Effect of Major Cations on the Behavior of Ammonia during Wastewater Reuse Using Batch Experiment

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DEDICATION

To the soul of my beloved brother,
The Martyr, Ashraf

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ABSTRACT

In this study the effect of main cations on the fate and bahaviour of ammonia in wastewater was investigated. A batch experiment techniques was implemented. Secondary treated wastewater from North Wastewater treatement Plant (NWWTP) and synthetic wastewater were used. The synthetic wastewater was made of NH_4CI, KNO_3, $C_6H_{12}O_6$ and $NaHCO_3$, to produce C to N ratio of 1 to 1, and 10mg/l as NH_3-N and 5mg/l as NO_3-N. The cations of interest during this study were Ca^{++}, Mg^{++}, K^+ and Na^+. A series of batch experiments were conducted to examine this effect, carried out with sandy clay loam soil and loamy sand soil. The data analysis indicated that the cations had a significant effect on the removal of NH_3 during nitrification and ion exchange process. It showed that the competitive effect of Na^+ high concentration was greatest for NH_3 ion exchange. Hence, it was concluded that the order of the effect of cations on NH_3 ion removal sorption process is $Ca^{++} > K^+ > Mg^{++} > Na^+$. The finding results indicated that the ion exchange process in the sandy clay loam soil considered the dominant mechanism for NH_3 removal from the soil solution, and the nitrification process in the loamy sand soil considered the dominant mechanism for NH_3 removal from the soil solution. The maximum removed of NH_3 from the soil solution was repoted to be 87.5% in the Sandy clay loam soil and in the presence of Ca^{++}. In the same soil, around 90% of ammonia from treated wastewater produced by (NWWTP) was observed to be removed both by nitrification and ion exchange process. In the loamy sand the maximum removed of NH_3 from soil solution was reported to be 71.1% in the presence of Ca^{++}. In the same soil, around 43.5% of ammonia from treated wastewater produced by (NGWWTP) was observed to be removed both by nitrification and ion exchange.

ملخص الدراسة

"تأثير الكاتيونات الرئيسية على سلوك الأمونيا خلال اعادة استخدام المياه العادمة بتجربة الدفع"

تقدم هذه الأطروحة دراسة عن تأثير الكاتيونات الرئيسة على سلوك و تحولات الأمونيا خلال إعادة استخدام مياه الصرف الصحي, وقد تم تنفيذ تقنية تجارب الدفع للدراسة باستخدام مياه صرف صحي ثانوية المعالجة من محطة معالجة مياه الصرف الصحية في منطقة الشمال, و باستخدام مياه صرف صناعية. و تكونت مياه الصرف الصناعية من كلوريد الأمونيوم و نترات البوتاسيم و الجلوكوز و بيكربونات الصوديم لتحقيق نسبة الكربون إلى النيتروجين بنسبة 1:1, وليكون تركيز الأمونيا كنيتروجين 10 مليغرام للتر, و تركيز النترات كنيتروجين 5 مليغرام للتر.

حيث تم دراسة الكاتيونات التالية الكاسيوم و الماغنيسيوم و الصوديم و البوتاسيوم, و نفذت سلسة من تجارب الدفع لدراسة هذا التأثير باستخدام تربة رملية طينية طميية و تربة طميية رملية, و أوضحت النتائج النهائية للدراسة بأن الكاتيونات لها تأثير واضح على إزالة الأمونيا من خلال عمليتي النترجة و التبادل الأيوني في التربة, و أظهرت التأثير التنافسي للتركيز العالي للصوديوم الذي كان له الأثر الأكبر على تحولات الأمونيا. فقد خلصت النتائج إلى أن تأثير الكاتيونات على إزالة الأمونيا تبعا للترتيب التالي البوتاسيم و الكالسيوم و الماغنسيوم و الصوديوم. كما أظهرت النتائج أن عملية التبادل الأيوني في التربة الرملية الطينية الطميية كانت المهيمنة على عملية إزالة الأمونيا من محلول التربة بينما كانت عملية النترجة في التربة الرملية الطميية هي المهيمنة على عملية إزالة الأمونيا من محلول التربة. و قد وصل الحد الأقصى لإزالة الأمونيا في التربة الرملية الطينية الطميية في وجود الكالسيوم إلى 87.5% , و في نفس التربة وصلت إزالة الأمونيا من خلال عمليتي النترجة و التبادل الأيوني للتربة في مياه صرف صحي ثانوية المعالجة الناتجة من محطة معالجة مياه الصرف الصحي في منطقة الشمال إلى 90%, بينما كان الحد الأقصى لإزالة الأمونيا في التربة الرملية الطميية في وجود الكالسيوم 71%, و في نفس التربة وصلت إزالة الأمونيا من خلال عمليتي النترجة و التبادل الأيوني للتربة في مياه صرف صحية ثانوية المعالجة الناتجة من محطة معالجة مياه الصرف الصحي في منطقة الشمال إلى 43.5%.

LIST OF ABBREVIATIONS

BWWTP	**Beit Lahia Wastewater Treatment Plant**
BOD	**Biological Oxygen Demand**
CEC	**Cation Exchange Capacity**
CMWU	**Coastal Municipalities Water Utility**
DOC	**Dissolved Organic Carbon**
DW	**Deionized Water**
EC	**Electrical Conductivity**
EPA	**Environmental Protection Agency**
GW	**Ground Water**
GWWTP	**Gaza Wastewater Treatment Plant**
Hr	**Hour**
MEQ/L	**Milliequivalent per Liter**
M S L	**Main Sea Level**
NCSWS	**National Center for Sustainable Water Supply**
NWWTP	**Northen Wastewater Treatment Plant**
PE	**Primary Effluent**
PWA	**Palestinian Water Authority**
RWWTP	**Rafah Wastewater Treatment Plant**
SAT	**Soil Aquifer Treatement**
SBR	**Sequencing Batch Reactor**
SE	**Secondary Effluent**
TDS	**Total Dissolved Solid**
W	**Weight**

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CHAPTER 1: INTRODUCTION

Water scarcity is likely to become more problematic in the near future due to rapid population growth, increasing per capita water consumption and geographical disparities between centers of population growth and availability of water (Postel, 1997). Water shortage is one of major concern in the world, due to population growth, rapid urbanization, increased domestic and industrial water use, pollution of fresh water sources and extreme weather patterns. With increasing shortages of freshwater, wastewater is now being recognized as a significant source of water for nonpotable uses (Miller, 2006; Metcalf & Eddy, 2007). In a world full of pollution, contaminated wastewater is considered to be one of the most serious threats to the environmental engineers, with mainly a civil engineering background, have placed a great effort and time on water pollution control (Viessman and Mark, 1998).

Artificial recharge of groundwater with treated wastewater or excess surface water is gaining wide acceptance as a method to replenish over drafted aquifers and provide sustainable water supplies (Bouwer et al., 1990).

This technique can provide the important link as a transition step between reclaimed municipal wastewater and groundwater and offers a higher level of acceptability and attractiveness in contrast to direct potable reuse due to psychological and esthetic reasons (Asano & Cotruvo, 2004). Soil Aquifer Treatment (SAT) represents a wastewater reclamation/reuse technology that has been gaining acceptance as an integral component in indirect potable reuse systems. SAT is a natural land treatment technology that uses soil infiltration and percolation through the unsaturated zone as treatment of the wastewater effluent before subsequent recharge to the underlying groundwater aquifer. Treatment by physical, chemical, and biological means continue

as the percolate passes through the unsaturated zone. Significant nitrification and simultaneously denitrification can occur during SAT, providing removal of nitrogen from the system (Pescod, 1992).

Wastewater contains a variety of contaminants, and nitrogen is considered as one of the undesirable pollutants. Nitrate NO_3^-, due to its high water solubility, is possibly the most widespread groundwater contaminant in the world, imposing a serious threat to drinking water supplies and promoting eutrophication. The presence of elevated concentrations of NO_3^- in potable water has become a serious concern worldwide over the recent decades. The increase in NO_3^- levels can be linked to several kinds of human activities especially the intensive use of fertilizers in agriculture, which have led to the higher NO_3^- contamination of ground and surface water sources. Nitrates in drinking water cause methemoglobinemia in infants (blue babies). The presence of nitrates can also lead to the formation of carcinogenic nitrosamines.

The adsorption of ammonia during SAT is a function of cation exchange capacity (CEC); the (CEC) is the total of the exchangeable cations that a soil can hold at a specified pH, and effluent cation composition. The large ratio of soil to water used during SAT makes moderate cation exchange capacities sufficient to remove ammonia by adsorption (NCSWS, 2001).

1.1 Problem statement:

The Gaza Strip is classified as a semi-arid region and suffers from water scarcity. The renewable amount of water that replenishes the groundwater system is much less than the demanded amount and this has resulted in deterioration of the groundwater system in both quantitative and qualitative aspects (PWA, 2000).

Water problem is expected to grow and the deficit in terms of quantity will reach to about 100 Mm3/y by year 2020, while the water quality will be deteriorated

dramatically according to Palestinian Water Authority report (PWA, 2003). Wastewater reuse is now the most significant source in quantity-deteriorated regions, as the Gaza Strip because of scarce presence of surface water.

