An-Najah National University

Faculty of Graduate Studies

Quantitative and Qualitative Assessment of Macronutrients and Micronutrients of Digestate from Biogas Units under different Feedstock Loadings

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This Thesis was defended successfully on 04 /11 /2014 and approved by:

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Dedication

To my parents who have given their love, encouragement, and sacrificed time and pleasure to teach me the great value of persistence in hard worthwhile work and study

To my dearest wife " Hana Qabaha ", who leads me through the valley of darkness with light of hope and support

To my brothers and sisters who have encouraged me all the time

To the committed teachers and good friends that have inspired me during my early years and throughout my life to seek for learning and greater education...

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Eng. Rafat Amarneh

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل عنوان:

Quantitative and Qualitative Assessment of Macronutrients and Micronutrients of Digestate from Biogas Units under different Feedstock Loadings

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، بإستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's Name: إسم الطالب: أمنة فتحي خالد عارف

Signature: التوقيع:

Date: التاريخ: 04.11.2016

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List of Abbreviations

AA**:**	Atomic Absorption
AD**:**	Anaerobic Digestion
ATP**:**	adenosine triphosphate
BOD**:**	Biochemical Oxygen Demand.
COD**:**	Chemical Oxygen Demand.
CEC**:**	Cation Exchange Capacity
C:N ratio**:**	proportional amount of carbon to nitrogen.
HRT**:**	Hydraulic Retention Time
ICP-MS**:**	Inductively coupled plasma mass spectrometry
ICP-OES**:**	Inductively coupled plasma Optical Emission
NIR**:**	near-infrared
OFMSW**:**	The organic fraction of Municipal Solid Waste
OLR**:**	Organic Loading Rate
TKN**:**	Total Kjeldahl Nitrogen
UV-Vis or UV/Vis**:**	Ultraviolet – visible spectroscopy or ultraviolet - visible spectrophotometry
VFA**:**	Volatile Fatty Acids
SPSS:	statistical package for social science

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Abstract

Digestate from biogas plants is a high quality product, suitable and safe for use as a fertilizer in agriculture. This study investigated the digestate produced from Anaerobic Digestion (AD) process through analyzing samples at specific times from digestate to estimate the nutrients concentration. The elements percentages of the macronutrients and micronutrients in digestate were evaluated, at different times for different feedstock.

Eighteen typical biogas units each of 250 liters in volume were used to digest six combinations of feedstock (three replications of each feedstock type) for 50 days period. The feedstock combinations used were manure of cows, manure of sheep and goats, manure of poultry chicken, olive waste, combination of olive waste and cow manure and Kitchen residues. A daily feeding volume of 4.25 litters was mixed with water at a ratio of 1:1 and then entered to the biogas unit. The starting date of digestion for all biogas units was on, Sep. 12th 2013; ninety samples collected every 10 days.

Using of digestate as fertilizer solves environmental problems of manure and organic wastes, and saves costs to farmers because they utilize their available resources. The digestate reduce manures and organic wastes

pathogens and of weed seeds during AD process so this improves safety on farms. Using of digestate as a fertilizer is limited in Palestine due to the lack of information about its qualities and it is advantages.

There was significant increase in the pH and macronutrients concentrations after digestion, this increase varied according to the type of feedstock. For the pH, the largest increase occurred in kitchen combination (6.57%) and the smallest increase occurred in cow combination (3.02%). For nitrogen, the highest percentage of nitrogen concentration increase was for poultry combination (13.88%) and the lowest for kitchen combination (11.10%). For phosphorous, the highest percentage of phosphorous concentration increase was for kitchen combination (16.8%) and the lowest was for olive combination (10.18%). For potassium, the highest percentage of potassium concentration increase was for cow combination (13.17%) and the lowest for olive combination (8.25%).

There was a small increase (not significant) in magnesium, magnesium and chlorides concentrations. There was a little increase (not significant) of calcium concentration and a little difference of iron, manganese, zinc, copper and molybdenum concentrations during digestion.

The best time to use digestate was found to be after 40 days .In average about 98% of changes of nutrients concentration occurred after 40 days. The changes of nutrients were from (65 to 80%) of total nutrients concentration after 30 days. Storage is required before digestate is applied to crops during the growing season. The most important issue in storage digestate is covering the storage because this protects nutrients from losses

through ammonia emissions. Digestate must be applied during the growing season in order to ensure the optimum uptake of the plant nutrients and to prevent ground water from pollution. Digestate must be applied at certain amount and special equipment.

Government support for farmers is required to establish biogas units and raise awareness among farmers to get the benefits of biogas and digestate. Agricultural researches are needed to clarify the needed nutrients for each type of soil and crop, the best combination of digestate for each crop type, the better method to applying digestate as fertilizer, monitoring crops growth during applying digestate and leakages of nitrogen.

This research was done in autumn (September and October) when temperature ranged from 22 to 26 ^{o}C. If temperature gets more or less, as in summer and winter, many parameters will change according to temperature so research is required in other season of the year.

Chapter One
Introduction

1. Introduction

1.1 Background

With increasing population around the world, problems associated with waste disposal increase, organic materials waste form higher ratio of waste (between 50-60 % of waste in Palestine). Because of that, special attention should be given to organic materials waste. There are many methods to get rid of organic wastes such as disposing to land fill, incineration and anaerobic digestion (AD) to produce energy and fertilizers. Organic waste dumping is not preferable nowadays because of many environmental problems of dumping them; also incineration is costly and difficult in applying specially in developing countries. Governments nowadays use prevention, reduction and reuse of waste in waste management.

The best method to get rid of organic materials is the use of AD process to break down the organic matter, recovery of biogas generated in the process and also to use the digestate as fertilizers. [1]

The use of fertilizers is going to be essential, because of increasing of population and growing need for food from agriculture. The industrial fertilizers have many problems and not sustainable. Using AD process to produce energy and fertilizers is one of the most sustainable methods to provide lands with biological fertilizers and also to produce energy.

Digestate produced from AD process has the nutrients needed for plants and good biological fertilizers. The use of digestate as a fertilizer is limited in many countries (especially Palestine) because of limited knowledge and available technology. Researches and quality managements are needed to

expand the use of digestate as fertilizers. Digestate quality management is performed through several instrumentation such as: criteria of digestate quality, digestate performance systems, nutrient laws and most essential through sustainable quality control practices along the total digestate production cycle. [1]

This study is focused on quantitative and qualitative assessment of nutrients of digestate in biogas plants where animal manures and slurries are the principal feedstock. In this study, different types of organic material would be processed by AD in constant time and volume. Samples of digestate would be taken at different times during digestion. Comparison and notice of quantitative and qualitative change would be done as illustrated through study.

1.2 History and definitions

Digestion is a process by which organic matter is hydrolysis and transformed due to chemical reactions and so it can be taken by the cells of microorganisms and used to keep body functions. During digestion, organic materials are reduced by hydrolytic enzymes, protease, and lipase excreted by glands of microorganisms. [2]

In final stages of AD process specific types of microorganisms are used in breaking down organic compounds and converting them into biogas which is a mixture of carbon dioxide and methane, and digestate which could be used as a good fertilizer. [3].

Nowadays, the developments of technology in AD throughout the world are in the option to get rid of industrial organic wastes and wastewater. The

new designs of the AD systems consider the requirement for small hydraulic retention times, higher retention of biomass, smaller reactor volume and higher loading rates. The municipal benefits of using biogas plants are in minimizing odor and the volume of digestate produced, as well as disinfecting the residue. Using AD process to the treatment of organic waste has many new challenges because of the variety in organic material and the area limitations where such instruments would be existing. The organic fraction of Municipal Solid Waste (OFMSW) may include agricultural, food, shed waste, or paper in varying concentrations, sizes, and composition. Moreover, MSW is polluted with non-organic materials, such as glass and metal, and so there is a need for pretreatment to isolate the organic waste. [4].

Future perspectives of AD as MSW management planning depend on many parameters ranging from environmental concerns to economic considerations: technology efficiency, minimizing biogas plant operation costs and high stable biogas output. It appears that AD technology will continue to play an essential function to dispose MSW organic material in other countries. However, the use of AD process in MSW is still limited in Palestine. [4].

1.3 Research question

- Is it technically feasible to use the digestate from biogas process as a fertilizer in Palestine?
- What are the percentage of macronutrients and micronutrients in digestate?

- At what time the digestate could be used as fertilizers?
- How can we use digestate as a sustainable source of nutrients?

1.4 Research objectives

The overall objective of this study is to analyze the digestate produced from AD process by taking samples at specific times from digestate and show its nutrient contents. Then, evaluate the elements percentage of the macronutrients and micronutrients (the elements percentage of main and secondary components of fertilizers) in digestate. This evaluation has to be done for different feedstock and combinations of feedstock to compare the results. The samples proposed to be taken after different times to inform the farmers at which time the digestate could be used as fertilizers. Then to illustrate how digestate can be used as a sustainable source of nutrients.

1.5 Significance of this research

More recently, the focus in the development of manure and digestate processing techniques has turned into techniques that recover a maximal amount of the present nutrients (N, P and K). This development is caused by the increasing worldwide awareness of the depletion of phosphorus and potassium, which are nowadays extracted through mining.

In this research the residue of AD process will be discussed for use as fertilizers. While the synthetic fertilizers had high cost, the fertilizers from AD process are cheap and feedstock is available for it. In addition to that, the research will assist farmers on knowing when the digestate could be

used as fertilizes. Significance is to dispose organic waste in a safety manner to producing fertilizers and energy.

1.6 Research approach:

To achieve the objectives of this study, the elements percentage of nutrients should be determined. To do that, 18 biogas units each of 250 liters volume is constructed with a different feedstock for each replication (three replications for each feedstock type). Then considering the retention time and organic feeding system, samples would be taken from each biogas unit at specific time. Testing of samples would be done using different instruments and methods. Final step is to compare and discuss the results.

Chapter Two

Literature Review

2. Literature Review

2.1. AD Strategy

2.1.1. Definitions

It is the microorganism procedure in which they break down organic substance, with the absence of oxygen, into biogas (a combination of carbon dioxide (CO_2), methane (CH_4) and small amounts of other gases) and digestate. The biogas can be used as fuel which creates power and energy producing heat, or electricity.

The digestate could be used as a fertilizer to increase the nutrient contents of soil and to optimize soil properties. AD process was known and applied over a hundred years ago in the UK for the treatment of sewage sludge. Nowadays, it has been used for the treatment of almost all organic types. [5]

The most organic substances commonly used in biogas plants are:

- Animal manure and their waste.
- Agricultural waste and residue.
- Organic waste from industries residue (plant and animal origin).
- Kitchen waste (vegetable and animal origin).
- Sewage sludge from waste water.[1]

2.1.2. Microbial Aspects of the AD process

Digestion of organic materials could be divided into four stages, which are hydrolysis or liquefaction, acidogenesis, acetogenesis and methanogenesis (see figure 2.1). These stages are a chain of Overlapping reactions

proceeding spatially as well as temporally in sequent and parallel steps and so, affect one another.

Hydrolysis is a process where complex macromolecular organic matter consisting carbohydrates, proteins and fats is subject to enzymatic dissolution and converted to monosaccharides, amino acids and long chain fatty acids (LCFA). Anaerobic fermentation finally Result from acidogenesis, acetogenesis and methanogenesis via intermediates and by products to biogas production (CH_4, CO_2).

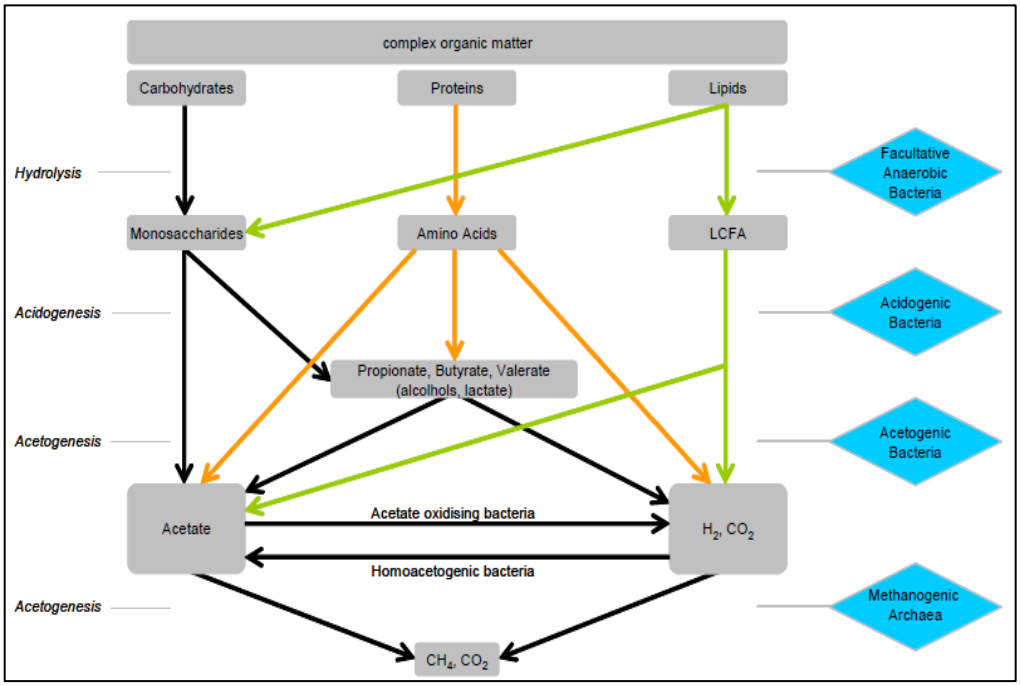

Figure 2.1: Main stages and steps of anaerobic digestion. [6].

2.1.2.1. Hydrolysis

Because the organisms could not be dealing with complex organic polymeric materials unless they are be in simple soluble compound, anaerobic digestion begins with the hydrolysis stage in which the organic compounds became simpler and more soluble intermediates which could then inter into the cell via membrane [7]. When these simple compounds

inter the cell they are used to supply energy and to synthesize cellular components. This stage is also named by liquefaction as the digestion processes involve the dissociation of water.

Hydrolytic reactions which include two steps are motivated by outer cellular enzymes excreted by bacteria which are making the anaerobes to work. In the first step a bacterial settlement takes place where the hydrolytic bacteria cover the surface of solids. Bacteria on the flake surface emit enzymes and create the monomers which can be used by the hydrolytic bacteria themselves, as well as by the other bacteria. In the second step the flake surface will be degraded by the bacteria at a constant depth per unit of time [8].

Emitted enzymes comprise cellulase, cellobiase, xylanase and amylase for degrading carbohydrates into simple sugars (monosaccharides), protease for degrading protein into amino acids and lipase for degrading lipids into glycerol and LCFA.

The reaction rate of hydrolysis depends on organic material itself,size, shape, surface area, concentration, enzyme production and adsorption. It is commonly found that hydrolysis is the slowest stage in digestion process when the substrate is in flake form while methanogenesis is the slowest stage for readily degradable substrate [8,12,17].

2.1.2.2. Acidogenesis

The stage come next of hydrolysis is named by acidogenesis (or fermentation) which is an anaerobic acid producing microbial process without an extra electron acceptor or donor [9]. The monosaccharides

and amino acids resulting previous stage are breaded down to a number of simpler products like volatile fatty acids (VFA) including propionic acid (CH_3CH_2COOH) and butyric acid ($CH_3CH_2CH_2COOH$) as well as acetic acid (CH_3COOH). However, the organisms oxidizing LCFA are wanted to use an external electron acceptor such as hydrogen ions or CO_2 to produce H_2 or format [6].

The degradation of monosaccharides (e.g. glucose) can occur in different pathways which leads to the development of different products (table 2.1) such as VFA, lactate, and ethanol with different production of energy. The controlling pathway depends on many factors like substrate concentration, pH and dissolved hydrogen concentrations. For example, for very high organic loads, lactic acid output will be significant. At pH greater than 5 the output of VFA is increased, whereas when pH smaller than 5 more ethanol is produced. At even lower pH (<4) all reactions may stop [6].

Table 2.1 Examples of different products from glucose degradation [6]

Products	**Reaction**		
Acetate	$C_6H_{12}O_6 + 2H_2O$	→	$2CH_3COOH + 2CO_2 + 4H_2$
Propionate + Acetate	$3C_6H_{12}O_6$	→	$4CH_3CH_2COOH + 2CH_3COOH + 2CO_2 + 2H_2O$
Butyrate	$C_6H_{12}O_6$	→	$CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$
Lactate	$C_6H_{12}O_6$	→	$2CH_3CHOHCOOH$
Ethanol	$C_6H_{12}O_6$	→	$2CH_3CH_2OH + 2CO_2$

However, hydrogen partial pressure has been having most influence on the fermentation pathway. At low partial pressures of hydrogen the fermentation pathway to acetate and hydrogen is preferable rather than

ethanol or butyrate formation. Thus, in a system where the hydrogen utilizing organisms (such as methanogens) preserve low partial pressure of hydrogen, the fermentation pathway to acetate and hydrogen give a share in the main carbon flow from carbohydrates to methane formation. However, higher VFA and alcohols are still produced constantly by the degradation of lipids and amino acids [10]. These products cannot be utilized instantly by the methanogens and must be degraded too in a next process that is named by acetogenesis [11].

Acidogenesis is often the fastest stage in the anaerobic transformation of complicated organic matter in liquid phase digestions. So, process failure in the anaerobic digestion of complex organic matter due to the influence of different toxic or restrained components leads to a hold of methane production and a collection of long- and short chain fatty acids [8].

2.1.2.3. Acetogenesis

The degradation of higher organic acids created in acidogenesis is an oxidation stage with no internal electron acceptor. Thus, the oxidizing organisms (normally bacteria) lack a supplemental electron acceptor such as hydrogen ions or CO_2 for the transformation to acetate, carbon dioxide and hydrogen [6]. This intermediate transformation is critical for the effective output of biogas, as these compounds cannot be used immediately by methanogens. Because of acetogens are force hydrogen creator and in the same time according to a low partial pressure of hydrogen, they keep a syntrophic (mutually beneficial) nexus with hydrogen exhaustion methanogenic archaea. This type of hydrogen transfer

where the methanogens work as a hydrogen sink allows the degrading reactions to complete. Syntrophy means "working together" and is a peculiar situation of symbiotic communion between two metabolically various types of microbial microorganisms which depend on each other for fermentation of a specific substrate, usually for energetic causes [10, 11].

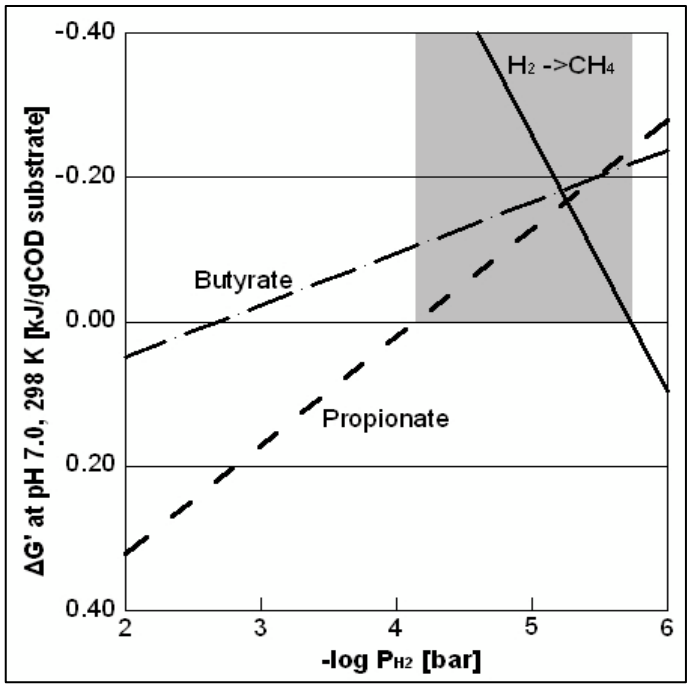

Figure 2.2: Thermodynamic (Gibb's energy $\Delta G'$) dependence on H_2 partial pressure. Calculations based on standard values for free energies at pH 7.0, 25°C [6].

Figure 2.2 shown low H2 partial pressure is primary for acetogenic reactions to be thermodynamically favorable ($\Delta G' < 0$), while hydrogen consumption methanogenesis comes more preferable at higher pressures. Therefore, these reactions can only take place with each other within a close range of very low pH2. The shaded area indicates the mathematical operating region for syntrophic acetogenesis from propionate.

An example of the free energy yield for the transformation of butyrate to acetate and methane is shown in table 2.2. The fermentation of butyrate to acetate is strongly unfeasible because it does a reaction which is endergonic under standard conditions, but is dependent on co-culture with hydrogen scavenging partner microorganism (hydrogenotrophic methanogens). The other reactions in table 2.2 supply a yield of energy which is half transported by the methanogens back to the acetogens. So, the overall syntrophic reaction is thermodynamically favorable with a small energy yield ($\Delta G' < 0$). The low energy yield affects negatively on the microorganisms growing and being sensitive to modification in organic load and flow rate. Acetogens are sensitive to environmental changes, and long periods are probable to be wanted for these bacteria to set to new environmental conditions [11].

Table 2.2 Energetics of syntrophic degradation [10,11].

Reaction			**$\Delta G°'$**
Acetogenesis from butyric acid: $2CH_3CH_2CH_2COOH + 4H_2O$	→	$4CH_3COO^- + 4H^+ + 4H_2$	[kJ mol^{-1}] 96 (2·48)
Methanogenesis from hydrogen:			
$4H_2 + CO_2$	→	$CH_4 + 2H_2O$	-131
Syntrophic reaction: $2CH_3CH_2CH_2COOH + CO_2 + 2H_2O$	→	$4CH_3COO^- + 4H^+ + CH_4$	-35

Acetogenic bacteria not solely gain from hydrogenotrophic methanogens, but also aceticlastic methanogens, like acetate removal has an effectuation on the energetics of VFA oxidizing reactions, particularly in isovalerate fermentation, where three molecules of acetate and just one molecule of

H_2 are created. Moreover, acetate accumulation may have a biochemical inhibitory impact on acetogenesis [12].

2.1.2.4. Methanogenesis

Through methanogenesis, the digestion outputs like acetate and H_2/CO_2 are transformed to CH_4 and CO_2 by methanogenic archaea that are firm obligate anaerobes. Other methanogens can grow on one carbon compounds like format, methanol and methylamine. In general methanogens are specialists in substrate use, as some of them can utilization only one substrate.

The archaea pertinent for anaerobic fermentation are generally divided into two groups: first one, named aceticlastic methanogens, split acetate into methane and carbon dioxide. The second one, named hydrogenotrophic methanogens utilised hydrogen as the electron donor and CO_2 as the electron acceptor to produce methane. Almost all known methanogenic types are able to output methane from H_2/CO_2, while only a few types of methanogens are believed to be able of using acetate as a substrate. But, it has been predestined from stoichiometric connections that about 70% of the methane formed in anaerobic digesters is come via the acetate pathway. The hydrogen pathway is more energy yielding than the acetate pathway, and is usually not rate limiting. It is, Nevertheless, of primary significance due to its capacity to keep the hydrogen pressure low in the system [11, 13].

Further, aside from methanogenic reactions, the inter-transmutation among hydrogen and acetate catalyzed termed by homoacetogenic bacteria also does an significant function in the methane forming pathway. Depending

on the external hydrogen concentration, homoacetogens can either oxidize or synthesize acetate which lets for contention with many different microbes, inclusive methanogens. As table 2.3 shown, the H_2 consuming by hydrogenotrophic methanogenesis is thermodynamically more favor than homoacetogenesis ($\Delta G°'<0$). Concerning acetate consuming, aceticlastic methanogenesis is too more favor than acetate oxidation. Hydrogenotrophic methanogenesis works more efficiently at high hydrogen partial pressure (figure 2.2), when aceticlastic methanogenesis is independent from hydrogen partial pressure. At high temperatures (> 30°C) the acetate oxidation pathway works more efficiently [12].

Table 2-3 Reactions related to methanogenesis (with standard temperatures) [10], [11], [12]

	Reaction			**$\Delta G°'$ [kJ mol^{-1}]**
Hydrogenotrophic methanogenesis Aceticlastic methanogenesis Acetate oxidation Homoacetogenesis	$4H_2 + CO_2$ CH_3COOH $CH_3COOH + 2H_2O$ $4H_2 + CO_2$	→ → → →	$CH_4 + 2H_2O$ $CH_4 + CO_2$ $4H_2 + 2CO_2$ $CH_3COOH + 2H_2O$	-135.0 -31.0 +104.0 -104.0

Hydrogenotrophic methanogenesis has been formed to be a main dominant process in the comprehensive scheme of anaerobic digestion. Its insufficiency will hardly affect the syntrophic acetogenic bacteria and the digestion process as an entire [10]. The collection of reduced digestion outputs in anaerobic digester is at most due to unsuitable elimination of hydrogen and acetate because of many Obstacles. For instance, high

organic load increases hydrogen and VFA production and the capacity of methanogens outputs in accumulation of VFA, or the decreasing in capacity of methanogens due to inhibition by toxic compounds or pH drop (<6) [12].

2.1.3. Main factors affecting the AD process

There are many factors affecting the steps of AD process and their efficiency of producing of biogas and digestate. Studying these factors is important to control and sittings the optimal range of this process during the AD process.

These factors are:

2.1.3.1. pH value:

Experiments of many biogas units show that to reach the optimal digestate production, the feedstock pH should be between 6 and 7 [11]. Also it is noticed that pH is different during the time of digestion, in the first step of digestion pH would be smaller than 5 because major amounts of organic matter would be in acid form [12]. This drop in pH would inhibits the digestion process because of methanogenic bacteria are very delicate to pH and do not work at pH below 6.5 [16].In spite of this, the digestion process continues and the concentration of biogas increases because of nitrogen would be digestion so pH will increase to above 8.Finally, when biogas production is stabilized, the pH range rest between 7.2 to 8.2. [17,18,19]

2.1.3.2. Temperature

There are three types of digestion depending upon temperature range, these are psychrophilic in which temperature range from (10-20°C), mesophilic in which temperature range from (20-42°C) and themophilic in which temperature range(43-55)°C [7]. The optimal temperature to digestion is 35°C, and when the temperature is less than 10°C digestion would be too slow or stop. [14,23].

