flask and make sure that no soil is left inside. Determine the weight of the dry soil in the evaporating dish (w_3).

by the following equation . The specific gravity can be calculated for the soil samples.

$$\text{Specific Gravity (Gs)} = \frac{\text{Weight of soil}}{\text{Weight of equal volume of water}}$$

Weight of soil = w_3

Weight of equal volume of water = $(w_1 + w_3) - w_2$

So

$$\text{Specific Gravity (Gs)} = \frac{W_3}{(W_1 + W_3)\, W_2} \qquad \text{(equation 3.4)}$$

Specific gravity is generally reported on the unit weight of water at T = 20 C°.

$$\text{Gs (at 20 C}^{o}\text{)} = \text{Gs (at } T_1\text{C)} \times A \qquad \text{(equation 3.5)}$$

The value of A are given in the Table (3.2)

Table (3.2): The value of A at different temperature [82].

TEMPERATURE (C)	A
16	1.007
18	1.004
19	1.002
20	1.000
22	0.9996
24	0.9991
26	0.9986
28	0.9980

3.11.4 Determination of pH, Electrical conductivity (EC) & Total Dissolved Solids (TDS):

Weight 10 g of three soil sample into 150 ml beakers and dissolve in 100 ml distilled water. Calibration pH meter by using buffers (4, 7) and then determine the pH for the three samples. Calibration the conductivity meter by using distilled water, then measure the conductivity (EC), total dissolved solid (TDS) in the same apparatus for the three samples.

3.11.5 Determination Salinity as (Sodium Chloride):

Weight about 5 g of three soil samples into three 250 mL Erlenmeyer flask. Add 100 mL distilled water into each one of the flasks, the agitate on hot plate using magnetic stirrer for 30 min. The samples cooled to room temperature then filtered by suction filtration. 25 mL 0.1N $AgNO_3$ and 5 mL conc. HNO_3 (1 : 3) were added to each flask and then 5 mL of ammoniumesien (Ш)-sulfate–12–hydrate indicator was added to the flasks, Then titration was made with 0.1 N NH_4SCN solution until a permanent light brown is reached. Calculation for salinity determination was done as follows:

mmol of $AgNO_3$ = Molarity (M) ×volume of $AgNO_3$ added

mmol of NH_4SCN = Molarity (M) ×volume of NH_4SCN added by titration

Differences = mmol of $AgNO_3$ - mmol of NH_4SCN

mg NaCl = differences × molecular weight (NaCl) ×1000

$$\%\,(\text{NaCl}) = \frac{\text{mg (NaCl)}}{\text{mg(weigh sample)}} \qquad \text{(equation 3.6)}$$

3.11.6 Determination of Phosphorous

Place 1.0 g each of the three soil samples in crucible, then burn in the furnance for 24 hours. After cooling to room temperature, transfer the samples to three 150 mL beakers. Add 5 mL conc. H_2SO_4 and 100 mL distilled water to each beaker and then boil for 30 minute. Cool the beakers to room temperature and adjust the pH to 5. Transfer the content of each beakers to 250 mL volumetric flask and add enough distilled water to reach the 250 mL mark. Take 0.132 g of ascorbic acid and dissolved in 25 mL phosphorus reagent. Using four 25 mL volumetric flasks, then add to each flask 4 mL of (ascorbic acid and phosphor reagent, add to each flask about 2 mL of distilled water and shake then add to the first three flask gradually miles of samples and wait about 15 minute to develop the blue color (1 mL, 5 mL, 5 mL), add distilled water to each flask to the mark. When the color in the flasks become light blue, then the concentration of the phosphor in each flask is determined by using spectrophotometer after making calibration. Calculation for estimating the concentration of phosphorous is made by the following equation [83, 84].

$$\mathrm{P}\,(\%) = \frac{\mathrm{conc.}(1)\times 250\times 25\times 100}{1000\times(\mathrm{mL\ added\ to\ flask})\times \mathrm{wt.\ of\ sample\,(mg)}} \qquad \text{(equation3.7)}$$

3.11.7 Determination of Total Organic Carbon (TOC):

Walkley Black titration method is used for determination total organic carbon (TOC) in the three soil samples. Place three-0.5 g of oven dried and sieved soil three 250 mL conical flask. Add 5 mL of 1N $K_2Cr_2O_7$ into each flask and swirled, then add 10 mL of conc. H_2SO_4 into the suspension and swirled gently until the soil was mixed. Swirled the mixture vigorously for about one minute. Let the three flasks cool to room temperature then add 100 mL of distilled water to each flask and then filter the suspension. Add 0.3 mL of (0.025 M) orthophenanthroline-ferrous indicator to each flask then titrate with 0.5 N $FeSO_4$. When the endpoint was approached the solution changed sharply from greenish-blue to red-brown. The amount of $FeSO_4$ used in the titration was recorded. The total organic carbon then calculated as following equations.

$$\text{Normality (N) FeSO}_4 = \frac{\text{mL K}_2\text{Cr}_2\text{O}_7 \times \text{N K}_2\text{Cr}_2\text{O}_7}{\text{mL FeSO}_4} \qquad \text{(equation 3.8)}$$

$$\text{meq FeSO}_4 = \text{mL FeSO}_4 \times \text{N FeSO}_4 \qquad \text{(equation 3.9)}$$

$$\text{TOC (\%)} = \frac{\text{meqK}_2\text{K2Cr}_2\text{O}_7 \text{ - meq FeSO}_4}{\text{weight of dry soil}} \qquad \text{(equation 3.10)}$$

$$\text{Organic Matter (\%)} = 1.72 \times \text{organic carbon \%} \qquad \text{(equation 3.11)}$$

3.11.8 Determination of nitrogen:

Kjeldahl method is used for determination nitrogen percent in the soil samples. Weight three soil samples of 1.0 g and placed them in digestion tube. A mixture of 0.8 g $CuSO_4.H_2O$, 7.0 g of K_2SO_4 catalysts and 15 mL of conc. H_2SO_4 were added to three digestion tubes, then swirl the three tubes until the acid was mixed with the samples. When all tubes are ready lower exhausted manifold on the top of the three tubes. Turn on the vacuum source to full with water. The water flow has been calibrated at 18 liter/minute. Put the rack on the three tubes in the block and heat to 420 C^o for 5 hours then leave the samples on to digest until the color turns clear, and then the mixture allowed to cool. Add 20 mL of deionized water slowly with shaking to each tube and swirl to bring any insoluble material into suspension, after that the tubes were transferred to the (Kjeldahl) distillation apparatus. The tubes were rinsed three time with water to complete the transfer. In 250 mL conical flask 50 mL of boric acid was added, and the flask was placed under the condenser of the distillation in a away that the end of the condenser in the apparatus was dipped into the solution. 20 mL of NaOH was added to the funnel of the apparatus into the digested tube, and the alkali was run slowly into the distillation chamber and about 100 mL of the condensate was distilled and the color changed from green to blue. The condenser of the apparatus was rinsed and few drops of phenolphthalein indicator was added to the distillate and titrated with 0.0869 M HCl acid to the violet end point. The nitrogen percent for the three samples were calculated using the following equation:

$$\mathrm{N}\,(\%) = \frac{\mathrm{V(mL\ of\ HCl)} \times \mathrm{M\ (HCl)} \times \mathrm{M_N} \times 100}{\mathrm{Wt.\ of\ sample} \times 1000} \qquad \text{(equation 3.12)}$$

Where

Wt.: is the mass of test sample.

M: molarity of HCl.

M_N: is the molar mass of N which equal 14.007 g/mole.

V: is the volume(mL) of the HCl used in titration of sample [63].

3.12 Optimum Time For Nitrate Ions (NO_3^{-1}) Adsorption Onto Soil:

For determination the optimum time for the of adsorption of nitrate (NO_3^{-1}) onto soil. Three different soil samples were collected from the municipality wells numbers (1, 3 and 5) and used in these test. Twenty four samples were prepared and these divided to the three parts according to the three types of soil that is collected from each well. 5 grams of oven dried sieved soil were prepared, and put in eight 125 mL Erlenmeyer flasks. An aqueous nitrate solution (50 mL of the water that contains 100 mg/L of nitrate) were added to each flask, in the same way another twenty four samples were prepared and 50 mL distilled water added to each flask. All samples were covered with Teflon screw caps and mounted on wrist action shaker model 75, Burrell at room temperature for shaking. All samples were kept on the shaker for 1, 2, 3, 4, 6, 12, 24 and 36 hours.

After shaking, the soil particles for all the samples were allowed to settle then each sample centrifuged using Hermel Z 200 A centrifuge for 3000 rpm for 10 minutes. After centrifuging, the concentration of nitrate for each sample was determined by using Jenway ion selective meter by taking 50 ml of each sample.

The actual conc. of (NO_3^{-1}) = conc.of the (NO_3^{-1}) in the water after addition 100 mg/L after certain period of time-conc.of the (NO_3^{-1}) in the distilled water that get from the soil after the same period of time.

3.13 Isotherms:

Freundlich equation and its parameters will be used in this study to describe the adsorption of nitrate ions onto soil because of its simplicity and versatility in fitting data.

Five different concentrations 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L & 500 mg/L of nitrate solutions were prepared .

Fifteen samples were prepared and these divided to the three parts according to the three types of soil that is collected from each well and each part contains five soil samples. 5 grams of oven dried and sieved soil were prepared and put in 125 mL Erlenmeyer flask, and 50 mL of different concentrations of prepared nitrate were added to each flask, in the same way another fifteen samples were prepared and 50 mL distilled water added to each flask, all samples were covered with Teflon screw caps and mounted on wrist action shaker model 75, Burrell at room temperature for 24 hours for shaking .

After shaking the soil was let to settle and centrifuged at 3000 rpm for 10 minute. After centrifuging, the concentration of nitrate for each sample was determined by using Jenway ion selective meter by taking 50 mL of each sample. The calculation done as before [59].

CHAPTER FOUR

Results And Discussion

4.1 Soil Texture & Hydrometer Test:

After drying the soil samples collected from Tulkarem Municipality wells no.s (1, 3 and 5), the samples then sieved and hydrometer test was performed in order to evaluate the soil texture for each soil sample. Table (4.1) shown below presents data of soil texture for each sample.

Table (4.1):Soil texture of the soil samples.

SOIL TEXTURE	SOIL OF WELL NO.1	SOIL OF WELL NO.3	SOIL OF WELL NO.5
Gravel fraction (%) ≥ 4.75 mm	4.03	10.09	24.23
Coarse sand (%) 4.75 mm – 2 mm	33.14	45.36	39.58
Medium sand (%) 2 mm – 0.20 mm	55.83	38.55	33.69
Fine sand (%) 0.20 mm – 0.075mm	2.48	4.69	1.79
Silt + Clay (%) < 0.075 mm	4.52	1.31	0.71

As shown in Table (4,1) above the main soil texture for, well no. (1) is sand (coarse + medium + fine) which mount to 91.45 %, well no. (3) is sand (coarse + medium + fine) which mount to 88.6 %, well no. (5) is sand (coarse + medium + fine) which mount to 75.06 %.

The highest percentage of sand is in well no. (1) located in the western part of Tulkarem, it is the nearest among all studied wells close to the coast of Meditation Sea, and it's about is 11 km far. The least percentage of sand is in well no. (5) located in the eastern part of Tulkarem in Thenabah, it is far from well no. (1) about 3-4 km and located on hill, the other components of soil is little like silt, clay and gravel.

Figures (4.1), (4.2) and (4.3) show graphs obtained from hydrometer tests for the three soil samples of percentage of passing soil through the sieve.