Nitrogen pollution in urban and rural groundwater is a common problem and it poses a major threat to groundwater-based drinking water supplies excessive nitrate concentration in groundwater is a significant public health problem. Monitoring of groundwater in the Gaza Strip indicated the presence of nitrates as early as the 1990s. It emerged that the elevated levels of nitrate were primarily caused by the infiltration of sewage from domestic septic tanks as well as agricultural runoff into the groundwater. A disturbing feature of nitrate as a contaminant it is colorless, tasteless and odorless. Fact indicates that the population has not been warned about it, means that people will continue to consume drinking water with high nitrates unless they are informed about it. Nitrate values in the Gaza Strip have continued to rise and currently present a health risk throughout the territory. Since the aquifer is a contiamin and pollution is occurring across the Gaza Strip, in varying degrees, it is not surprising that high levels of nitrate NO_3^- are found throughout the Gaza Strip. (UNEP, 2009). However the practical operation of SAT facilities still relies upon experience. Systems that have been poorly operated because of the lack of operation criteria have failed, and seriously damaged the groundwater causing environmental health, social and economic problems (Benham-Blair and Affiliates, 1979). So studying the effect of major cations on ammonia behavior during wastewater reuse is expected to help in understanding the behavior of ammonia in SAT to prevent groundwater from becoming contaminated.

1.2 Aims and Objectives:

This research aims to assess the function of soil type on the behavior of ammonia in the presence of cations Ca^{++}, Mg^{++}, K^+, and Na^+.

The specified objectives of this research are studying the following: _

a-The effect of the concentration of Ca^{++}, Mg^{++}, K^+, Na^+ on the sorption of NH_4^+ on soil particles.

b-The effect of the concentration of Ca^{++}, Mg^{++}, K^+, Na^+ on the nitrification of NH_4^+ in wastewater.

1.3 Research Structure

The thesis focused on the effect of major cations on the behavior of ammonia during wastewater reuse using batch experiment with synthetic wastewater and real wastewater with two different types of soils. The study is divided into six chapters.

- Chapter one includes a general introduction, Problem statement, aims and objectives of the study, and research structure.

- Chapter two the Soil Aquifer Treatment (SAT) and the technology of SAT is identified. Components of SAT are described. Factors affecting SAT performance are reviewed and discussed. Nitrogen Removal process are described. Fate of nitrogen in SAT is discussed. Uses of treated wastewater effluent are presented. Ion exchange and Cation Exchange Capacity are defined. The adsorption of ammonia in soil is reviewed. Soil properties are described. Batch experiment theory is defined.

- Chapter three describes geography of the Gaza Strip, topography, soil, climate and Population, Water resources problem at the study area, wastewater treatment plant in The Gaza Strip and (Northern) wastewater treatment plant (NWWTP).

- Chapter four describes the Methodology in this thesis.

- Chapter five includes discussion the results of the thesis, soil characterization, runs with sandy clay loam soil, runs with loamy sand soil, and runs with secondary treated wastewater.

- Chapter six, a summary of conclusion and recommendations of the study are presented.

CHAPTER 2: LITERATURE REVIEW

SAT is a sustainable technology for wastewater treatment prior to indirect potable reuse. It is a low cost and operation is not highly technical and therefore suitable to arid and semi arid developing countries.

2.1 Soil Aquifer Treatment (SAT)

Soil Aquifer Treatment (SAT) is artificial recharge process wherein the groundwater is recharged with pre-treated wastewater effluent (Houston et al., 1999). This concept can be broadened to a SAT system that adds the additional components of effluent pretreatment, SAT site operation and the recovery of groundwater after infiltration and aquifer storage for water reuse. The SAT technology involves infiltration of secondary effluent through a recharge basin with subsequent extraction through recovery wells, and embodies both treatment, dominant in the vadose (unsaturated) zone, and storage within the saturated zone (aquifer). It is an advanced wastewater treatment process that is both natural and sustainable, and is dominated by biodegradation, initially aerobic and subsequently anoxic (Amy and Drewes, 2007). It represents a wastewater reclamation/reuse technology that has been gaining acceptance as an integral component in indirect potable reuse systems. Treatment by physical, chemical, and biological means continue as the percolate passes through the unsaturated zone. SAT, when combined with other available water treatment technology can produce an effluent quality appropriate for potable reuse. Municipal wastewater can be an important water resource but its use must be carefully planned and regulated to avoid adverse health impacts (Bouwer, 2000).

Types and quantities of contaminants of reclaimed wastewater as well as degree of pretreatment has to be assessed prior to surface spreading or injection to groundwater aquifers (Asano and Cotruvo, 2004).

2.2 The Technology of SAT

The SAT technology consists of infiltrating wastewater effluent through a recharge basin with eventual extraction through recovery wells. Figure 2.1 shows the schematic diagram of SAT, it is a natural land treatment technology that uses soil infiltration and percolation through the unsaturated zone as treatment of the wastewater effluent before subsequent recharge to the underlying groundwater aquifer. A number of treatment processes operate as the wastewater flows vertically downward through the unsaturated soil of the vadose zone to the underlying aquifer. The major purification processes occurring in the soil aquifer system are: slow sand filtration, chemical precipitation, adsorption, ion exchange, biological degradation, nitrification, denitrification and disinfection (Houston et al., 1999; Kanarek & Michail, 1996). These mechanisms can be very effective in removing nitrogen, phosphorous, biochemical oxygen demand (BOD), suspended solids, organic compounds and trace metals (Kopchynski et al., 1996).
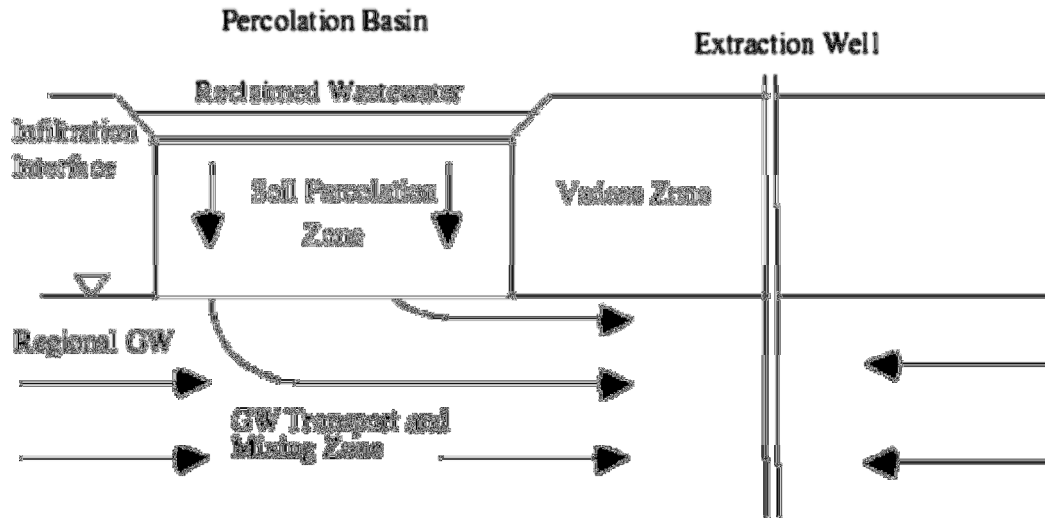
Figure 2. 1: Schematic diagram of soil aquifer treatment (SAT) (Source: Amy & Drewes, 2007; Fox et al., 2005).

2.3 Components of SAT

American Water Works Association Research Foundation (AWWARF, 1998) and

U.S. Environmental Protection Agency (EPA, 1973) defined five main components

as a requirement for any SAT distribution system, Figure 2.2 as:

1. The pipeline that carries the treated effluent from the wastewater treatment plant to

the infiltration basins (percolation ponds). This transmission to the site can be done by

gravity or by pumping. At the end of the line there must be an outlet facility. This

usually consists of a single riser pipe in each basin or the application can be done by

sprinklers (EPA, 1973).

2. Infiltration basins or percolation ponds where the treated effluent infiltrates into the

ground. It could be one basin or more. A SAT system with large numbers of small

basins is always preferable to one with only few large basins. A system with large

numbers of basins offers more flexibility in scheduling wetting and drying times and

in performing maintenance work.

3. The soil immediately below the infiltration basins which consists of the unsaturated

soil (vadose zone) where all the physical and chemical transformations will take place

in.

4. The unconfined aquifer where the applied wastewater is stored for long or short

duration.