2.1.3.3. Retention Time.

The Hydraulic Retention Time (HRT) is the time needed for organic material input to flow out from digester as digestate or digested compounds. The HRT is determined experimentally by examining the out flow of digested material, as measured by the COD and BOD of the exiting material. The HRT is dependent on many factors such as temperature, type of feedstock, volume of daily feedstock, volume of biogas unit and technology used. So that The HRT for specific biogas unit may be different from one day to another day or from one month to another month, table 2.1 demonstrates experimentally minimum HRT with different temperature. [21]

Table 2.1: minimum HRT with different temperature. [21]

Thermal stage Process	Temperatures(°C)	Minimum retention time (days)
psychrophilic	10-20	70 - 80
mesophilic	20 - 42	30 - 40
thermophilic	43 - 55	15 - 20

Often the HRT ranges from 15 and 30 days for dry feedstock and this time would be less with increasing moisture content of feedstock, the HRT may reach 7 days in the case of very high moisture contents(80%) of feedstock.

[23].The volume of biogas unit is a basic design parameter and directly influences the HRT. Minimizing of unitizes reduces the HRT, this results in cost saving and in getting digestate in less time.[16]

There are two experimental practices to reduce the HRT to get digestate in less time which is an important issue to farmers. The first practice is continuously mixing of organic; this helps the various types of bacteria to work faster. Other practice is to use large water content in feedstock, this will make the digestion more easy to bacteria and more quick. [21].

2.1.3.4. Organic Loading Rate.

The Organic Loading Rate (OLR) is the amount or mass of feedstock that would be put in biogas unit in specific time period (often one day) and per unit volume of biogas unit. This parameter affects microorganism's activation, amount of biogas production, CO2 production and stabilization of the system. [16]

When OLR is more, demand of bacterial consumption may cause undigested martial in effluent and loss amount of biogas and get digestate with less quality. Other disadvantage of high OLR is the excess growing of acidogenic bacteria which increases the acidity of the system in hydrolysis step, this hinders the next steps to work because the high acidity kills many of methanogenic bacteria. This may cause a failure in digestion system. [17]

2.1.3.5. Toxicity

It is industrial chemicals that when exist at high concentrations in the digestion system could inhibit the work of the system by inhibiting the

growing of bacterial. The most familiar toxicity forms are mineral ions, heavy metals and detergents. [6]

A small amount of mineral ions (e.g. sulphur, ammonium, magnesium, calcium, potassium and sodium) motivates growing of microorganisms while high concentration of it would have toxic effect. Detergents affect methanogenic bacteria and inhibit their growth. [21]

Detergents should not found in high concentrations with feedstock and toxic material should be illuminated before placing feedstock into system. [24].

2.1.3.6. Volatile fatty acids (VFA)

The VFA are intermediate compounds such as acetate, propionate, butyrate and lactate which found in system during acidogenesis step, and the VFA often have six carbon chains. [19]

Gathering of these compounds with time causes a problem because they influence directly pH dropping and so inhibit the work of microorganism. The accumulation of VFA depending on type of feedstock and HRT. Animals manure have more VFA than kitchen and agricultural wastes, and when HRT is smaller than accumulation of VFA would be more. If the concentration in a system is so high the digestion would be approximately stopped. [6]

2.1.3.7. Ammonia

Ammonia (NH_3) is an important compound for digestion process, also it is an important nutrient and essential as a fertilizer for plants. It is often found

as gas and it has severe smell. The main origin of NH_3 is the protein of organic materials. [20]

High concentrations of ammonia (especially free ammonia) in a system are the main factors of process inhibition, concentration of ammonia depending on the type of feedstock. Feedstock from animal origin has more ammonia concentration in digestion system. [16]

Experiments show that ammonia concentration should not be more than 80 mg/l, because methanogenic bacteria inhibit at this concentration. The concentration of free ammonia depends on temperature, so when temperature increases the free ammonia increases. Free ammonia is the main problem of themophilic digestion. [21]

2.2. Biogas Plants

Biogas plants are constructed units in which AD process take place. There are many types and forms of biogas units; they could be also named as bio-digesters, microbial reactors, bio-reactors or anaerobic reactors.

The basic purpose of biogas plants is to contain the organic material of feedstock and microorganisms for digestion process work and biogas and digestate produced in good quality. [25].

2.2.1. Biogas technology in the world

The first biogas unit was constructed in Guangdong in 1929 by Lou's and was approved by the industry and commerce ministry in 1930. From that time biogas units were developed with time by organizations and institutions.

Luo setin Shanghai China a company for gas, and then biogas technology was traded in the beginning of 1930s, this company made training courses to farmers and people, so this helped the spread of biogas technology. [26].

Nowadays concern in biogas has increased because of interest in clean and renewable technology. Biogas technology is the best solution to get rid of organic waste and animal manure in clean and economical manner. Biogas units spread widely in the world, there are millions of home units in china and India which provide energy for cooking and lighting, in Europe and North America many thousands of agricultural units are used to provide energy and fertilizers to plants. [1].

2.2.2. Main applications of AD process

2.2.2.1. Agricultural biogas plants

The agricultural biogas plants are the biogas units that receive feedstock from agricultural origin. The main feedstock used in these plants are animal manure and slurries, agricultural plants and vegetable residue, food and kitchen waste and other organic waste of industries. Animal manure is the main feedstock of this type of plant. [1]

These digestion units have abundance benefits for farmers which are:

- **Economic benefits**

  Production of biogas is of economic benefits for farmers, they use biogas for cooking and lighting, and if the amount of feedstock is large then biogas could be marketed and return money to farmers. Another economic benefit is to get rid of agricultural wastes without any cost.

❖ **Digestate is a good fertilizer**

In addition of energy, biogas plants produce digestate which is rich in nutrients for soil such as nitrogen, potassium, phosphorus and others.

❖ **Closed nutrient cycle**

The main cycle of elements that digestion achieve is carbon cycle, when biogas unit release biogas (mostly combination of methane (CH_4) and carbon dioxide (CO_2)) methane is used to produce energy and carbon dioxide is released to atmosphere, then carbon dioxide taken by plants to complete process of photosynthesis. There are amounts of carbon compounds that remain in digestate which are beneficial for soil as nutrients. Other cycle elements digestion could achieve are: nitrogen, potassium and phosphorus.

❖ **Flexibility to use different feedstock**

Farmers have flexibility to use feedstock; there is no limit to use any organic material as feedstock.

❖ **Veterinary safety**

It is obvious that dealing with digestate is more safe comparing dealing with raw feedstock. During digestion process almost all harmful pathogens due to high temperature of the system, high pressure which can also inactivate the weed seeds. [1]

2.2.2.2. Waste water treatment plants

AD process is commonly used for handling of sludge in primary and secondary steps resulted from aerobic treatment of municipal waste water. This process is applied in many waste water treatment plants with

combination to AD process to eliminate and reduce the amount of sludge and get energy and fertilizers. For example in most European countries between 30 and 70% of sewage sludge is handled by AD process, depending on demand and properties of sludge. The treated sludge by AD process could be used as fertilizers or to produce energy by incineration.[1]

2.2.2.3. Municipal solid waste (MSW) treatment plants

The traditional disposal of municipal solid waste around the world is collecting solid waste without sorting to be buried in special landfill or burned by incinerators. This work is a waste of nutrient and energy, because organic materials could be separated and used as feedstock to AD process to get energy.

Advanced municipal solid waste treatment had technology to separate types of wastes; the percentage of waste type is basic determination of the disposal technology of waste. The most important types of waste that determine the technology used is organic material type because high percentage of organic waste could create problems in waste disposal. Organic waste collected often too wet so it is considered good feedstock for AD process. It is rarely used for aerobic composting. On the opposite side wood material or organic waste that contain high proportions of lignocelluloses material are suitable for composting or it should treated before used as feedstock of AD process.

There are many advantages of AD process in (MSW) treatment plants, energy and nutrients could be obtained from AD process and reduction the amount of leachate through landfill. [1]

2.2.2.4. Industrial biogas plants

Industrial wastes could have good percentages of organic matter especially those which deal with food and animal origin, also waste water from industries could be used as feedstock for AD process. Most AD plants need pre-treatment to their waste before used as feedstock, industrial biogas plants have new concern in Europe and they are rarely spread around the world. [1]

2.2.2.5. Landfill gas recovery plants

Landfills can be considered as large anaerobic plants but the difference here is that the digestion process is limited in time according to the age of the landfill. Landfill gas has properties approximately the same as biogas in AD units, but it may have toxic gases which come from different chemical reactions in the landfill.

Recovery of landfill gas is important for environmental protection and reduction of emissions of methane and other landfill gases and avoid of burning in landfill and safety, also it is a source of energy to use to light the landfill or to sell if the landfill is a big one. [1]

2.2.3. Biogas plants types

2.2.3.1. Size types

Biogas plants can classified according to their size as follows:

- **The family - size units**

  These units are the widely spread units globally. These units can obtain feedstock of organic wastes of approximately four animals and kitchen

waste and municipal waste for eight persons' family. One unit enough to produce biogas for this family size to cooking purposes and it gives fertilizer for about 81 donums.

- **The community - type units**

  These units are larger in volume than family units, many families could be partners in one unit, and this unit can receive organic waste of animal or kitchen origin. It could be found in schools, hospitals, companies or in small industries. These units often face some problems concerning with operation and maintenance.

- **The large - scale systems**

  These units are larger in volume than community units, they are used when there are large numbers of animals in farms and huge organic waste. In these units often combined with electric generator for lighting and operating houses in villages or using the energy for other purposes such as cooking and car fuel. [27].

2.2.3.2. Continuity types

Biogas plants can be classified according to their times and types of take feedstock as following:

- **Continuous digester**

  In these plants, the unit receives daily or regular feedstock, the effluent of the unit is the same quantity of organic have digested and out regularly from unit. This type is given excellent and homogenous digestate, and high quality biogas, also this type take the organic waste

daily and we do not need to collect the waste, this avoiding odor problem.

❖ **Batch digester**

In these plants, the unit receives all amount of organic feedstock once and fills the digester; the effluent of the unit is then removed once after digestion takes place.

❖ **Semi – continuous digester**

In these plants, the unit receives regular or once feedstock, the effluent of the unit is taken once or regularly as farmers need.

These three plant types required continuous good monitoring and maintenance because they are sensitive to the circumstances surrounding and basic properties (especially pH and total solids). [28].

2.2.3.3. Design types

Biogas plants can be classified according to their design, there are many design types of reactors the following are examples and figures of the most commonly spread:

❖ **Floating drum digester**

This digester is constructed under-ground by stones and has a gas-holder. The gas-holder move manually or mechanically (free movement) and it is storing and collecting the gas produced in process. It is going up or down according to gas pressure collected. Floating drum digester sketch is given in figure 2.6. [27]

❖ **Fixed dome digester**

This digester is constructed under-ground by stones, it was designed in 1936 in china. Its components are an inlet trough, a down digestion reservoir with, storing dome capping which has free movement as shown in figure 2.7.[27]

❖ **Deenbandhu model**

This digester is constructed under-ground by stones or concrete. The main components of a Deenbandhu biogas plant is digester spherical tank connected with input and output storage, digester connected with pipe that is considered as an exit of gas. Deenbandhu sketch is given in figure 2.8. [27]

❖ **Bag digester**

This type of digester is constructed under-ground or on-ground by stones, concrete or plastic material. This type is widely used for domestic use. Bag digester sketch is given in figure 2.9. [27]

❖ **Plug flow digester**

The components of this reactor are a mix tank which makes formation process faster, a digester tank, an effluent storage for digestate, biogas inlet. Plug flow digester sketch is given in figure 2.10. [27]

❖ **Anaerobic filter**

This type of reactor used mainly for waste water treatment. Its sketch is given in figure 2.11. [27]

❖ **Up flow anaerobic sludge blanket**

This type of reactor used mainly for waste water treatment. Its sketch is given in figure 2.12. [29].

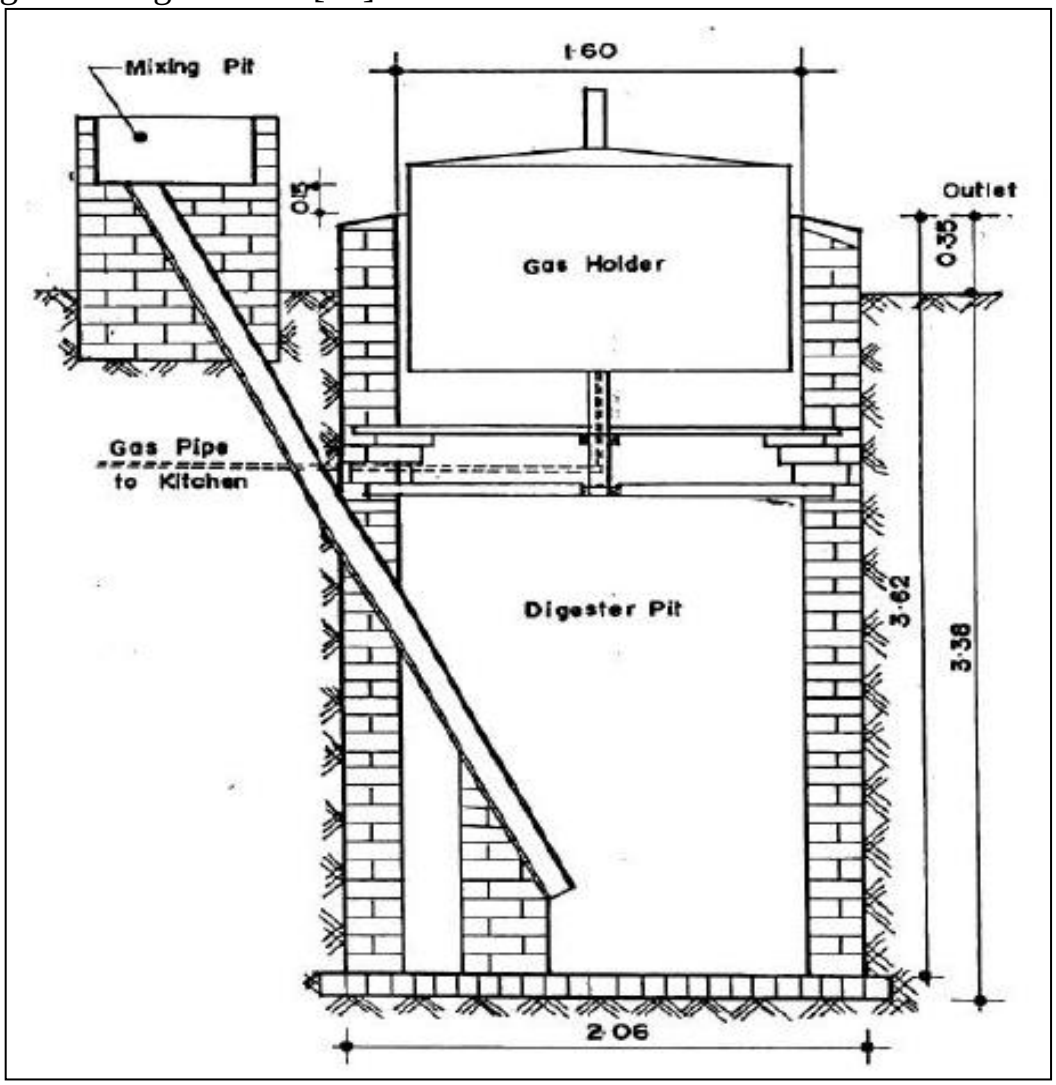

Figure2.6: Floating drum digester [27]

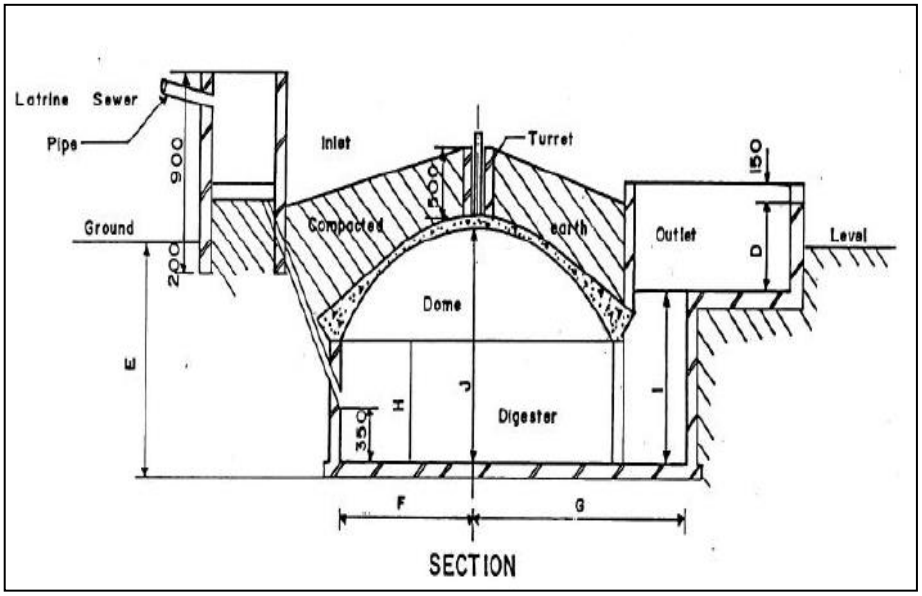

Figure 2.7: Fixed dome digester [27]

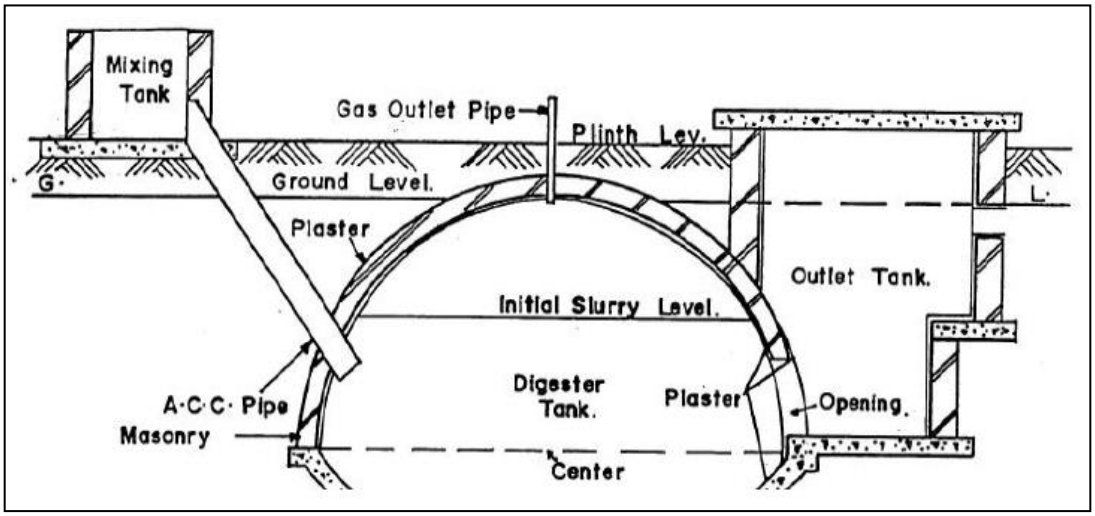

Figure 2.8: Deenbandhu biogas plant [27]

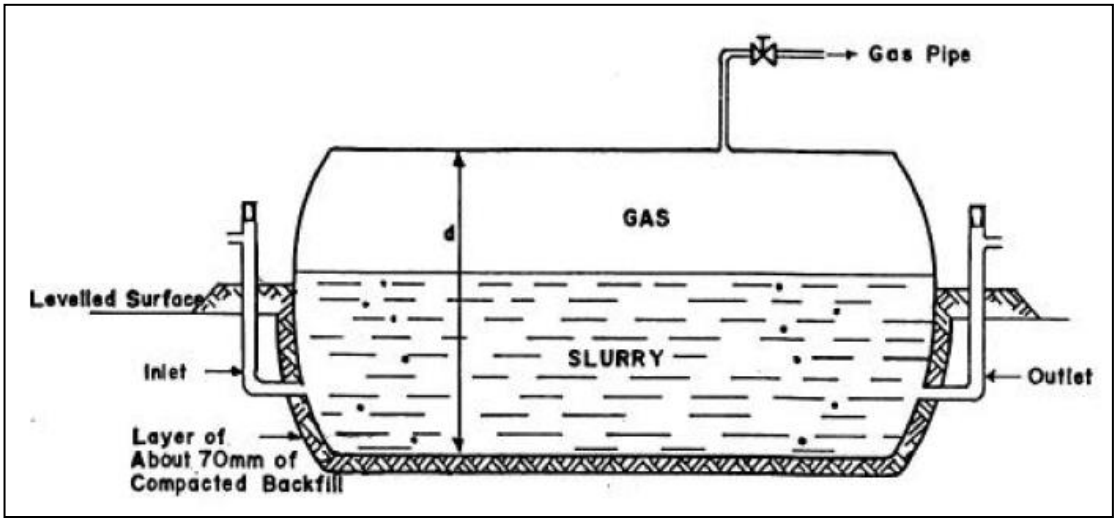

Figure 2.9: Bag digester [27]

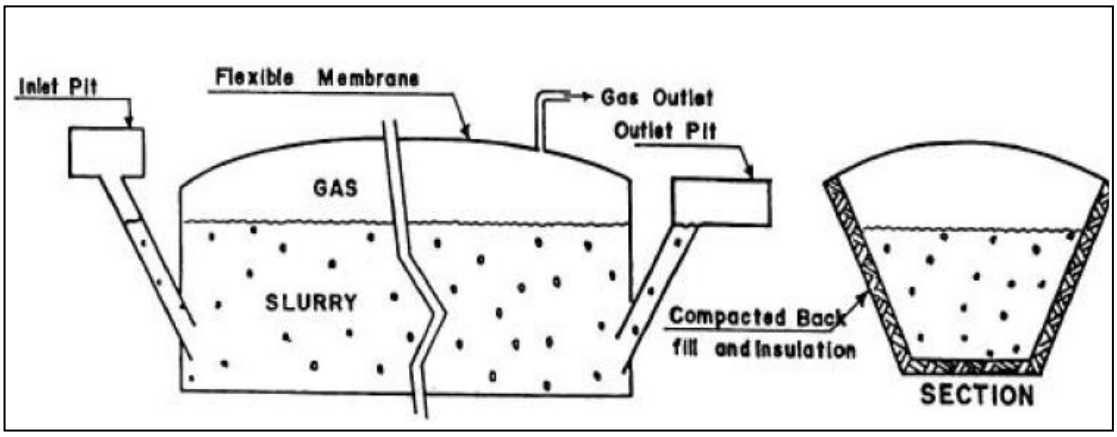

Figure 2.10: Plug flow digester [27]

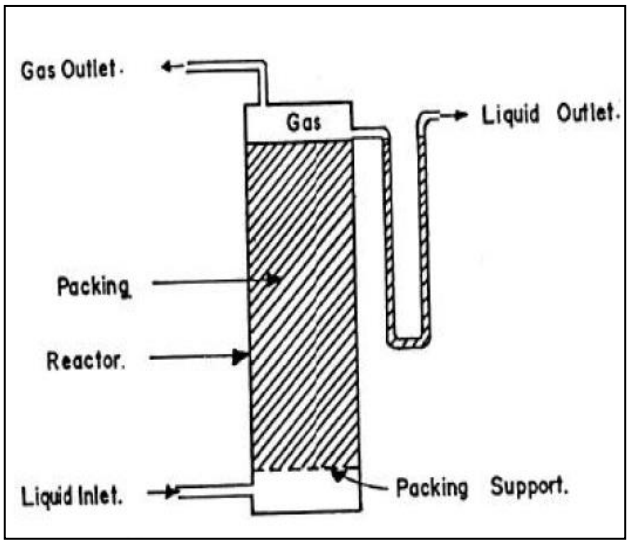

Figure 2.11: Anaerobic Filter [27]

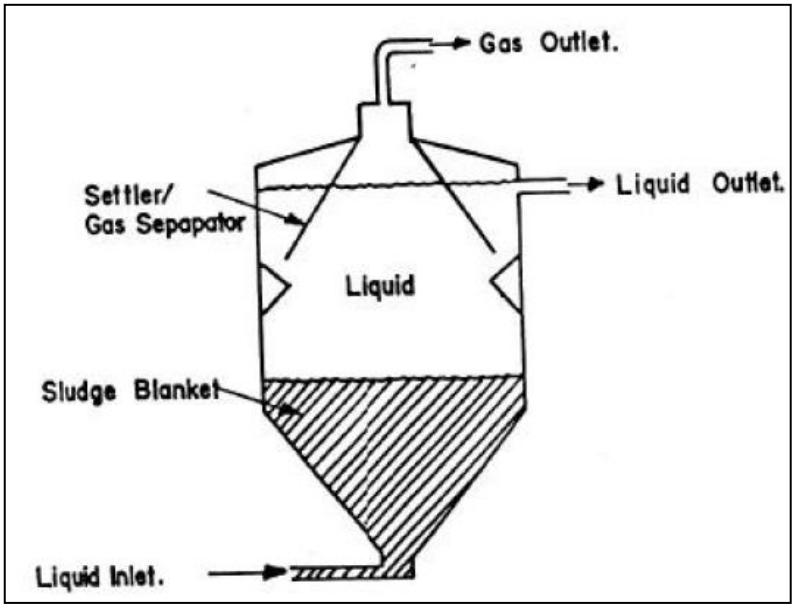

Figure 2.12: Up Flow Anaerobic Sludge Blanket [27]

2.2.4. Main factors influencing the selection of biogas design

There are many types and designs for reactors, these factors should be taken into consideration when selecting the biogas design, these main factors are:

- **Economy:**

  Economy in selecting the type of design is important, construction cost is the main cost in the design and it should be selected such that cost-benefits of the project are taken into consideration.

- **Availability of local materials:**

  Materials available in local place should be taken into consideration to have an economic and practical project.

- **Sustainability:**

  A question should be asked on how long that reactor will work. The answer to this question needs specific analysis to select the most cost effective and sustainable design.

- **Suitable design for the type of inputs:**

  The design should take into consideration the feedstock types, the plant materials which are affected with input types. The size of reactor should be designed in a way that is consistent with organic material produced. [27].

2.3. Feedstock

2.3.1. Feedstock used in AD process

The organic materials that could be used as feedstock to AD process were published in European Waste Catalogue in 2002; table 2.4 shows "the Codes for “bio wastes” suitable for biological treatment according to the European Waste Catalogue".