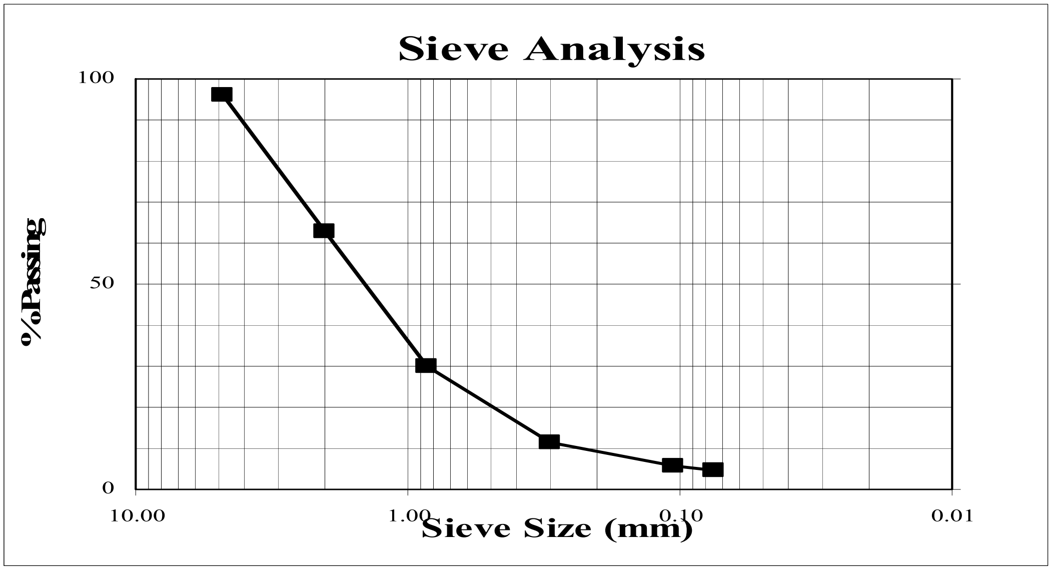


Figure (4.1): Particle size distribution curve (hydrometer test) for soil sample from well no. (1) as 4.03 % gravel, 91.45 % sand (coarse , medium, fine), 4.52 % silt and clay.

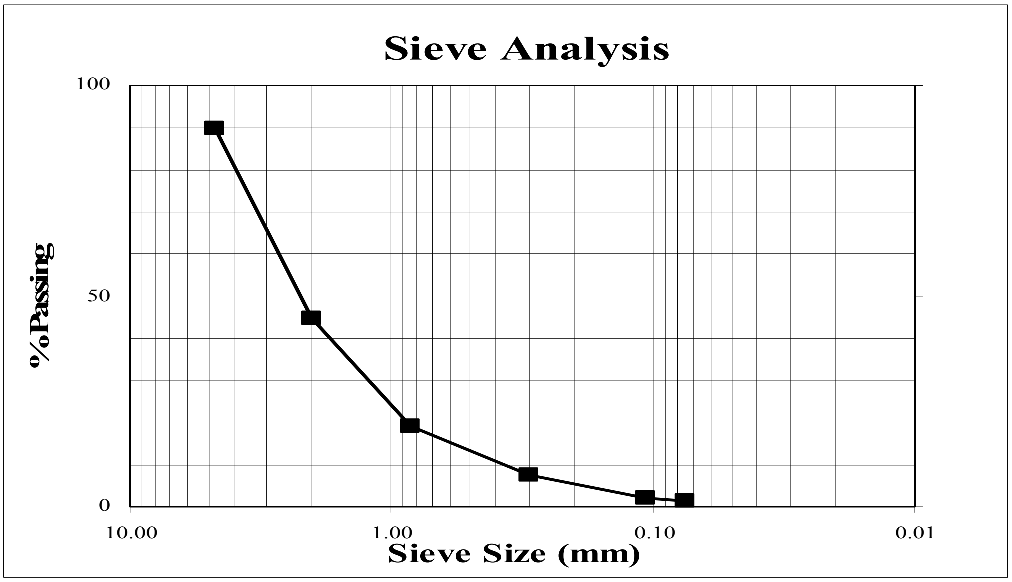


Figure (4.2): Particle size distribution curve (hydrometer test) for soil sample from well no. (3) as 10.09 % gravel, 88.6 % sand (coarse, medium, fine) and 1.31 % silt and clay.

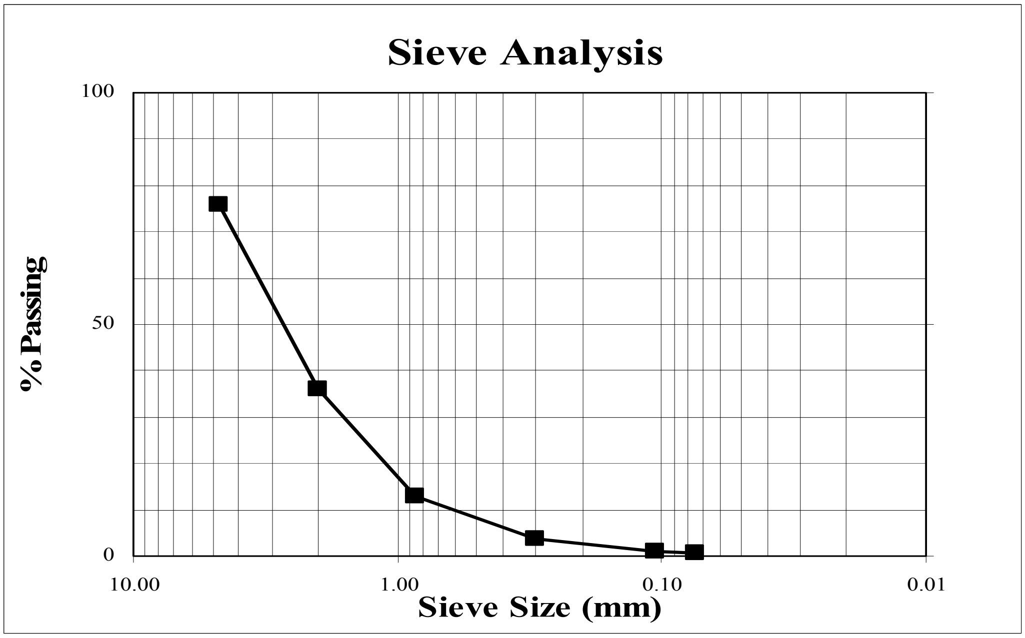


Figure (4.3): Particle size distribution curve (hydrometer test) for soil sample from well no. (5) as 24.23 % gravel, 75.06 % sand (coarse, medium, fine) and 0.71 % silt and clay.

4.2 Chemical & Physical Parameters For Soil Samples:

Each soil sample was analyzed in order to evaluate pH, total dissolved solids, electrical conductivity, salinity, organic carbon, organic matter, phosphorous, nitrogen. All of parameters are shown in Table (4.2).

Table (4.2): pH, total dissolved solids, electrical conductivity, salinity, organic carbon, organic matter, phosphorous, nitrogen.

TEST	**SOIL OF WELL NO.1**	**SOIL OF WELL NO.3**	**SOIL OF WELL NO.5**
pH	9.43	9.77	9.66
Total dissolve solids(TDS) (mg/L)	55.20	92.80	61.90
Conductivity (EC) (µs/cm)	81.30	192.30	101.40
Salinity (%)	**0.130**	**0.103**	**0.023**
Moisture content (%)	5.1	8.3	18.2
Specific gravity (%)	2.23	2.38	2.30
Organic carbon (%)	2.44	2.16	2.47
Organic matter(%)	4.20	3.71	4.25
Nitrogen (%)	0.33	0.21	0.32
Phosphorous (%)	0.129	0.004	0.015

The concentration of nitrate ions in each of the nine columns studied is shown in the Table (4.3) below. These concentration are determined for the nine columns when only distilled water was added to all columns

Table (4.3): The concentration of nitrate ions in each column leached.

WELL NUMBER	TIME-TERM CONC.	COLUMN NO.	CONCENTRATION OF (NO_3^{-1}) (MG/L)
Well number 1	**Blank**	**Column 1**	**270**
	1 year	**Column 2**	**240**
	25 year	**Column 3**	**280**
Well number 3	**Blank**	**Column 4**	**210**
	1 year	**Column 5**	**190**
	25 year	**Column 6**	**250**
Well number 5	**Blank**	**Column 7**	**840**
	1 year	**Column 8**	**780**
	25 year	**Column 9**	**777**

The average concentration of nitrate ions in the soil, in the first three columns that is collected from near well no.1 is equal 263.3 mg/L, while the average concentration of nitrate ions in the soil in the second three columns that is collected from near well no. 3 is equal 216.7 mg/L, and finally the average concentration of nitrate ions in the soil, in the first three columns that is collected from near well no.1 is equal 799 mg/L.

4.3 The Effect of Organic Matter:

The function of organic matter can be classified into three groups: physical, chemical and biological.

- Physical functions:

It influences water-retention and holding capacity of the soil properties, alters soil thermal properties, and improves structural stability of soil .

- Chemical functions:

Reduces concentrations of toxic cations, contributes in the buffering changes in pH-complexes cations, promotes the binding of soluble organic matter to soil minerals, and contributes to the cation exchange capacity.

- Biological functions:

It is a reservoir of nutrients like nitrogen, phosphorus, sulfur, and carbon, provides sources of energy for essential biological processes, and contributes to flexibility of soil/plant system [85].

The texture of the soil is important because it determines the amount of the nitrate ions that is hold in the soil. In general it is the non living materials that include clay, silt, sand, and organic matter. The soil that contain clay, silt, and sand in equal amounts is called a loam soil.

One of the most important soil components is clay, the clay particles are very small and the spaces among the particles is also small and have negatively charged surfaces, and for this reasons clay has a major effect on the leaching of nitrate. Nitrate has a negative charge and it is not attracted to the clay surface, so it stays in the water between the soil particles and this water is called the soil solution. Also clay can attract positive ions such as potassium and ammonium and others to its surface.

The organic residue of plants and animals degraded and converted to the humic compounds that have positively charged ions, when the organic matter is high this will give the soil an overall positive charge that can bind nitrate and reduce or prevent it from leaching to the groundwater [86].

From the Table (4.2) we can see the organic matter content in the soil ranges from 3.71 % to 4.25 %, and this percentage of the organic matter considered to be high compared to the normal percentage which equal 5 %, so the soil texture in the study area is sandy to sandy loam, and the particles size is big and the spaces among this particles is large and the surface area is small. This higher amount of organic matter presents on the soil particles and between them to block this spaces. As a result the organic matter gives the soil an overall positive charge that can bind nitrate ions that have negative charge, so it reduces or prevents the nitrate ions from leaching to the groundwater. Organic matter acts as a reservoir to hold the water that contain nitrate for period of time, but also there is leaching of nitrate to the groundwater because the organic matter doesn't blocked all the spaces among the soil particles.

4.4 Measurement of The Nitrate Concentrations Leached From The Soil Vertical Columns:

In order to study the effect of different soils, collected from different locations near the municipality wells no. (1, 3 and 5) in Tulkarem City, on nitrate leaching from the nine vertical (PVC) that filled with soils, distilled water and different concentrations of nitrate that were added to the columns for 44 days.

The concentrations of nitrate that get out (leached) of soil columns are shown in the table (4.4) below

Table (4.4): Different concentrations of nitrate that leached from nine columns that filled with different soils after the addition distilled water and varies concentrations of nitrate.