5. The recovery well/wells to pump out the treated wastewater from the aquifer again.
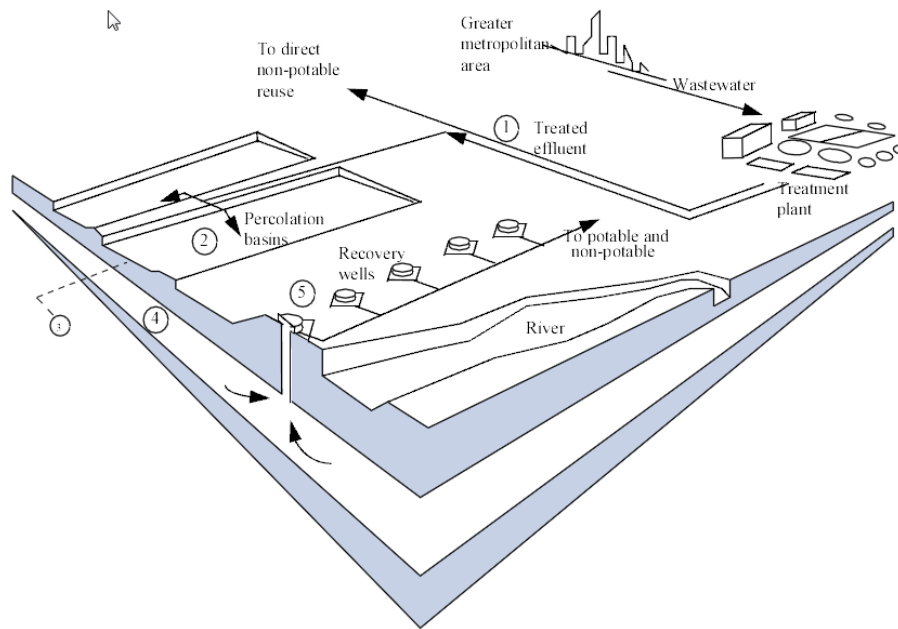
Figure 2. 2: A schematic diagram of various SAT components: (1) pipeline (2) basins (3) soil (4) unconfined aquifer and (5) recovery wells.

2.4 Factors affecting SAT performance

The factors that influence infiltration rates and soil aquifer treatment are soil type,

surface clogging material, pond depth and wetting/drying cycles.

1. Soil type

The best surface soils for SAT systems are in the fine sand, loamy sand, and sandy

loam range. Materials deeper in the vadose zone should be granular and preferably

coarser than the surface soils (Pescod, 1992).

Significant differences in removal efficiencies of non-purgable dissolved organic carbon (NPDOC) were reported by Quanrud et al., (1996). 56% removal was reported for colums containing Sandy loam. However, 48% and 44% were reported for sand and silty sand soils, respectively. No significant differences in the removal of UV-absorbing organics were observed in the same experiment for columns containing sand (22%) and sandy loam (20%). Soil properties can affect infiltration rates, bacterial attachment, reaeration rates and adsorption (Fox *et al.*, 2001). Soils with high hydraulic conductivities provide high infiltration rates during the beginning of wetting cycles during SAT and infiltration rates decrease as clogging layers develop (Pescod, 1992). In addition surface infiltration system requires transmissive aquifers to get lateral flow away from the infiltration system without excessive groundwater mounding (Bouwer, 2002). The nature of soils beneath the vadose zone affects the filtration rate. Previous studies have shown that fine clay result in low filtration rates (Fox *et al.*, 2001a).

Depending on the soil type, removal of DOC is rapid during percolation through the first 1.5 m (Quanrud *et al.*, 2003). Therefore, SAT technology can be applied in tertiary wastewater treatment without polluting the deeper soil layers. However, soil characteristics vary from place to place with the depth making the rational design and operation of SAT systems difficult since it would require detailed hydrogeological investigations for each site. According to Bouwer, (2002) SAT systems require permeable soils to get water into the ground and to the aquifer. Permeability depends on types of soil and porosity. During SAT clogging caused by biological processes and suspended solids at the infiltration interface reduces the permeability of soil leading to declined infiltration rates.

2. Surface clogging material

The hydraulics of wastewater infiltration basins are affected by the formation of a low conductivity clogging layer on and within the upper few millimeters of the surface soils (Bouwer, 1996). Surface clogging phenomenon is also present even in freshwater recharge basins. This clogging layer impedes wastewater infiltration (Quanrud et al., 1996).

There is two type of clogging layers the first is physical filter cake, as particulate material (organic and inorganic suspended solid) accumulates on the bottom of the basin to form the clogging layer it exists in a loose, compressible state. An increase in water depth translates to compression of this loose material because of the action of the seepage forces exerted by the infiltrating water, eventually resulting in the reduction of hydraulic conductivity of the clogging layer and the infiltration rate (Houston et al., 1999).

The second type is microbial film growth, it is biological clogging, is bacteria adsorped to the soil surface.

3. Pond depth

The pond depth in the infiltration basin should be kept relatively shallow. Small depths promote fast turnover of the wastewater in the basins during wetting time and minimize growth of suspended algae that can form a filter cake on the surface (Bouwer and Rice, 1984), which causes precipitation of calcium carbonate due to pH increases as the algae remove carbon dioxide from the water during photosynthesis or other biological activities. However, as the water depth is increased, the clogging layer is compressed and becomes less permeable (Bouwer *et al.*, 1984). As a result of this, the increase in infiltration rate may only be moderate or even a decrease. In other words the infiltration rate does not increase in direct proportion to increasing the

water depth in the basin. (Bouwer and Rice, 1989) reported an increase in the hydraulic loading rate from 20 m per year to 100 m per year when the water depth was decreased from 1 m to 0.2 m in basins with fine loamy sand. Unlike this, results from their lab experiments reported an increase in the infiltration rate from 30 cm per day to 40 per cm day in one day as the water depth was increased from 20 cm to 85 cm in columns filled with the same loamy sand. This is a simple illustration how the system under field conditions behaves different from laboratory experiment outcome

4. Wetting/Drying Cycles

During soil aquifer treatment, cyclic flooding/drying of the basins is necessary for improvement of infiltration rates and to control aerobic conditions in the soil (Kopchynski et al., 1996). Recharge basins function under wet and dry cycles, alternately. A clogging layer called schmutzdecke develops at the soil surface during flooding due to the combined effects of algal growth, suspended solids deposition, and bacterial growth in soil pore spaces and slows down the infiltration rate. However, infiltration rates are restored during the drying cycles by allowing the soil surface to dry and develop cracks (Quanrud et al., 1996).

Wet-dry cycle operations consist of filling the pond to a certain depth, stopping the inflow (loading) and allowing the water to infiltrate into the ground. After all the water has infiltrated into the soil, the pond is left to dry for a period so that natural aeration can take place. During the drying period, water percolates and the infiltration potential for the next application period increases. When clogging occurs, the recharge basin can be cleaned and possibly restored to their original capacity by draining, drying and scraping. Another method of wet-dry cycle operation is to maintain a full pond, i.e., the influent water is maintained at a rate equal to the recharge rate. When the recharge rate reaches an unacceptable value, the operation is

stopped so that the clogging layer can be removed (Li et al., 2000). The best soils are in the texture range of sandy loam, loamy sand, and fine sand (EPA, 1973: Bouwer, 1985: NRC, 1994).

Nitrogen species present in the recharged wastewater before SAT usually include various forms of inorganic and organic nitrogen. Signicant nitrication and simultaneous denitrication can occur during SAT, providing removal of nitrogen from the system (Kanarek *et al.,* 1993). Nitrogen species present in wastewater usually include various form of organic and inorganic nitrogen (ammonium*,* nitrite and nitrate); raw sewage has considerable organic nitrogen (Brdjanovic, 2006).

2.5 Nitrogen Removal Process

The nitrogen compounds such as ammonia and nitrite can be toxic to aquatic life if presented at sufficiently high concentrations, while nitrate is known to cause "blue baby syndrome" and is therefore a potential public health threat. Furthermore, nutrient such as nitrogen and phosphorus are known to stimulate growth of algae and other photosynthetic aquatic life, which leads to excessive eutrophication, excessive loss of oxygen resources, and undesirable changes in the aquatic ecosystem (Jang et al., 2004). The most common forms of nitrogen in wastewater are ammonia (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) ions and organic nitrogen, determined as total nitrogen. The organic fraction of nitrogen consists of a complex mixture of compounds including amino acids, and proteins (polymers of amino acids), (Metcalf and Eddy 2003). Biological nitrogen removal is usually achieved by a sequence of ammonification, nitrification and denitrification processes, ammonification is the conversion of soluble organic nitrogen into ammonia-N that occurs as bacteria consume soluble organic matter containing nitrogen (Grady et al., 1999), During

nitrification ammonia is biologically oxidized to nitrite which is then reduced to nitrogen gas during the denitrification process, as shown in the Figure 2.3.
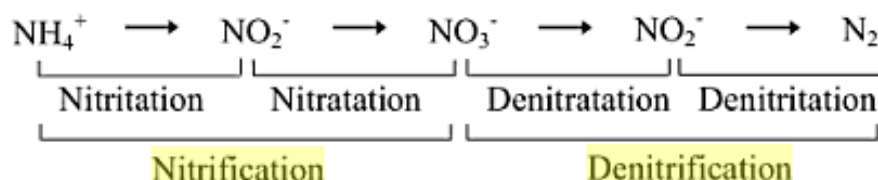
Figure 2. 3: Nitrification and Denitrification process.