Table 2.4: "The Codes for “bio wastes” suitable for biological treatment according to the European Waste Catalogue"[1]

Waste code	Waste description	
02 00 00	Waste from agriculture, horticulture, aquaculture, forestry, hunting and fishing, food preparation and processing	Waste from agriculture, horticulture, aquaculture, forestry, hunting and fishing
		Waste from the preparation and processing of meat, fish and other foods of animal origin
		Wastes from the fruit, vegetables, cereals, edible oils, cocoa, tea and tobacco preparation and processing:

		conserve production; yeast and yeast extract production, molasses preparation and fermentation
		Wastes from sugar processing
		Wastes from the dairy products industry
		Wastes from the baking and confectionery industry
		Wastes from the production of alcoholic and / nonalcoholic beverages (except coffee, tea and cocoa)
03 00 00	Wastes form wood processing and the production of panels and furniture, pulp, paper and Cardboard	Wastes from wood processing and the production of panels and furniture
		Wastes from pulp, paper and cardboard production and processing
04 00 00	Waste from the leather, fur and textile industries	Wastes from the leather and fur industry
		Wastes from the textile industry
15 00 00	Waste packing; absorbents, wiping cloths, filter materials and protective clothing not otherwise Specified	Packaging (including separately collected municipal packaging waste)
19 00 00	Waste from waste management facilities, off site wastewater treatment plants and the preparation of water intended for human consumption and water for industrial use	Wastes from anaerobic treatment of waste
		Wastes from wastewater treatment plants not otherwise specified
		Wastes from the preparation of water intended for human consumption or water for industrial use
20 00 00	Municipal wastes (household waste and similar commercial, industrial and institutional wastes) including separately collected fractions	Separately collected fractions (except 15 01)
		Garden and park wastes (including cemetery waste)
		Other municipal wastes

The widely organic materials used for AD process are:

- Animal manure.

- Plants residue, vegetables and agricultural wastes.
- Waste water and organic wastes of human origin
- Organic kitchen waste of food origin
- Pieces and waste of animals in Slaughterhouses.
- Industrial residue of food, animal and plants origin
- Sewage sludge from waste water treatment plants. [1]

2.3.2. Feedstock properties

The most familiar feedstock used are animal manure and organic fraction of municipal solid waste, the nutrients contents in animal manure mostly depending on what they eat.

2.3.2.1. Manure of cows

Cow manure, that is often a dark purple color, is usually used as agricultural fertilizer. If it not reused as soil fertilizer, by soil organisms such as earthworms and dung beetles, it can dry out and lie on the grassland. In many countries caked and dried cow manure is utilized as fuel. Cow manure supply food for a many animals and fungus types.[30]

2.3.2.2. Manure of sheep and goats

Goat manure is drier than cow manure. It has fewer odors and is easier to work with and spread. Goat manure is higher in nitrogen than cow manures, it has approximately 10 kilograms of nitrogen in 1 ton but cow manure has approximately 4.5 kilograms of nitrogen in 1 ton. Cow manure may have weed seeds due to eat grass and hay. Composting or digestions of the manure help to break down these seeds. [30]

2.3.2.3. Manure of poultry chicken (Laying hen)

Poultry are good source of eggs and meat which main source of animal protein to people everywhere the world. Due to Increased demand on animal protein and the ease of breeding chicken, many countries adapted intensive poultry production. Layers are active egg producers. Chosen and hybridization mechanisms have resulted in productive laying hens producing 15 – 19 kg of eggs per year. Often two stages of production are familiar: (1) growing stage up to approximately 140 days; and (2) productive stage from 140 – 560 days. The big amount of chicken waste cause soil, water and air pollution. Most effects are caused by the transport from manure of nitrogen (N), phosphorus (P) and heavy metals (Zn and Cd). Release of these from manure occur in the chicken houses, during storage, after spreading on soils or when manure is simply get rid of. [30]

2.3.2.4. Olive solid waste

Solid and liquid OMW (olive mill wastes) are dark-colored wastes and contain large amounts of organic materials. They are consisting of several complicated substances that are not easily dissociation. Bad odorous released from OMW during production due to strongly volatile compounds. OMW affected negatively on water resources and soils, so special procedure should be done to get rid of OMW. [31]

2.3.2.5. Kitchen organic residues

Kitchen residues include the following:

- Fruit and vegetable scraps

- Food leftovers, plate scrapings
- Meat, fish, bones
- Dairy products, eggs, eggshells, butter
- Bread, cereal, grains, baked goods and ingredients
- Pasta, pizza
- Coffee filters and grounds, tea bags
- Nuts and shells, herbs, spices
- Solidified grease and fats
- Soiled paper towel and tissue
- Used paper cups and plates [30]

2.3.2.6. Nutrient content of farm livestock manures

It is known that animal manures are good sources of nutrients and organic materials that soil needed. Nevertheless, for credible fertilizer application it is needed to know the nutrient content of the manures. [32] Table 2.5 shows the nutrients average content for different types of animal manure in Asia.

Table 2.5 nutrients average content in slurry and manure for different types of animals manure in Asia (g/kg). [30]

Manure type	Note	Dry mater (g/kg)	N (g/kg)	NH_4^+-N (g/kg)	P (g/kg)	K (g/kg)	Mg (g/kg)
Slurry							
Pigs	Average	51	4.8	3.5	0.9	2.7	0.6
	range	15-92	1.2-8.2	1.9-6.1	0.13-2.2	0.5-6.6	0.1-1.8
Sow and piglets	Average	50	4.2	2.5	1.3	3.6	0.66
Fattening pigs	Average	90	7.2	4.2	1.8	6.0	1.08
Poultry	Average	170	11.1	5.2	3.9	4.4	1.7
	range	10-300	2-18	1.9-7.8	0.39-6.5	2.1-7.5	0.2-3.6
Laying hens	Average	145	10.2	5.8	3.4	5.3	1.3
Cattle	Average	60	3.0	1.5	0.5	2.9	0.4
Cattle	Average	86	4.4	2.2	0.7	5.1	0.78
Solid manure							
Pigs	Average	243	6.9	2.2	2.4	5.4	1.6
	range	150-330	3.5-11	0.5-6.0	0.74-6.5	2.3-13.3	0.9-2.5
Pigs and straw	Average	230	7.5	1.5	3.9	2.9	1.5
Laying hens	Average	406	23.6	10.9	7.2	8.9	3.1
	range	220-550	5.1-25	37-60	3.5-11.8	5.0-12.5	1.2-6.0
Laying hens	Average	515	24.1	2.4	8.2	18.8	2.9
Broilers	Average	605	30.5	5.5	7.4	18.7	3.9
	range	450-850	21.8-40	2.0-15	3.0-10.9	5.6-19.1	2.5-6.5
Broiler litter	Average	605	30.5	5.5	7.4	18.7	3.9
Cattle FYM	Average	250	6.0	0.6-1.5	1.5	6.6	0.4
Cattle FYM	Average	248	6.4	1.2	1.8	7.3	1.3

2.4. Digestate

2.4.1. Digestate definition

Digestate is the effluent of AD process; digestate can be used as fertilizer because it has many nutrients that plants need. Digestate consists of material that indigestible organic material and dead bacteria and its wastes.

The volume of feedstock is reduced approximately 5-10 % of the basic volume. Digestate use as fertilizer is more suitable than raw manure and synthetic fertilizer, comparisons between these types of fertilizer are illustrated in the next sections. [33]

2.4.2. Composition of digestate

The components of a digestate is depending on the digestion process itself and the composition of Digestates subsequently the agricultural utilization and activity of the resultant materials could be dissimilar. But, several connected principles could be found in the pathway of the digestion process that assists to evaluate the results of a digestion process.

2.4.2.1 pH of digestate

Usually, the pH of digested organic material is alkaline (see table 2.6). [34].

Table 2.6 Changes of the pH in different digestion systems [35,36].

Type of ingestate	Type of digestion process	pH of ingestate	pH of digestate
Pharmaceutical industry sludge	mesophilic, solid type digester	7.0	7.8
Cattle manure	mesophilic, liquid type digester	6.9	7.6
Primary sludge from municipal waste water treatment plant and organic fractions of municipal solid wastes	thermophilic (co-digestion), liquid type digester	3.58	7.5
Energy crops, cow manure slurry and agro- industrial waste	thermophilic (codigestion), liquid type digeste	4.8	8.7
Energy crops, cow manure slurry, agro- industrial waste and OFMSW	thermophilic (codigestion), liquid type digester	4.0	8.3

2.4.2.1. Macronutrient content of digestate

The macronutrient content of digestate also depend on organic materials type. Table 2.7 shows some characteristics for different digestates, however these are mean values which may be changed during the digestion process.

Table 2.7 Characteristics of liquid digestates from different origin [36,37,38,39,40].

Type of ingestate	Type of digestion process	Total-N (Nt)	NH4-N	Total-P	Total-K
Swine manure	Mesophilic	2.93 (g L^{-1})	2.23 (g L^{-1})	0.93 (g L^{-1})	1.37 (g L^{-1})
Liquid cattle slurry	Mesophilic	4.27 (% DM)	52.9 (‰ Nt)	0.66 (% DM)	4.71 (% DM)
Energy crops, cow manure slurry and agro-industrial waste	Thermophilic	105 (g kg^{-1} TS)	2.499 (g L^{-1})	10.92 (g kg^{-1} TS)	-
Energy crops, cow manure slurry, agro-industrial waste and OFMSW	Thermophilic	110 (g kg^{-1} TS)	2.427 (g L^{-1})	11.79 (g kg^{-1} TS)	-
Cow manure, plant residues and offal	mesophilic and thermophilic	0.2013 (%m/m, fresh matter)	0.157 (%m/m, fresh matter)	274.5 mg kg^{-1} (fresh matter)	736.45 mg kg^{-1} (fresh matter)
Clover/grass or pea straw or cereal straw or silage maize and clover/grass silage (mean)	mesophilic	0.253 (%m/m, fresh matter)	0.176 (%m/m, fresh matter)	0.62 (% DM)	18.5 (% DM)

The NH4 content of the digestate is approximately range from 60 to 80% of its total N content. In general, the NH4-N content is decreased by the decrease of protein content in feedstock [42] like animal by-products and

altar wastes [43]. The transformation of organic N to NH4-N lets its direct utilization by crops [44].

Digestate has Relatively high phosphorus (P) and potassium (K) content so it is appropriate for complements of these lost macronutrients in soils. [11]

2.4.2.3. Microelement content of digestate

Plants need small amounts of several heavy metals like copper (Cu), zinc (Zn), however some heavy metals like cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) are toxic for plants. The major origins of the heavy metals are animal feed additives, food processing industry, flotation sludge, fat residues and domestic sewage [45].

2.4.2.4 Organic matter content of digestate

The content of organic dry matter and the carbon content of digestate are reduced by the fermentation of degradable carbon compounds in the digestion process (see table 2.8) [39]. It is reported that the degree of organic matter (OM) degradation ranged between 10.9% and 38.5%. [43].

The sufficiency of digestate as soil improvement is depending on its modified OM content. Most OM is transformed into biogas, however the biological constancy of remaining OM was increased during AD with the increase of more recalcitrant molecules like lignin, cutin, humic acids, steroids, complex proteins [41].

Table 2.8 Changes in macromolecules content on the course of AD [36]

Type of ingestate	Total solid (TS) (g kg^{-1} ww)		Lignin (g kg^{-1} TS)		Hemicelluloses (g kg^{-1} TS)		Celluloses (g kg^{-1} TS)	
	Ingestate	Digestate	Ingestate	Digestate	Ingestate	Digestate	Ingestate	Digestate
Energy crops, cow manure slurry and agro-industrial waste	127	35	49	280	35	42	50	68
Energy crops, cow manure slurry, agro-industrial waste and OFMSW	143	36	72	243	27	54	71	79

2.4.3. Effects of digestate on soil properties

Digestate is a sophisticated material thus its using has wide influence on soil properties [38].

2.4.3.1. Effect of digestate on soil pH

It is reported that small change in the pH after four yearlong applying digestate [46]. It is assumed an increase of the soil pH due to the alkaline pH of digestates. The polycondensation, connection to organic and inorganic colloids and transformation of acids can have an effect also on the soil chemical properties and finally the decrease of soil pH , more particularly at the soils with high organic and inorganic colloid contents. So the regular control of soil pH is seeded in case of long term digestate application. [46]

2.4.3.2. Effect of digestate on soil macroelement content

As other fertilizers, the main problem of applying digestate is nitrogen losses. It is reported that the N leaching was dependent on the use of cover crops. This means that the use of cover crops is an suitable method to prevent N leaching and to requite for higher N application [37]

Digestate contains high ratio of NH4-N so it is expected to increase NH4-N content of treated soil. Generally, the digestate application does not cause any considerable changes in the total-N and available P content, while the available K content was increased by the application of biogas residue [47].

2.4.3.3. Effect of digestate on soil microelement

After the application of the digestate the Cd, Co, Cu, Ni and Sr content of soil solutions did not change. The Zn content decreased significantly, while the amount of manganese (Mn) increased by almost 40% [48].

The increasing soluble P content of digestate treated soil decreased the available Zn content in the soil solution by building small soluble zinc-phosphate remnant [48].

2.4.3.4. Effect of digestate on soil organic matter content

Digestate contains high amount of volatile fatty acid (C2-C5) which could be decomposed within few days in the soil [49]. The greatest rates of fermentation were observed in the first day after the treatment but the mineralization rate were high during the first 30 days. [38]

2.4.3.5. Effect of digestate on the microbiological activity of soil

The high amount of easy-degradable carbon increased the substrate induced breathing (SIR), which was promoted by the higher carbon content generated from the higher litter and root exudates of higher plant growth. In accordance with these results, the largest proportion of active microorganisms was found in the digestate treated samples [49].

Besides the macronutrient and micronutrient content of digestate which are important not for the crops but for soil microorganisms too, it contains growth promoters and hormones, also. [38]

2.4.4. Effects of digestate on crop yield

On the bases of the plant reaction on the digestate treatment, plants could be divided into the sensitive (alfalfa, sunflower, soybean) and the non-sensitive (winter wheat, triticale, sweet corn, silage maize) groups. In the case of sensitive plants the burning effect of digestate can be observed but it follows a strong and quick recovering process. For the non- sensitive plants the digestate can be used in any developmental stage. It is favorable, because in rainy period the digestate technically could not be applied [38]. The right application rate of liquid or solid digestate depends on the plant nitrogen demand. It should be applied when plant N demand arises. This time for non-legume scpecies is the late winter and spring [39].

2.4.5. Effects of digestate on the quality of crops

Digestate treatment seems to be very effective to increase the protein content of plants. It is reported that digestate used as supplement with rice

straw for preparation of mushroom beds. [50] Other reported that significant increase of protein content of treated soybean.

2.4.6 Legislation of digestate utilization in agriculture

Sustainable applying of digestate needs regulations, the used digestion methods and the monitoring of products. These regulation processes for the digestate are different in specific countries.

“ In Hungary, the digestate is regarded as other non-hazardous waste if the ingestate does not contain sewage or sewage sludge, while in the presence of these materials the conditions of the digestate utilisation depend on the quality of the given material. In Scotland the BSI PAS110:2010 digestate quality assurance scheme is applied. If a digestate complies with the standards for the quality, the usage criteria and the certification system stated in the worked scheme, the Scottish Environment Protection Agency (SEPA) does not apply the waste regulatory control for it. In Swiss the digestate which suits the limits, can be used as soil conditioner and fertilizer in “bio” agriculture. In Germany the origin of the input materials determines the quality label of digestate product by bio waste and renewable energy crops. Digestates have to fulfil the minimum quality criteria for liquid and solid types which determine the minimum of nutrients and the maximum of pollutions in the digestate. Pollutions mean toxic elements, physical contaminants and pathogen organisms. The quality of digestate products is regularly controlled by “Bundesgütegemeinschaft Kompost e.V.” (BGK) ” [52].

2.4.7. Other advantages of digestate

❖ **Bio-digestion of organic material**

AD process converts the organic material of animal and agricultural origin to inorganic material and biogas, the digestion period depends on type of feedstock and temperature. Digestate is a dense liquid which has rich nutrient content, it is easy to dealing, pumping and applying as fertilizer and do not need heavy equipment.

❖ **Reduction of odors**

Organic materials have bad smells because they contain compounds that have bad odors such as volatile acids, phenol and phenol derivatives. These compounds found in more concentration in animal manure than other organic materials. AD process reduces the presence of these compounds in digestate to approximately 80% of feedstock odor. Another advantage of digestate in reducing odors is the release of ammonia when digestate stored for a long period, so the odor would be reduced with time.

❖ **Sanitation**

AD process offer sanitation to digestate, pathogens such as viruses, bacteria and parasites become dead or inactive. The percentage of cleaning of digestate from pathogens depending basically on temperature and HRT of process, as temperature and HRT increase, sanitation increased. At enough HRT, the best purification obtained at temperature between 50 and 55°C, the percentage of pathogens that breaking down may reach 99%.

❖ **Destruction of weed seeds**

AD process can destroy weed seeds, as in sanitation the percentage of destruction of weed seeds depends basically on temperature and HRT of process. The seeds can lose the ability to germinate as a result of high temperatures and chemical reactions occurring in system. There are many types of seeds in organic materials, some types are easy to destroy and others are difficult. Experience show that time needed for the destruction of seeds is between 10 and 16 days.

❖ **Avoidance of plant burns**

Organic waste (especially animal manure) contains fatty acids which high concentration of it in soil may cause burning the plants leaves. Fatty acids such as acetic acid breaking down throw AD process, so burning of plants is avoided. Also digestate flow slowly by pipes to plants without harm to the plant. [33]

2.4.8. Comparison between digestate and raw manure

Raw manure of animals is the most commonly type of organic waste, traditional disposal of animal manure is spread manure on soil around plants. This practice has many disadvantages when applied as fertilizer, these are:

- Nutrients of manure may be seeped to groundwater and pollute it.
- Affecting negatively the soil structure and microorganisms in soil.
- Some plants may die or reduction in their growth or burning their leaves because of acidity compounds in manure.

- High amounts of methane and ammonia leakage that affect negatively soil structure.
- Worse smells and spread of harmful insects from manure storage and through application.
- Low safety because of pathogen growth and odors.

In digestate application as fertilizers the above problems are reduced through formation and chemical reactions occurring during AD process. [33]

2.4.9. Issues that should be taken into consideration during the application of digestate as fertilizers

The most important issue that should be taken into consideration is the problem of loss of nitrogen (the most important nutrient) through ammonia (NH_3) emission and nitrate (NO_3^-) leakage. To reduce or prevent this problem from occurring the following agricultural practices should be followed:

- Keeping the digestate away from unwanted movement and transportation.
- Use the digestate cool during application if it is possible.
- Move or transport the digestate as pressurized in pipes or pump it.
- Combine the digestate with soil if possible.
- Apply the digestate in the beginning of growth period or during Vegetative growth.
- The best time to apply the digestate as fertilizer is when the weather is cold, rainy, high humidity and no strong wind. [1]

2.5. Soil

2.5.1. Introduction

The main component of earth crust is soil; it is formation takes over millions of years via weathering, erosion, human and plants factors and others. These basic components come from different resources which form the soil types such as: alluvial soils that formed from residue and sediments from rivers and seas, and Aeolian soils that formed by wind.

The soil is important for plants, as it provides the area that roots extend in and supplying the plant with its basic needs. The main requirements are water and nutrients which are contained in soil according to its type and formation method. There are many nutrients that the plant utilizes from the soil when they are less than the demand, it will be essential to use fertilizers to cover the shortage of nutrients in soils. [53]

2.5.2. Soil Constituents, Texture and Structure

Soils consist of mineralogical particles that vary in size because of weathering. The particles of soil are sorted by their size into: gravel and stones (diameter is more than 2 mm), sand (diameter from 0.02 to 2.0 mm), silt (diameter from 0.002 to 0.02 mm) and clay (diameter is less than 0.002 mm).

Soil texture indicates the relative amounts or percentages of sand, silt and clay available in a soil. Soils are classified according to texture as sands, sandy loams, loams, clay loams, clays, etc according to proportions of sand, silt and clay in soil. Soil structure is how the soil particles are

combined or aggregated in larger aggregates. Soil structure could be classified according to strength as weak as “light” (e.g. sands and sandy loams), “medium” (e.g. loams) or “heavy” (e.g. clay loams and clay).

Soil structure is important for plants growth and the application of fertilizers. Sandy soils do not hold large amount of water and nutrients so when applying fertilizers it is necessary to take care of leakage of nutrients to groundwater. On the other side, clay soil can hold large amount of water and nutrient for a long time but this type of soil has low aeration, this problem could be reduced by adding organic material or limning. Organic matter improves soil structure thus it improves soil aeration especially for clay soils.

Cultivation and agricultural practice change the property and arrangement of soil structure, so applying fertilizers is needed when the soil has low contents of nutrients and organic matter. [53]

2.5.3. Organic matter in the soil

The main components of organic matter in the soil are fresh organic material and humus material. Fresh organic materials are residue organic material from animals, plants and humans that have not been broken down yet. When organic matter is decomposed by microorganisms that exist in soil, the plants could take the nutrients from the organic matter. The formation of stable organic material in soils is called humus or soil organic matter. The formation of organic matter provides soil with nutrients needed for plants and give the soil black color. Plants cannot take the nutrients

from fresh organic material because these nutrients are in organic form and plants absorb nutrient when they are in inorganic forms.

Humus is rich in nutrients and has many benefits to soil, improving soil water holding capacity. The main problem of organic matter that the formation takes a long time to convert fresh organic material to humus. The importance of existing organic matter in the soil is essential for soil for the following:

- The humus is rich with nutrients which are available to plants
- The humus improves water holding capacity of the soil.
- The organic matter enhances the soil property when it mixed with soil. Organic matter improves soil chemical and physical properties. [54]

2.5.4. Soil microorganisms and organisms

There are millions of organisms in the soil; most of them cannot be seen with naked eyes which are the microorganisms. These microorganisms are important to the soil, plants growth and nutrients cycles. The main microorganisms in the soil are bacteria, moulds and Protozoa. There are some other types of organisms that live in the soil that can be seen by eyes and important, most of them are beneficial to the soil such as earthworms, beetles, mites, nematodes and termites, also there are many insects that benefit soil and plants.

The microorganisms and insects have many benefits to the soil such as:

- Many types of worms such as earth worms dig in soil and make pores and voids, these pores are important for aeration especially for clay soil.

- The existences of microorganisms in soil help the structure to be more stable.
- The microorganisms decompose the complex organic material in soil to simple compounds and nutrients that the plants easy to absorb it as illustrated above. [54]

2.5.5. Chemical characteristics of the soil

There are two important properties of soils that affect directly soil texture and nutrients in soil, these are: the acidity (pH) and the cation exchange capacity (CEC).

- **Soil pH**

  Soil pH is an indication of acidity or basicity of soil solution, pH for most of soil solutions range from 5.5 to 8.5, any increase or reduction in acidity may be harmful to the plant and affects soil properties.[55]

- **Cation Exchange Capacity (CEC)**

  The type and value of negative charge on soil colloids which is responsible for the ability of soil to exchange positive cations (nutrients) with the soil solution. Soils with high cation exchange capacity can exchange and hold more nutrients, these nutrients held by soil CEC are exchanged with plant roots to provide the plant with needed nutrients.[56]

2.6. Nutrients of plants

There are sixteen essential elements for plant growth. Three elements are widely available for plant which supplied by air, these are oxygen,

hydrogen and carbon. Other thirteen elements are obtained from soil components or from added fertilizers.

The nutrients are classified to primary nutrients (macronutrients) and micronutrients. The primary nutrients are six elements (nitrogen, phosphorus, potassium, Calcium, magnesium and sulfur) which are needed for the growth of plants in large amounts compared with other elements needed. Soil gets calcium and magnesium usually from limestone available in soil by liming materials, and sulfur usually supplied by applying fertilizers. Micronutrients are seven elements (boron, copper, chlorine, iron, manganese, molybdenum and zinc) and needed in very small amounts compared with primary nutrients (macronutrients), but this small amount is essential for growth of plants.

A shortage or absence of one or more of essential element nutrients affect negatively plants growth, yield, and crop quality (result in deficiency symptoms). In this case nutrients should be added to soil to by applying natural or synthetic fertilizers. [56]

The following table illustrates the nutrients and their forms.

Table 2.9: Essential nutrient elements showing element, symbol and primary forms used by plants. [55]

Element	Symbol	Primary form used by plant
Elements from air		
Carbon	C	CO_2 (g)
Hydrogen	H	H_2O (l), H+
Oxygen	O	H_2O (l), O_2(g)
Mineralelements / Primary or Macro- Nutrients		
Nitrogen	N	NH_4^+ , NO_3^-
Phosphorous	P	HPO_4^{2-} , $H2PO_4^-$
Potassium	K	K+
Calcium	Ca	Ca^{2+}
Magnesium	Mg	Mg^{2+}
Sulfur	S	SO_4^{2-}
Mineral elements / Micro-Nutrients		
Iron	Fe	Fe^{3+} , Fe^{2+}
Manganese	Mn	Mn^{2+}
Zinc	Zn	Zn^{2+}
Copper	Cu	Cu^{2+}
Boron	B	$B(OH)_3^o$ (Boric acid)
Molybdenum	Mo	MoO_4^{2-}
Chlorine	Cl	Cl^-

2.6.1. Functions of basic elements for plants

It is important to know the function of each element needed for plants growth to ensure existing of these elements. The main function of each element is illustrated as:

Carbon (C), Hydrogen (H), and Oxygen (O)

- Essential in photosynthesis directly, that responsible for the plants growth.

Nitrogen (N)

- It is used in large percentage in forming chlorophyll, nucleic acids, and amino acids.

- It enters in large percentage in forming of protein and enzymes, that controlling whole biological reactions.

Phosphorus (P)

- Main formed of adenosine triphosphate (ATP) that is responsible directly for energy transmission process in the plant and of DNA and RNA.
- Main element in the formation of phospholipids, those do basic function in cell membranes of plants.
- It is essential for plant up growth including development of a well root groups, ordinary seed up growth, and photosynthesis breathing, cell division, and other reactions.

Potassium (K)

- Dependable for organization of plants water purpose, sickness fights, and root strength.
- It enters in photosynthesis, dry allowance, winter temerity, and protein composition.

Calcium (Ca)

- Fundamental for cell extension and division.
- Directly needed for stem and leaf growth, job of cell membranes, and formation of cell wall components.
- participate in the function of many plant enzymes.

Magnesium (Mg)

- Basic formation of chlorophyll, and so, it is essential in photosynthesis.

- Involved in formation of ribosome that is needed for protein components.
- Basic formation in phosphate metabolism, respiration, and the function of many enzyme systems.