	Well no. 1			Well no. 3			Well no. 5		
Date	Column 1 Blank	Column 2 1year (78 mg/L)	Column 3 25year (1950 mg/L)	Column 4 Blank	Column 5 1year (59 mg/L)	Column 6 25year (1475 mg/L)	Column7 Blank	Column 8 1year (57 mg/L)	Column 9 25year (1425 mg/L)
(1)12/9	115	253	364	194	253	500	807	867	1162
(2)13/9	107	248	344	185	239	492	783	842	1134
(3)14/9	95	240	333	177	230	470	774	830	1111
4)15/9(	87	215	327	163	214	460	760	813	1097
(5)16/9	82	201	307	166	216	444	730	779	1038
(6)17/9	77	188	307	157	205	420	717	764	989
(7)18/9	75	174	304	147	196	382	703	752	973
8)19/9(	74	168	290	143	189	350	684	732	913
(9)20/9	72	160	280	141	188	314	633	679	898
(10)21/9	68	147	268	135	180	280	611	655	834
(11)22/9	69	140	260	134	177	272	611	657	815
(12)23/9	69	137	255	136	179	289	573	616	777
(13)24/9	66	123	243	132	171	291	586	631	780
(14)25/9	64	121	230	126	167	280	565	607	774
(15)26/9	63	117	224	122	161	274	535	576	739
(16)27/9	62	113	210	125	160	265	522	561	722
(17)28/9	63	109	200	121	153	260	526	563	739
(18)29/9	61	104	193	113	147	250	492	532	696
(19)30/9	60	111	194	111	142	243	475	515	693
(20)1/10	58	106	189	106	138	280	467	506	680
(21)2/10	57	103	188	105	138	280	440	480	644
(22)3/10	56	104	186	106	140	280	450	491	709
(23)4/10	55	104	186	107	140	314	445	487	707
(24)5/10	55	104	190	101	133	340	431	475	695

	Well no. 1			Well no. 3			Well no. 5		
Date	Column 1 Blank	Column 2 1year (78 mg/L)	Column 3 25year (1950 mg/L)	Column 4 Blank	Column 5 1year (59 mg/L)	Column 6 25year (1475 mg/L)	Column7 Blank	Column 8 1year (57 mg/L)	Column 9 25year (1425 mg/L)
(25)6/10	55	106	196	108	142	382	385	429	654
26)7/10(	56	104	191	105	141	400	374	423	642
(27)8/10	55.5	108	187	105	143	425	387	440	657
(28)9/10	56.8	108	195	99	136	467	395	449	718
(29)10/10	56.8	113	198	100	140	535	386	442	728
11/10)(30	56.8	111	204	105	149	577	392	452	767
(31)12/10	56.8	118	220	107	156	620	400	461	813
13/10)(32	58.8	121	224	110	162	654	374	441	839
14/10)(33	59.4	123	227	112	165	713	380	451	831
(34)15/10	60.8	130	243	112	167	832	396	470	880
(35)16/10	64	127	254	112	168	760	410	488	930
(36)17/10	63.4	135	257	112	172	942	386	469	926
(37)18/10	67	144	271	113	175	998	416	503	1016
(38)19/10	68	149	285	110	175	1096	429	517	1119
20/10)(39	70	154	289	112	182	1200	433	526	1133
(40)21/10	69	162	294	114	182	1325	429	526	1239
(41)22/10	72	168	307	118	192	1460	446	544	1316
(42)23/10	73	180	325	124	201	1480	509	609	1511
(43)24/10	75	200	345	129	209	1490	547	645	1597
(44)25/10	80	212	356	130	214	1613	594	705	1686

To calculate the concentration of nitrate leached from the nine soil columns after the addition of different concentrations (distilled water, short and long term concentrations) of nitrate for 44 days. The concentration of nitrate leached from columns for short & long term concentrations is equal to that of short or long term concentration subtracted from the concentration of nitrate for blank column, the results are illustrated in Table (4.5) & Figure (4.4) to (4.6).

Table (4.5): Different concentration of the nitrate ions leached from the nine columns after subtracting short and long term concentrations from blank columns

	Well no. 1			Well no. 3			Well no. 5		
Date	Column 1 Blank	Column 2 1year (78 mg/L)	Column 3 25year (1950 mg/L)	Column 4 Blank	Column 5 1year (59 mg/L)	Column6 25year (1475 mg/L)	Column7 Blank	Column 8 1year (57 mg/L)	Column 9 25year (1425 mg/L)
(1)12/9	115	138	249	194	59	306	807	60	365
(2)13/9	107	141	237	185	54	307	783	59	351
(3)14/9	95	145	238	177	53	293	774	56	337
4)15/9(	87	128	240	163	51	297	760	53	337
(5)16/9	82	119	225	166	50	278	730	49	308
(6)17/9	77	111	230	157	48	263	717	47	272
(7)18/9	75	99	229	147	49	235	703	49	270
8)19/9(	74	94	216	143	46	207	684	48	229
(9)20/9	72	88	208	141	47	173	633	46	265
(10)21/9	68	79	200	135	45	145	611	44	223
(11)22/9	69	71	191	134	43	138	611	46	204
(12)23/9	69	68	186	136	43	153	573	43	204
(13)24/9	66	57	177	132	39	159	586	45	194
(14)25/9	64	57	166	126	41	154	565	42	209
(15)26/9	63	54	161	122	39	152	535	41	204
(16)27/9	62	51	148	125	35	140	522	39	200
(17)28/9	63	46	137	121	32	139	526	37	213
(18)29/9	61	43	132	113	34	137	492	40	204
(19)30/9	60	50	134	111	31	132	475	40	218
(20)1/10	58	48	131	106	32	174	467	39	213
(21)2/10	57	46	131	105	33	175	440	40	204
(22)3/10	56	48	130	106	34	174	450	41	259
(23)4/10	55	49	131	107	33	207	445	42	262
(24)5/10	55	49	135	101	32	239	431	44	264
(25)6/10	55	50	141	108	34	274	385	44	269
26)7/10(	56	48	135	105	36	295	374	49	268

	Well no. 1			Well no. 3			Well no. 5		
Date	**Column 1 Blank**	**Column 2 1year (78 mg/L)**	**Column 3 25year (1950 mg/L)**	**Column 4 Blank**	**Column 5 1year (59 mg/L)**	**Column6 25year (1475 mg/L)**	**Column7 Blank**	**Column 8 1year (57 mg/L)**	**Column 9 25year (1425 mg/L)**
(27)8/10	55.5	52.5	131	105	38	320	387	53	270
(28)9/10	56.8	51.2	138	99	37	368	395	54	290
(29)10/10	56.8	56.2	141	100	40	435	386	56	295
11/10)(30	56.8	54.2	147	105	44	472	392	60	300
(31)12/10	56.8	61.2	163	107	49	513	400	61	310
13/10)(32	58.8	62.2	165	110	52	544	374	67	340
14/10)(33	59.4	63.6	168	112	53	601	380	71	380
(34)15/10	60.8	69.2	182	112	55	720	396	74	450
(35)16/10	64	63	190	112	56	748	410	78	480
(36)17/10	63.4	71.6	194	112	60	830	386	83	540
(37)18/10	67	77	204	113	62	885	416	87	600
(38)19/10	68	81	217	110	65	986	429	88	690
20/10)(39	70	84	219	112	70	1088	433	93	700
(40)21/10	69	93	225	114	68	1211	429	97	810
(41)22/10	72	96	235	118	74	1342	446	98	870
(42)23/10	73	107	252	124	77	1356	509	100	1002
(43)24/10	75	125	270	129	80	1361	547	104	1050
(44)25/10	80	132	276	130	84	1483	594	111	1092

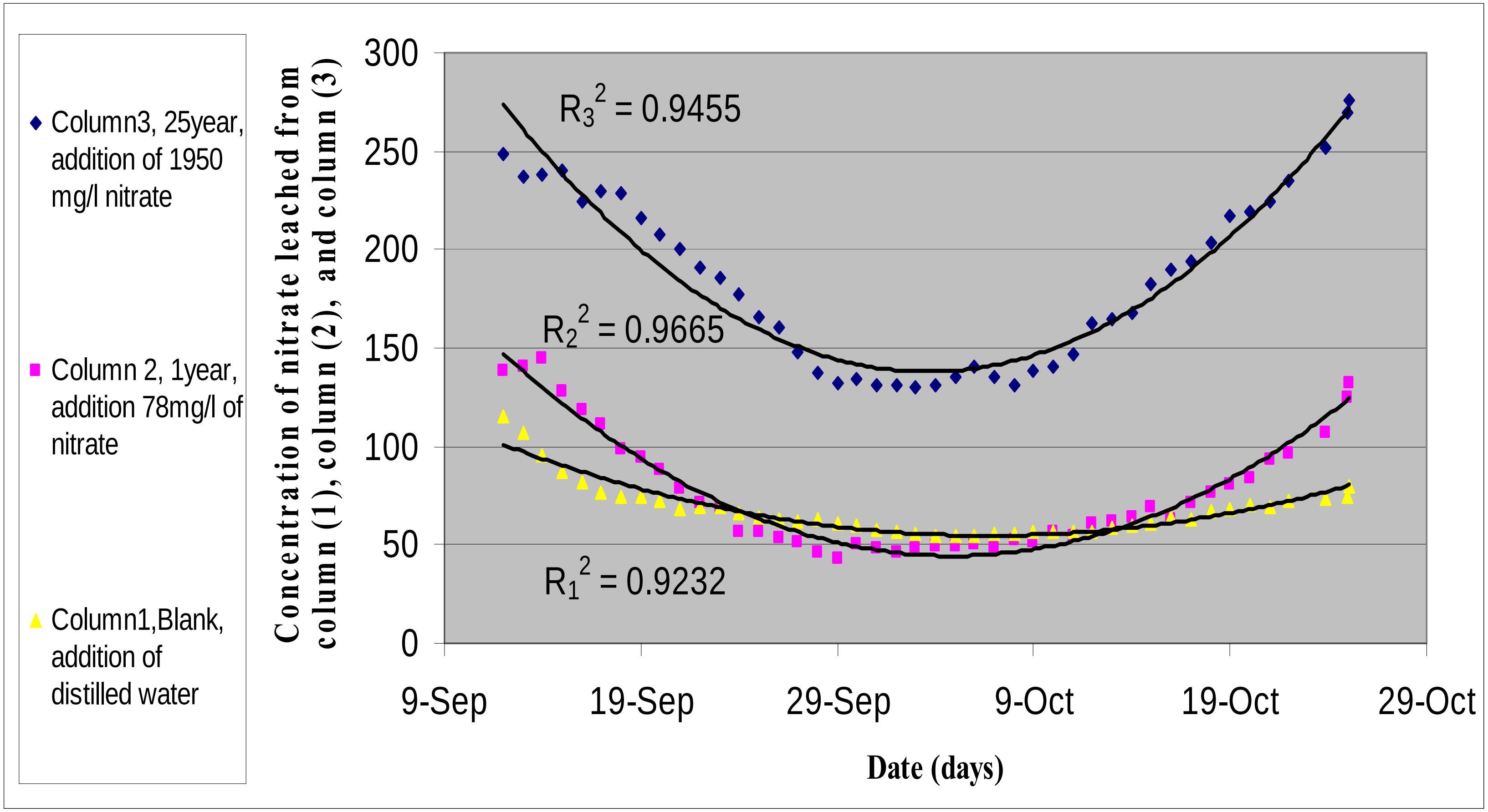


Figure (4.4): Concentration of nitrate leached from column (1), column (2), and column (3) vs. date (44 days).

Figure (4.4) represents the concentration of the nitrate ions leached from the column 1 (0.0 mg/L, blank), column 2 (78 mg/L, 1year), and column 3 (1950 mg/L, 25 years) for well no. 1. For the column 1 (0.0 mg/L, blank), it was noticed that after the addition of distilled water for 44 days, the concentration of nitrate ions decrease to nearly one-half in the first period (25 days) and then the concentration increase in the second period (19 days). These differences in the concentrations are due to the high concentration of nitrate content in the soil samples, so the adsorption of nitrate in the beginning in the first 25 days to the soil particles is higher than desorption and then by the effect of distilled water flush and earth gravity the desorption increase and adsorption decrease in the second period in the 19 days.

For the column 2, that represents short term concentration for one year, the addition of water-containing nitrates in concentration 78 mg/L to the soil of these column for 44 days. The main soil texture for the sample is sand and the spaces between the sand particles is large and enough to enter nitrate ions between the soil particles and the surface area is small. Besides the presence of high concentration of both nitrate ions and organic matter in the soil content, for these reasons the adsorption in the beginning (29 days) is higher than desorption, then desorption increase and adsorption decrease in the second period (16 days), these is because the soil is unable to hold excess nitrate between the soil particles and by the effect of water flux and earth gravity the nitrate ions moves downward.

For the column 3, that represents long term concentration for 25 year, the addition of water-containing nitrates in concentration 1950 mg/L to the soil of these column for 44 days. The main soil texture for the sample is sand and the spaces between the sand particles is large and enough to enter nitrate ions between the soil particles and the surface area is small. Besides the presence of high concentration of both nitrate ions and organic matter in the soil content, for these reasons the adsorption in the beginning (22 days) is higher than desorption, then desorption increase and adsorption decrease in the second period (22 days), these is because the soil is unable to hold excess nitrate in large amount between the soil particles and by the effect of water flux and earth gravity the nitrate ions moves downward.