Nitrification is conducted in two sequential oxidative stage: ammonia oxidation to nitrite (nitritation) and nitrite oxidation to nitrate (nitratation) with oxygen (an aerobic process that requires oxygen). Each stage is performed by different bacterial genera that are for instance Nitrosomonas, Nitrosococccus for nitritation and Nitrobacter, Nitrospira for nitratation. The nitrifiers use ammonia or nitrite as an energy source, oxygen as an electron acceptor and carbon dioxide as carbon source. Equations for nitritation, nitratation and total oxidation generating energy are as follows (Metcalf and Eddy 2003).

$$2\ NH_4^+ + 3\ O_2 \quad \rightarrow \quad 2NO_2^- + 4H^+ + 2H_2O + \text{Energy} \qquad \text{(Nitrosomonas)} \qquad 2.1$$

$$2NO_2^- + O_2 \quad \rightarrow \quad 2NO_3^- + \text{Energy} \qquad\qquad\qquad \text{(Nitrobacter)} \qquad 2.2$$
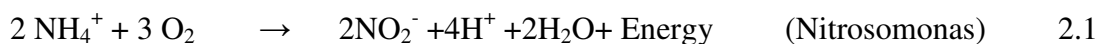
Thus, the total oxidation equation is expressed by:

$$NH_4^+ + 2O_2 \quad \rightarrow \quad NO_3^- + 2H^+ + H_2O \qquad\qquad\qquad \text{(Nitrifies)} \qquad 2.3$$

From equations (2.1), (2.2), and (2.3), it can be noticed that the nitrification process does not remove nitrogen from the wastewater, instead, it only change the nitrogen compounds oxidation states.

The biomass synthesis reaction in nitrification is represented as follows:

$$4CO_2 + HCO_3^- + NH_4^+ + H_2O \rightarrow C_5H_7O_2N + 5O_2 \qquad\qquad\qquad 2.4$$
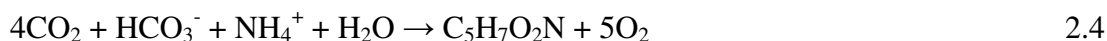
The over all synthesis and oxidation reaction in nitrification can be represented as follows:

$$NH_4^+ + 1.863O_2 + 0.098CO_2 \rightarrow 0.0196C_5H_7NO_2 + 0.98NO_3^- + 0.0941H_2O + 1.98H^+ \quad 2.5$$

The chemical formula $C_5H_7NO_2$ represent the synthesized bacterial cells.

According to the above equation for each g of ammonia (as N) oxidized, 4.25 g of O_2 are utilized, 0.16 g of new cells are formed, 7.07 g of alkalinity (as $CaCO_3$) are consumed it is a large amount of alkalinty, and 0.08 g of inoganic carbon are required for the formation of new cells.

Denitrification is accomplished in two sequential reductions under anoxic condition by a heterotrophic bioconversion process. Nitrate is reduced to nitrite (denitrataion), and then the nitrite is reduced to nitrogen gas (denitritation). During denitrification, microorganisms utilize nitrite and or nitate as electron acceptors and organic matter as carbon and energy source. A variety of carbon sources, such methanol, acetate, glucose and ethanol can serve for denitrification. Denitrification is an important process because it closes the loop of the nitrogen cycle. Without this process the atmospheric nitrogen would be depleted. Denitrification is favored in the absence of oxygen (anaerobic) although most denitrifiers are facultative (Metcalf and Eddy, 2004). The denitrification, according to Hammer, (2007), has several benefits, including the recovery of approximately 60% of the energy dispended during the nitrification and about 50% of the alkalinity consumed by nitrification.

2.5.1 Factors effect nitrification and denitrification

According to Henze et al., (2001) there are many factors that affect nitrification and denitrification processes, such as temperature, pH, oxygen, alkalinity energy sources and Cations.

- **Temperature** WEF et al., (2005) affirm that nitrification has been shown to occur in wastewater temperatures from 4 to 45ºC, with an optimum growth rate occurring in the temperature range 35 to 42ºC. However, studies carried out by Fontenot et al. (2007), testing different temperatures (22, 28, 37 and 45ºC) on shrimp wastewater treatment using a sequencing batch reactors SBR system, showed that the temperature range of 22-37 ºC worked well and removed more than 89% of all nitrogen species (nitrite, nitrate, ammonia nitrogen) and carbon. According to Henze et al., (2001), denitrification rate is very low below 5 ºC and increases with increasing temperature until 35 ºC. However, most wastewater treatment plants operate with liquid temperature between 20 and 30ºC.

- **pH** Metcalf & Eddy, (2003) suggest that the nitrification rate decline significantly at pH values below 6.8;(Metcalf & Eddy, 2003) recommend that 6.5 to 7.5 is the optimum pH rang for denitrifying bacteria.

- **Dissolved oxygen** (DO) Ferreira, (2000) affirm that optimum nitrification rates can be obtained using DO levels higher than 4.0 mg/l, provided that there is a sufficient population of nitrifying bacteria. In denitrifying systems, the maintenance of low dissolved oxygen concentration is very important to obtain good nitrate removal rates. The denitrification can be completely inhibited at DO concentrations lower than 0.2 mg/l (Wiesmann et al., 2007).

- **Alkalinity** In agreement with Grady et al., (1999), while the nitrification process consumes alkalinity, denitrification generates it. If both processes occur in the same tank, as in a SBR (sequencing batch reactor) system, the effluent alkalinity is the overall result of alkalinity consumed in nitrification and alkalinity generated in denitrification. Theoretically the difference between influent alkalinity and effluent alkalinity (as CaCO3) is 7.14 - 3.57 = 3.57 mg/l per mg/l removed (LI & Irvin, 2007).

- **Energy source** the energy needed for cell synthesis may be supplied by light or by a chemical oxidation reaction. Those organisms that are able to use light as an energy source are called phototrophs. Phototrophic organisms may be either heterotrophic (certain sulfur bacteria) or autotrophic (algae and photosynthetic bacteria). Organisms that derive their energy from chemical reactions are known as chemotrophs. Like the phototrophs, chemotrophs may be either heterotrophic (protozoa, fungi, and most bacteria) or autotrophic (nitrifying bacteria). Chemoautotrophs obtain energy from the oxidation of reduced inorganic compounds, such as ammonia, nitrite, and sulfide. Chemoheterotrophs usually derive their energy from the oxidation of organic compounds.

- Wastewater contains amount of major **cations** in different concentration which effects on nitrification process. As reported by Hileman, (1974) high level of soluble salts, increased salinity in the soil, this led to decrease the nitrification process. Major cations Ca^{++}, Mg^{++}, K^+, Na^+ compete with NH_4^+ for adsorption sites, which reduces the adsorption of ammonia on soil, result decreased nitrification process and increased the concentration of ammonium in solution of soil. Furthermore, there is a competition in the wastewater for exchange

sites between ammonium ions and other cations, resulting in a lower ammonium exchange compared to if only an ammonium solution would have been applied (Koon and Kaufmann, 1975).

2.6 Fate of Nitrogen in SAT

Nitrogen is very important in wastewater management because nitrogen has many effects in environment like eutrophication, oxygen depletion and toxicity. Ammonia is extremely toxic to fish and other aquatic organism, it is also oxygen consuming compound which can deplete dissolved oxygen in aquatic environment (Chacha, 2007).

Nitrogen removal from the percolated water in the SAT system is important because nitrogen may contaminate the groundwater and cause serious health problems if consumed by humans. The total nitrogen levels in conventionally treated domestic wastewater are on the order of 20 mg-N/l unless effluent is at least partially nitrified. The dominant nitrogen species are ammonium ion and organic nitrogen. During SAT nitrogen conversions tend to produce oxidized nitrogen forms (predominantly nitrate) that may have groundwater quality implications (Fox *et al.*, 2001).

Biological denitrification has received much attention as a method of removing nitrogen because it returns nitrogen to the atmosphere as inert N_2 gas. The main difficulty in using denitrification is that N in the applied wastewater is mostly in the NH_4^+ and organic N forms, which must be first oxidized to NO_3^- before denitrification can proceed (Abushbak, 2004).

Particulate kjeldahl nitrogen is also removed by filtration in the upper soil layer and the dissolved part by adsorption onto soil particles. Ammonia is removed by adsorption and nitrification-denitrification biological process (Idelovitch *et al.*, 2003).

Nitrogen removal has been observed during SAT at many sites recharging effluent containing ammonia-nitrogen. A common hypothesis for this nitrogen removal is the two-step process of autotrophic nitrification and heterotrophic denitrification. Recharge basins are typically operated to consist of a wetting cycle when water is applied followed by a drying cycle. Due to the net positive charge of the ammonium ion, it is adsorbed onto the soil in the upper region of the vadose zone during the wetting cycle Figure 2.4. During wetting, oxygen is not available for nitrification. As the soil dries and air/oxygen enters the soil, the oxidation of ammonia to nitrate by autotrophic nitrifiers may occur. This process results in a high nitrate concentration at the beginning of the following wetting cycle. This nitrate, which tends to be more mobile, is transported with the water deeper into the vadose zone. Once the nitrate reaches an anoxic zone, heterotrophic denitrification may convert the nitrate to nitrogen gas in the absence of oxygen and in the presence of an organic carbon electron donor (Fox *et al.*, 2001).
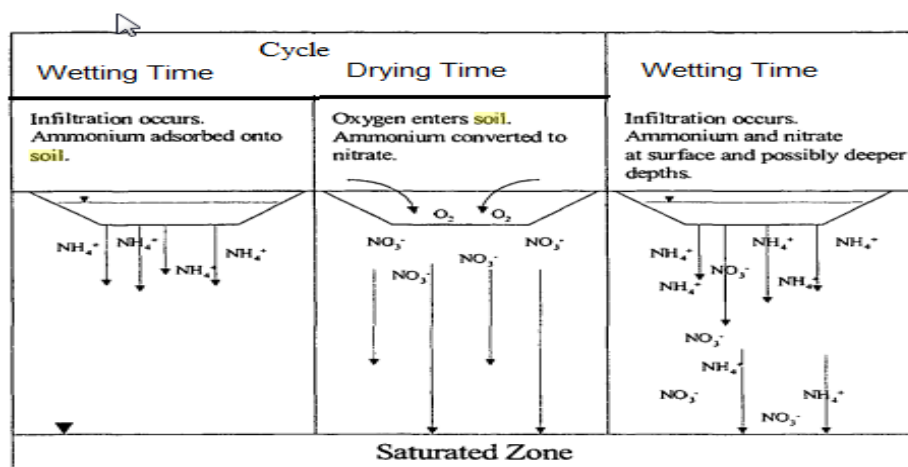
Figure 2. 4: The Wetting and Drying Cycle.