Sulfur (S)

- needed for the function of the sulfur-containing amino acids cystine, cysteine, and methionine, which are basic compounds for protein components.
- Basic component of enzymes and vitamins, chlorophyll consistence, and consistence of many organic components that allow special odors to garlic, mustard, and onion.

Iron (Fe)

- Do as a catalyst in chlorophyll formation.
- Main essential for many oxidation-reduction reactions during breathing and photosynthesis.

Manganese (Mn)

- Main component of enzyme systems in plants.
- Involved in many essential metabolic reactions.
- Involved in photosynthesis.
- Do as a catalyst in chlorophyll formation.

Boron (B)

- Important for development of vaccine grains and growth of pollen pipes, seed, and cell wall components.
- Important for growth of fresh cells in meristematic tissue.

- Essential in protein formation.

Zinc (Zn)

- Important for certain metabolic/enzymatic process.
- Important for the formation of chlorophyll, carbohydrates, and development hormones.

Copper (Cu)

- Important for chlorophyll synthetic.
- Do as a catalyst for many enzymes.

Molybdenum (Mo)

- Needed for the formation and activity of the enzyme system that minimize nitrate to ammonium in the plant.
- Important in the reactions of symbiotic nitrogen fixation by Rhizobia bacteria in legume stem nodules.

Chlorine (Cl)

- Existing in energy formation in the plant, breakdown of water, organization of stomata guard cells, conservation of turgor, and the ratio of water seepage.
- Existing in plant reaction to moisture stress and fight to some illness.
- Activates many enzyme systems.
- Do as an opposite ion in the transform of many cations in the plant.

Cobalt (Co)

- Important in the formation of symbiotic nitrogen fixation by *Rhizobia* bacteria in legume stem nodules.
- May be important for the growth and development of plants.

Nickel (Ni)

- Main formation of the urease enzyme.
- Important for plants in which uredines are essential in nitrogen metabolism. [55]

2.6.2. Nitrogen

2.6.2.1.The Nitrogen Cycle

The most essential element of nutrients that has many transformations is nitrogen. The loss, increase, reduction and transformation of nitrogen are called the “nitrogen cycle” (see figure 2.13).The main source of nitrogen is nitrogen molecules (N_2 gas) in the atmosphere which forms 78 percent of atmosphere. N_2 gas in the atmosphere is not available for the plant, to be taken by plant it should be transformed by biological or synthetic methods to formation that plants could absorb. The most important components of the N cycle are illustrated below. [55]

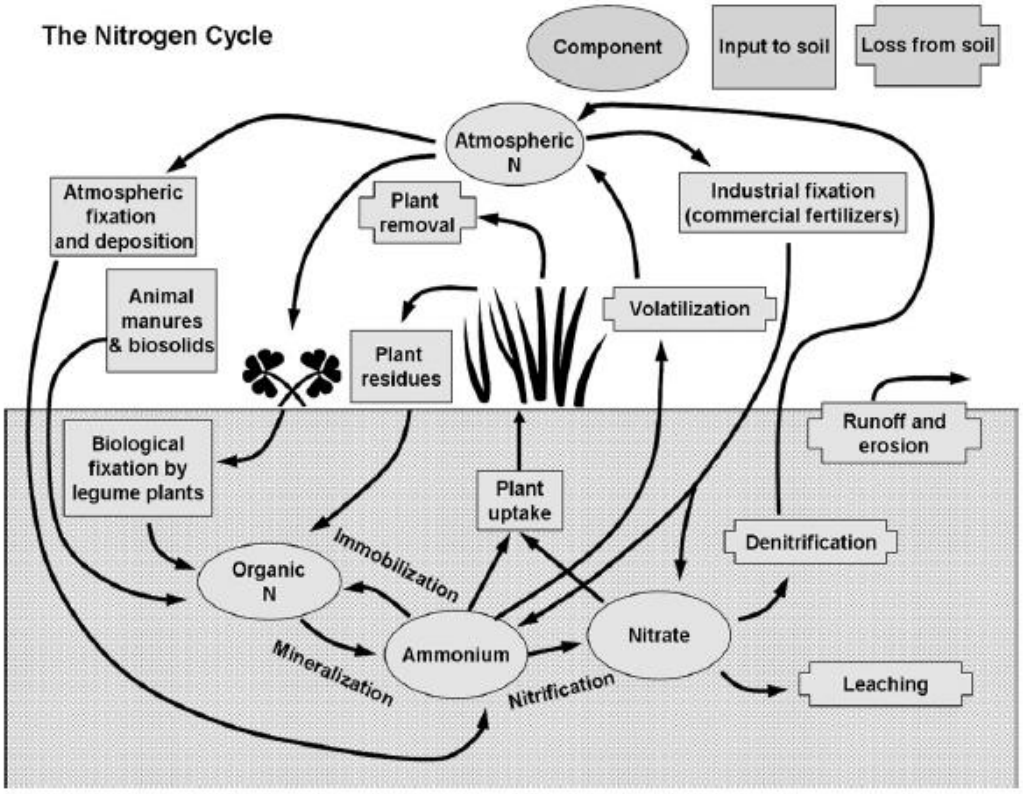

Figure 2.13: Nitrogen Cycle [30]

2.6.2.2. Nitrogen Fixation

Nitrogen fixation is the conversion of N_2gas to compounds in soil that plants could take them, such as NH^{+4} and NO^{-3} compounds. This transformation may be by biological or synthetic methods, the biological and synthetic method are illustrated blow:

- **Biological processes:**

  Biological fixation could be symbiotic or non-symbiotic. Symbiotic N fixation indicates that microorganisms fixing N when growing in corporation with a host plant. The plant and the microorganisms profit from their symbiotic relationship. An obvious example of this relationship is among Rhizobium bacteria and plants including legumes

such as soya, peanut and alfalfa. These bacteria contract with plant's stems and make nodules. The bacteria involved in these nodules fix N2 from the atmosphere and convert it to a form that the plant could take.

Non-symbiotic N fixation is done by independent-living bacteria and blue-green algae in the soil without relationship with plant. The quantities of N fixed by non-symbiotic organisms are less than the quantities fixed by symbiotic bacteria. So this nitrogen is ignored agriculturally because it is small amount.

- **Fixation of Nitrogen from Lightning:**

  Nitrogen could fixed by the electrical discharge of lightning in the air. The temperature from lightning could compose NO^{3-}-N, that is then transported to the soil by rainfall.

- **Synthetic or industrial methods of nitrogen fixation**:

Industrial methods could be functionally fix N in soil to be available for plants. The wide industrial method is synthesizing ammonia (NH3) from N and hydrogen (H), as shown:

$N_2 + 3H_2 \rightarrow 2NH_3$

The hydrogen (H_2) is often gained from normal gas and the nitrogen (N_2) is derived immediately from the atmosphere. When the ammonia formed (NH_3), it preface as the basic fresh material for abundant of other materials that involve nitrogen, such as ammonium nitrate, ammonium sulfate, sodium nitrate, urea aqua ammonia, nitrogen solutions and ammonium phosphates. Basically all commercially used N fertilizers produced as NH_3setup from atmospheric N. [56]

2.6.2.3. Format of Soil Nitrogen

Soil N exists in organic and inorganic format. Often the entire total N in the top soils exist as organic nitrogen. Organic soil N take place in the formula of amino acids, amino sugars, and other complicated nitrogen components. Inorganic formula of soil nitrogen involve ammonium (NH^{4+}), nitrite (NO^{2}), nitrate (NO^{3-}), nitrous oxide (N_2O_{gas}), nitric oxide (NO_{gas}), and elemental nitrogen ($N_{2\ gas}$). Ammonium, nitrite, and nitrate are the extreme essential plant nutrient formulas of N and often consist 2 to 5 percent of the whole soil N.

Nitrogen "mineralization" (see figure 2.14) is the transformation of organic nitrogen to NH^{4+}. This is an essential component in the N cycle which converts nitrogen from organic to inorganic form which plants could take from soil.

Nitrogen "immobilization" is the transformation of inorganic (NH^{4+} or NO^{3-}) byplants or bacteria to organic N forms (amino acids and proteins). This transformation is the opposite of mineralization, the compound produced by this process is not available for plants. [55]

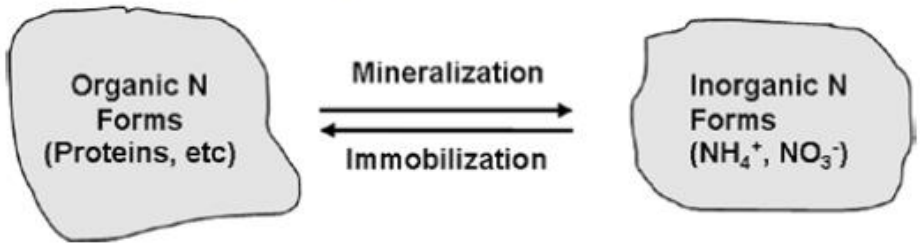

Figure 2.14: Mineralization and immobilization of soil nitrogen. [55]

2.6.2.4. Carbon-to-Nitrogen Ratios

Mineralization and immobilization are continuous reactions in the soil and are often in equilibrium with each other. This equivalent could be broken

by the conjunction of organic materials which have higher carbon to nitrogen ratios (C:N). The C:N ratio could be defined as the proportional amount of organic elements residues and living tissues. The breaking down of organic material depends on C:N ratio as follows:

- Higher C:N ratios (more than 30-to-1): Immobilization of soil N will be preferable.
- C:N ratios between 20-to-1 to 30-to-1: Immobilization and mineralization would be almost similar.
- Small C:N ratios of smaller than 20-to-1:mineralization of N is preferable.[56]

2.6.2.5. Nitrification

The transformation of ammonium to nitrate is named nitrification. Nitrification is an oxidation reaction and emission of energy by soil organisms. The transformation passes through two reactions, in the first ammonium is transformed to nitrite (NO_2^-) and in second nitrite is transformed to nitrate (NO_3^-). The transformation of ammonium to nitrite is completed by many microorganisms in the soil, the familiar type of bacteria transforming ammonium to nitrite is known as Nitrosomonas. The first reaction can be illustrated as follows:

$2\ NH^{+4} + 3O_2 \rightarrow 2\ NO_2^- + 2H2O + 4\ H^+$The transformation of nitrite to nitrate is also completed by many microorganisms in the soil, the familiar type of bacteria completing this reaction is known as Nitrobacter. The second reaction can be illustrated as follows:

$2NO_2^- + O_2 \rightarrow 2NO_3^-$

The product of this reaction is NO^{-3} which is often movable through soil due to its negative charge and it may be leached from the soil through water movement downward to groundwater. NO_3^- is a source of contamination of surface and ground water.

Aeration is essential for nitrification process so it occurs more quickly in soils with good aeration. Other factors which the reaction depends upon include the surrounding status of the soil, such as temperature, moisture, pH, cultivation practice, agricultural system, the existing of other elements and properties of organic material in the soil.[56]

2.6.2.6. Denitrification

Denitrification is the transformation of nitrates to N_2 and N_2O gases by reduction reaction under anaerobic conditions. Nitrogen gases may be spread to the atmosphere later. The losses of nitrogen through this process depend on the soil concentration with nitrite, duration of saturation, organic material and soil pH. It is noticed the concentration of nitrite is higher more denitrification occurs.

From agricultural practical point of view, it is noticeable that the best method to keep nitrate from seeping due to denitrification is to develop agriculture practices that support enough soil aeration, decrease soil water saturation, and keep soil pH in the range of 5.5 to 7.0.[56]

2.6.3. Phosphorus

The main source of P is weathering of soil minerals, such as apatite, and from applying fertilizers or organic material residues containing P (see

figure 2.15). Orthophosphate ions ($HPO4^{-2}$ and $H2PO^{4-}$) are created when apatite crashes, organic residues are broken down, or fertilizer P origins dissolve. These formations of P are absorbed by plant stems and they exist in small ratios in the soil solution.

Several soils have large P content, unfortunately most of it is not available to plants. The species of P-bearing minerals that exist in soil are related to soil pH. The reaction of soluble P with free iron or free aluminum, in acid soils form compounds that cannot be absorbed by plants root, is called fixed phosphorous. The following figure shows the main components and reaction in phosphorus cycle. [56]

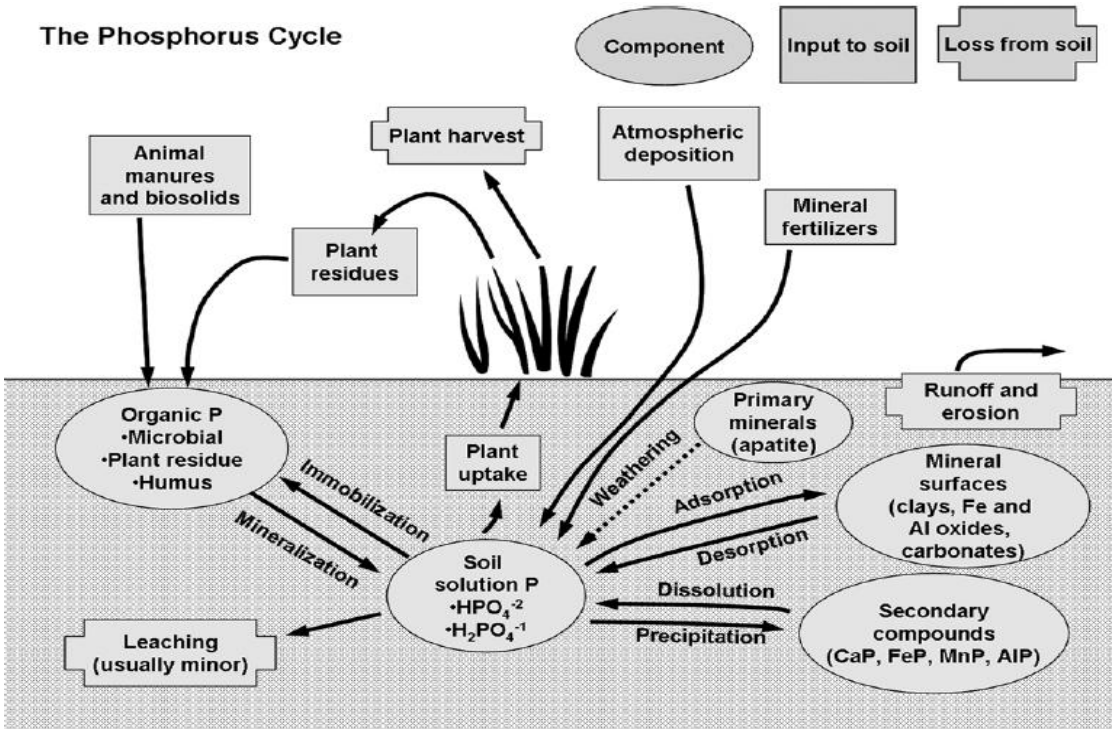

Figure 2.15: Phosphorus cycle [55]

2.6.4. Potassium

Plants absorb K as the monovalent cation K^+. Potassium of ten exists in soils in with large amounts; unfortunately a little part of the total soil K is available for the plant.

The K cycle is shown in figure 2.16. Some types of minerals, spatially feldspars and micas, are broken down to form K ions. The breaking down to K+ could be absorbed by plant roots, transported by the cation exchange of clay and organic material, or “fixed” in the inside composition of specific clay minerals. Fixed potassium by these clay minerals is not available for the plant. [55]

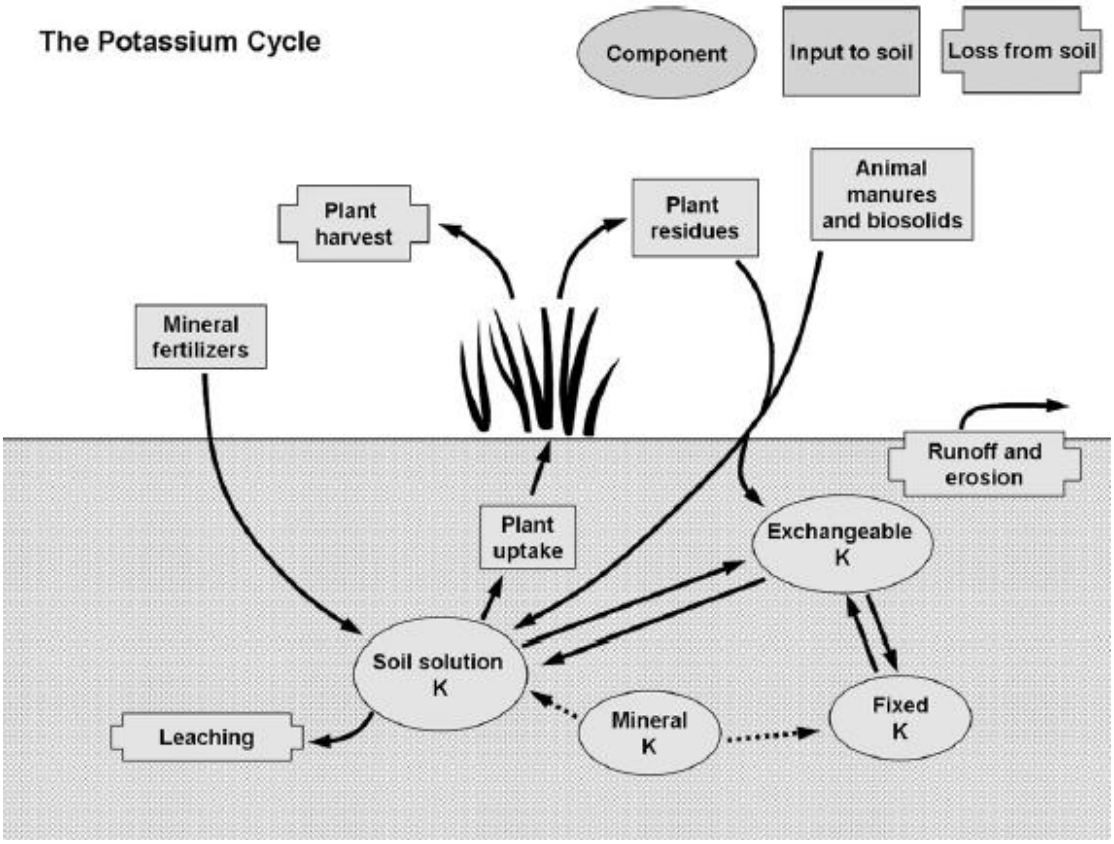

Figure 2.16: Potassium Cycle.[55]

2.6.5. Calcium, Magnesium and Sulfur

❖ **Calcium and Magnesium**

Calcium and magnesium are almost with the same chemical characteristics and processes in the soil. The mobility of Ca and Mg is smaller than other cations, and so the movement of cations through soil profile is small.

The Ca amount is high in almost all soils, calcium is a portion of the component of many minerals and almost all soil calcium take place from the weathering of popular minerals, which include dolomite, calcite, apatite and calcium-feldspars.

❖ **Sulfur**

Sulfur exists in soil as inorganic and organic forms. Almost all of the sulfur present in soils from the breaking down of sulfate metals such as gypsum. Inorganic sulfur often exists in the sulfate (SO_4^{-2}) type, which is available for the plants. [55]

2.6.6 Micronutrients (trace elements)

❖ **Boron**

Boron presents an anion joint in soil organic material, and in the soil solution.

❖ **Copper**

Cu exists in the soil solution depending on soil pH, the amount of Cu available on clay minerals and soil organic material. Cu^{+2}cation make

strong bounds with organic material in the soil, so the soils that have small amounts of organic material may have shortage in Cu^{+2}cation.

- **Iron**

  Iron has little solubility in soil solution, because its solubility depends on the pH of soil solution.

- **Manganese**

  Availability of Mn to plants is detected by the equivalent between solutions, commutable, organic and metals formation of soil Mn. Chemical reactions influence on Mn solubility involve oxidation, reduction and combination with soil organic material.

- **Molybdenum**

  Molybdenum exists in soil metals as commutable Mo on the face of iron/aluminum oxides and solution of soil organic material. The ion (MoO^{-4}) could be soluble or taken by plant roots.

- **Zinc**

  The different formation of soil Zn involve soil metals, organic materials, adsorbed Zn on the face of organic material and clay, and dissolved Zn in the soil solution. Zinc emitted from soil materials during weathering could be absorbed into the cation exchange sites, inserted into soil organic material, or react with organic material to make soluble compounds. [55]

2.7. Soil and good agricultural practice

For effective soil management a farmer should develop the attractive soil property by instrumentation of good agricultural practices. These practices

should be consistent with technically available, economically engaging, environmentally safe, functional in practice and socially reasonable, so as to include sustainable and high agricultural fertility. The essential issues of good agricultural practices are:

- Choice of good seeds of a high productive variety.
- Selecting the better time and suitable method of planting, with best seed rate.
- A suitable selection of fertilizers style and time of application.
- Refresh of organic material.
- Conservation of a suitable soil processing specially pH.
- Suitable measures versus probable insect epidemic and diseases.
- Soil and weed erosion monitoring.
- Conditioning of irrigation and drainage system. [53]

Chapter Three

Experimental Work

3. Experimental Work

3.1. Constructing biogas units

There are many types and volumes of biogas units around the word, as discussed in the previous chapter. Choosing a typical unit to achieve the objectives of this study depends upon available material for biogas units, available volumes, cost of materials, cost of construction, volume of feedstock and other technical matters relating to biogas unit operation.

The volume of a typical biogas unit was chosen to be 250 liters because this volume is available and easy for construction. The components needed for the construction of each biogas unit were:

- A closed plastic tank of 250 liters in volume.
- A plastic pipe of 3 inches in diameter (1.00 meter long), for inflow control.
- A plastic right angle elbow of 2 inches in diameter and a plastic pipe of 3 inches in diameter (0.45 meter long), for effluent control.
- Gas dart of 3/4 inches and gas valve of 3/4 inches, for gas control.
- Stones between 1-3 inches in diameter, to help microorganisms to settlement.
- Gas collector.
- A grinding machine and funnel to cut organic matter into small parts.

The following two figures show the components of a typical biogas unit

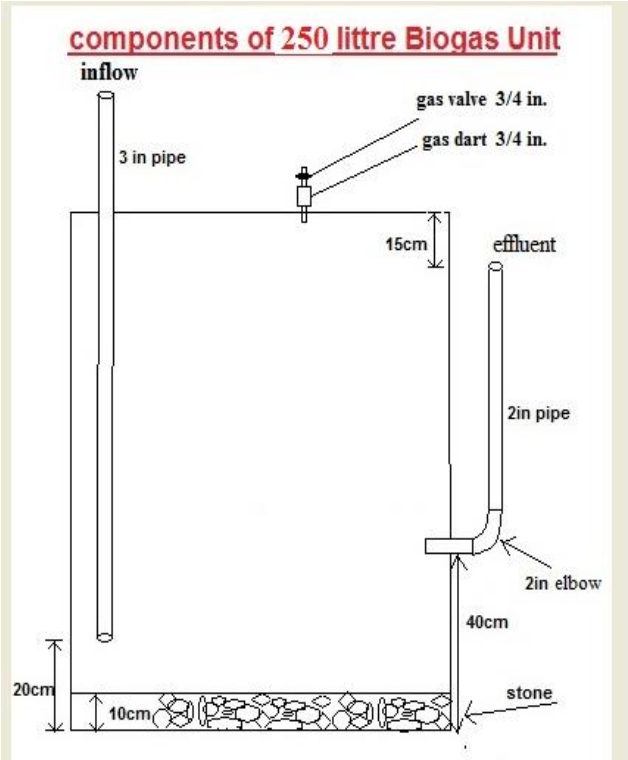

Figure 3.1: Schematic diagram for the components of a typical biogas unit

Figure 3.2: a photo of two typical biogas units

3.2. Combination of feedstock

There are six types of organic waste used in this study, these are:

- Manure of cows
- Manure of sheep and goats
- Manure of poultry chicken (laying hens)
- Olive solid waste
- Combination of olive waste and cow manure
- Kitchen residues.

The above combinations are available in Palestine and it is important to investigate them. Olive solid waste is one of important waste residues of olive oil extraction process which is mostly lost as waste and thus it is important to include it in combination with other organic materials.

3.3. Retention time and feeding system

Retention time is important for the digestion process; it varies according to the circumstances surrounding the biogas unit. The most important factor affecting retention time is temperature. As shown in figure 2.1 in chapter 2, when temperature ranges from 20 to 42 °C, then the retention time would be in the range of30 to 40 days. The experimental work of this study was conducted in September and October of 2013 during which temperature ranged from 15 to 35 °C. Thus, it was safe to use a retention time of 50 days for this range of temperature values.

The daily feeding organic waste depends on the available volume of biogas unit and the retention time. For our experiment, the available volume for organics is:

Available volume = total volume of biogas unit – empty volume

= 250 liters–0.15*250 liters

= 212.5 liters.

So, the volume of organics that must be added to the system in 50 days was 212.5 liters. The daily organic feed was:

Daily organic feed = $\frac{\text{avalable volume}}{\text{retention time}} = \frac{212.5 \text{ liters}}{50 \text{ days}}$ = 4.25 liters of organics per day.

The daily feeding volume of organics were mixed with water at a ratio of 1:1 and then entered the biogas unit through inflow pipe as illustrated in figure 3.1.

3.4. Sampling

Sampling included taking samples from the biogas units and preparing them for testing. To make comparisons and analyses for the different mixtures, five samples from each biogas unit with three replications were taken from effluent (see figure 3.1) and analyzed.

The volume of each sample should not be less than 50 milliliters to allow testing for several parameters under consideration. The starting date of digestion for all biogas units was, Sep. 12th 2013, and samples were collected every 10 days to cover the changes in nutrient contents during the digestion period. Table 3.1 shows the sample dates and number:

Table 3.1: dates and numbers of samples

Sample	Date	Replicates	# of combinations	Total number
Start	Sep. 12th 2013	-	-	-
Sample 1	Sep. 22th 2013	3	6	18
Sample 2	Oct. 1th 2013	3	6	18
Sample 3	Oct. 10th 2013	3	6	18
Sample 4	Oct. 20th 2013	3	6	18
Sample 5	Oct. 30th 2013	3	6	18
			Total samples	**90**

As shown in the table above, the total number of digestate samples was 90 samples taken from biogas units at regular times. These samples were stored in a refrigerator at temperatures less than 4°C to avoid anaerobic digestion and emission of nitrate.

The three replications of each combination are important to do statistical analysis for each combination type. Two way ANOVA using SPSS program (statistical package for social science) in which Time and combination type are independent variables and concentration is dependent variable. Null hypothesis is defined as the independent variables or factors (Time and combination type) have no significant effect on depending or variable tested (concentration).