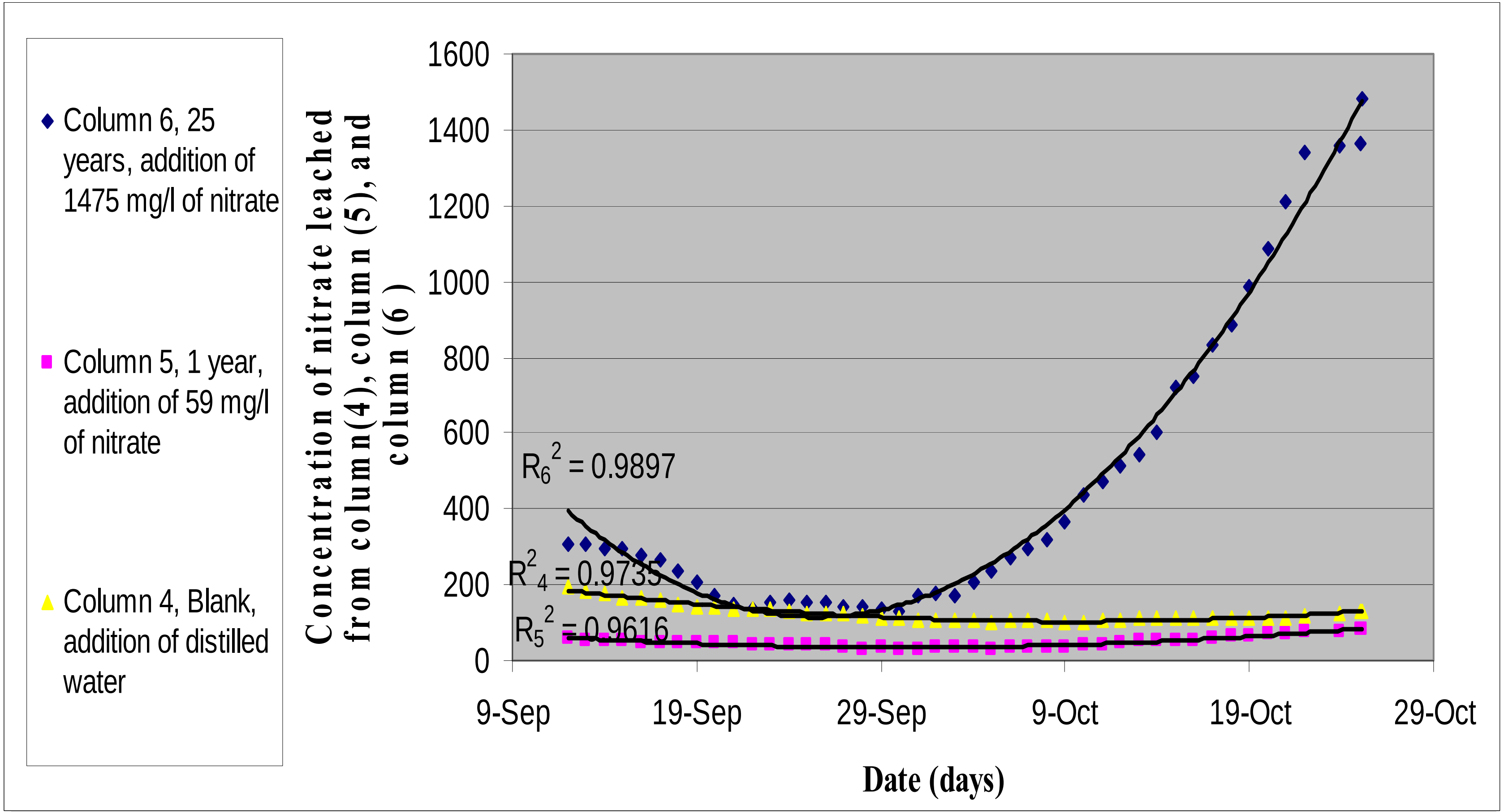


Figure (4.5): Concentration of nitrate leached from column (4), column (5), and column (6) vs. date (44 days).

Figure (4.5) represents the concentration of the nitrate ions leached from the column 4 (0.0 mg/L, blank), column 5 (59 mg/L, 1year), and column 3 (1475 mg/L, 25 years) for well no. 3. For the column 4 (0.0 mg/L, blank), it was noticed that after the addition of distilled water for 44 days, the concentration of nitrate ions decrease in the first period (28 days) and then the concentration increase in the second period (16 days). These differences in the concentrations are due to the high concentration of nitrate content in the soil samples, so the adsorption of nitrate in the beginning in the first 28 days to the soil particles is higher than desorption these is because the sand content for the soil is less which is about 89 % and also by the effect of distilled water flush and earth gravity the desorption increase and adsorption decrease in the second period in the 16 days.

For the column 5, that represents short term concentration for one year, the addition of water-containing nitrates in concentration 59 mg/L to the soil of these column for 44 days. The main soil texture for the sample is sand and the spaces between the sand particles is large and enough to enter nitrate ions between the soil particles and the surface area is small. Besides the presence of high concentration of both nitrate ions and organic matter in the soil content, for these reasons the adsorption in the beginning (28 days) is higher than desorption, then desorption increase and adsorption decrease in the second period (16 days), these is because the soil is unable to hold excess nitrate between the soil particles and by the effect of water flux and earth gravity the nitrate ions moves downward.

For the column 6, that represents long term concentration for 25 year, the addition of water-containing nitrates in concentration 1475 mg/L to the soil of these column for 44 days. The main soil texture for the sample is sand and the spaces between the sand particles is large and enough to enter nitrate ions between the soil particles and the surface area is small. Besides the presence of high concentration of both nitrate ions and organic matter in the soil content, for these reasons the adsorption in the beginning (19 days) is higher than desorption, then desorption increase and adsorption decrease in the second period (25 days), these is because the soil is unable to hold excess nitrate in large amount between the soil particles and by the effect of water flux and earth gravity the nitrate ions moves downward.

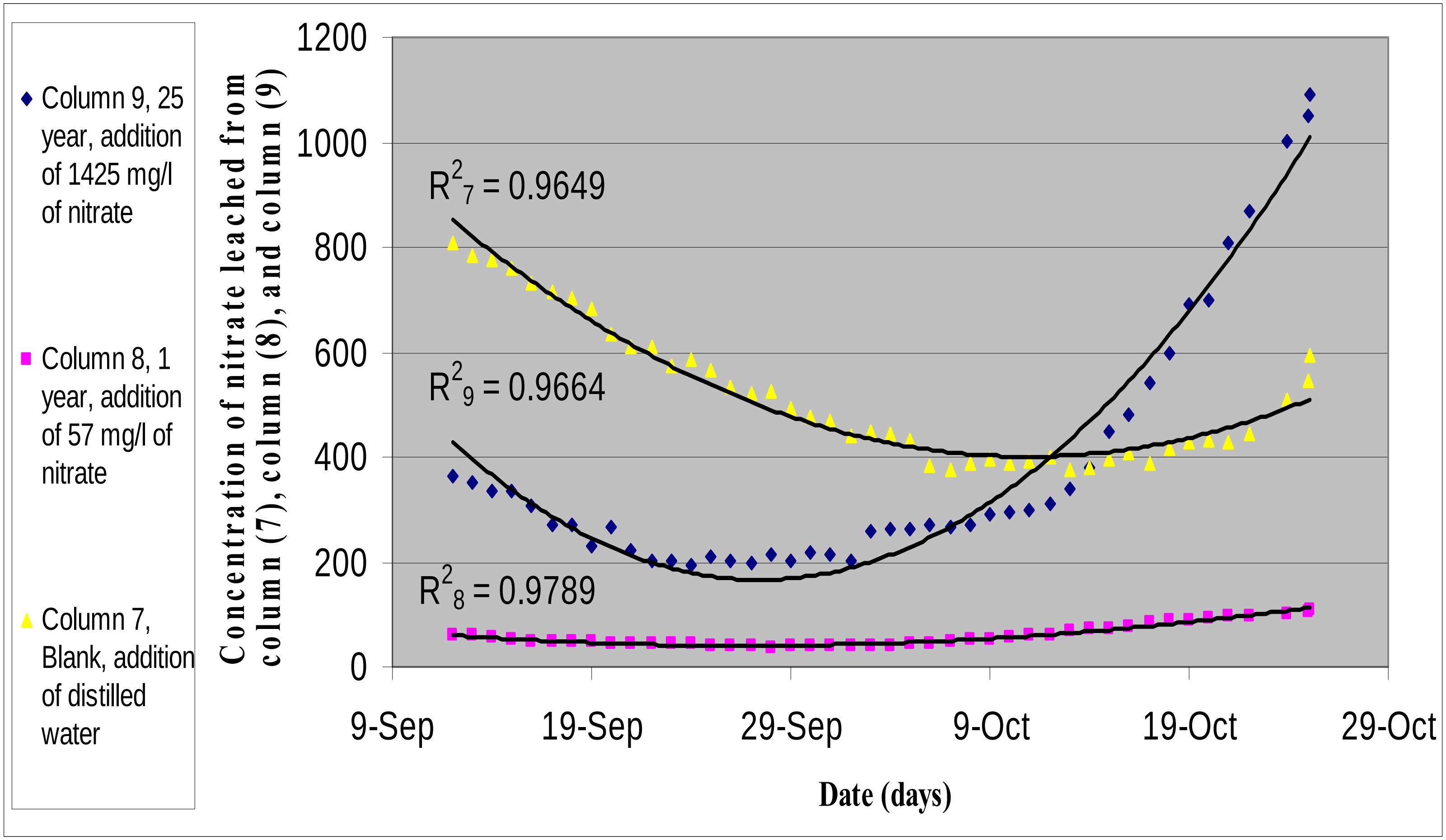


Figure (4.6):Concentration of nitrate leached from column (7), column (8), and column (9) vs. date (44 days).

Figure (4.6) represents the concentration of the nitrate ions leached from the column 7 (0.0 mg/L, blank), column 8 (57 mg/L, 1year), and column 9 (1425 mg/L, 25 years) for well no. 5. For the column 7 (0.0 mg/L, blank), it was noticed that after the addition of distilled water for 44 days, the concentration of nitrate ions decrease in the first period (32 days) and then the concentration increase in the second period (12 days). These differences in the concentrations are due to the high concentration of nitrate content in the soil samples, so the adsorption of nitrate in the beginning in the first 32 days to the soil particles is higher than desorption these is because the sand content for the soil is less which is about 75 % and also by the effect of distilled water flush and earth gravity the desorption increase and adsorption decrease in the second period in the 12 days.

For the column 8, that represents short term concentration for one year, the addition of water-containing nitrates in concentration 57 mg/L to the soil of these column for 44 days. The main soil texture for the sample is sand and the spaces between the sand particles is large and enough to enter nitrate ions between the soil particles and the surface area is small. Besides the presence of high concentration of both nitrate ions and organic matter in the soil content, for these reasons the adsorption in the beginning (20 days) is higher than desorption, then desorption increase and adsorption decrease in the second period (24 days), these is because the soil is unable to hold excess nitrate between the soil particles and by the effect of water flux and earth gravity the nitrate ions moves downward.

For the column 6, that represents long term concentration for 25 year, the addition of water-containing nitrates in concentration 1425 mg/L to the soil of these column for 44 days. The main soil texture for the sample is sand and the spaces between the sand particles is large and enough to enter nitrate ions between the soil particles and the surface area is small. Besides the presence of high concentration of both nitrate ions and organic matter in the soil content, for these reasons the adsorption in the beginning (26 days) is higher than desorption, then desorption increase and adsorption decrease in the second period (18 days), these is because the soil is unable to hold excess nitrate in large amount between the soil particles and by the effect of water flux and earth gravity the nitrate ions moves downward.

4.5 Testing of Nitrate Content For Soil Samples From Columns-Contain Nitrate Ions:

After the complete addition of distilled water and contaminated nitrated-water to each one of the nine columns for 44 days, the excess water goes from down columns until no water goes out in order to cut the nine columns.

Each column of the nine 2-meters vertical columns length is divided into four 50 cm equal parts, hence 36 parts of the nine columns are resulted. Each part of the columns is designated with a specific number which is necessary to keep track of the samples. The columns are cut by electrical disk into 36 equal parts. All parts were emptied from there contents of soil-containing nitrate ions in order to dry the soil, then the nitrate concentration is determined and illustrated in the following tables, Table (4.6) to Table (4.8) .

Table (4.6): Concentration of nitrate ions in soil of cut columns for the column (1), blank, column (2), 1 year, column (3), 25 years after addition of distilled water and nitrate solutions.