In order to achieve denitrification, wetting period must be long enough to obtain anaerobic conditions that allow adsorption of the ammonium to the clay particles. The adsorbed ammonium will be nitrified under aerobic conditions during drying part of cycle while at the same time the nitrate will be denitrified in micro anaerobic zones present in the aerobic vadose zone. At the beginning of the wetting time of the basin sufficient oxygen is available. This leads the organic matter (usually stated as $C_5H_7O_2N$ to be degraded aerobically to form ammonium as described by the reaction:

$$C_5H_7O_2N + 5O_2 \rightarrow NH_4^+ + 4CO_2 + H_2O + HCO_3^- \hspace{3cm} 2.7$$
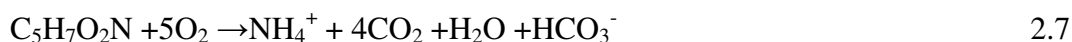
Amount of produced and original NH_4^+ is adsorbed to the clay particles in the soil. The amount to be adsorbed depends on the cation exchange capacity of the soil. As the drying process starts, oxygen from the atmosphere starts to enter the soil to create the aerobic conditions in the system. The adsorbed ammonium is oxidized by the nitrosomonas and nitrosococcus bacteria (nitrifying bacteria) as described by the chemical reaction:

$$NH_4^+ + 3/2O_2 + H_2O \rightarrow NO_2^- + HCO_3^- \hspace{3cm} 2.8$$

The total nitrification of NH_4^+ during the aerobic or drying time is desirable to promote the denitrification process during subsequent anaerobic or wetting time and for avoiding NH_4^+ accumulation in the soil. This accumulation can happen if the amount of NH_4^+ applied during the wetting time exceeds that which can be nitrified during the following dry time. This causes a subsequent increase in the NH_4^+ content of the water during the next wetting time. The formed nitrite NO_2^- in soil environment is so quickly oxidized to nitrate NO_3^- that it rarely accumulates. In most soils NO_3^- is not adsorbed to the clay particles. It moves readily with the soil solution. If large quantities of wastewater are applied to the land NO_3^- will move downward and may eventually reach the groundwater. However, whether NO_3^- is formed from oxidizing NH_4^+ or is initially present in the wastewater, it is subject to denitrification under the denitrification conditions of the soil which may prevent at least some of it from moving downward:

$$5CH_2O + 4H^+ + 4NO_3^- \rightarrow 5CO_2 + 7H_2O + N_2 \uparrow \qquad\qquad 2.9$$
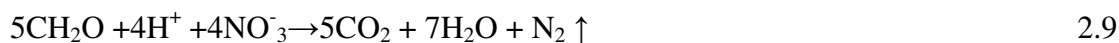
This mechanism of denitrification is known as heterotrophic denitrification. When sulfide replaces organic carbon as the electron donor the mechanism for denitrification is known as autotrophic. Both mechanisms were found to take place when oxygen levels are limited, but heterotrophic mechanism was found to be the dominant in the SAT systems. Therefore, denitrifiers prefer very wet soil conditions, where there is available organic carbon. The un-denitrified NO_3^- from this process will leached out to the groundwater by the next wetting process. The remaining nitrate that may leach out during the wetting period of the following cycle will be removed with distance of travel and dilution in aquifer (Abushbak, 2004).

The necessary conditions for denitrification include absence or near absence of molecular oxygen and adequate supply of electron donors and a capable bacteria population (Miller *et al.*, 2006).

2.7 Uses of Treated Wastewater Effluents

Treated wastewater effluents, free from health hazards, must be considered as a valuable water resource for irrigation of certain crops, greening enhancement, landscaping, land reclamation, car washing, industrial process water, and toilet flushing. Treated wastewater may also be used for recharging aquifers in the areas with water shortages or where the aquifers have been depleted by overexploitation to augment water supply for drinking purposes (Akber *et al.*, 2003).

2.8 Ion Exchange

Ion exchange is similar to sorption since a substance is captured by a solid in both processes, there is a characteristic difference between them; ion exchange is a stoichiometric process in contrast to sorption (Hellfferich, 1995). It means that in the ion exchange process, for every ion that is removed, another ion of the same sign is released into the solution, in contrast in sorption no replacement of solute take place.

2.8.1 The rate of ion exchange
 The rate of ion exchange in soils is dependent on the type and quantity of inorganic and organic components and the charge and radius of the ion being considered (Sparks, 1989). With clay minerals like Kaolinite, where only external exchange sites are present, the rate of ion exchange is rapid. With 2:1 clay minerals that contain both external and internal exchange sites, particularly with vermiculite and micas where partially collapsed interlayer space sites exist, the Kinetics is slower. The charge of

ion also affects the Kinetics of ion exchange. Generally, the rate of exchange decreases as the charge of the exchanging species increases (Hellfferich, 1962).

2.8.2 Characteristics of ion exchange reaction

It is usually rapid, diffusion-controlled, reversible (Treypal,1980, Perry and Green,1999), and stoichiometric means that any ions that leave the colloidal surface are replaced by an equivalent(in terms of ion charge)amount of other ions for example, two K^+ ions are necessary to replace one Ca^{++} ion, and in most cases there is some selectivity of one ion over another by exchange surface,

2.8.3 Ion exchange reaction

Ions adsorbed by outer-sphere complexation and diffuse-ion adsorption are readily exchangeable with similar ions in solution.

Exchange reactions involving common, major cations are treated as equilibrium $processes.$ A $specific$ $example$ of $monovalen$ $divalent$ $cation$ $exchange$ $reaction$ in $soil$ is:

$$2NaX + Ca^{2+} \leftrightarrow CaX + 2Na^+ \hspace{4cm} 2.10$$

The equilibrium constant for this reaction is given by:

$$K = (CaX)\ (Na^+)^2/(NaX)^2\ (Ca^{2+}) \hspace{4cm} 2.11$$

2.9 Cation Exchange Capacity (CEC)

Cation Exchange Capacity (CEC) can be defined as follows;

1. **Cation** the positively charged elements in the soil that are electrically attracted to the negatively charged sites on soil colloids (clay). Examples of cations are Al^{+++}, Ca^{++}, Mg^{++}, K^+, NH_4^+, Na^+ & H^+.

2. **Exchange** cations are held on the surface of negatively charge clay particles in a form that they can be exchanged with other cations. For example, a plant can send out two acid cations (2 H^+) in exchange for a Ca^{++}, which is taken up into the plant.

3. **Capacity** is simply defined as the sum of the total cations that a particular soil is capable of absorbing. This is a way of measuring the "volume".

The cation exchange capacity (CEC) of a soil represents the total amount of negative charges available to attract positively charged ions (cations) in solution (soluble). On most soil tests CEC is expressed as milliequivalents of negative charge per 100 grams of soil (meq/100 g). The milliequivalent per 100 grams also represents the total amount of charge of cations in the soil. Milliequivalents (meq) is used instead of mass (pounds, tons, etc) because CEC represents the total charge involved.

The adsorption strength for cations with similar charges (Ca^{++} & Mg^{++}) is determined by the size of the hydrated (attached water) cation. For example, calcium has 2 charges and a hydrated radius (size) of 0.96nm, whereas; magnesium also has 2 charges, but a hydrated radius of 1.08nm. Therefore, magnesium cannot get as "close" to the colloid because of the water present. These two forces of strength of adsorption result in a "preference" of soil colloids for cations in the following order;

$Al^{+++} > H^+ > Ca^{++} > Mg^{++} > K^+ = NH_4^+ > Na^+$
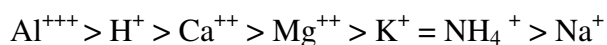
Soil cation exchange capacity (CEC) is the total of the exchangeable cations that a soil can hold at a specified pH. Soil components known to contribute to soil CEC are clay and organic matter, and to a lesser extent, silt (Martel *et al.* 1978; Manrique et al. 1991).

The relationship between clay content (% by weight) and CEC can be highly variable because different clay minerals have very different CEC values. In addition, the

relative proportion of pH-dependant and permanent CEC varies among clay minerals (Miller 1970).