An informal interpretation of a *p*-value, based on a significance level of about 5%, might be:

- $P_{value} \leq 0.001$: very strong presumption against null hypothesis
- $0.001 < P_{value} \leq 0.01$: strong presumption against null hypothesis
- $0.01 < P_{value} < 0.05$: low presumption against null hypothesis
- $P_{value} \geq 0.05$: no presumption against the null hypothesis

The mean separation of times and combination factors is done using LSD method in which means with different superscripts (letters) are significantly different.

3.5. Testing

There are four method of testing specific micronutrients and macro nutrients, these are illustrated in the following table:

Table 3.2: testing methods for each nutrient type

Elements	Testing method
K, Ca, Mg, Fe, Mn, Zn, Cu, Mo	**ICP-MS**
N	**TKN**
P	**UVspectroscopy**

The following sections illustrate the details of these methods:

3.5.1. ICP-MS device

There are a lot of similarities between ICP-MS and the other analytical apparatuses used in the laboratory, such as Atomic Absorption and ICP Optical Emission Spectrometry. The ICP-MS is a way to determine the elemental content of samples. ICP-MS perform this by counting the number of ions at a certain mass of the element in state the light released by the element, as in optical techniques. Sample preparation for ICP-MS is very similar to that used in AA and ICP-OES, and in many cases is identical. Standards are analyzed to generate a calibration curve and the signals from unknown samples are compared against the calibration curve to determine the concentration of each element in the sample. The software

reports data and results for quantitative, semi-quantitative, isotope ratio, or isotope dilution analyses. [57]

ICP-MS has many advantages over other technologies, such as AA and ICP-OES, for determining the elemental composition of samples. ICP-MS generally has less interference than ICP-OES and is much faster than AA and Graphite Furnace AA for the determination of multiple analyses per sample. ICP-MS detection limits are generally much lower than those that can be achieved by ICP-OES. Quadrupole ICP-MS instruments are capable of measuring as many as 35 elements in a sample in two to three minutes. Because the spectrometer and all the accessories are under computer control, the system can literally operate 24 hours per day, 7 days per week, and analyze over 300 samples per 24-hour day. In short, no other technology can provide the low detection limits and the high productivity for elemental analysis offered by ICP-MS. [57]

3.5.2. Total Kjeldahl Nitrogen (TKN)

This method is used to determine N content in solutions, TKN is mainly composed of heating an organic substance with sulfuric acid, that to break down the organic matter by oxidation to release the nitrogen as ammonium sulfate [$(NH_4)_2SO_4$]. Here potassium sulfate (K_2SO_4) is added to raise the boiling degree of the solution (from 337°C to 373°C). Full chemical breaking down of the sample occurs when the very dark-coloring of the sample has become clear and colorless.

The clear sample is distilled with a small volume of sodium hydroxide (NaOH), that transforms the ammonium salt to ammonia (NH_3). The

amount of ammonia is equal to the total nitrogen that is decided by back titration using excess of boric acid. The ammonia reacts with the boric acid and the residue of the boric acid is titrated with a sodium carbonate using of a methyl orange indicator. [57]

3.5.3. UV Spectroscopy

Ultraviolet – visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.[58]

Chapter Four
Results and Discussion

4. Result and Discussion

4.1. Temperature

The experimental works were done during September and October, in which temperature ranged from 22 to 26 ^{o}C, so the type of digestion occurred was mesophilic digestion. Table 4.1 shows the temperature of the days when the samples were taken:

Table 4.1: temperature of the days when the samples were taken.

time (days)	0	10	20	30	40	50
temperature (^{o}C)	22.5	23.6	25.7	23.9	25.1	23.1

4.2. pH

The results of pH with time are illustrated in table 4.2, and figure 4.1 illustrates these results for each combination type.

Table 4.2 Average pH value with time.

time (days)	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	7.33	7.32	7.40	7.46	7.56	7.55	0.0065	0.0084
sheep	7.98	7.99	8.14	8.27	8.38	8.40	0.0038	0.0067
poultry	7.54	7.53	7.73	7.85	7.99	7.98	0.0053	0.0035
olive	7.27	7.27	7.44	7.62	7.73	7.72	0.0041	0.0076
olive+cow	8.00	8.01	8.22	8.38	8.44	8.45	0.0084	0.0043
kitchen	7.79	7.79	8.00	8.15	8.31	8.32	0.0050	0.0018

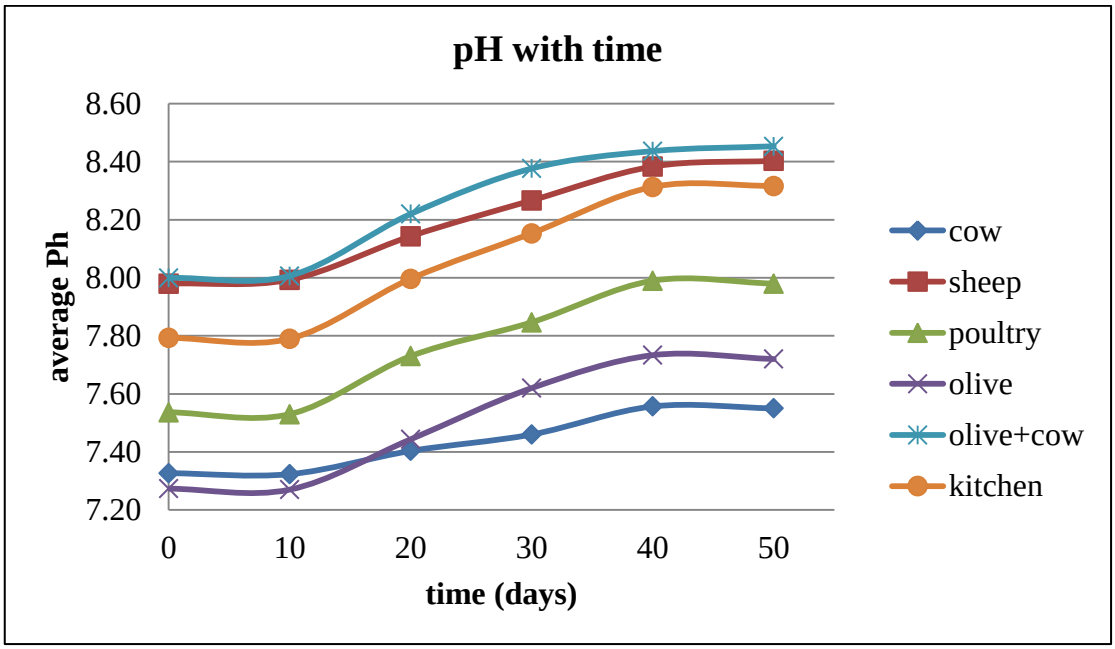

Figure 4.1 Average pH values with time for each combination.

Table 4.2a Mean separation.

Time	0 d	10 d	20 c	30 b	40 a	50 a
Combination	Cow a	Sheep a	Poultry c	Olive d	olive+cow f	Kitchen b

*** * "Means with different superchips (letters) are significantly different (P<5%) "**

pH of digestate was alkaline and the values of pH increased significantly with time, the percentage change and accumulative changes of pH are shown in table 4.3, also figure 4.2 shows the total change in pH during digestion.

The reason of increase in pH was the reduction of acidity due to consumption acids and production of Carbone dioxide and methane especially in methanogens is stage. The alkaline pH of digestate is a useful property because of the worldwide problem of soil acidification. The increase in pH is different according to the type of combination. As shown in tables and figures the largest change occurred in kitchen combination

(6.57%) that means the reduction of acidity is highest, and the smallest changes occurred in cow combination (3.02%) that means the reduction of acidity is smallest.

The first reading of pH depending on the content of acids in organic combination, so it is obvious that (olive + cow) combination contain the highest acidity.

Table 4.3 the percentage changes and accumulative changes of pH

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	-0.05	1.09	0.77	1.30	-0.09
Interval Change% for sheep	0.17	1.88	1.51	1.41	0.24
Interval Change% for poultry	-0.09	2.66	1.51	1.83	-0.13
Interval Change% for olive	-0.05	2.38	2.37	1.49	-0.17
Interval Change% for olive+cow	0.08	2.66	1.91	0.72	0.20
Interval Change% for kitchen	-0.04	2.65	1.96	1.96	0.04
at time (day)	10	20	30	40	50
Cumulative Change for cow %	-0.05	1.05	1.81	3.11	3.02
Cumulative Change for sheep %	0.17	2.04	3.56	4.97	5.21
Cumulative Change for poultry %	-0.09	2.57	4.08	5.90	5.78
Cumulative Change for olive %	-0.05	2.34	4.71	6.20	6.03
Cumulative Change for olive+cow%	0.08	2.75	4.65	5.37	5.57
Cumulative Change for kitchen %	-0.04	2.61	4.57	6.53	6.57

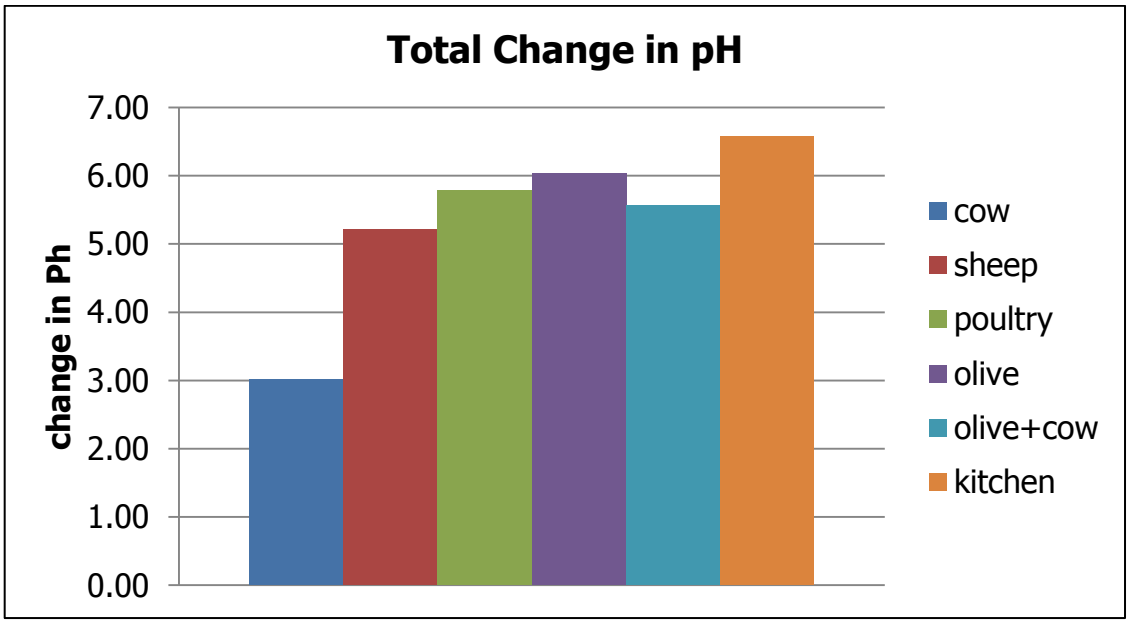

Figure 4.2: total percentage changes in pH during digestion.

4.3. Nitrogen

The average concentration of Nitrogen for each sample combination is illustrated in table 4.4 and figure 4.3.

Table 4.4 the average concentration of Nitrogen (gm/L)

time (days)	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
Cow	23.2695	23.7132	24.5098	25.2448	26.2146	26.2264	0.0065	0.0011
Sheep	30.1460	30.3658	32.0597	33.1485	34.3466	34.1841	0.0038	0.0015
Poultry	25.2547	26.2466	26.9852	27.7697	28.9453	28.9457	0.0053	0.0008
Olive	16.2245	16.6640	17.2125	17.7300	18.3658	18.3761	0.0071	0.0014
Olive +cow	19.5178	19.9864	20.6234	21.2531	21.9968	22.0138	0.0084	0.0013
Kitchen	14.0109	14.3336	14.5671	14.8880	15.6136	15.6271	0.0122	0.0025

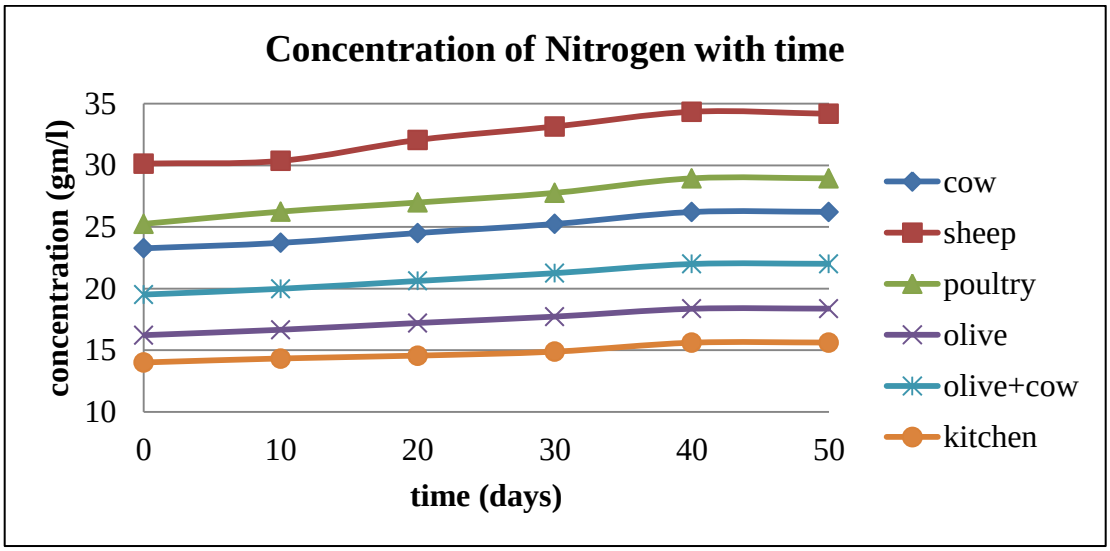

Figure 4.3: Concentration of Nitrogen with time

Table 4.4a Mean separation.

Time	0 d	10 d	20 c	30 b	40 a	50 a
Combination	Cow b	Sheep a	Poultry b	Olive d	olive+cow c	Kitchen f

*** * "Means with different superchips (letters) are significantly different (P<5%) "**

The obvious change in nitrogen is significantly increase for all combination is according to ammonification which makes the Earth's supply of this essential element available to living organisms. It is carried out by various microorganisms found in water, which break down proteins and amino acids in organic matter, releasing ammonia, which is usually retained in water in the form of the ammonium ion.

According to significance of type of combination, the most significant combination effect on concentration is sheep combination. And according to time the most significant combination is poultry combination.

The percentage changes of Nitrogen and accumulative changes of Nitrogen are shown in table 4.5; also figure 4.4 shows the total change in Nitrogen during digestion.

Table 4.5 the percentage changes and accumulative changes of N (gm/L)

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	1.91	3.36	3.00	3.84	0.04
Interval Change% for sheep	0.73	5.58	3.40	3.61	-0.47
Interval Change% for poutry	3.93	2.81	2.91	4.23	0.00
Interval Change% for olive	2.71	3.29	3.01	3.59	0.06
Interval Change% for olive+cow	2.40	3.19	3.05	3.50	0.08
Interval Change% for kitchen	2.30	1.63	2.20	4.87	0.09
at time (day)	10	20	30	40	50
Cumulative Change for cow %	1.91	5.27	8.26	12.11	12.15
Cumulative Change for sheep %	0.73	6.31	9.70	13.32	12.84
Cumulative Change for poultry %	3.93	6.74	9.65	13.88	13.88
Cumulative Change for olive %	2.71	6.00	9.01	12.59	12.65
Cumulative Change for olive+cow%	2.40	5.59	8.64	12.14	12.22
Cumulative Change for kitchen %	2.30	3.93	6.13	11.01	11.10

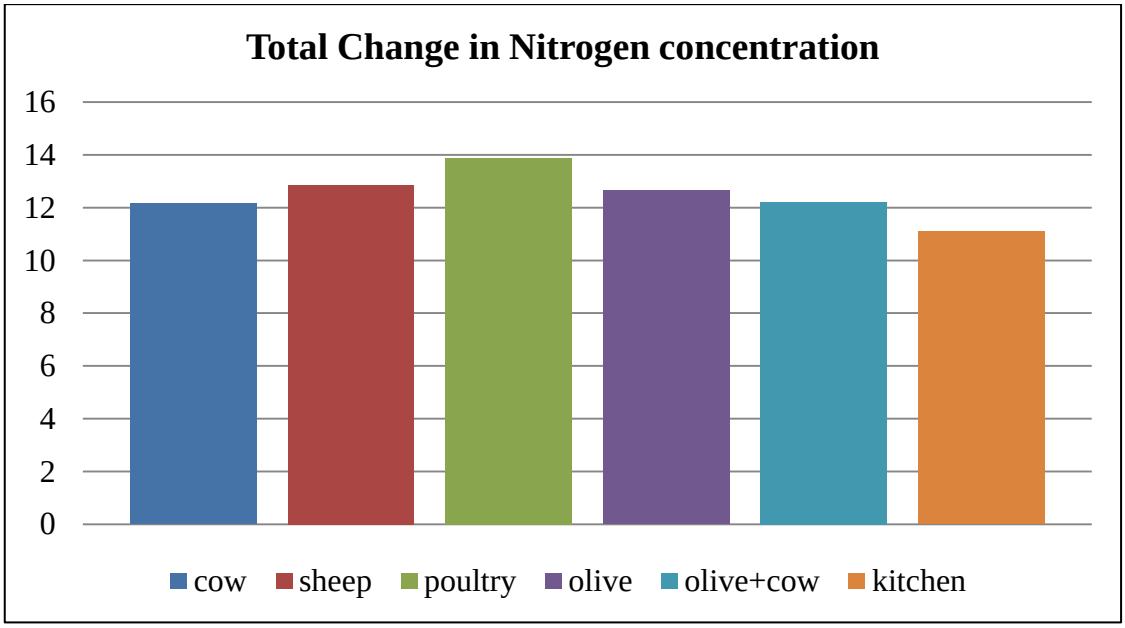

Figure 4.4: total percentage changes in N during digestion.

The higher percentage of nitrogen concentration increase is for poultry combination (13.88%) and the lowest for kitchen combination (11.10%).

4.4. Phosphorous

The average concentration of Phosphorous for each sample combination is illustrated in table 4.6 and figure 4.5.

Table 4.6 the average concentration of P (gm/L)

time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	1.7850	1.7867	1.8220	1.8550	1.8907	2.0093	0.0045	0.0091
sheep	1.8607	1.8643	1.9123	1.9533	1.9937	2.1360	0.0036	0.0073
poultry	3.4590	3.4750	3.6220	3.7667	3.7847	3.8433	0.0015	0.0081
olive	1.5330	1.5417	1.5677	1.5930	1.6137	1.6947	0.0051	0.0114
olive+cow	1.6947	1.6930	1.7423	1.7877	1.8257	1.9727	0.0065	0.0061
kitchen	1.5150	1.5227	1.5630	1.6417	1.6403	1.7830	0.0076	0.0046

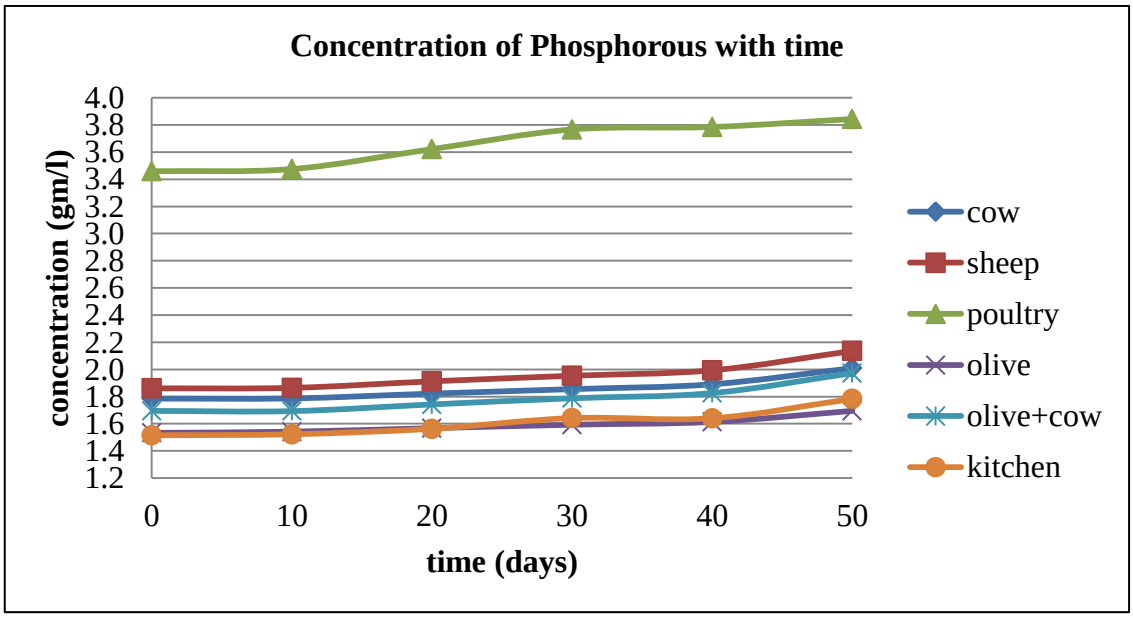

Figure 4.5: Concentration of P with time

Table 4.6a Mean separation.

Time	0 d	10 d	20 c	30 b	40 b	50 a
Combination	Cow c	Sheep b	Poultry a	Olive d	olive+cow c	Kitchen d

*** * "Means with different superchips (letters) are significantly different (P<5%) "**

The obvious significant increase in phosphorous for all combinations are according to biological processes during digestion (the biological processes depend on the type of organic combination) in which organic material breaks down and induces phosphorous ions.

According to significance of type of combination, the most significant combination effect on concentration is poultry combination. And according to time the most significant combination is kitchen combination.

The percentage changes of Phosphorous and accumulative changes of Phosphorous are shown in table 4.7; also figure 4.6 shows the total change in Phosphorous during digestion.

Table 4.7 the percentage changes and accumulative changes of P

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	0.09	1.98	1.81	1.92	6.28
Interval Change% for sheep	0.20	2.57	2.14	2.06	7.14
Interval Change% for poultry	0.46	4.23	3.99	0.48	1.55
Interval Change% for olive	0.57	1.69	1.62	1.30	5.02
Interval Change% for olive+cow	-0.10	2.91	2.60	2.13	8.05
Interval Change% for kitchen	0.51	2.65	5.03	-0.08	8.70
at time (day)	10	20	30	40	50
Cumulative Change for cow %	0.09	2.07	3.88	5.80	12.08
Cumulative Change for sheep %	0.20	2.77	4.92	6.98	14.12
Cumulative Change for poultry %	0.46	4.69	8.69	9.16	10.71
Cumulative Change for olive %	0.57	2.25	3.87	5.17	10.18
Cumulative Change for olive+cow%	-0.10	2.82	5.42	7.54	15.60
Cumulative Change for kitchen %	0.51	3.15	8.19	8.11	16.80

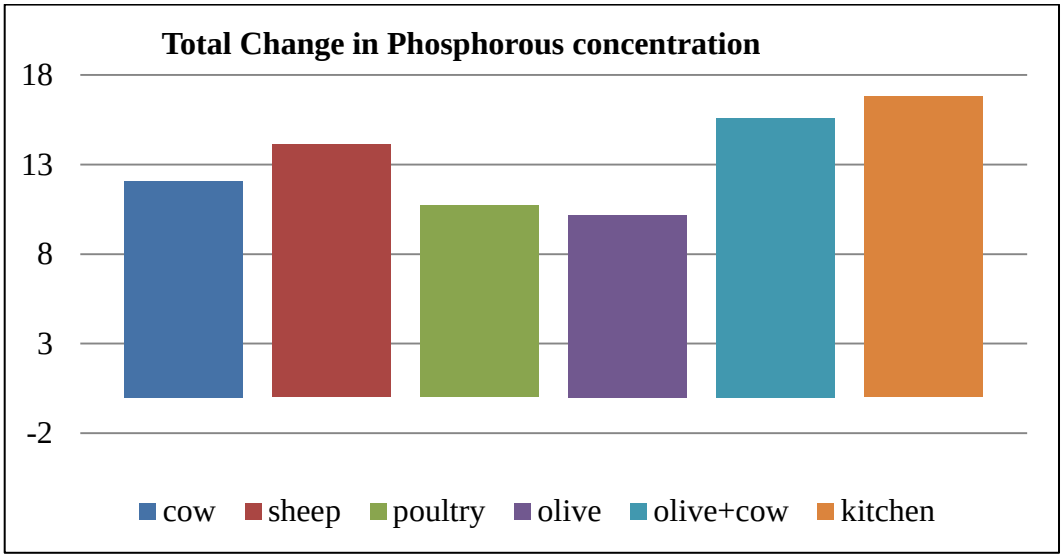

Figure 4.6: total percentage changes in P during digestion.

The highest percentage of phosphorous concentration increase is for kitchen combination (16.8%) and the lowest for olive combination (10.18%).

4.5. Potassium

The average concentration of Potassium for each sample combination is illustrated in table 4.8 and figure 4.7.