SOIL FROM WELL NO. 1			
Piece no. and length of columns cut in (cm)	**Column (1) Blank (0 mg/L) (NO_3^{-1})**	**Column (2) 1year (78mg/L) (NO_3^{-1})**	**Column (3) 25 years (1950 mg/L) (NO_3^{-1})**
	Concentration of (NO_3^{1}) (mg/L)	**Concentration of (NO_3^{-1}) (mg/L)**	**Concentration of (NO_3^{-1}) (mg/L)**
131-(0-50)	56	88	363
132 -(50-100)	67	109	331
133-(100-150)	74	130	291
134-(15-200)	85	160	255

As we see in Table (4.6) which represents the concentration of the nitrate ions in soil of cut columns for column 1 (0.0 mg/L, blank), column 2 (78 mg/L, 1year), and column 3 (1950 mg/L, 25 years) for well no. 1. The concentration of nitrate ions in the soil of the column 1, increases from 56 mg/L to 85 mg/L, when the length of column increase from up to down from 0 cm to 200 cm. Because in these column distilled water is added for 44 days, making gradual washing (cleaning) for the soil from nitrate and the concentration of nitrate increase from up to down the column, so the adsorption of nitrate in soil decreases with increase of length of column. By the effect of the earth gravity the nitrate ions move from up to down and high concentration of nitrate concentrated in the bottom of columns while the concentration of nitrate increase with increase of column length. While for column 2 the concentration of the nitrate ions in the soil of these column increase from 88 mg/L to 160 mg/L, when the length of the column increase from up 0 cm to down 200 cm. Because in these column distilled water that contaminated with nitrate is added for 44 days to the soil that contain high nitrate content, and the soil texture is sandy and the spaces between the soil particle is large and able to enter the nitrate ions between them. By the effect of both water flush and earth gravity the nitrate ions moves from up to down, and the adsorption of nitrate decrease in the soil of the column with the increase of the column length. The higher concentration of nitrate concentrated in the bottom of column, while the lower concentration concentrated in the top of the column. Finally, the concentration of the nitrate ions in the column 3 decrease from 363 mg/L to 255 mg/L, when the length of the column increase from up 0 cm to down 200 cm. Because in these column distilled water that contaminated with nitrate in large amount which is 1950 mg/L added for 44 days to the soil of these column that contain high nitrate content. The soil texture is sandy and the spaces between the soil particle is large and able to enter the nitrate ions between them, so by addition of large amount of nitrate ions to the soil there is accumulation of the nitrate ions in the soil along the column. By the effect of both water flush and earth gravity the nitrate ions moves slowly from up to down, and the adsorption of nitrate increase in the soil of the column with the increase of the column length. The higher concentration of nitrate concentrated in the top of column, while the lower concentration concentrated in the bottom of the column.

Table (4.7): Concentration of nitrate ions in soil of cut columns for the column (4), blank , column (5), 1 year, column (5), 25 years after addition of distilled water and nitrate solutions.

SOIL FROM WELL NO. 3			
Piece no. and length of columns cut in (cm)	**Column (4) Blank (0 mg/L) (NO_3^{-1}**	**Column (5) 1year (59mg/L) (NO_3^{-1})**	**Column (6) 25 years (1475 mg/L) (NO_3^{-1})**
	Concentration of (NO_3^{1}) (mg/L)	**Concentration of (NO_3^{-1}) (mg/L)**	**Concentration of (NO_3^{-1}) (mg/L)**
131-(0-50)	22	38	226
132 -(50-100)	24	45	206
133-(100-150)	26	54	186
134-(150-200)	28	64	161

Also Table (4.7) represents the concentration of the nitrate ions in soil of cut columns for column 4 (0.0 mg/L, blank), column 5 (59 mg/L, 1year), and column 6 (1475 mg/L, 25 years) for well no. 3. The concentration of nitrate ions in the soil of the column 4, increases from 22 mg/L to 28 mg/L, when the length of column increase from up to down from 0 cm to 200 cm. Because in these column distilled water is added for 44 days, making gradual washing (cleaning) for the soil from nitrate and the concentration of nitrate increase from up to down the column, so the adsorption of nitrate in soil decreases with increase of length of column. By the effect of the earth gravity the nitrate ions move from up to down and high concentration of nitrate concentrated in the bottom of columns while the concentration of nitrate increase with increase of column length. While for column 5 the concentration of the nitrate ions in the soil of these column increase from 38 mg/L to 64 mg/L, when the length of the column increase from up 0 cm to down 200 cm. Because in these column distilled water that contaminated with nitrate is added for 44 days to the soil that contain high nitrate content, and the soil texture is sandy and the spaces between the soil particle is large and able to enter the nitrate ions between them. By the effect of both water flush and earth gravity the nitrate ions moves from up to down, and the adsorption of nitrate decrease in the soil of the column with the increase of the column length. The higher concentration of nitrate concentrated in the bottom of column, while the lower concentration concentrated in the top of the column. Finally, the concentration of the nitrate ions in the column 6 decrease from 226 mg/L to 161 mg/L, when the length of the column increase from up 0 cm to down 200 cm. Because in these column distilled water that contaminated with nitrate in large amount which is 1475 mg/L added for 44 days to the soil of these column that contain high nitrate content. The soil texture is sandy and the spaces between the soil particle is large and able to enter the nitrate ions between them, so by addition of large amount of nitrate ions to the soil there is accumulation of the nitrate ions in the soil along the column. By the effect of both water flush and earth gravity the nitrate ions moves slowly from up to down, and the adsorption of nitrate increase in the soil of the column with the increase of the column length. The higher concentration of nitrate concentrated in the top of column, while the lower concentration concentrated in the bottom of the column.

Table (4.8): Concentration of nitrate ions in soil of cut columns for the column (7), blank , column (8), 1 year, column (9), 25 years after addition of distilled water and nitrate solutions .

SOIL FROM WELL NO. 5			
Piece no. and length of columns cut in (cm)	**Column (7) Blank (0 mg/L) (NO_3^{-1})**	**Column (8) 1year (57mg/L) (NO_3^{-1})**	**Column (9) 25 years (1425 mg/L) (NO_3^{-1})**
	Concentration of (NO_3^{1}) (mg/L)	**Concentration of (NO_3^{-1}) (mg/L)**	**Concentration of (NO_3^{-1}) (mg/L)**
131-(0-50)	26	51	385
132 -(50-100)	34	67	360
133-(100-150)	40	83	324
134-(150-200)	47	101	297

Finally, for the Table (4.8) which represents the concentration of the nitrate ions in soil of cut columns for column 7 (0.0 mg/L, blank), column 8 (57 mg/L, 1year), and column 9 (1425 mg/L, 25 years) for well no. 5. The concentration of nitrate ions in the soil of the column 7, increases from 26 mg/L to 47 mg/L, when the length of column increase from up to down from 0 cm to 200 cm. Because in these column distilled water is added for 44 days, making gradual washing (cleaning) for the soil from nitrate and the concentration of nitrate increase from up to down the column, so the adsorption of nitrate in soil decreases with increase of length of column. By the effect of the earth gravity the nitrate ions move from up to down and high concentration of nitrate concentrated in the bottom of columns while the concentration of nitrate increase with increase of column length. While for column 8 the concentration of the nitrate ions in the soil of these column increase from 51 mg/L to 101 mg/L, when the length of the column increase from up 0 cm to down 200 cm. Because in these column distilled water that contaminated with nitrate is added for 44 days to the soil that contain high nitrate content, and the soil texture is sandy and the spaces between the soil particle is large and able to enter the nitrate ions between them. By the effect of both water flush and earth gravity the nitrate ions moves from up to down, and the adsorption of nitrate decrease in the soil of the column with the increase of the column length. The higher concentration of nitrate concentrated in the bottom of column, while the lower concentration concentrated in the top of the column. Finally, the concentration of the nitrate ions in the column 9 decrease from 385 mg/L to 297 mg/L, when the length of the column increase from up 0 cm to down 200 cm. Because in these column distilled water that contaminated with nitrate in large amount which is 1950 mg/L added for 44 days to the soil of these column that contain high nitrate content. The soil texture is sandy and the spaces between the soil particle is large and able to enter the nitrate ions between them, so by addition of large amount of nitrate ions to the soil there is accumulation of the nitrate ions in the soil along the column. By the effect of both water flush and earth gravity the nitrate ions moves slowly from up to down, and the adsorption of nitrate increase in the soil of the column with the increase of the column length. The higher concentration of nitrate concentrated in the top of column, while the lower concentration concentrated in the bottom of the column.

4.6 Adsorption Isotherm:

The equilibrium adsorption data could be described by the Freundlich adsorption equation (4.1) :

$$x/m = k\,(Ce)^{1/n} \qquad \text{equation (4.1)}$$

The Freundlich equation constants " k" & "n" could be obtained from the empirical Freundlich adsorption equation (4.1):

Where:

x: moles of compound adsorbed.

m: weight of soil (g).

Ce: equilibrium concentration (mole/L).

x/m: amount adsorbed soil (mole/g).

K& n: Freundlich adsorption constants.

The isotherm equilibrium results are shown in Tables (4.9), (4.10) & (4.11) and Figures (4.7), (4.8) & (4.9), as the amount adsorbed against the equilibrium concentrations after 24 hours of adsorption.

Table (4.9): Equilibrium concentration (Ce) & amount of nitrate adsorbed per gram of sample soil from well no. (1) (x/m).

CONC. OF (NO$_3^{-1}$) ADDED(MG/L)	CONC. OF NO$_3^{-1}$) IN(SOIL (MG/L)	CONC. OF (NO$_3^{-1}$) OUT OF SOIL (MG/L)	X/M (MOLE/G)	CE (MOLE/L)
100	3	97	1.06×10^{-5}	1.56×10^{-3}
200	12	188	3.20×10^{-5}	3.03×10^{-3}
300	21	279	5.40×10^{-5}	4.50×10^{-3}
400	30	370	6.20×10^{-5}	5.97×10^{-3}
500	39	461	7.90×10^{-5}	7.44×10^{-3}

Table (4.10): Equilibrium concentration (Ce) & amount of nitrate adsorbed per gram of sample soil from well no. (3) (x/m).

CONC. OF (NO$_3^{-1}$) ADDED (MG/L)	CONC. OF NO$_3^{-1}$) IN(SOIL (MG/L)	CONC. OF (NO$_3^{-1}$) OUT OF SOIL (MG/L)	X/M (MOLE/G)	CE (MOLE/L)
100	30	70	9.68×10^{-5}	1.13×10^{-3}
200	60.14	139.86	1.94×10^{-4}	2.26×10^{-3}
300	90.83	209.17	2.93×10^{-4}	3.37×10^{-3}
400	142.6	257.4	4.60×10^{-4}	4.15×10^{-3}
500	199.02	300.98	6.42×10^{-4}	4.86×10^{-3}

Table (4.11): Equilibrium concentration (Ce) & amount of nitrate adsorbed per gram of sample soil from well no. (5) (x/m).

CONC. OF (NO_3^{-1}) ADDED (MG/L)	CONC. OF (NO_3^{-1}) IN SOIL (MG/L)	CONC. OF (NO_3^{-1}) OUT OF SOIL (MG/L)	X/M (MOLE/G)	CE (MOLE/L)
100	30.47	69.53	9.83×10^{-5}	1.12×10^{-3}
200	63.11	136.9	2.04×10^{-4}	2.21×10^{-3}
300	105.36	194.64	3.39×10^{-4}	3.14×10^{-3}
400	151.02	248.99	4.87×10^{-4}	4.02×10^{-3}
500	183.78	318.45	5.93×10^{-4}	5.14×10^{-3}

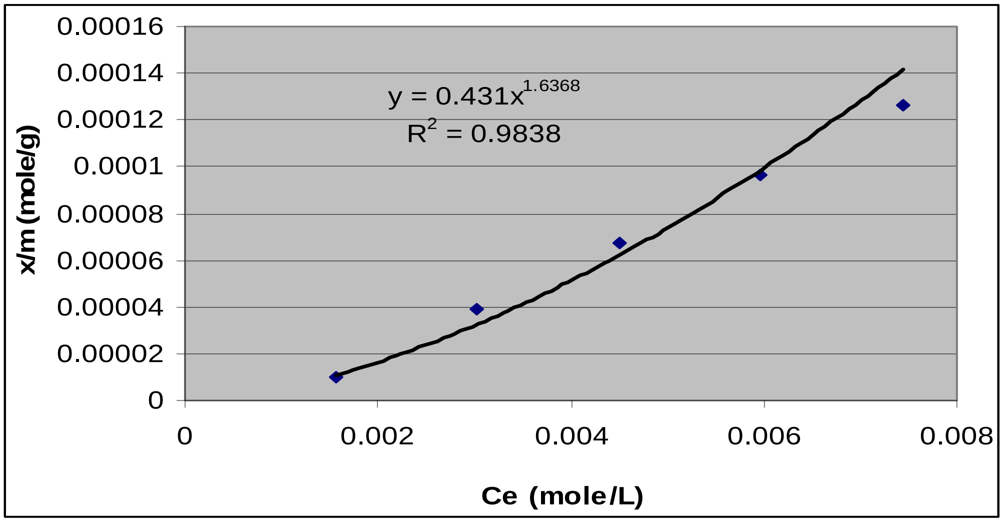


Figure (4.7): Plot of x/m vs. Ce for nitrate for soil sample from well no. (1).