Figure 2.5 shown that the Soil low in clay and humus has a low CEC, whereas soil high in clay and/or humus has a higher CEC. Soils that contain equal amounts of 1:1 clay in comparison to soils that contain 2:1 clay will be lower in CEC because 1:1 clay only holds cations on the outside of the clay particle. By this we can see the importance of clay type in determining CEC of soils.
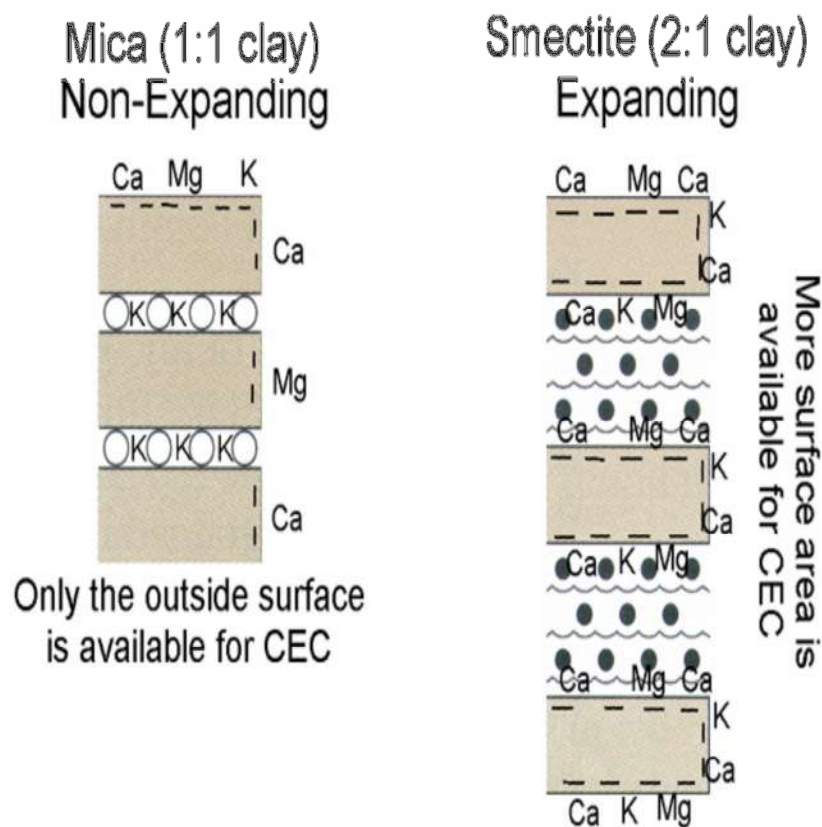
Figure 2. 5:A schematic diagram of the importance of clay type in determining CEC of soils.

A SCHEMATIC LOOK AT CATION EXCHANGE

CEC 25
MORE CLAY, MORE POSITIONS
TO HOLD CATIONS

CEC 5
LOW CLAY CONTENT,
FEWER POSITIONS TO HOLD CATIONS

H^+
CA^{++}
Mg^{++}
NH_4^+
NA^+
K^+

Sand

Clay

H^+ H^+

H^+ K^+

50 CEC
(Heavy Clay)

Common CEC Range

0 CEC
(Sand)

SOME PRACTICAL APPLICATIONS	
Soils with CEC 11-50 Range	Soils with CEC 1-10 Range
• High clay content • More lime required to correct a given pH • Greater capacity to hold nutrients in a given soil depth • Physical ramifications of a soil with a high clay content • High water-holding capacity	• High sand content • Nitrogen and potassium leaching more likely • Less lime required to correct a given pH • Physical ramifications of a soil with a high sand content • Low water-holding capacity

Figure 2. 6:A schematic diagram look at Cation Exchange.

2.10 The adsorption of ammonia in soil

In any given soil, the number of exchange sites is dependent on the soil pH, type, size and amount of clay; and amount and source of the organic material (Kamprath and Welch 1962; Parfitt *et al.* 1995; Syers *et al.* 1970; Miller 1970).

Conditions are favorable for adsorption and cation exchange on clay particles in the vadose zone (Martin and Koerner, 1984). The sorption of ammonia during SAT is a function of cation exchange capacity and effluent cation composition. The large ratio of soil to water used during SAT makes moderate cation exchange capacities sufficient to remove ammonia by sorption (NCSWS, 2001). The mechanism

suggested for ammonia sorption by soil clays is a combination of protonation on water associated with metal cations, coordination to exchangeable cations and dissolution in pore water. Soil clays can retain significant amounts of ammonium in excess of the cation exchange capacity (CEC) and out of competition for exchange sites. Dissolved NH_3 can also undergo hydrolysis in the local coordination sphere of hydrated exchangeable cations (Mortland and Raman, 1968). Ammonium ions in the soil solution can subsequently enter into cation-exchange reactions with the soil matrix (Mortland, 1966).

2.11 Soil Properties

The surface of an individual clay particle or organic colloid is negatively (-) charged (Brady and Weil, 2002). As a consequence their surfaces attract and adsorb positively charged ions called cations. When water is added to soil, cations can move into solution, however, they are still attracted to the clay particle or organic colloid surface and as a result swarm around them. The mechanism of adsorption and desorption is important, even though less than 1 % of cations will do this at any one time. Positively charged ions capable of being readily substituted from the soil solution and onto the surface of a negatively charged soil particle, and vice-a-versa, are termed exchangeable cations. (Dontsova, 2004) The exchangeable cations of most importance are Cation exchange is therefore defined as the interchange between a cation on the surface of any negatively charged particle (i.e. clay mineral or organic colloid) and the soil solution. Whilst the cations themselves are still attracted to the clay particle, the force of attraction on the cations diminishes rapidly with increasing distance from the negatively charged surface. This is because the binding force of individual cations is a function of various factors, including; Cation charge (i.e. valence), Size of hydrated cation (i.e. ionic radius), and Concentration of charge, and

Thickness of the double layer outside the surface of clay particles.In the first instance, the more strongly attracted a cation is to the exchange surface, the greater is the chance of adsorption. This is known as the energy of adsorption. The energy of adsorption of a cation is a function of the valence (i.e. charge). This is the reason why trivalent (+3 charge) cations such as aluminium and divalent (i.e. +2 charge) cations such as calcium and magnesium, have an energy of adsorption respectively, almost three and two times that of monovalent (i.e. +1 charge) cations such as potassium or sodium. (Brady and Weil, 2002) As a consequence an exchangeable cation of aluminum, calcium or magnesium stays close to the clay particle and does not interfere with the cohesion between aggregated particles. In fact these cations initiate the process of particle aggregation in soil. The valence of an exchangeable cation therefore determines the double layer thickness. So that, the higher the valence of the dominant exchangeable cation, the thinner the double layer. However, differences in the thickness of the double layer can still occur even when the cations are of equivalent charge or valency. When the valence of the cations are equal (i.e. both +1 charge) the cation with the smallest hydrated radius is more strongly adsorbed. In the case of the monovalent cations of potassium and sodium, the potassium ion is more strongly adsorbed since it has a smaller hydrated radius and hence is more strongly adsorbed to the site of the negative charge. In comparison the sodium ion is so loosely held and so ready to hydrate that sodium rich soil will disperse. This is similarly the case with the divalent cations of calcium and magnesium. Because the hydrated magnesium ion is larger than that of calcium, the magnesium ion is held more weakly and behaves in some instances in soil (i.e. when calcium is low) like sodium. The charge of the cation and the size of the hydrated cation essentially govern the preferences of cation exchange equilibria. In summary, highly charged cations tend to

be held more tightly than cations with less charge and secondly, cations with a small hydrated radius are bound more tightly and are less likely to be removed from the exchange complex. The combined influence of these two criteria can be summarized generally by the lysotrpoic series. Aluminium > calcium > magnesium > potassium, ammonium > sodium > hydrogen. It indicates, from left to right, the decreasing strength of adsorption of the various cations (Helfferich, 1995) . As such, the less tightly held cations are located furthest from the surface of colloids and are most likely to be leached away or further down the profile most quickly. Conversely, the most strongly adsorbed cations will tend to move the slowest down through the profile.The proportion and kinds of cations adsorbed on soil mineral particles and organic colloids is also a function of the concentration of cations in the soil solution. If the concentration of a cation in soil solution is high, there is an increased chance or tendency for that cation to be adsorbed.

2.12 Batch experiment

2.12.1 Theory of batch experiment

Batch experiments are essentially slurries of soil (or sand) and water that are given significant contact time to allow leaching and geochemical reactions to occur. Containers are used to isolate the batch experiments from any changes in environmental conditions. Water temperature should remain constant, Mechanical shaking of the containers is recommended to ensure adequate mixing and contact between the soil particles and the water.   In a batch test, a known mass of solid (S_m) is mixed and allowed to equilibrate with a known volume of solution (V) containing a known initial concentration of a solute (C_i). The solid and solution are then separated

and the concentration ($C^)$ of the solute remaining is measured. The difference $C_i - C$ is the concentration of solute adsorbed and convert.

Batch experiments have been used in feasibility studies to evaluate geochemical changes for planning managed aquifer recharge schemes (e.g. Johnson *et al.*, 1999; Cavé, 2000; Cavé *et al.*, 2001). In these examples, the focus was on the effectiveness of the aquifer material to remove contaminants and identifying readily soluble components in the aquifer. Although batch experiments are commonly used in different types of studies involving leaching.

(Yona, 2011) laboratory –scale batch and soil column studies were carried out to study the effect of temperature and redox conditions on removal of bulk organic matter, nutrient (nitrogen and phosphorous) and pathogens with primary effluent (PE) and secondary effluent (SE).