Table 4.8 the average concentration of k (gm/L)

time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	3.4457	3.5847	3.7057	3.8517	3.9163	3.9220	0.0045	0.0051
sheep	6.3533	6.5753	6.7887	7.0340	7.1937	7.2103	0.0014	0.0073
poultry	4.3323	4.5117	4.6110	4.8357	4.9140	4.9227	0.0025	0.0081
olive	2.3630	2.3533	2.4217	2.5110	2.5560	2.5630	0.0081	0.0123
olive+cow	3.1417	3.1963	3.3043	3.4250	3.4750	3.4857	0.0065	0.0091
kitchen	2.6957	2.6837	2.7803	2.8943	2.9417	2.9440	0.0076	0.0086

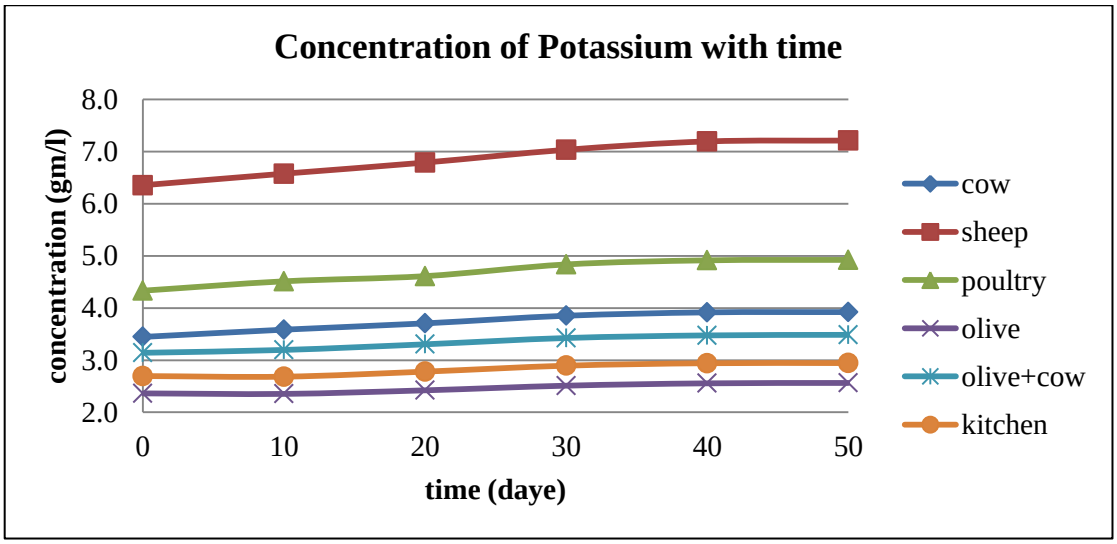

Figure 4.7: Concentration of k with time

Table 4.8a Mean separation.

Time	0 d	10 d	20 c	30 b	40 a	50 a
Combination	Cow c	Sheep a	Poultry b	Olive d	olive+cow c	Kitchen c

*** * "Means with different superchips (letters) are significantly different (P<5%) "**

The obvious significant increase in potassium for all combinations is according to biological processes during digestion (the biological processes depend on the type of organic combination) in which organic material breaks down and induces potassium ions.

According to significance of type of combination, the most significant combination effect on concentration is sheep combination. And according to time the most significant combination is cow combination.

The percentage changes of Potassium and accumulative changes of Potassium are shown in table 4.9; also figure 4.8 shows the total change in Potassium during digestion.

Table 4.9 the percentage changes and accumulative changes of K

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	4.03	3.38	3.94	1.68	0.14
Interval Change% for sheep	3.49	3.24	3.61	2.27	0.23
Interval Change% for poultry	4.14	2.20	4.87	1.62	0.18
Interval Change% for olive	-0.41	2.90	3.69	1.79	0.27
Interval Change% for olive+cow	1.74	3.38	3.65	1.46	0.31
Interval Change% for kitchen	-0.45	3.60	4.10	1.64	0.08
at time (day)	10	20	30	40	50
Cumulative Change for cow %	4.03	7.41	11.35	13.03	13.17
Cumulative Change for sheep %	3.49	6.74	10.35	12.62	12.85
Cumulative Change for poultry %	4.14	6.34	11.21	12.83	13.01
Cumulative Change for olive %	-0.41	2.49	6.18	7.98	8.25
Cumulative Change for olive+cow%	1.74	5.12	8.77	10.23	10.54
Cumulative Change for kitchen %	-0.45	3.16	7.26	8.89	8.97

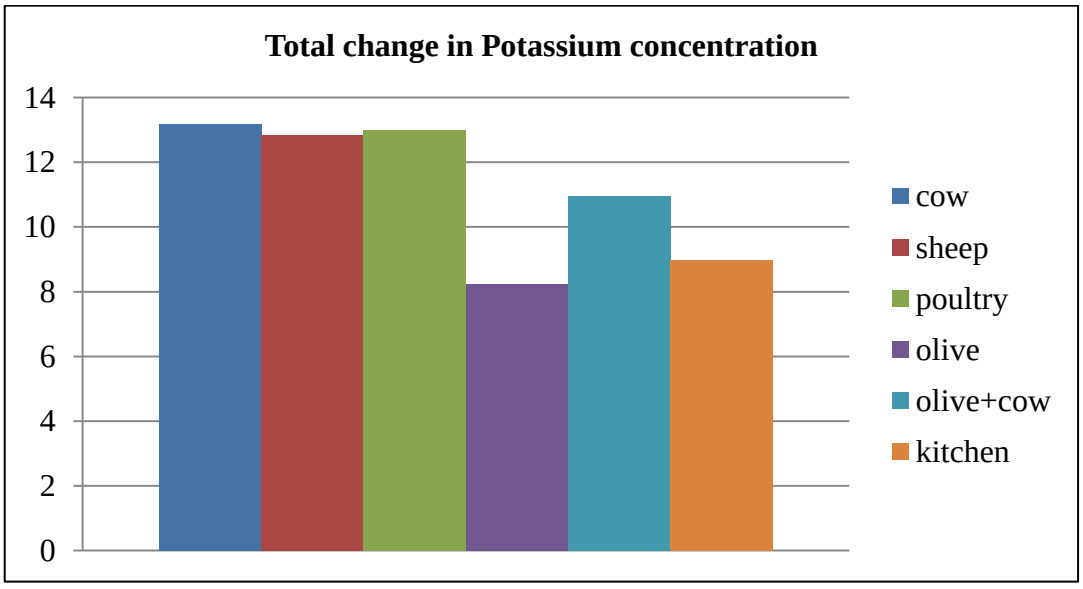

Figure 4.8: total percentage changes in K during digestion.

The highest percentage of potassium concentration increase is for cow combination (13.17%) and the lowest for olive combination (8.25%).

4.6. Calcium

The average concentration of Calcium for each sample combination is illustrated in table 4.10 and figure 4.9.

Table 4.10 the average concentration of Ca (gm/L)

time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	3.2581	3.2644	3.2674	3.2775	3.2858	3.2894	0.0045	0.063
sheep	3.8215	3.8324	3.8387	3.8434	3.8504	3.8547	0.0064	0.063
poultry	8.1240	8.1094	8.1508	8.1816	8.2204	8.2271	0.0035	0.031
olive	2.1030	2.1091	2.1155	2.1175	2.1181	2.1215	0.0051	0.045
olive+cow	2.7534	2.7591	2.7638	2.7670	2.7689	2.7716	0.0075	0.062
kitchen	1.9525	1.9552	1.9606	1.9608	1.9626	1.9633	0.0096	0.087

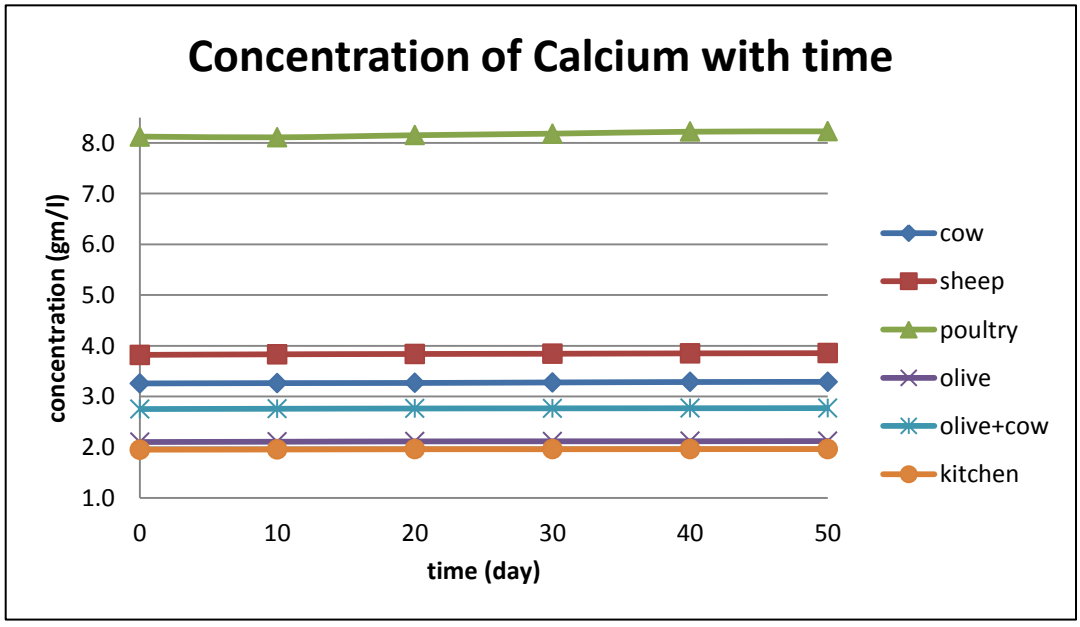

Figure 4.9: Concentration of Ca with time

The percentage changes of Calcium and accumulative changes of Calcium are shown in table 4.11; also figure 4.10 shows the total change in Calcium during digestion.

Table 4.11 the percentage changes and accumulative changes of Ca

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	0.19	0.09	0.31	0.25	0.11
Interval Change% for sheep	0.29	0.16	0.12	0.18	0.11
Interval Change% for poultry	-0.18	0.51	0.38	0.47	0.08
Interval Change% for olive	0.29	0.31	0.09	0.03	0.16
Interval Change% for olive+cow	0.21	0.17	0.12	0.07	0.10
Interval Change% for kitchen	0.14	0.28	0.01	0.09	0.03
at time (day)	10	20	30	40	50
Cumulative Change for cow %	0.19	0.29	0.59	0.85	0.96
Cumulative Change for sheep %	0.29	0.45	0.57	0.76	0.87
Cumulative Change for poultry %	-0.18	0.33	0.71	1.18	1.26
Cumulative Change for olive %	0.29	0.60	0.69	0.72	0.88
Cumulative Change for olive+cow%	0.21	0.38	0.49	0.56	0.66
Cumulative Change for kitchen %	0.14	0.42	0.43	0.52	0.55

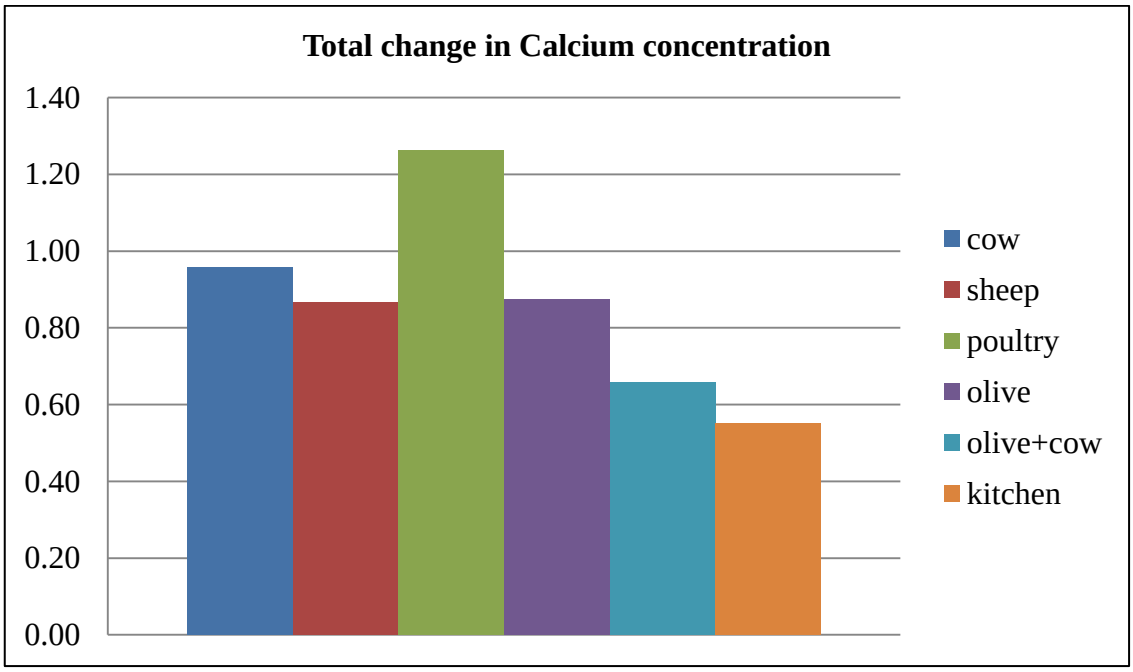

Figure 4.10: total percentage changes in Ca during digestion.

The above results show a few increasing of calcium concentration, the highest percentage of calcium concentration increase is for poultry combination (1.26%) and the lowest for kitchen combination (0.55%).

4.7. Magnesium

The average concentration of Magnesium for each sample combination is illustrated in table 4.12 and figure 4.11.

Table 4.12 the average concentration of Mg (gm/L)

time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	1.1544	1.1562	1.1807	1.2015	1.2147	1.2241	0.0035	0.091
sheep	0.8024	0.8044	0.8264	0.8425	0.8555	0.8593	0.0045	0.063
poultry	1.9256	1.9334	1.9839	2.0036	2.0357	2.0422	0.0021	0.079
olive	0.2565	0.2575	0.2592	0.2628	0.2656	0.2656	0.0078	0.102
olive+cow	0.6855	0.6866	0.6945	0.7019	0.7097	0.7107	0.0059	0.117
kitchen	0.3155	0.3194	0.3245	0.3276	0.3316	0.3326	0.0082	0.082

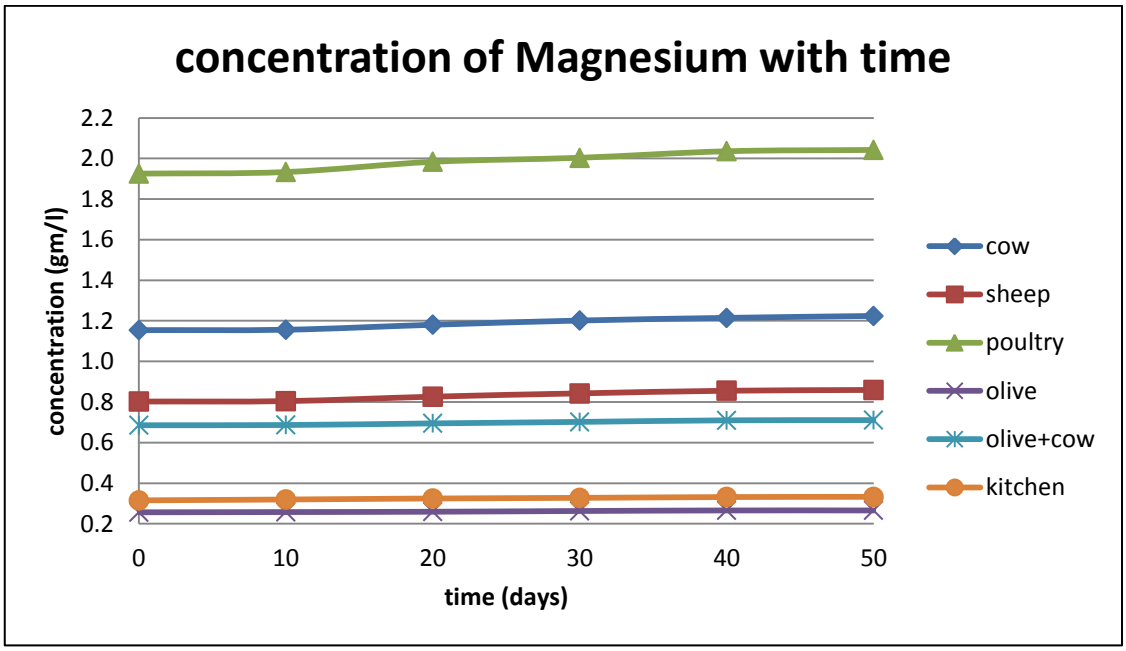

Figure 4.11: Concentration of Mg with time

The percentage changes of Magnesium and accumulative changes of Magnesium are shown in table 4.13; also figure 4.12 shows the total change in Magnesium during digestion.

Table 4.13 the percentage changes and accumulative changes of Mg

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	0.16	2.12	1.77	1.10	0.77
Interval Change% for sheep	0.25	2.73	1.95	1.54	0.45
Interval Change% for poultry	0.41	2.61	1.00	1.60	0.32
Interval Change% for olive	0.42	0.66	1.38	1.08	-0.01
Interval Change% for olive+cow	0.16	1.16	1.06	1.12	0.13
Interval Change% for kitchen	1.26	1.58	0.97	1.22	0.31
at time (day)	10	20	30	40	50
Cumulative Change for cow %	0.16	2.27	4.04	5.14	5.91
Cumulative Change for sheep %	0.25	2.98	4.93	6.48	6.92
Cumulative Change for poultry %	0.41	3.02	4.01	5.62	5.93
Cumulative Change for olive %	0.42	1.08	2.45	3.53	3.52
Cumulative Change for olive+cow%	0.16	1.32	2.38	3.49	3.62
Cumulative Change for kitchen %	1.26	2.83	3.80	5.02	5.33

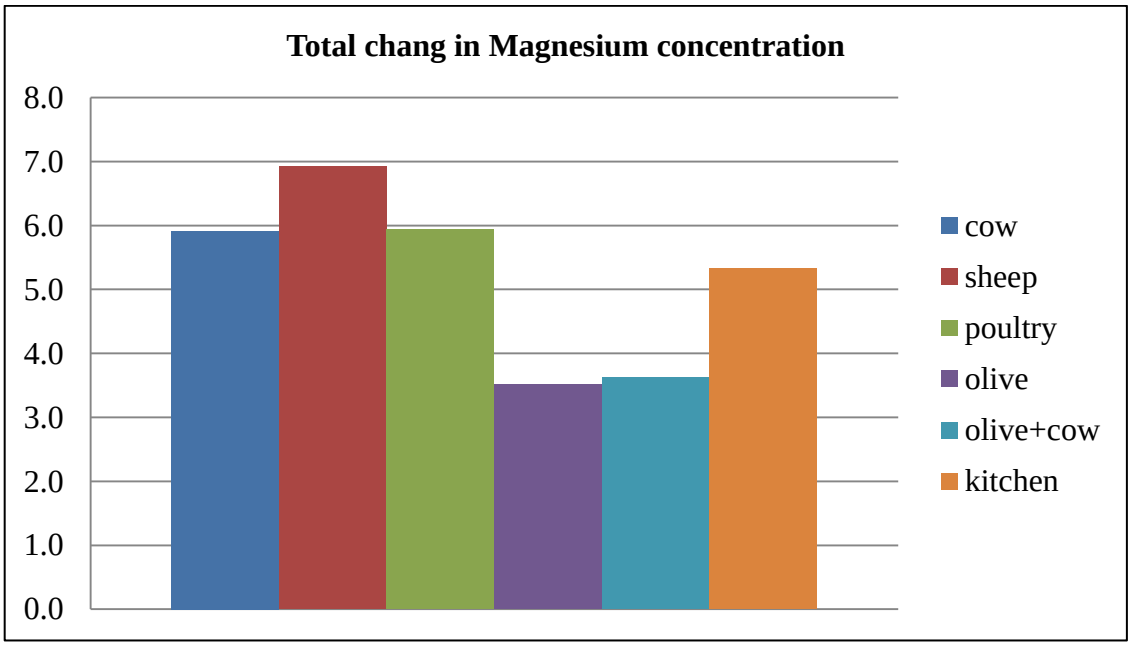

Figure 4.12: total percentage changes in Mg during digestion.

The above results show small increasing (not significant change) in magnesium concentration, the highest percentage of magnesium concentration increase is for sheep combination (6.92 %) and the lowest for olive combination (3.52 %).

4.8. Iron

The average concentration of Iron for each sample combination is illustrated in table 4.14 and figure 4.13.

Table 4.14 the average concentration of Fe (gm/L)

Time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	1.9364	1.9343	1.9346	1.9704	1.9868	1.9886	0.0058	0.112
sheep	2.5966	2.5917	2.6136	2.6387	2.6635	2.6662	0.0046	0.103
poultry	1.6215	1.6153	1.6307	1.6446	1.6572	1.6586	0.0063	0.092
olive	0.4576	0.4547	0.4566	0.4593	0.4604	0.4606	0.0095	0.126
olive+cow	0.9325	0.9275	0.9322	0.9336	0.9343	0.9368	0.0087	0.164
kitchen	0.3055	0.3049	0.3063	0.3066	0.3066	0.3077	0.0108	0.142

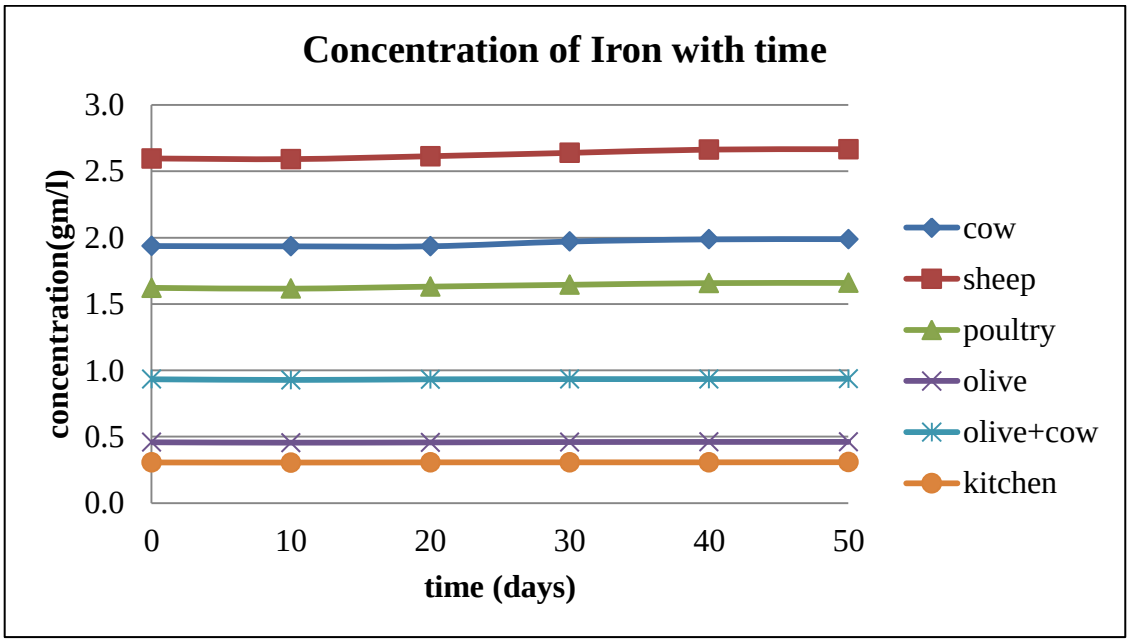

Figure 4.13: Concentration of Fe with time

The percentage changes of Iron and accumulative changes of Iron are shown in table 4.15; also figure 4.14 shows the total change in Iron during digestion.

Table 4.15 the percentage changes and accumulative changes of Fe

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	-0.11	0.02	1.85	0.83	0.09
Interval Change% for sheep	-0.19	0.85	0.96	0.94	0.10
Interval Change% for poultry	-0.38	0.95	0.85	0.76	0.09
Interval Change% for olive	-0.63	0.43	0.59	0.24	0.03
Interval Change% for olive+cow	-0.54	0.51	0.15	0.07	0.27
Interval Change% for kitchen	-0.19	0.46	0.09	-0.01	0.37
at time (day)	10	20	30	40	50
Cumulative Change for cow %	-0.11	-0.09	1.76	2.59	2.68
Cumulative Change for sheep %	-0.19	0.66	1.62	2.56	2.66
Cumulative Change for poultry %	-0.38	0.57	1.42	2.19	2.28
Cumulative Change for olive %	-0.63	-0.21	0.38	0.62	0.65
Cumulative Change for olive+cow%	-0.54	-0.03	0.12	0.20	0.47
Cumulative Change for kitchen %	-0.19	0.27	0.36	0.35	0.72

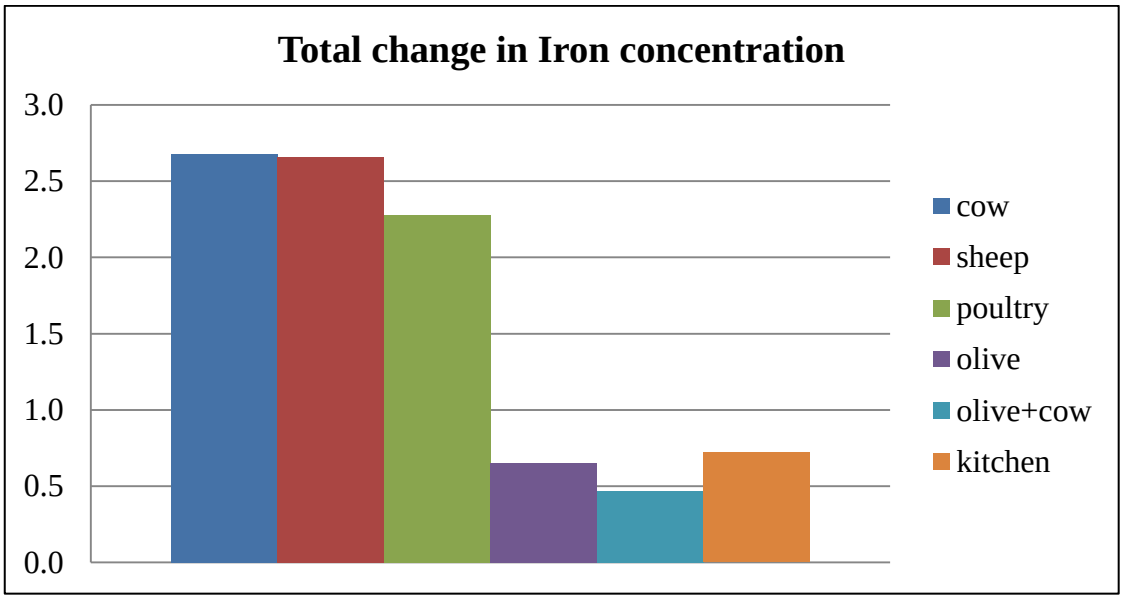

Figure 4.14: total percentage changes in Fe during digestion.

The above results show a small increase (not significant change) of iron concentration, the highest percentage of iron concentration increase is for cow combination (2.68 %) and the lowest for olive+cow combination (0.47 %).

4.9. Manganese

The average concentration of Manganese for each sample combination is illustrated in table 4.16 and figure 4.15.