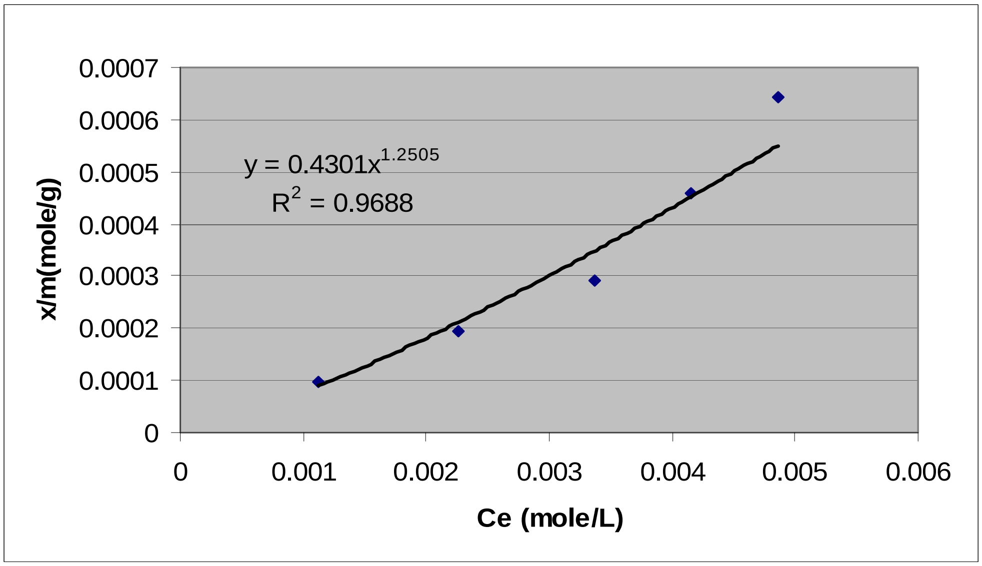


Figure (4.8): Plot of x/m vs. Ce for nitrate for soil sample from well no. (3).

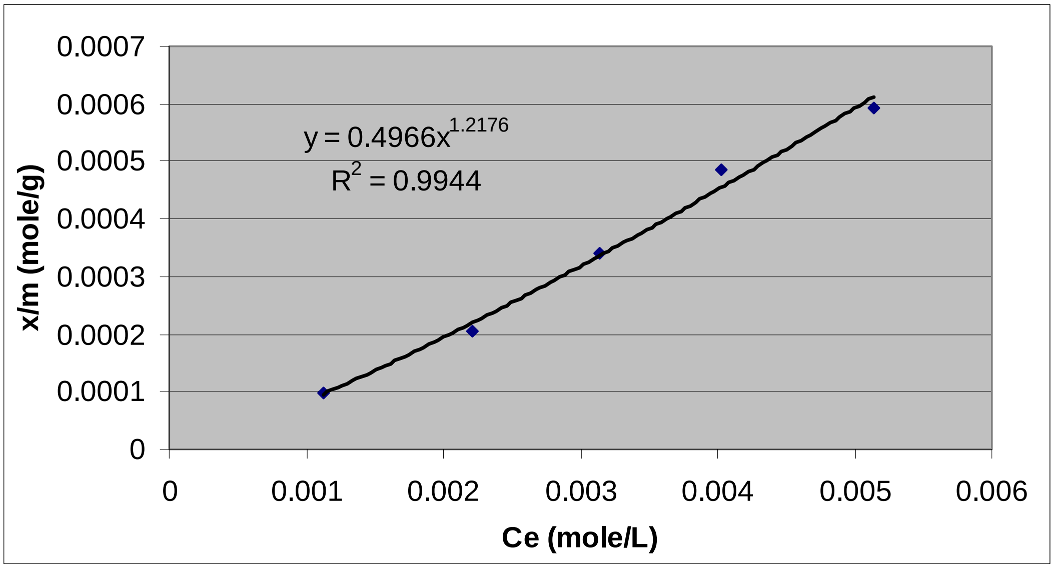


Figure (4.9): Plot of x/m vs. Ce for nitrate for soil sample from well no. (5).

After plotting amount of adsorbed soil (x/m) against equilibrium concentration of solute (Ce) a straight line is obtained from the three figures after applying Freundlich equation, and from the figures (4.7), (4.8) & (4.9) the following equations are obtained

Soil sample from well no.(1) $y = 0.431X^{1.6368}$ $R^2 = 0.9838$

Soil sample from well no.(3) $y = 0.4301X^{1.2505}$ $R^2 = 0.9688$

Soil sample from well no.(5) $y = 0.4966X^{1.2176}$ $R^2 = 0.9944$

Freundlich isotherms constants (k & n) for nitrate & the correlation coefficient "R" were obtained from the above equations and listed in the Table (4.12) below

Table (4.12): Freundlich isotherms constants (k & n) & the correlation coefficient " R" for nitrate.

SOIL SAMPLE	K	1/N	N	R^2	R
Well no. (1)	0.431	1.6368	0.611	0.9838	0.9919
Well no. (3)	0.4301	1.2505	0.799	0.9688	0.9843
Well no. (5)	0.4966	1.2176	0.821	0.9944	0.9972

From the Table (4.12), the values of (n) for nitrate were found to be 0.611, 0.799, and 0.821 respectively, and these results are satisfactory where n for well no. 5 close to 1, while the linear adsorption 1/n = 1, and for (k) values its found to be also (0.4301- 0.4966).

4.7 Optimum Time For Nitrate (NO_3^{-1}) Adsorption onto soil:

The aim of this work is to determine the optimum time for the process of adsorption of nitrate (NO_3^{-1}) onto soil to reach equilibrium.

Tables (4.13), (4.14 & (4.15) show the concentrations of nitrate (NO_3^{-1}) solutions after the addition of 50 mL of 100 mg/L of prepared solution, to each 5 grams of soil sample at different mixing time (1, 2, 3, 4, 6, 12, 24, & 36 hours) equilibrium occurred after 24 hours of adsorption for nitrate (NO_3^{-1}). Figures (4.10), (4.11) & (4.12) shows plotted graphs of nitrate concentration vs. time intervals.

Table (4.13):Concentration of nitrate (NO_3^{-1}) for soil sample from well no. (1) at different times.

TIME (HOURS)	CONC. OF (NO_3^{-1}) MG/L
1	82
2	79.5
3	76.5
4	78
6	75
12	72
24	60
36	60.29

Table (4.14): Concentration of nitrate (NO_3^{-1}) for soil sample from well no. (3) at different times.

TIME (HOURS)	CONC. OF (NO_3^{-1}) MG/L
1	83
2	81
3	80
4	79
6	74
12	70
24	51
36	51.23

Table (4.15): Concentration of nitrate (NO_3^{-1}) for soil sample from well no. (5) at different times.

TIME (HOURS)	CONC. OF (NO_3^{-1}) MG/L
1	79
2	79
3	77
4	74
6	74
12	70
24	50.06
36	49.91

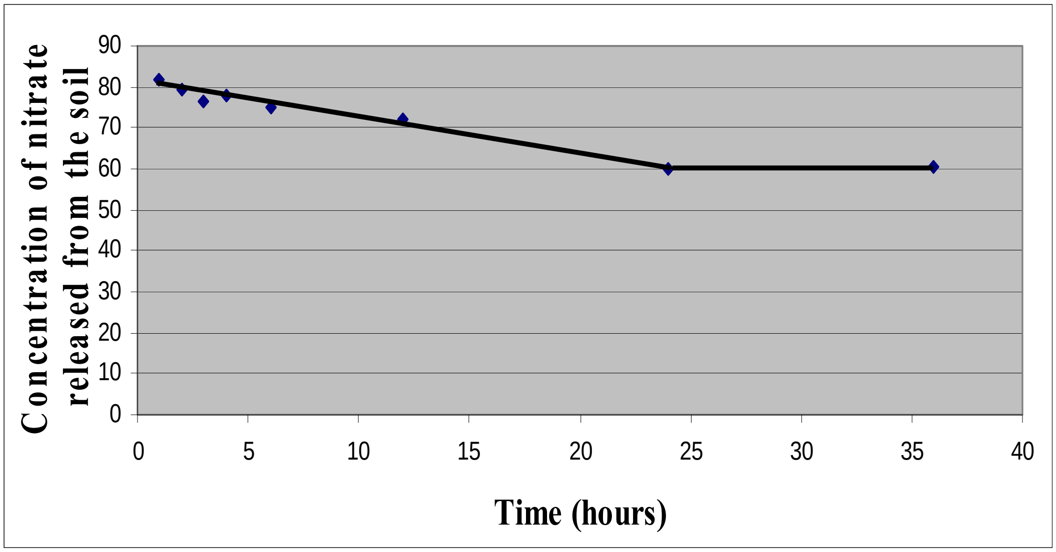


Figure (4.10): Plot of concentration of nitrate released from the soil sample for well no (1). vs. time.

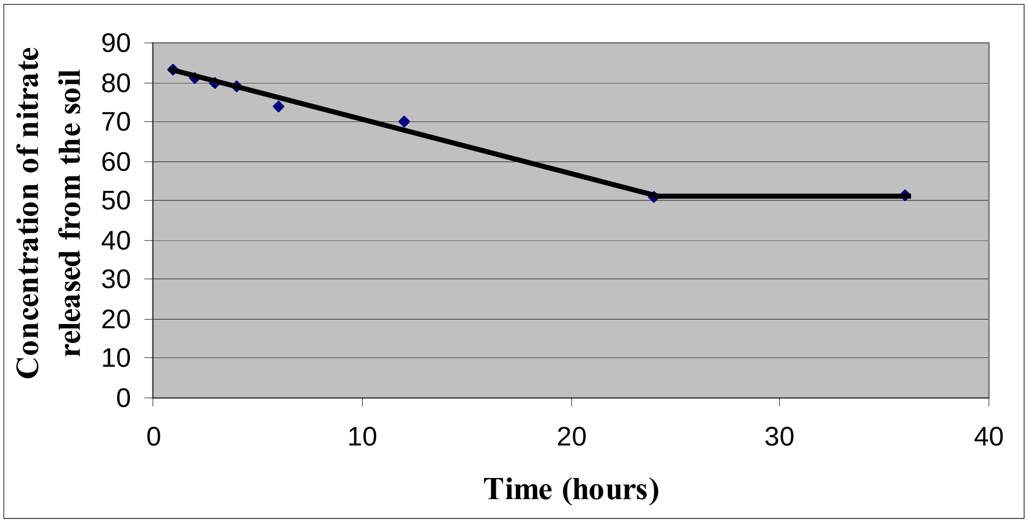


Figure (4.11): Plot of concentration of nitrate released from the soil sample for well no (3). vs. time.

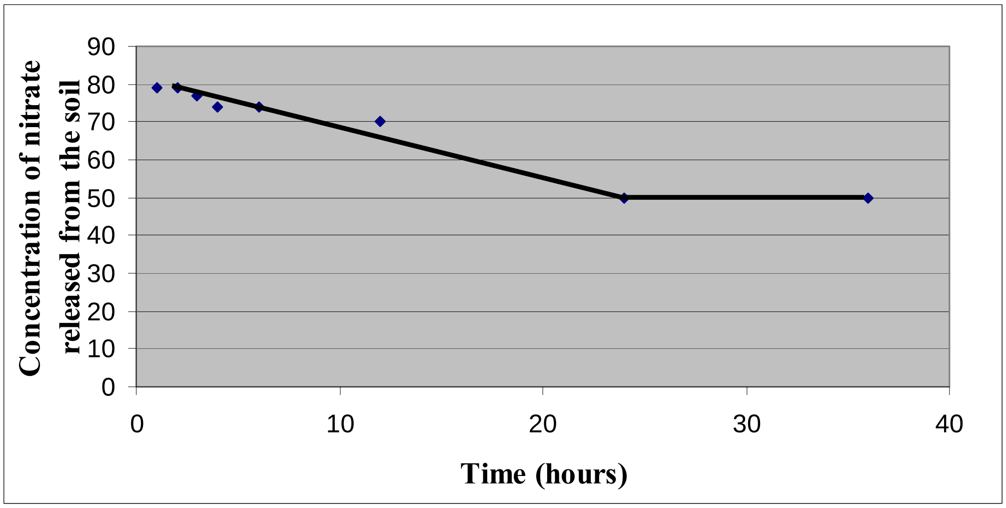


Figure (4.12): Plot of concentration of nitrate released from the soil sample for well no (5). vs. time.