Wang et al. (2007), studied the effect of aerobic denitrification process on sequencing batch reactors, managed to isolate and characterize bacteria belonging to four genera: Pseudomonas, Delftia, Herbaspirillum and Comamonas.

Fontenot et al., (2007) tested the effect of different C/N ratios (5:1, 10:1, 20:1, 30:1, and 40:1) on a sequencing batch reactor applied for shrimp wastewater treatment with both nitrification and denitrification occurring in the same reactor. They observed a performance of nitrogen reduction higher than 91% for all species of nitrogen (nitrite, nitrate and ammonia nitrogen) when working with C:N =10, and similar removal nitrogen values with C:N = 5. The higher C:N ratios tested did not show satisfactory results.

Huanga et al., (2009) studied the removal of ammonium ion from aqueous solutions using natural Chinese (Chende) zeolite. A series of experiments was conducted to examine the effects of solution pH, particle size, contact time, adsorbent dosage, and

the presence of other cation- and anion species on ammonium removal. The findings indicated that these parameters named had a significant effect on the removal of ammonium by the zeolite. The effect of other cations on the removal of ammonium followed the order of preference $Na^+ > K^+ > Ca^{++} > Mg^{++}$ at identical mass concentrations, and the effect of the presence of individual anions followed the order of preference carbonate > chloride > sulfate > phosphate. At identical mass concentrations of ammonium ions. Kinetic analysis showed that the adsorption of ammonium on zeolite at different ranges of particle size well followed the pseudo-second-order model and followed the intra-particle diffusion model only during the initial 60 min of the adsorption process.

(Wan Cho et al. 2010) Bench-scale batch experiments were performed to investigate the feasibility of using different types of clay minerals (bentonite, fuller's earth, and biotite) with zero-valent iron for their potential utility in enhancing nitrate reduction and ammonium control. Kinetics experiments performed with deionized water (DW) and groundwater (GW) revealed nitrate reduction by Fe proceeded at significantly faster rate in GW than in DW, and such a difference was attributed to the formation of green rust in GW. The amendment of the minerals at the dose of 25 g/ L in Fe reaction in GW resulted in approximately 41%, 43%, and 33% more removal of nitrate in 64 h reaction for bentonite, fuller's earth, and biotite, respectively, compared to Fe alone reaction. The presumed role of the minerals in the rate enhancement was to provide sites for the formation of surface bound green rust. Bentonite and fuller's earth also effectively removed ammonium produced from nitrate reduction by adsorption, with the removal efficiencies significantly increased with the increase in mineral dose above 5:1 Fe to mineral mass ratio. Such a removal of ammonium was not observed for biotite, presumably due to its lack of swelling property.

Equilibrium adsorption experiments indicated bentonite and fuller's earth had maximum ammonium adsorption capacity of 5.6 and 2.1 mg /g, respectively.

(Johnson et al, 1999) Six soils from two vadose-zone injection wells were used in conjunction with three types of recharge waters (microfiltered reclaimed wastewater; reverse osmosis-treated reclaimed wastewater and membrane-filtered Colorado River water) to evaluate soil water chemical processes that may alter water quality during recharge of these waters. Batch studies (soil water slurries; 30-day contact time, 40 rpm) and flow-through column studies (up flow mode columns; 100 pore volumes over 30 to 100 days) showed that Fluorine, and Arsenic were leached in appreciable concentrations, whereas leaching of Boron, Chromium, lead and Selenium was minimal. In the column study, concentrations often peaked during the first few days of operation (a ``washout'' phenomenon) and then declined. Precipitation and dissolution reactions may be important from a standpoint of sustained infiltration rates.

CHAPTER 3: STUDY AREA

3.1 Geography of the Gaza Strip

The Gaza Strip is located in the Middle East (at 31º 25˝ N, 34 º 20˝ E) and consists of around 360 km^2. It has an 11km border with Egypt, near the city of Rafah, and a 51km border with Israel. It has a 40 km coastline onto the Mediterranean Sea, but has no maritime claims due to Israeli administration. The Gaza is located on the coast of the Mediterranean Sea, north of the Sinai Peninsula and southwest of Jerusalem, on a road that links Egypt with central Israel. Gaza Strip forms part of the coastal foreshore plain bordering the Hebron Mountains in the north-east, the Northern Negev desert in the south-east, and the Northern Sinai desert in the south. It is situated in the shadow of the Nile Delta and Northern Sinai. The curve in the coastal starting from El Arish towards north of Gaza.
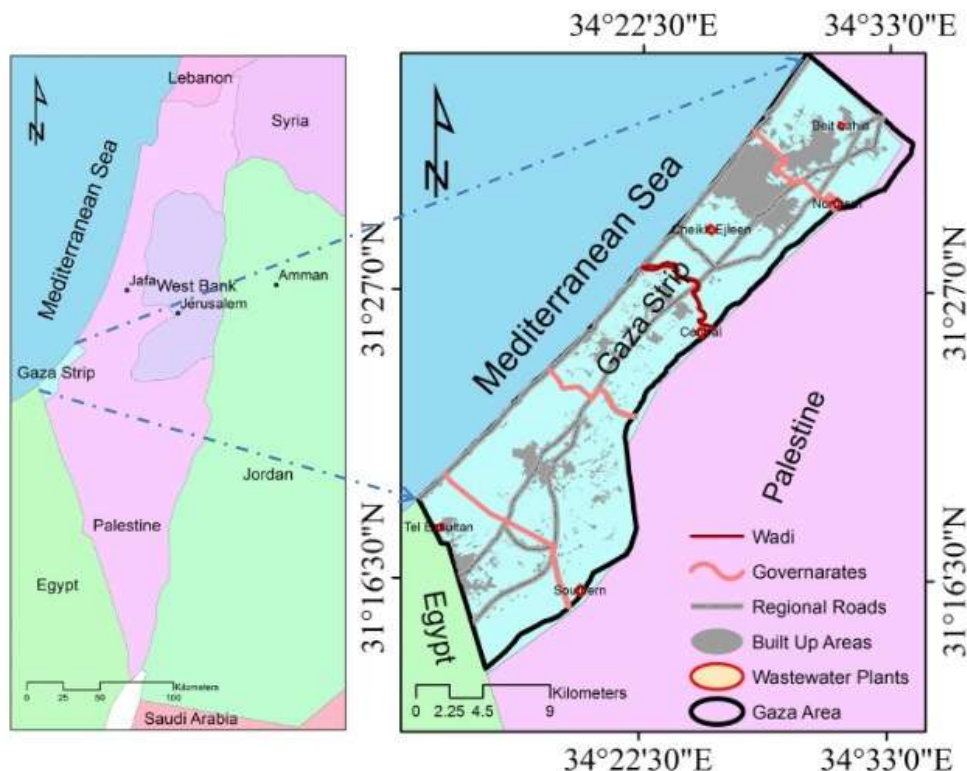
Figure 3. 1:The location of Gaza Strip map.

3.2 Topography

The coastal plain is determined by the exposure of Kurkar ridges. The age of these ridges increases from the coastline eastwards. In the north of the Gaza Strip there are four ridges: the coastal ridge (20 m MSL), the Gaza ridge (up to 50 m MSL), the El Muntar ridge (80 m MSL), and the Beit Hanoun ridge (90 m MSL). The ridges are separated by deep depression (20-40 m MSL) with alluvial deposits. There is evidence that there are at least three to four younger Kurkar ridges on the continental shelf, parallel to the present coastal line and several kilometers offshore. Kurkar ridges of calcareous sandstone appear all along the coast positioned in a south-west-northerly direction parallel to the coast. The influence of these Kurkar ridges on sedimentation and erosion processes is however limited to local disruption of waves and currents.

3.3 Soil

The soil in the Gaza Strip is composed mainly of three types, sands, clay and loess. The sandy soil is found along the coastline extending from south to outside the northern border of the Strip, at the form of sand dunes. The thickness of sand fluctuates from two meters to about 50 meters due to the hilly shape of the dunes. Clay soil is found in the north eastern part of the Gaza Strip. Loess soil is found around Wadis, where the approximate thickness reaches about 25 to 30 m. (Jury and Gardner, 1991).

3.4 Climate

The Gaza Strip is located in the transitional zone between the arid desert climates of the Sinai Peninsula and the semi humid Mediterranean climate along the coast.

- Temperature: The average daily mean temperature in the Gaza Strip ranges between 25.8 ^{0}C in summer to 13.4 ^{0}C in winter. The hottest month is August with an average

temperature of 25 to 28 ^{0}C and the coldest month is January with average temperature of 12 to 14 ^{0}C.

- Humidity: The relative humidity fluctuates between 60% and 85%.

- Wind: In summer, sea breeze blow all day and land breeze blows at night. Wind speed reaches its maximum value at noon period and decrease during night. During the winter, most of the wind blow from the Southwest and the average wind speed is 4.2 m/s. In summer, strong winds blow regularly at certain hours, and the daily average wind speed is 3.9 m/s and come from the Northwest direction. Storms have been observed in winter with maximum hourly wind speed of 18 m/s.