Table 4.16 the average concentration of Mn (gm/L)

time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	0.0853	0.0854	0.0854	0.0855	0.0856	0.0856	0.0053	0.161
sheep	0.0702	0.0701	0.0701	0.0702	0.0702	0.0703	0.0062	0.131
poultry	0.3803	0.3805	0.3802	0.3804	0.3807	0.3807	0.0041	0.142
olive	0.0092	0.0093	0.0092	0.0093	0.0092	0.0093	0.0075	0.135
olive+cow	0.0223	0.0222	0.0223	0.0222	0.0223	0.0222	0.0093	0.156
kitchen	0.0059	0.0059	0.0060	0.0059	0.0060	0.0060	0.0113	0.142

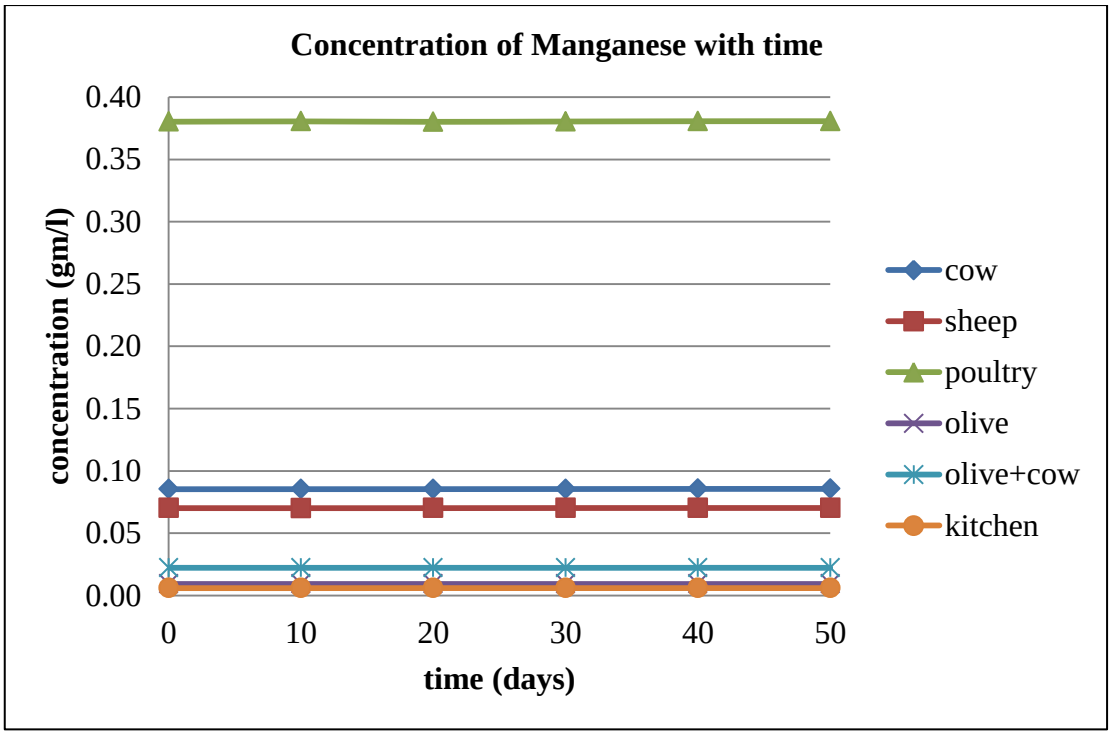

Figure 4.15: Concentration of Mn with time

The percentage changes of Manganese and accumulative changes of Manganese are shown in table 4.17; also figure 4.16 shows the total change in Manganese during digestion.

Table 4.17 the percentage changes and accumulative changes of Mn

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	0.05	0.01	0.11	0.10	0.02
Interval Change% for sheep	-0.06	0.05	0.10	0.04	0.01
Interval Change% for poultry	0.06	-0.09	0.07	0.06	0.01
Interval Change% for olive	0.04	-0.04	0.07	-0.25	0.29
Interval Change% for olive+cow	-0.09	0.09	-0.16	0.15	-0.16
Interval Change% for kitchen	0.22	0.39	-0.34	0.34	-0.11
at time (day)	10	20	30	40	50
Cumulative Change for cow %	0.05	0.06	0.16	0.27	0.28
Cumulative Change for sheep %	-0.06	0.00	0.10	0.14	0.15
Cumulative Change for poultry %	0.06	-0.03	0.04	0.10	0.11
Cumulative Change for olive %	0.04	0.00	0.07	-0.18	0.11
Cumulative Change for olive+cow%	-0.09	0.00	-0.16	-0.01	-0.18
Cumulative Change for kitchen %	0.22	0.62	0.28	0.62	0.51

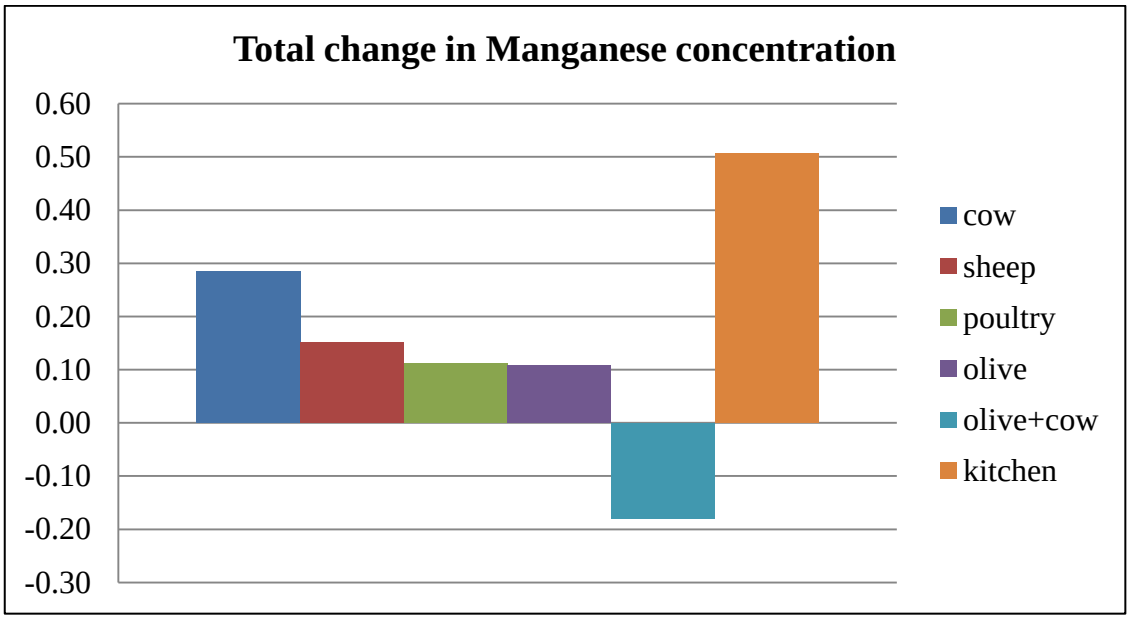

Figure 4.16: total percentage changes in Mn during digestion.

The above results show a few increasing (not significant change) of manganese concentration, the highest percentage of manganese concentration increase is for kitchen combination (0.51 %) and the lowest for olive+cow combination

(-0.18 %).

4.10. Zinc

The average concentration of Zinc for each sample combination is illustrated in table 4.18 and figure 4.17.

Table 4.18 the average concentration of Zn (gm/L)

time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	0.1025	0.1025	0.1025	0.1026	0.1027	0.1027	0.0053	0.312
sheep	0.0950	0.0950	0.0950	0.0951	0.0951	0.0952	0.0062	0.234
poultry	0.2737	0.2737	0.2737	0.2740	0.2742	0.2742	0.0041	0.210
olive	0.0029	0.0028	0.0028	0.0029	0.0028	0.0028	0.0075	0.362
olive+cow	0.0306	0.0307	0.0306	0.0306	0.0307	0.0307	0.0093	0.417
kitchen	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0113	0.595

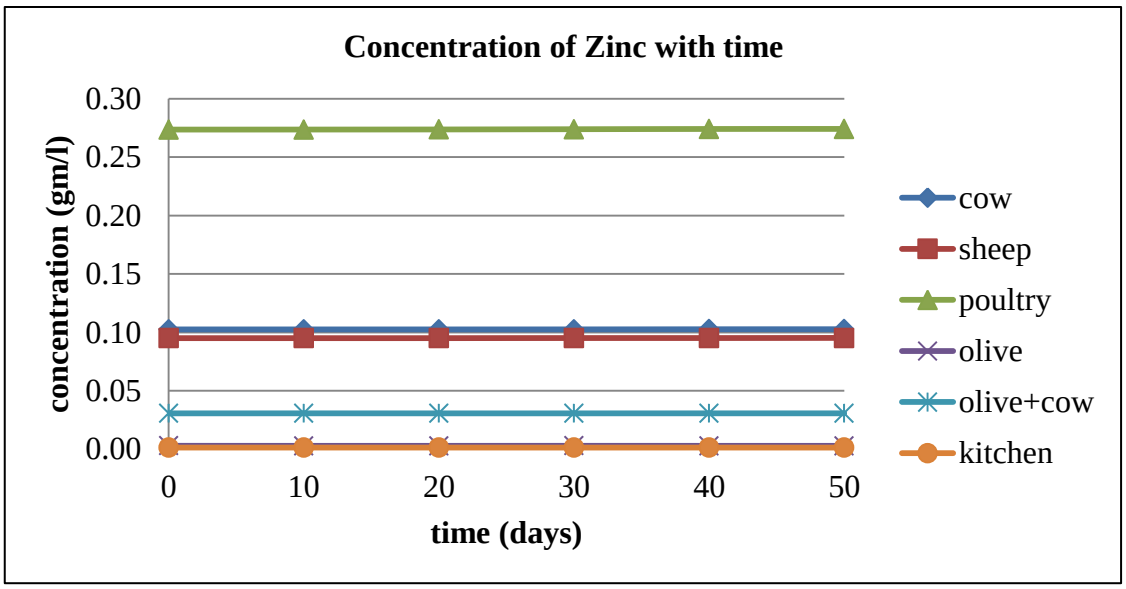

Figure 4.17: Concentration of Zn with time

The percentage changes of Zinc and accumulative changes of Zinc are shown in table 4.19, also figure 4.18 shows the total change in Zinc during digestion.

Table 4.19 the percentage changes and accumulative changes of Zn

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	-0.01	0.01	0.02	0.11	0.02
Interval Change% for sheep	0.01	0.00	0.11	0.00	0.11
Interval Change% for poultry	0.01	0.03	0.08	0.07	0.02
Interval Change% for olive	-1.16	0.00	0.82	-1.05	0.47
Interval Change% for olive+cow	0.05	-0.07	-0.02	0.10	-0.01
Interval Change% for kitchen	-0.25	0.25	-0.50	0.50	-0.50
at time (day)	10	20	30	40	50
Cumulative Change for cow %	-0.01	0.00	0.02	0.13	0.15
Cumulative Change for sheep %	0.01	0.01	0.12	0.12	0.22
Cumulative Change for poultry %	0.01	0.03	0.11	0.19	0.20
Cumulative Change for olive %	-1.16	-1.16	-0.34	-1.39	-0.92
Cumulative Change for olive+cow%	0.05	-0.01	-0.03	0.07	0.05
Cumulative Change for kitchen %	-0.25	0.00	-0.50	0.00	-0.49

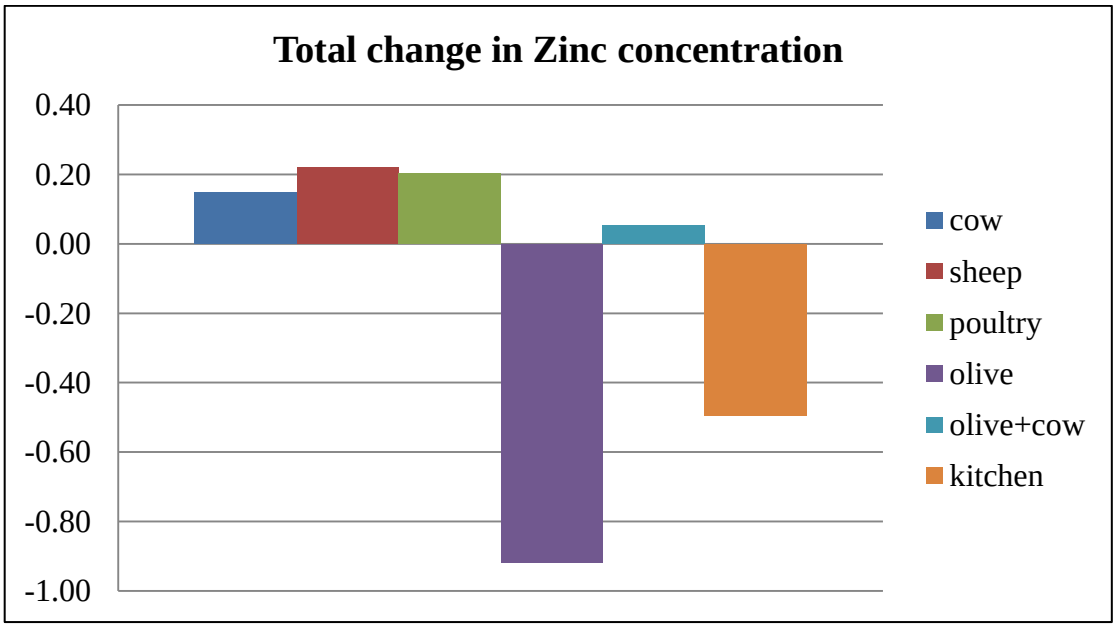

Figure 4.18: total percentage changes in Zn during digestion.

The above results show a minor increase (not significant change) in zinc concentration, the highest percentage of zinc concentration increase is for sheep combination (0.22 %) and the lowest for olive combination (- 0.92 %).

4.11. Copper

The average concentration of Copper for each sample combination is illustrated in table 4.20 and figure 4.19.

Table 4.20 the average concentration of Cu (gm/L)

Time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	0.0250	0.0250	0.0251	0.0251	0.0251	0.0251	0.0075	0.245
sheep	0.0224	0.0224	0.0224	0.0225	0.0225	0.0225	0.0042	0.652
poultry	0.0433	0.0433	0.0432	0.0433	0.0433	0.0433	0.0063	0.412
olive	0.0050	0.0050	0.0050	0.0050	0.0050	0.0050	0.0068	0.532
olive+cow	0.0083	0.0080	0.0083	0.0083	0.0083	0.0083	0.0124	0.424
kitchen	0.0032	0.0032	0.0032	0.0032	0.0033	0.0033	0.0094	0.356

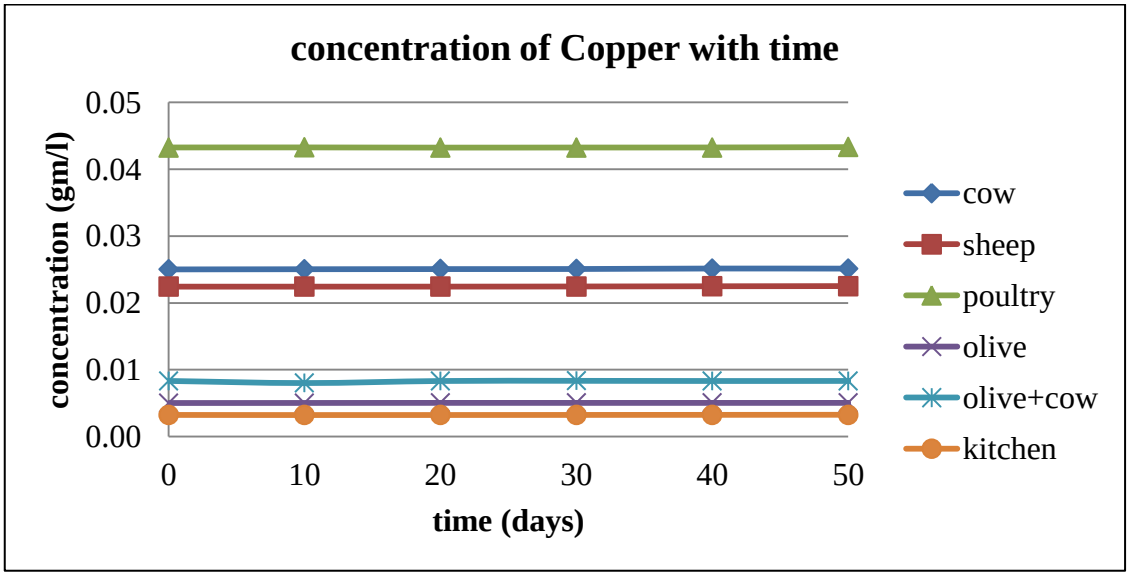

Figure 4.19: Concentration of Cu with time

The percentage changes of Copper and accumulative changes of Copper are shown in table 4.21, also figure 4.20 shows the total change in Copper during digestion.

Table 4.21 the percentage changes and accumulative changes of Cu

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	0.11	0.08	0.05	0.28	-0.04
Interval Change% for sheep	0.00	0.03	0.07	0.15	0.12
Interval Change% for poultry	0.02	-0.06	0.03	0.02	0.12
Interval Change% for olive	0.20	0.20	-0.07	0.00	0.07
Interval Change% for olive+cow	-3.80	3.83	0.32	-0.32	0.12
Interval Change% for kitchen	-0.51	0.21	0.31	0.41	0.31
at time (day)	10	20	30	40	50
Cumulative Change for cow %	0.11	0.19	0.24	0.52	0.48
Cumulative Change for sheep %	0.00	0.03	0.10	0.25	0.37
Cumulative Change for poultry %	0.02	-0.05	-0.02	0.00	0.12
Cumulative Change for olive %	0.20	0.40	0.33	0.33	0.40
Cumulative Change for olive+cow%	-3.80	0.03	0.35	0.03	0.15
Cumulative Change for kitchen %	-0.51	-0.31	0.00	0.41	0.72

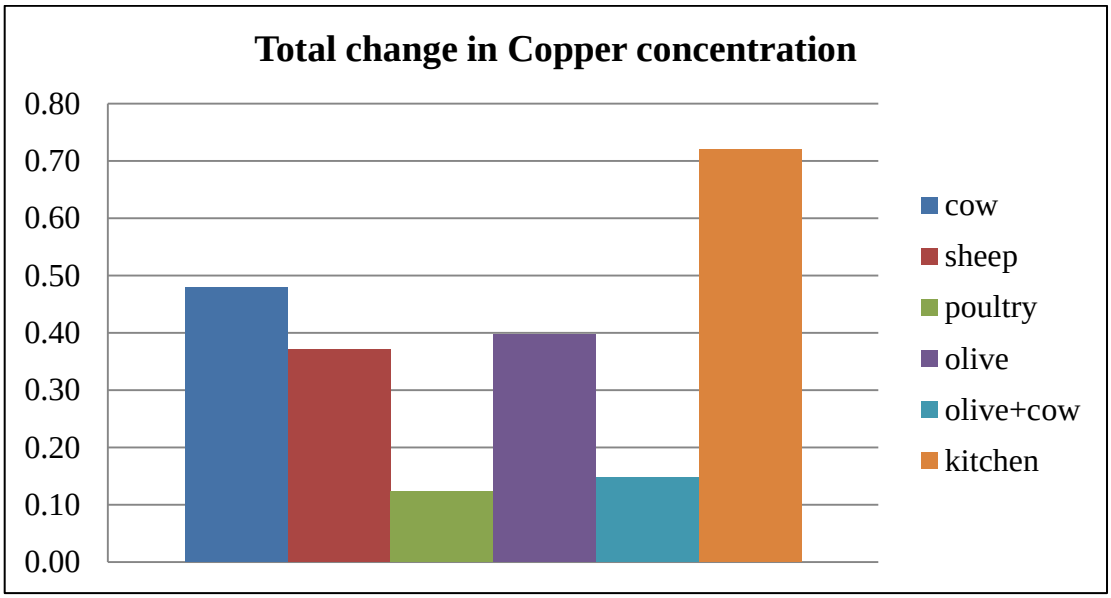

Figure 4.20: total percentage changes in Cu during digestion.

The above results show a minor increasing (not significant change) of copper concentration, the highest percentage of copper concentration increase is for kitchen combination (0.72 %) and the lowest for poultry combination (0.12 %).

4.12. Molybdenum

The average concentration of Molybdenum for each sample combination is illustrated in table 4.22 and figure 4.21.

Table 4.22 the average concentration of Mo (gm/L)

time day	0	10	20	30	40	50	Combination P_{value}	Time P_{value}
cow	0.0023	0.0023	0.0023	0.0023	0.0024	0.0023	0.0068	0.361
sheep	0.0032	0.0031	0.0031	0.0032	0.0032	0.0032	0.0058	0.546
poultry	0.0033	0.0033	0.0033	0.0033	0.0033	0.0034	0.0042	0.316
olive	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0059	0.742
olive+cow	0.0011	0.0011	0.0011	0.0011	0.0011	0.0011	0.0142	0.418
kitchen	0.0003	0.0003	0.0004	0.0004	0.0004	0.0004	0.0089	0.401

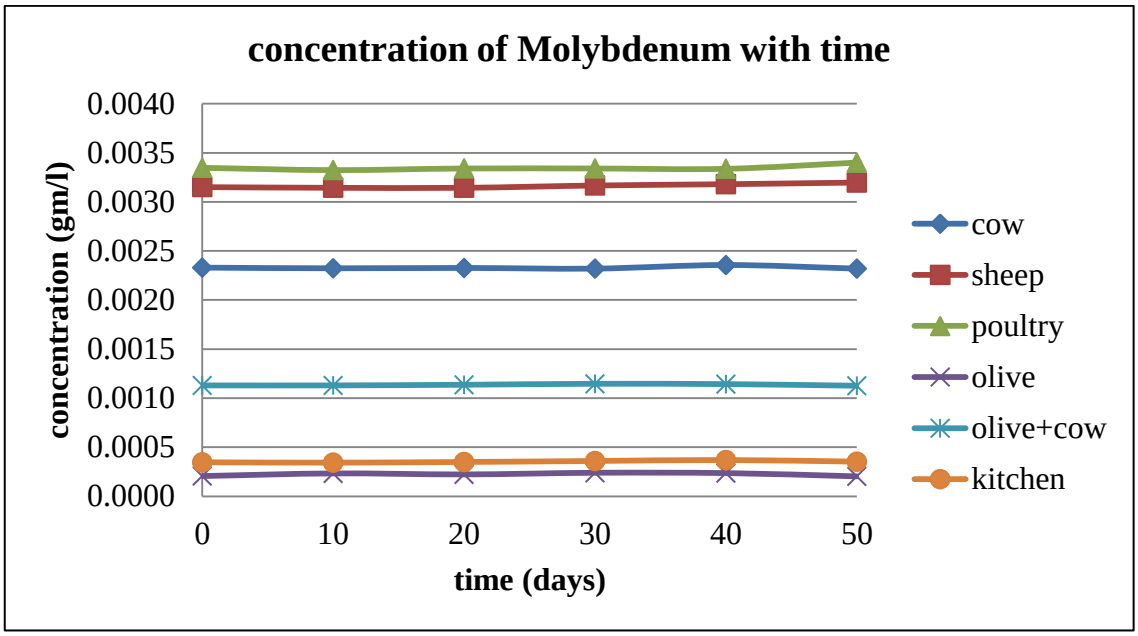

Figure 4.21: Concentration of Mo with time

The percentage changes of Molybdenum and accumulative changes of Molybdenum are shown in table 4.23; also figure 4.22 shows the total change in Molybdenum during digestion.

Table 4.23 the percentage changes and accumulative changes of Mo

Interval	(0-10) day	(10-20) day	(20-30) day	(30-40) day	(40-50) day
Interval Change% for cow	-0.29	0.14	-0.29	1.58	-1.56
Interval Change% for sheep	-0.21	0.00	0.74	0.42	0.52
Interval Change% for poultry	-0.70	0.50	0.00	-0.10	1.90
Interval Change% for olive	12.90	-4.29	7.46	-1.39	-14.08
Interval Change% for olive+cow	0.00	0.59	0.88	-0.29	-1.46
Interval Change% for kitchen	-0.96	1.94	2.86	2.78	-4.50
at time (day)	10	20	30	40	50
Cumulative Change for cow %	-0.29	-0.14	-0.43	1.15	-0.40
Cumulative Change for sheep %	-0.21	-0.21	0.53	0.95	1.48
Cumulative Change for poultry %	-0.70	-0.20	-0.20	-0.30	1.60
Cumulative Change for olive %	12.90	8.62	16.08	14.69	0.61
Cumulative Change for olive+cow%	0.00	0.59	1.47	1.18	-0.28
Cumulative Change for kitchen %	-0.96	0.98	3.84	6.62	2.11

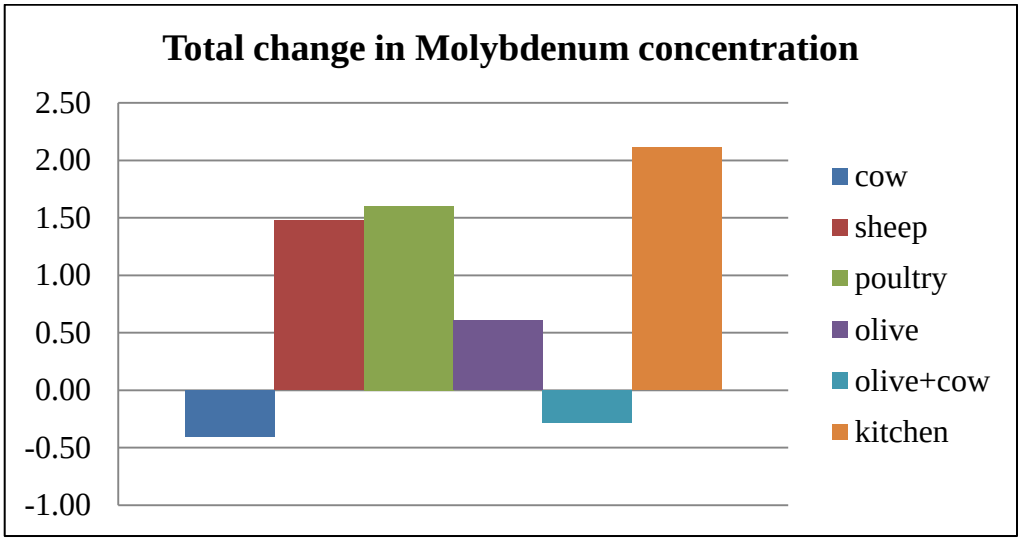

Figure 4.22: total percentage changes in Mo during digestion.

The above results show a minor increase (not significant change) of molybdenum concentration, the highest percentage of molybdenum concentration increase is for kitchen combination (2.11 %) and the lowest for cow combination

(-0.40 %).