According to the above results from the tables (4.13), (4.14) & (4.15) and figures (4.10), (4.11) & (4.12), when 100 mg/L of nitrate solutions were added to the three soil samples that collected from wells no. 1, 3, and 5, there is a decrease in the nitrate concentration when the time increase from 1 hour to 24 hour, the optimum time for adsorption of nitrate ions was after 24 hours of adsorption because there is no change occur for the concentration of nitrate ions after 24 hour.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS:

Many regions in the world and especially Palestine use the groundwater as the only source of drinking water and agriculture, thus nitrate in drinking water becomes a significant concern for people.

Soil texture, organic matter content, water flux, certain fertilizer, fertilizer application may have a major influence on nitrate leaching in groundwater.

The results clearly indicate, that soil present in the columns taken from wells no. (1, 3, and 5) is mainly sandy to sandy loam soil that contains sand in high percentage (75 %-92 %), small amount of silt & clay (0.74 %-4.52 %), and considerably high percentage organic matters (3.71 %-4.25%). The soil content in Tulkarem City consider to be high in the concentration of the nitrate ions that range from 261,7 mg/L to 799 mg/L, and these elevation in the nitrate concentrations is due to the intensive use of fertilizers, animal manures, and wastewater from Wadi Zaimer and septic tanks. This higher concentrations of nitrate leach from the soil to the ground water in large amount, this because the major component of the soil is sand, and sand has large particle size and large spaces that enable nitrate ions to enter between them for a period of time until irrigation or rain full that move nitrate ions downward to the ground water. However, there are high amount of organic matters, that close some spaces between the sandy particles, so it reduces the rate of the water that contain nitrate from leaching to the groundwater.

Using large amount of the water in the irrigation of the agricultural land makes the percolating of nitrate and other chemicals at greater potentially risk. This large amount that is used in irrigation dissolves excess nitrate that is present in the soil and makes it more susceptible to leach downward until reaching the groundwater. The microbial activity will raise in the soil, and as a result mineralization increase which is necessary in making nitrate ions .

Nitrate percolating from fertilizer depends upon the climate condition, fertilizer types (organic, nitrate, or ammonium) and method of application. Nitrate percolating may be greater when fertilizer contains ammonium nitrogen as major component of the fertilizer with nitrate as another part of fertilizer [87].

Adding distilled water to the blank columns for 44 days, made washing (cleaning) for the soil from the higher concentration of nitrate ions, which is present in the soil content. This happened by the effect of distilled water flux, that forces nitrate ions that is adsorbed to the soil particles to dissolve in distilled water and move in the soil under influence of the earth gravity until reach the bottom of the soil column. In the first addition of distilled water adsorption of nitrate ions to the soil particles is higher than desorption, then as the addition of distilled water continue the desorption is higher than adsorption. As a result the higher concentration of nitrate ions are concentrated in the bottom of the columns, while the top of the soil has lower concentration, and these is a benefit way to remove nitrate from soil.

Adding contaminated water with nitrate to the soil in the columns according to the short-term concentration (one year) and long–term concentration (25 years), resulted in having a higher concentration of nitrate at the bottom of the columns and a lower concentration of nitrate concentrated at the top of the columns. It is worth noticing that the concentration of nitrate ions is doubled in quantity of the short-term concentration relative to that of the blank columns. However, in short–term concentration (57 mg/L-78 mg/L), this higher concentration of nitrate that added for 44 days to the soil that contain high nitrate content. By the effect of both water flush and earth gravity the nitrate ions moves from top to down column, hence the higher concentration of nitrate concentrated at the bottom of column, comparing the lower concentration at the top of the column. While in long–term concentration (1400 mg/L-1950 mg/L), this higher concentration of nitrate that added for 44 days to the soil that contain high nitrate content, making accumulation of the nitrate ions in the soil along the column. By the effect of both water flush and earth gravity the nitrate ions moves very slowly from up to down the column, so the higher concentration of nitrate concentrated at the top, while the lower concentration concentrated in the bottom of the column.

The values of "n" in Freundlich equation were close to "one" for well no. (5) and less for wells no. (1 & 3), which indicate good adsorption for nitrate, while the optimum time for adsorption was after 24 hours.

The groundwater in Tulkarem city is shallow which is about 80 m-200 m in depth, and that makes it at greater potential risk for leaching of nitrate into groundwater in a relatively short time, whereas in areas where the groundwater is deep enough it may take decades before nitrate reaches the groundwater in large quantities to raise the nitrate concentration above the standards value.

The soil texture in Tulkarem city is sandy to sandy loam because Tulkarem is a coastal city, about 10 km–12 km far of the Mediterranean sea. Going further east, the percentage of sand in soil becomes less which in return mean, that the other components like clay and silt will be higher in concentration.

5. 2 RECOMMENDATIONS:

- In the case of sandy soil, mixing soil with organic matter decrease the pores among the soil particles therefore restrict the flux of water and other solute through soil, hence nitrate leaching to the groundwater will be reduced.
- To reduce nitrification in the soil, chemicals known as nitrification inhibitors can be added to the soil.
- There must be full awareness for the farmers of how to use fertilizers and animal manures and the proper time for application, and how to calculate the real need of land from fertilizers and manures by making chemical tests that illustrate the components of the soil and its need from fertilizers and manure .

- There must be real plan from the municipality to finish the spreading of septic tanks, by connecting all houses, shops, restaurants, factories and others with public sewage network.

- Full responsibility laying on the municipality when drilling for new well, they should have them further away from polluted areas. Also well must be clean in the inside and tubes and the top must be sealed.

- To reduce the nitrate in Tulkarem City and in the area surrounding, the wastewater from western part of Nablus city along with that of the villages in the path to Tulkarem must pumped their sewage in trunk line made of concrete and not dumped in Wadi Zaimer.

- If there is high nitrate in any well, that well must be stopped from pumping drinking water and find other source of water with low nitrate or solve the problem by diluting it. with water of other well with low nitrate.

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Appendices

APPENDIX 1.1

Preparation of Reagents and Standards Solutions

In this research sodium nitrate ($NaNO_3$) is used as source of nitrate ion (NO_3^{-1}). Molecular weigh of $NaNO_3$ = 84.9947 g, molecular weigh of (NO_3^{-1}) ion = 62.0049 g.

A. Sodium nitrate standard solution (2000 mg/L).

2000 mg/L = 2.0 g.

1 mole $NaNO_3$ (84.9947 g) $\longrightarrow$ 1mole (NO_3^{-1}) (62.0049 g)

$NaNO_3$ (x g) $\longrightarrow$ (NO_3^{-1}) (2.0 g)

Grams of (NO_3^{-1}) = (2.0 × 84.9947) ÷ 62.0049 = 2.7416 g

2.7416 g $NaNO_3$ was dissolved in one liter distilled water gradually by shaking.

B. Sodium nitrate solution for well no. 1 one year (78 mg/L).

78 mg/L = 0. 078 g.

84.9947 g $\longrightarrow$ 62.0049 g

(x) g $\longrightarrow$ 0. 078 g

Grams of (NO_3^{-1}) = (0 . 078 × 84.9947) ÷ 62.0049 = 0.1069 g

0.1069 g $NaNO_3$ was dissolved in one liter distilled water gradually by shaking.

C. Sodium nitrate solution for well no. 25 one year (1950 mg/L).

1950 mg/L = 1.950 mg/L

84.9947 g → 62.0049 g

(x) g → 1.950 g

Grams of (NO_3^{-1}) = (1.950 × 84.9947) ÷ 62.0049 = 2.6730 g

2.6730 g $NaNO_3$ was dissolved in one liter distilled water gradually by shaking.

D. Sodium nitrate solution for well no. 3 one year (59 mg/L).

59 mg/L = 0.059 g

84.9947 g → 62.0049 g

(x) g → 0.059 g

Grams of (NO_3^{-1}) = (0.059 × 84.9947) ÷ 62.0049 = 0.0809 g

0.0809 g $NaNO_3$ was dissolved in one liter distilled water gradually by shaking.

E. Sodium nitrate solution for well no. 3 25 year (1475 mg/L).

1475 mg/L = 1.475 g

84.9947 g → 62.0049 g

(x) g → 1.475 g

Grams of (NO_3^{-1}) = (1.475 × 84.9947) ÷ 62.0049 = 2.0219 g

2.0219 g $NaNO_3$ was dissolved in one liter distilled water gradually by shaking.

G. Sodium nitrate reagent for well no. 5 one year (57 mg/L).

57 mg/L = 0.057 g

84.9947 g → 62.0049 g

(x) g → 0.057 g

Grams of (NO_3^{-1}) = (0.057 × 84.9947) ÷ 62.0049 = 0.07813 g

0.07813 g $NaNO_3$ was dissolved in one liter of distilled water gradually by shaking.

H. Sodium nitrate reagent for well no. 5 25 year (1425 mg/L).

1425 mg/L = 1.425 g

84.9947 g → 62.0049 g

(x) g → 1.425 g

Grams of (NO_3^{-1}) = (1.425 × 84.9947) ÷ 62.0049 = 1.9534 g

1.9534 g ($NaNO_3$) was dissolved in one liter of distilled water gradually by shaking.

I. Standard calibration solutions.

This solutions prepared from stock solution (2000 mg/L) so the required calibration solutions are (200 mg/L, 600 mg/L, 1000 mg/L, 1400 mg/L). By the following equation the calibration solution is prepared

$M_{(1)}(\text{ mg/L}) \times V_{(1)(\text{mL})} = M_{(2)}(\text{ mg/L}) \times M_{(2)(\text{mL})}$

● 200 mg/L calibration solution .

200 mg/L × 100 mL = 2000 mg/L × $V_{(2)}$ (mL)

$V_{(2)}$ (mL) = (200 mg/L ×100 mL) ÷ 2000 mg/L = 10 mL stock solution

10 mL stock solution is added to 90 mL distilled water to making volume 100 mL.

● 600 mg/L calibration solution .

600 mg/L × 100 mL = 2000 mg/L × $V_{(2)}$ (mL)

$V_{(2)}$ (mL) = (600 mg/L ×100 mL) ÷ 2000 mg/L = 30 mL stock solution

30 mL stock solution is added to 70 mL distilled water to making volume 100 mL.

● 1000 mg/L calibration solution .

1000 mg/L × 100 mL = 2000 mg/L × $V_{(2)}$ (mL)

$V_{(2)}$ (mL) = (1000 mg/L ×100 mL) ÷ 2000 mg/L = 50 mL stock solution

50 mL stock solution is added to 50 mL distilled water to making volume 100 mL.

● 1400 mg/L calibration solution .

$1400\ \text{mg/L} \times 100\ \text{mL} = 2000\ \text{mg/L} \times V_{(2)}\ (\text{mL})$

$V_{(2)}\ (\text{mL}) = (1400\ \text{mg/L} \times 100\ \text{mL}) \div 2000\ \text{mg/L} = 70\ \text{mL}$ stock solution

70 mL stock solution is added to 30 mL distilled water to making volume 100 mL.

J. Recommended ISAB 1 M [KH_2PO_4] reagent.

This reagent is prepared by the following:

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liter of solution}} \longrightarrow 1\text{M} = \frac{\text{moles of } KH_2PO_4}{0.1\ \text{liter}}$$

Moles of $KH_2PO_4 = 0.1$

Molecular weigh of $KH_2PO_4 = 136.0892$ g

$$\text{Moles of } KH_2PO_4 = \frac{\text{weigh of } KH_2PO_4}{\text{molecular weigh of } KH_2PO_4}$$

$$0.1 = \frac{\text{wt . of } KH_2PO_4}{136.0892} \longrightarrow \text{wt. of } KH_2PO_4 = 13.6089\ \text{g}$$

13.6089 g is dissolved in 100 mL distilled water for making 1 M.