4.13. Time of taking digestate from digester and storage it.

Most of the changes in the concentrations of nutrients (especially macronutrients) occur between day 10 and 40 because of most organic waste had converted into their basic component due to biochemical reactions. In average about 98% of changes of nutrients concentration occurs after 40 days, so the best time to use digestate is after 40 days. After 30 days the changes of nutrients between (65-80%) of total nutrients concentration so if we take digestate after 30 days it is possible to lose 20-35% of nutrients concentration.

Production of digestate is a continuous process, so storage is required before digestate applied to crops during the growing season. The needed storage capacity and the duration of the storage depend on location, soil type, rainfall, crop rotation etc. Digestate can be stored at the biogas plant, or at a location near to the fields where it will be applied as fertilizer. Regardless of location, digestate storages are often above ground in storage tanks. Lagoons and storage bags can also be used. The most important issue in storage digestate is covering the storage because this protect nutrient from expected losses through ammonia emissions, as well as protect digestate dilution by rainwater. [1]

4.14. Applying digestate as fertilizer.

Like any other fertilizer, digestate must be applied during the growing season in order to ensure the optimum uptake of the plant nutrients and to prevent ground water from pollution. Digestate must be applied at a certain amount, this need special equipment that preserve applications throughout the land. The equipment used to apply digestate should minimize the surface area exposed to air and ensure rapid incorporation of digestate into the soil. For these reasons, digestate is best applied with trailing hoses, trailing shoes or by direct injection into the top soil. These methods of application will also minimize ammonia volatilization. [1]

4.15. Future prospects

Beside the fertilizer or amendment properties of digestate, nowadays there are some other ways to use it. These new methods are very creative and make the possibility of proper use of digestates with different quality.

A new promising alternative of the digestate utilization is its use as solid fuel after drying. Kratzeisen et al. (2010) used liquid digestate originated from silage maize co-digestion with different field crops and animal residues. After drying the digestate, the water content of pellets made was 9.2-9.9%. Their mechanical durability fulfilled the requirements of standards for pellets. Moreover, the calorific value of these pellets was similar to the calorific value of wood. Therefore digestate fuel pellet seems to be a good alternative fuel for wood.[59]

Another interesting possibility of digestate utilization is the using of digestate effluent to replace freshwater and nutrients for bioethanol

production. Gao & Li (2011) found that ethanol production was enhanced with digestate effluent by as much as 18% comparing to the freshwater utilization.[59]

Digestate can be separated to liquid and solid fraction. Liquid fraction is suitable for irrigation and it has high N and K content. Solid fraction contains a great amount of volatile solid and P [60] and – by its fertilizer effect – has also high biogas and methane potential, therefore it could be used as a co-ferment for anaerobic digestion [61]

Chapter Five
Conclusions and Recommendations

5. Conclusions and Recommendations

5.1. Conclusions

- pH increase due to the consistence of (NH4)2CO3 resulted from reactions; this increase varied according to the type of combination. The largest change occurs in kitchen combination (6.57%) and the smallest change occurred in cow combination (3.02%).
- The obvious increase in nitrogen for all combination is according to ammonification .The higher percentage of nitrogen concentration increase is for poultry combination (13.88%) and the lowest for kitchen combination (11.10%).
- The obvious increase in phosphorous for all combination is according to biological processes during digestion .The highest percentage of phosphorous concentration increase is for kitchen combination (16.8%) and the lowest for olive combination (10.18%).
- The obvious increase in potassium for all combination is according to biological processes during digestion .The highest percentage of potassium concentration increase is for cow combination (13.17%) and the lowest for olive combination (8.25%).
- Minor or no change in concentrations of all micro-elements because of small reaction occurred on these elements during digestion process.
- The best time to use digestate is after 40 days because most changes in the concentrations of nutrients (especially macronutrients) occur between day 10 and 40. In average about 98% of changes of

nutrients concentration occurs after 40 days, after 30 days the changes of nutrients between (65-80%) of total nutrients concentration.

5.2. Recommendations

- It is technically feasible to use digestate as fertilizer in Palestine.
- Government support for farmers is required to establish biogas units and raise awareness among farmers to get the benefits of biogas and digestate.
- Agricultural research is needed to clarify the needed nutrients for each type of soil and crops, the best combination of digestate to each crop type, the better method to applying digestate as fertilizer, monitoring crops growth during applying digestate and other aquiculture issues.
- Studies of leakages of nitrogen during digestion and storage monitoring are needed.
- This research done in autumn (September and October) at which temperature range from 22 to 26 ^{o}C. If temperature gets more or less, as in summer and winter, many parameters will change according to temperature so research is required in other season of the year.
- Research of toxicity and its impact on nutrient, digestion process, soil and crops.
- Production of digestate is a continuous process, so storage is required before digestate applied to crops during the growing season. Digestate storages are often above ground in storage tanks. Lagoons

and storage bags can also be used. The most important issue in storage digestate is covering the storage because this protect nutrient from losses through ammonia emissions.

- Like any other fertilizer, digestate must be applied during the growing season in order to ensure the optimum uptake of the plant nutrients and to prevent ground water from pollution. Digestate must be applied at certain amount and special equipment.

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Appendix (A) pH and concentrations of nutrients for each sample pH

time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	7.36	7.37	7.25	7.33	7.35	7.29	7.42	7.38	7.41
sheep	7.97	8.04	7.93	7.98	8.03	7.97	8.15	8.16	8.12
poultry	7.55	7.59	7.47	7.52	7.58	7.49	7.72	7.69	7.78
olive	7.23	7.25	7.34	7.22	7.26	7.33	7.41	7.45	7.47
olive+cow	7.97	8.09	7.94	7.96	8.13	7.93	8.22	8.23	8.21
kitchen	7.78	7.77	7.83	7.77	7.76	7.84	8.02	7.93	8.04

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
7.46	7.44	7.48	7.58	7.52	7.57	7.56	7.58	7.51
8.31	8.22	8.27	8.41	8.36	8.38	8.39	8.43	8.39
7.85	7.83	7.86	8.08	7.95	7.94	7.91	8.04	7.99
7.59	7.63	7.64	7.73	7.72	7.75	7.71	7.74	7.71
8.34	8.43	8.36	8.45	8.42	8.44	8.41	8.47	8.48
8.14	8.21	8.11	8.31	8.35	8.28	8.34	8.32	8.29

Nitrogen

Nitrogen (N)	gm/L	Testing method: TKN							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	23.3861	23.2695	23.1530	23.7026	23.7150	23.7221	24.5084	24.5021	24.5189
sheep	30.0346	30.1977	30.2058	30.3544	30.3681	30.3750	32.0843	32.0933	32.0016
poultry	25.4039	25.2537	25.1064	26.2493	26.2447	26.2459	26.9874	26.9847	26.9834
olive	16.1257	16.2369	16.3110	16.6513	16.6660	16.6746	17.2195	17.2126	17.2053
olive+cow	19.4872	19.5122	19.5539	19.9880	19.9893	19.9818	20.6324	20.6224	20.6154
kitchen	14.0088	14.0143	14.0097	14.3432	14.3310	14.3265	14.5736	14.5684	14.5592

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
25.2442	25.2390	25.2511	26.2145	26.2180	26.2114	26.2266	26.2210	26.2316
33.1482	33.1391	33.1582	34.3450	34.3516	34.3431	33.8516	34.3456	34.3550
27.7674	27.7664	27.7754	28.9464	28.9482	28.9412	28.9464	28.9420	28.9486
17.7182	17.7182	17.7134	18.3652	18.3736	18.3585	18.3769	18.3785	18.3729
21.1998	21.1998	21.1936	21.9981	21.9947	21.9977	22.0127	22.0170	22.0116
14.9867	14.9867	14.9790	15.6151	15.6210	15.6048	15.6269	15.6313	15.6231

Phosphorous

Phosphorous (P)	gm/L	Testing method: UV spectroscopy							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	1.788	1.785	1.782	1.784	1.789	1.787	1.819	1.825	1.822
sheep	1.854	1.865	1.863	1.867	1.865	1.861	1.908	1.915	1.914
poultry	3.453	3.465	3.459	3.475	3.479	3.471	3.622	3.619	3.625
olive	1.531	1.536	1.532	1.549	1.541	1.535	1.568	1.569	1.566
olive+cow	1.698	1.695	1.691	1.689	1.691	1.699	1.745	1.739	1.743
kitchen	1.521	1.513	1.511	1.528	1.522	1.518	1.562	1.569	1.558

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
1.853	1.858	1.854	1.891	1.893	1.888	2.017	2.004	2.007
1.953	1.951	1.956	1.997	1.993	1.991	2.137	2.139	2.132
3.769	3.767	3.764	3.784	3.781	3.789	3.846	3.841	3.843
1.591	1.592	1.596	1.607	1.613	1.621	1.699	1.691	1.694
1.791	1.788	1.784	1.821	1.824	1.832	1.975	1.971	1.972
1.642	1.644	1.639	1.641	1.645	1.635	1.779	1.781	1.789

Potassium

Potassium (K)	gm/L	Testing method: ICP-MS							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	3.445	3.443	3.449	3.598	3.562	3.594	3.701	3.705	3.711
sheep	6.356	6.359	6.345	6.575	6.573	6.578	6.786	6.789	6.791
poultry	4.336	4.333	4.328	4.51	4.514	4.511	4.612	4.613	4.608
olive	2.361	2.365	2.363	2.352	2.353	2.355	2.421	2.425	2.419
olive+cow	3.141	3.137	3.147	3.196	3.195	3.198	3.305	3.302	3.306
kitchen	2.693	2.703	2.691	2.683	2.687	2.681	2.778	2.782	2.781

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
3.845	3.859	3.851	3.914	3.919	3.916	3.925	3.919	3.922
7.031	7.037	7.034	7.192	7.193	7.196	7.211	7.212	7.208
4.836	4.832	4.839	4.913	4.912	4.917	4.923	4.921	4.924
2.507	2.511	2.515	2.559	2.556	2.553	2.561	2.565	2.563
3.423	3.421	3.431	3.471	3.476	3.478	3.486	3.482	3.489
2.894	2.897	2.892	2.945	2.938	2.942	2.948	2.943	2.941

Calcium

Calcium (Ca)	gm/L	Testing method: ICP-MS							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	3.2571	3.2590	3.2583	3.2645	3.2641	3.2646	3.2680	3.2672	3.2671
sheep	3.8218	3.8211	3.8215	3.8328	3.8322	3.8323	3.8391	3.8383	3.8387
poultry	8.1237	8.1237	8.1247	8.1091	8.1097	8.1093	8.1509	8.1506	8.1508
olive	2.1032	2.1029	2.1029	2.1095	2.1095	2.1083	2.1155	2.1159	2.1152
olive+cow	2.7536	2.7531	2.7535	2.7598	2.7583	2.7593	2.7636	2.7640	2.7637
kitchen	1.9522	1.9528	1.9525	1.9551	1.9551	1.9554	1.9607	1.9611	1.9601

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
3.2776	3.2772	3.2776	3.2852	3.2862	3.2859	3.2896	3.2896	3.2891
3.8433	3.8436	3.8434	3.8502	3.8504	3.8506	3.8544	3.8549	3.8548
8.1817	8.1819	8.1812	8.2203	8.2201	8.2207	8.2271	8.2267	8.2275
2.1171	2.1176	2.1178	2.1181	2.1181	2.1182	2.1218	2.1214	2.1212
2.7666	2.7667	2.7676	2.7695	2.7688	2.7683	2.7719	2.7717	2.7711
1.9607	1.9601	1.9617	1.9628	1.9627	1.9624	1.9637	1.9634	1.9628

Magnesium

Magnesium (Mg)	gm/L	Testing method: ICP-MS							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	1.1541	1.1542	1.1548	1.1564	1.1562	1.1560	1.1809	1.1803	1.1808
sheep	0.8023	0.8025	0.8023	0.8042	0.8041	0.8049	0.8266	0.8261	0.8264
poultry	1.9259	1.9257	1.9251	1.9336	1.9334	1.9331	1.9833	1.9845	1.9838
olive	0.2560	0.2566	0.2568	0.2579	0.2576	0.2571	0.2589	0.2597	0.2591
olive+cow	0.6859	0.6852	0.6854	0.6861	0.6870	0.6866	0.6941	0.6949	0.6946
kitchen	0.3152	0.3153	0.3159	0.3197	0.3191	0.3195	0.3249	0.3241	0.3244

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
1.2012	1.2015	1.2019	1.2152	1.2142	1.2147	1.2242	1.2244	1.2237
0.8429	0.8424	0.8421	0.8557	0.8556	0.8551	0.8599	0.8591	0.8589
2.0040	2.0032	2.0037	2.0363	2.0351	2.0358	2.0426	2.0421	2.0419
0.2631	0.2626	0.2627	0.2657	0.2653	0.2659	0.2653	0.2654	0.2661
0.7023	0.7015	0.7019	0.7102	0.7099	0.7091	0.7101	0.7107	0.7112
0.3277	0.3278	0.3273	0.3320	0.3316	0.3312	0.3329	0.3329	0.3321

Iron

Iron (Fe)	gm/L	Testing method: ICP-MS							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	1.9361	1.9364	1.9368	1.9345	1.9343	1.9342	1.9349	1.9342	1.9348
sheep	2.5969	2.5961	2.5967	2.5914	2.5919	2.5917	2.6131	2.6137	2.6139
poultry	1.6212	1.6218	1.6215	1.6153	1.6152	1.6155	1.6302	1.6308	1.6311
olive	0.4571	0.4578	0.4579	0.4542	0.4551	0.4548	0.4565	0.4568	0.4566
olive+cow	0.9329	0.9324	0.9321	0.9271	0.928	0.9273	0.9321	0.9323	0.9322
kitchen	0.3058	0.3056	0.3051	0.3049	0.3053	0.3046	0.3067	0.3060	0.3063

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
1.9709	1.9702	1.9701	1.9861	1.9869	1.9873	1.9892	1.9879	1.9887
2.6386	2.6392	2.6382	2.6632	2.6633	2.6639	2.6661	2.6663	2.6663
1.6447	1.6450	1.6441	1.6569	1.6571	1.6575	1.6593	1.6581	1.6585
0.4593	0.4591	0.4596	0.4604	0.4601	0.4608	0.4601	0.4611	0.4605
0.9340	0.9332	0.9336	0.9346	0.9342	0.9341	0.9373	0.9364	0.9368
0.3065	0.3062	0.3071	0.3061	0.3069	0.3067	0.3082	0.3076	0.3073

Manganese

Manganese (Mn)	gm/L	Testing method: ICP-MS							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	0.08531	0.08536	0.08532	0.08531	0.08538	0.08543	0.08532	0.08539	0.08543
sheep	0.07012	0.07016	0.07017	0.07015	0.07007	0.07011	0.07018	0.07012	0.07014
poultry	0.38029	0.38028	0.38025	0.38059	0.38051	0.38045	0.38013	0.38017	0.38023
olive	0.00928	0.00925	0.00921	0.00921	0.00929	0.00925	0.00921	0.0093	0.00923
olive+cow	0.02229	0.02223	0.02228	0.02222	0.02223	0.02229	0.02226	0.02222	0.02232
kitchen	0.00588	0.00597	0.00593	0.00593	0.00591	0.00598	0.00589	0.00603	0.00597

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
0.08543	0.08547	0.08551	0.08552	0.08557	0.08558	0.08561	0.08557	0.08554
0.07018	0.07026	0.07021	0.07028	0.07021	0.07025	0.07022	0.07029	0.07026
0.38047	0.38043	0.38041	0.38063	0.38066	0.38067	0.38073	0.38071	0.38065
0.00929	0.00921	0.00926	0.00921	0.00922	0.00926	0.00923	0.00928	0.00926
0.02221	0.02223	0.02225	0.02227	0.02223	0.02229	0.02220	0.02223	0.02225
0.00593	0.00593	0.00597	0.00593	0.00599	0.00597	0.00592	0.00598	0.00597

Zinc

Zinc (Zn)	gm/L	Testing method: ICP-MS							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	0.10252	0.10253	0.10254	0.10255	0.10252	0.10249	0.10258	0.10250	0.10252
sheep	0.09505	0.09502	0.09500	0.09503	0.09501	0.09505	0.09502	0.09500	0.09507
poultry	0.27369	0.27365	0.27361	0.27371	0.27368	0.27362	0.27372	0.27376	0.27375
olive	0.00287	0.00289	0.00285	0.00284	0.00282	0.00285	0.00284	0.00282	0.00285
olive+cow	0.03061	0.03063	0.03066	0.03068	0.03064	0.03063	0.03061	0.03063	0.03065
kitchen	0.00136	0.00132	0.00134	0.00136	0.00131	0.00134	0.00137	0.00131	0.00134

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
0.10252	0.10256	0.10258	0.10262	0.10267	0.10271	0.10263	0.10269	0.10273
0.09516	0.09511	0.09513	0.09515	0.09513	0.09512	0.09526	0.09521	0.09523
0.27399	0.27396	0.27392	0.27412	0.27417	0.27419	0.27421	0.27423	0.27418
0.00288	0.00285	0.00285	0.00281	0.00283	0.00285	0.00287	0.00281	0.00285
0.03061	0.03062	0.03064	0.03068	0.03065	0.03063	0.03062	0.03068	0.03065
0.00131	0.00135	0.00134	0.00137	0.00133	0.00132	0.00129	0.00132	0.00139

Copper

Copper (Cu)	gm/L	Testing method: ICP-MS							
time	0 days			10 days			20 days		
combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
cow	0.02501	0.02500	0.02503	0.02504	0.02505	0.02503	0.02502	0.02507	0.02509
sheep	0.02242	0.02243	0.02245	0.02243	0.02242	0.02245	0.02245	0.02246	0.02241
poultry	0.04326	0.04324	0.04327	0.04329	0.04323	0.04327	0.04329	0.04319	0.04323
olive	0.00502	0.00504	0.00501	0.00503	0.00505	0.00502	0.00508	0.00504	0.00501
olive+cow	0.00831	0.00833	0.00834	0.00798	0.00801	0.00804	0.00837	0.00827	0.00831
kitchen	0.00324	0.00322	0.00326	0.00322	0.00321	0.00324	0.00323	0.00322	0.00324

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
0.02503	0.02511	0.02508	0.02515	0.02517	0.02511	0.02516	0.02513	0.02511
0.02242	0.02248	0.02247	0.02253	0.02245	0.02249	0.02253	0.02252	0.0225
0.04321	0.04325	0.04329	0.04326	0.04323	0.04328	0.04333	0.04329	0.04331
0.00507	0.00503	0.00502	0.00508	0.00501	0.00503	0.00504	0.00506	0.00503
0.00835	0.00836	0.00832	0.00836	0.00828	0.00831	0.00833	0.00834	0.00831
0.00324	0.00326	0.00322	0.00324	0.00327	0.00325	0.00328	0.00327	0.00324

Molybdenum

Molybdenum (Mo)	gm/L	Testing method: ICP-MS							
Time	0 days			10 days			20 days		
Combination	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
Cow	0.00232	0.00231	0.00236	0.00233	0.00231	0.00233	0.00232	0.00231	0.00235
Sheep	0.00315	0.00317	0.00313	0.00315	0.00314	0.00314	0.00312	0.00315	0.00316
Poultry	0.00335	0.00337	0.00332	0.00334	0.00332	0.00331	0.00334	0.00332	0.00336
Olive	0.00019	0.00021	0.00022	0.00026	0.00023	0.00021	0.00023	0.00021	0.00023
olive+cow	0.00115	0.00111	0.00113	0.00117	0.00109	0.00113	0.00116	0.00112	0.00113
Kitchen	0.00036	0.00033	0.00035	0.00031	0.00037	0.00035	0.00031	0.00039	0.00035

30 days			40 days			50 days		
sample 1	sample 2	sample 3	sample 1	sample 2	sample 3	sample 1	sample 2	sample 3
0.00239	0.00226	0.00231	0.00239	0.00236	0.00232	0.00231	0.00233	0.00232
0.00318	0.00317	0.00315	0.00319	0.00320	0.00315	0.00319	0.00318	0.00322
0.00336	0.00334	0.00332	0.00331	0.00338	0.00332	0.00341	0.00339	0.00340
0.00024	0.00027	0.00021	0.00021	0.00023	0.00027	0.00021	0.00021	0.00019
0.00116	0.00115	0.00113	0.00114	0.00113	0.00116	0.00111	0.00112	0.00115
0.00036	0.00037	0.00035	0.00036	0.00038	0.00037	0.00033	0.00035	0.00038

جامعة النجاح الوطنية
كلية الدراسات العليا

تقييم نوعية و كمية المغذيات الصغرى و الكبرى للناتج من عملية التخمر من وحدات الغاز الحيوي مع اختلاف المواد العضوية المدخلة

إعداد
رأفت عمارنه

إشراف
د.نعمان مزيد

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في هندسة المياه والبيئة بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2014

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اشراف

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الملخص

ان المخلفات الصلبة المتبقية من وحدات انتاج الغاز الحيوي ذات جودة عالية و مناسبة للاستخدام كسماد زراعي. هذا البحث يبحث في هذه المخلفات الناتجة من عملية التخمر اللاهوائي من خلال تحليل العينات عند وقت محدد من عملية التخمر لمعرفة و تقدير نسبة تركيز المغذيات اللازمة للنبات. وقد تم ايجاد وتقدير نسبة العناصر الرئيسة و الثانوية المغذية للنبات و ذلك باستتخدام مواد عضوية اولية مختلفة.

تم انشاء و تركيب ثمانية عشر وحدة غاز حيوي ذات حجم 250 لتر و تم استخدام ستة مجموعات من المواد العضوية الاولية (ثلاث متكررات لكل مجموعة من المواد العضوية الاولية) وكانت مدة التخمر 50 يوما. و تم استخدام المجموعات التالية في التخمر اللاهوائي:

- الروث البقري
- روث الاغنام البيضاء و السوداء
- روث الدجاج البياض و مخلفاتها
- المخلفات الصلبة الناتجة عن عصر الزيتون (الجفت)
- خليط من مخلفات الزيتون الصلبة و الروث البقري
- مخلفات المطبخ

كانت التغذية اليومية لكل وحدة غاز حيوي 4.25 لتر من المواد العضوية حيث كانت تخلط بماء بنسبة 1:1 و تدخل الي وحدة الغاز. لقد بدأت عملية التخمر في الثاني عشر من شهر أيلول و

تم جمع العينات كل عشرة ايام كما تم استخدام طريقة TKN و UV و ICPM spectroscopy في ايجاد نسبة العناصر المغذية للنبات في مخلفات الغاز الحيوي.

ان استخدام مخلفات الغاز الحيوي في فلسطين يحل جزء كبير من مشكلة المخلفات العضوية ويوفر المال للمزارعين. كما ان عملية التخمر اللاهوائي تتخلص من اغلب مسببات الامراض و تقتل اغلب البذور العشبية و هذا يعطي امان اكثر في استخدام المواد العضوية من للمزارعين. ان استخدام المخلفات العضوية الناتجة عن التخمر اللاهوائي في فلسطين قليلة جدا و ذلك يعود الي قلة المعلومات و المعرفة عن كمياتها و محاسنها.

في تحليل النتائج تم ايجاد زيادة واضحة في الرقم الهيدروجيني و المغذيات الرئيسة بعد انتهاء عملية الهضم. هذه الزيادة اختلفت حسب نوع المواد العضوية المستخدمة في عملية الهضم.

كانت اعلى نسبة زيادة للرقم الهيدروجيني في مخلفات المطبخ حيث بلغت 6.57% و اقل نسبة زيادة في الروث البقري حيث بلغت 3.02%. و للنيتروجين كانت اعلى نسبة زيادة في مخلفات المطبخ حيث بلغت 17.26% و اقل نسبة زيادة في الروث البقري حيث بلغت 12.15%. و كانت اعلى نسبة زيادة للفوسفور في روث الدواجن حيث بلغت 13.88% و اقل نسبة زيادة في مخلفات الزيتون حيث بلغت 10.18%. اما البوتاسيوم كانت اعلى نسبة زيادة في الروث البقري حيث بلغت 13.17% و اقل نسبة زيادة في مخلفات الزيتون حيث بلغت 8.25%.

و كانت نسبة الزيادة قليلة لكل من المغنيسيوم و الكلوريدات حيث كانت اعلى نسبة زيادة للمغنيسيوم في روث الاغنام حيث بلغت 6.92% و اقل نسبة زيادة في مخلفات الزيتون حيث بلغت 3.52%.

كما كانت نسبة الزيادة في تركيز الكالسيوم ضئيلة اما التغير في تركيز كل من الحديد و المنغنيز و النحاس و الموليبدينوم فكانت ضئيلة جدا لا تكاد تذكر.

من خلال الدراسة وجد أن افضل وقت لتطبيق المخلفات العضوية على المزروعات كان بعد 40 يوم من عملية الهضم حيث ان ما يقارب 98% من التغيرات في نسب المغذيات تحصل في هذه الفترة. كما وجد ان (65–80%) من التغيرات على المغذيات تحصل خلال اول 30 يوم من عملية الهضم.

ان تخزين المخلفات العضوية المهضومة ضروري قبل تطبيقها على المزروعات و اهم خطوة في تخزينها هي تغطيتها لحماية المغذيات و خاصة النيتروجين من التسرب من خلال انبعاثات الامونيا. كمان ان افضل وقت لتطبيق المخلفات العضوية المهضومة هو موسم النمو من أجل ضمان امتصاص امثل للمغذيات و تجنب تلوث المياه الجوفية بها. و يجب تطبيق هذه المخلفات بكمية معينه و ادوات خاصة.

المزارعين في فلسطين بحاجة لدعم الحكومة لانشاء وحدات الغاز الحيوي و زيادة الوعي بينهم للحصول على منافع المرجوة من هذا البحث. كما ان البحوث الزراعية مطلوبة لتوضيع متطلبات كل تربة من المغذيات و الكميات المطلوبة من المخلفات لكل نوع تربة و افضل انواع المواد العضوية اللازمة لكل نوع تربة و افضل الطرق لتطبيق المخلفات العضوية المخمرة على التربة و مراقبة المحاصيل خلال تطبيق هذه المخلفات عليها والتحكم بتسرب النيتروجين.

تم عمل هذا البحث في فصل الخريف (شهر أيلول و تشرين الأول) من عام 2013 حيث تراوحت درجة الحرارة بين (22–26) درجة سيلسيوس. و في حال ان درجة الحراة قلت او زادت فان كثيرا من المتغيرات المتعلقة بعملية التخمر اللاهوائي ستختلف لذلك فان بحوث في اوقات اخرى من السنه مطلوبة.