K. Ionic strength adjustor (ISA) 2 M $(NH_4)_2SO_4$ reagent.

26.4 g powder of $(NH_4)_2SO_4$ is added to 100 mL distilled water and shaking well.

L. Extraction solution 0.04 M of $(NH_4)_2SO_4$.

20 mL of ISAB is added to 1 liter volumetric flask and making to volume with distilled water.

M. (50 %) NaOH solution.

500 g NaOH (Pellets) added to 500 mL distilled water (carefully-slowly in sink in heat resistant container–cool before adding to alkali reservoir.

N. Boric acid solution.

80 g of boric acid added to 1000 mL distilled water, 20 mL of bromocrysol green indicator and 14 mL methyl red indicator was added to the content in 2 L volumetric flask and distilled water added to the mark of 2 L.

O. Phosphor reagent.

1- Dissolve 1.2 g of ammonium paramolybdate in 25 mL distilled water.

2- Dissolve 0.02908 g of potassium antimony tartarate in 10 mL distilled water.

3- Prepare 100 ml of 5 N H_2SO_4 by diluting 13.8 mL of concentrated H_2SO_4 into 100 mL distilled water .

4- Add both (1)+(2) and complete the volume to 200 mL by distilled water.

5- Take 100 mL of solution in (4), add to it 0.528 g ascorbic acid (this step is done as fresh as possible before testing).

APPENDIX 1.2

Amount of nitrate solutions added to soil columns, by knowing the following parameters

- Average rainfall in Tulkarm city which equal about 602.2 mm = 602.2 ÷ 10 = 60.22 cm
- Raining days in Tulkarem City (44 days),
- Surface area of cylinder (tube) = area of circle = $R^2 \times \pi$, (R = radius)

Volume of water added to each tube = average rainfall (mm) × surface area of tube (mm^2) ÷ raining days.

Note: diameter = 6 inch , Radius = 3 inch = 3 × 2.54 = 7.62 cm

$= 60.22\ (\text{cm}) \times (7.62\ \text{cm} \times 7.62\ \text{cm}) \times (3.14) \div 44\ \text{days} \approx 250\ \text{mL}$

This is the amount of water (distilled or contaminated with nitrate) that must be added everyday for 44 days to the to the plastic columns that filled with soil .

APPENDIX 1.3

1.3.1Operating Instructions For Jenway ion selective electrode meter:

he JENWAY ion selective electrode meter model 3340 is used in this research and is highly sophisticated product offering a host of valuable features, but retaining simplicity of operation. The meter is connected to ion selective electrode which has a solid-state PVC polymer membrane and integer reference. The electrode is designed for the detection and analysis of nitrate ion in aqueous solutions and suitable for use in both field and laboratory application and the meter is illustrated in Figure (1.1) bellow.

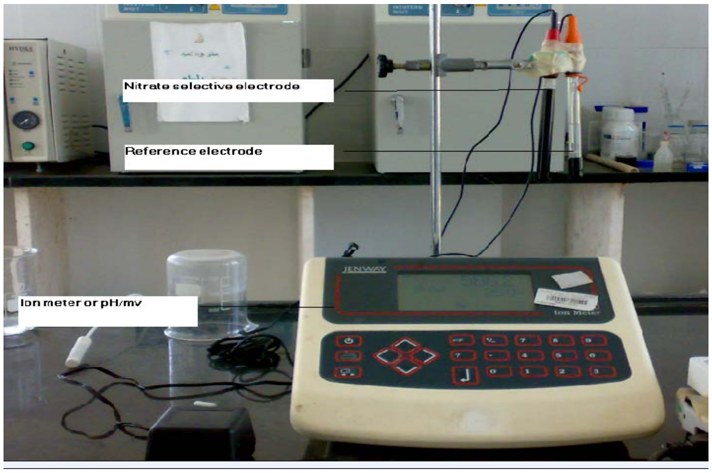

Figure (1.1): Jenway ion selective electrode meter with main part.

1.3.2 Installation:

Connect the ISE and reference electrode to the pH/mV or ion meter. Remove the black protective cap from the two electrodes and keep it in a safe place. The ISE can be used immediately but pre soaking is recommended if the electrode has been stored dry for more than 2 week or if very precise measurements are required. To condition the electrode, immerse electrode for 5 minutes in a 1000 mg/L nitrate solution. When soaking is completed rinse electrode with deionized water and dray. The electrode is now ready for calibration.

1.3.3 Operation

Calibration is carried out using standard solutions at decade intervals (200 mg/L, 600 mg/L, 1000 mg/L, 1400 mg/L). The ionic strength of the standards and solutions should be kept constant between all standards and samples. This is achieved by the simple addition of an ionic strength adjustment buffer (ISAB), recommended potassium dihydrogen phosphate 1 M KH_2PO_4 or ammonium sulphate $(NH_4)SO_4$. Atypical addition would be 2 mL of 1 M ISAB to 100 mL of standard and sample. However, if the ionic strength of the sample is less than 10-4 M no buffer is needed. Constant temperature of both standards and samples solutions should be maintained ± 2 C^o. In most cases it is suggested that both standards and sample solutions are stirred slowly at the same rate ~100 rpm. Begin calibration from the lowest concentration standard to avoid cross contamination. Calibration should cover the anticipated range of the samples and this can be shown in the Figure bellow (1.2). Rinse tip with deionized water between measurements. Avoid strongly acidic or alkaline samples, strong detergents and organic solvents.

1.3.4 Calibration Ion Selective Electrode Meter:

Ion selective electrode meter is calibrated in the following way:

Switch the meter from on/off button. Menu appear choose by arrows cal. Button and press enter and illustrate in the Figure (1.2) bellow. Another menu appear choose cal. buffer by arrows from the menu and enter.

Another menu appear showing cal. 1 to cal. 5 enter the values of calibration solution by numeric keys cal. 1 = 200 mg/L, cal. 2 = 600 mg/L, cal. 3 = 1000 mg/L, cal. 4 = 14000 mg/L and press enter after each value and then press exit to go to previous menu and this illustrate in Figure (1.3) bellow. In the menu that shown in Figure (1.3) choose cal.1 and press enter, it goes to cal. 1 = 200 mg/L, immerse the ISE and reference electrode in standard solution 200 mg/L that contain 2 mL of ISAB in 100 mL solution and stir well at ~100 rpm. The reading that appear in the screen approach to or become 200 mg/L then press enter to accept the value, then goes to another cal. 2 and so on until reach cal. 4 then press exit, it return to menu that appear in Figure (1.2), then the meter ready for measuring the samples.

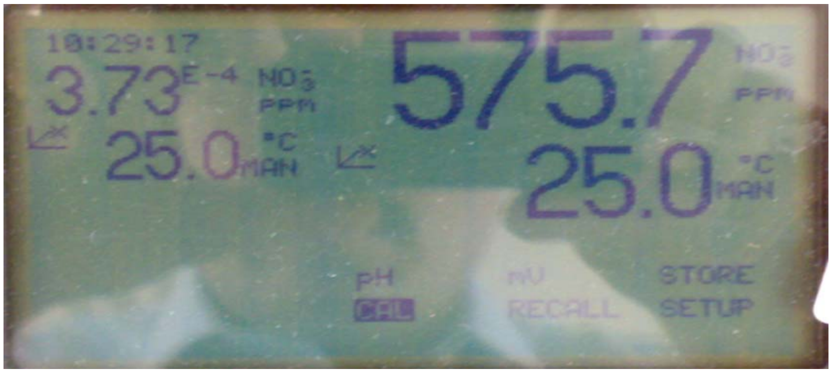

Figure (1.2): The main menu in the meter that shows cal. and other icons.

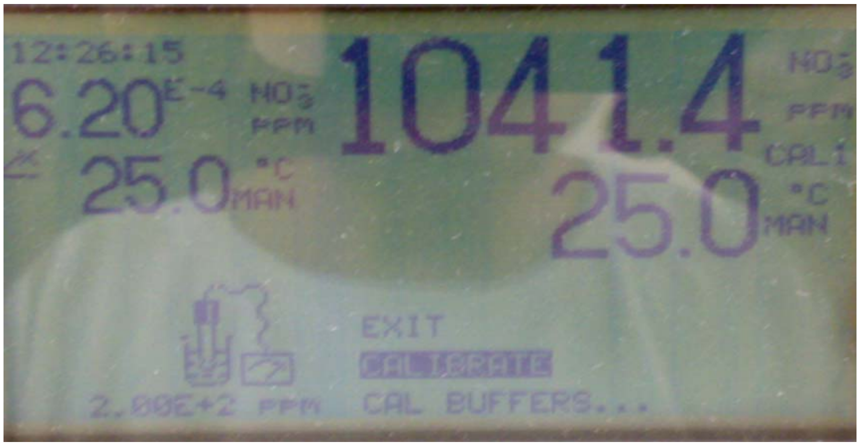

Figure (1.3): Menu shows calibrate and cal buffer icon

جامعة النجاح الوطنية
كلية الدراسات العليا

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إعداد
أسامة زكي محمد ناصر

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء من كلية الدراسات العليا في جامعة النجاح الوطنية، نابلس – فلسطين.

2011

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الملخص

كما نعرف أن ايونات النترات هي ملوثات عالمية تلوث مصادر المياه والتي تتضمن المياه السطحية والجوفية. وهذا التلوث ينتج بشكل أساسي من الأسمدة النيتروجينية في المناطق الزراعية، المياه العادمة وروث الحيوانات . منظمة الصحة العالمية (WHO) وضعت المعايير لتركيز ايون النترات والذي يساوي 45 ملغم / لتر، لذلك أي مصدر للمياه يتعدى هذه القيمة يعتبر ملوث ويوضع تحت الأنظار للمعالجة. طريقة الأعمدة العمودية التي ملئت بأنواع مختلفة من التربة المأخوذة من مدينة طولكرم هي لدراسة تأثيرات التربة على المياه الجوفية إذ ترشح المياه الملوثة بالنترات خلال التربة وعلاقتها بارتفاع النترات في هذه المناطق.

ثلاثة عينات من الأتربة المختلفة في تراكيز النترات ستجمع من جانب آبار بلدية طولكرم رقم (1)، رقم (3)، ورقم (5). هذه العينات ستوضع في تسعة أنابيب عمودية من البلاستيك (PVC). بعد ذلك هذه الأنابيب ستقسم إلى ثلاثة أقسام زمنية معينة للتراكيز وهي صفر مدة زمنية (صفر سنة) – مدة زمنية قصيرة (سنة واحدة) – مدة زمنية طويلة (25 سنة) لكل عينة تراب. ثلاثة تراكيز مختلفة من المياه الملوثة بالنترات ستضاف كتراكيز زمنية للأنابيب التسعة بشكل يومي.

للأنابيب، التي تضاف لها النترات بتراكيز لمدة زمنية قصيرة (سنة واحدة) وتركيز مياه مقطرة خالية من النترات (بلانك) وجد أن التراكيز العالية للنترات تتركز في أسفل الأنابيب بينما التراكيز المنخفضة تتركز في أعلى الأنابيب. للأنابيب التي تضاف إليها النترات بتركيز

لمدة زمنية طويلة (25 سنة) التراكيز العالية لنترات تتركز في أعلى الأنابيب بينما التراكيز المنخفضة تتركز في أسفل الأنابيب.

النتائج أيضا أشارت أن بنية (تركيب) التربة هي رملية إلى رملية طفالية وتحتوي على نسبة عالية من المواد العضوية التي تتراوح ما بين 3.71% و 4.25%. وجد أن متوسط تراكيز ايونات النترات في محتوى عينات التراب من الآبار رقم (1)، رقم (3) و رقم (5) يساوي 263.3 ملغم/ لتر، 216.7 ملغم / لتر و 799 ملغم / لتر على التوالي.

دراسات حركية (مبدأ فرندلخ للالتصاق) طبقت لدراسة التصاق النترات لذرات التراب في الآبار رقم (1)، رقم (3) ورقم (5) . نتائج دراسة الالتصاق للآبار رقم (1)، رقم (3)، ورقم (5) يساوي 0.611، 0.779 و 0.821 بشكل متوالي. هذه النتائج مرضية بينما الالتصاق الأمثل لايونات النترات هو بعد 24 ساعة.