- Rainfall: The winter is the rainy season, which stretches from October up to March. Rainfall is the main source of recharge for groundwater. The rate of rainfall is varying in the Gaza Strip and ranges between 160mm/year in the south to about 400mm/year in the north, while the long term average rainfall rate in all over the Gaza Strip is about 317mm/year (CMWU, 2011). For the last ten years, between 2001 and 2011, the average annual rainfall of The Gaza Strip ranged between 220 mm/year to 520 mm/year (MOA, 2011).

3.5 Population

Gaza Strip is considered as one of the most densely populated areas all over the world. According to the Ministry of Interior (MOI) records in September 2012 the number of inhabitants of the Gaza Strip in 2012 is 1.8 million people, including more than 200 thousand new baby born during the past four years. In 2011 more than 929,019 inhabitants were crowded in the Northern area of about 135 Km^2. The natural rate of population growth in the Gaza Strip is estimated at 3.8% per year (MOI, 2011),

3.6 Water Resources Problem at the Study Area

The water resource problems which Gaza Strip is facing are immense. 1.8 million habitants suffer from overexploitation of groundwater resources and pollution due to inadequate wastewater collection, treatment and disposal. The overexploitation of groundwater resources in The Gaza Strip refers to the unsustainable extraction rates of groundwater from the Coastal Aquifer of Northern Gaza Strip. Currently, the Coastal Aquifer is facing severe quality and quantity problems, which are a result of excessive exploiration, resulting in a water deficit between natural recharge and extraction about 40 to 50 Mm^3/yr (GABARDINE 2009).

3.7 Wastewater treatment plant in Gaza strip

There are five wastewater disposal and treatment facilities in The Gaza strip which are Beit Lahia (BLWWTP), Gaza City (GWWTP), Northen Gaza wastewater treatment plant (NGWWTP), Rafah (RWWTP) and Khan Younis wastewater treatment plant.

All of these plant are facing difficulties in operation and don't work properly (PWA, 2012).

3.7.1   (Northern) Gaza wastewater treatment plant (NGWWTP)

The Northern Wastewater Treatment Plant is designed to replace Beit Lahia WWTP. It will serve the whole of the Northern Governorate to a design horizon of 2025. At that year the NGWWTP will be operating with full capacity of 60,000 m3/d. Processes will include primary sedimentation followed by an oxidation ditch, sand filtration and UV disinfection. The effluent is planned to be reused in agriculture. It is proposed to cover a command area of 21,000 dunum. Excess wastewater will be recharged into the groundwater through infiltration basins located near the WWTP.

The total project area is around 16,500 dunums located at the north-east of the Gaza Strip adjacent to the eastern border with Israel. The agricultural area is about 13,700 dunums whereas the industrial and residential area account for 546 dunums.
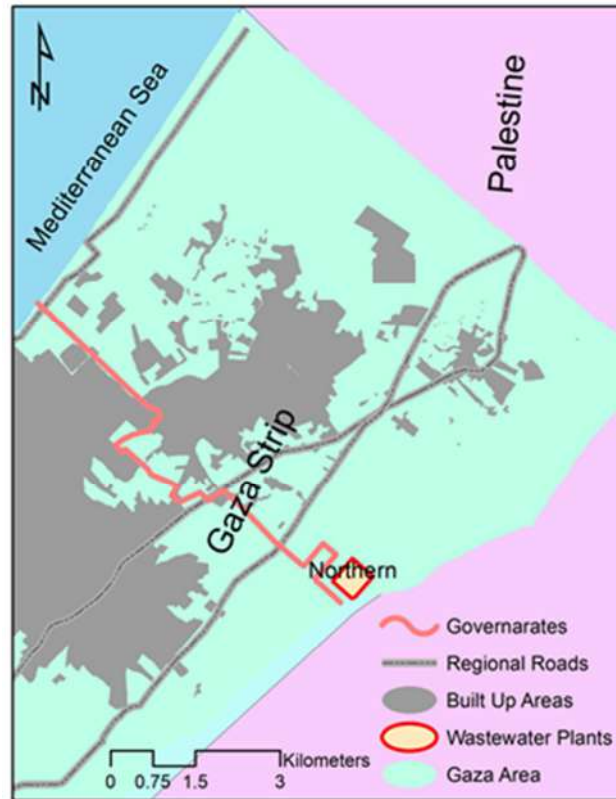
Figure 3. 2: The location of the Northen Gaza Wastewater Treatment Plant.

CHAPTER 4: METHODOLOGY

To achieve the previously mentioned objectives, a batch experiment technique was adapted and implantated for two local soil types.

4.1 Soil sampling

Two types of soil samples were used in this experiment. Both soils were collected for the North part of Gaza Strip near the NGWWTP. The zigzag random method technique was adapted for the sampling (Petersen & Calvin, 1986). The augur was used to collect samples from depth 20-30cm. the collected samples were mixed to create composite soil sample. The two samples were dried at 30 ºC for 24 hrs; samples were grounded in stainless steel soil grinder and passed through a2-mm sieve, before characterization at laboratory of Al Azhar University.

4.1.1 Soil characterization

Before any application of the synthetic wastewater to batch experiment both the physical and chemical characterization of the two types of soil was investigated. (See **A-3-3**)

4.1.1.1 Physical characterization

The textures of the soils were analyzed using the hydrometer analysis (Gee & Bauder, 1986), the results were applied to the soil texture triangle to recognize the type of the soil. (See **A-3-1**)

Cation Exchange Capacity CEC meq/100g was analyzed the method described by (Ryan *et al.* 1996) was implemented to measure the cation exchange capacity (CEC) for the soil. Six g air-dried soil sample was saturated with sodium (Na^+) and then subsequent replaced by ammonium (NH_4^+). The sodium concentration in the final

extract was detected by a flame photometer. For a weight W (g) of the oven-dry soil

sample. CEC in (meq/100g) was calculated as:

$$CEC = C_{Na+} \times 10/W \qquad (4.1)$$

Where C_{Na+} is the concentration of ion Na^+ in the extract (meq/ L). All analysis was

conducted according to A Soil and Plant Analysis Manual Adapted for the West Asia

and North Africa Region.

4.1.1.2 Chemical characterization

Soil water extracts prepared from 1:5 soil water ratio shaker for 1 hour, filtered

through whatman No.1 filter paper, this filtrate was distributed for the determination

of the different chemical species in the soil as described by soil analysis (1986). **(See**

A-3-2)

Soil pH is a measure of hydronium ion (H_3O^+, or more commonly the H^+) activity in

the soil solution. The Soil pH is defined as the negative logarithm (base 10) of the H^+

activity (moles per liter) in the soil solution. As the activity of H^+ in the soil solution

increases, the soil pH value decreases. It was measured for each sample using a pH

meter model HI3220, Electrical conductivity (EC) refers to the ability of a material or

solution to conduct an electrical current. As soluble salts increase in the soil, the soil

solution becomes a better conductor of electricity and EC increases, it was measured

using E.C meter HI4321, and Total Dissolve Soild (TDS), (Dhyan et al., 1999),

Soluble cations Calcium Ca^{++}, Magnesium Mg^{++}, Potassium K^+, Sodium Na^+,was

measured in the soil water extracts by prepareing 1:5 soil-water suspension, shake for

one hour on a shaker and filter through Whatman #1 filter paper and using the

supernatant for analysis, by using flame photometer. **(See A-3-5) (See A-3-6)**. Soluble

anion Chloride Cl^-, the determination was done by $AgNO_3$ (Mohrs's titration) method.

Potassium chromate shows the brick red colour at the end point due to formation of silver chromate.

Nitrate NO_3^- water soluble was extracted by shaking with 2.0 M KCl to prepare, dissolve 150 g of KCl in 1 L of distilled water 5 g of soil air dried, ground, and sieved (2mm) soil into a 125 mL Erlenmeyer flask, Add 50 mL of the desired extractant 2M KCl. then Shake for 15 minutes on a reciprocating shaker at 160 round per minute, as describe at, (Keeney and Nelson, 1982). The filtrate was used to detect NO_3^- using spectrophotometer type UV-1601PC (SHIMADZU, 1995) at wavelength 220 nm, (See **A-3-4)**

$CaCO_3\%$ Calcium carbonate in the soil sample is dissolved in the excess of hydrochloric acid, the remained of the acid is titrated against sodium hydroxide, and this method is known as Piper method (Piper, 1966).

Table 4. 1:Method and Equipments used for water solution test.

Parameter	Unit	Method	Equipment
pH		Electrometric	pH meter HI 3220
E.C	µs/cm	Electrode Method	E.C meter HI4321
TDS	mg/l	Calculation	E.C meter HI4321
Mg^{++}	mg/l	Calculation Method	
Ca^{++}	mg/l	Titrametric Method	
Na^+	mg/l	Flame Emission Photometric Method	Flame photometer Jenway PFP7
K^+	mg/l	Flame Emission Photometric Method	Flame photometer Jenway PFP7
Cl^-	mg/l	Titrametric method	

NO_3^--N	mg/l	UV Spectrophotometric Screening Method	UV1601Spectrophotometer
$CaCO_3\%$		Titrametric Method	

4.2 Synthetic wastewater

The synthetic wastewater with C:N ratio 1:1   contained the following (per liter of DW) 38.2 mg/l NH_4Cl to produce 10 mg/l NH_3-N, 36.1 mg/l KNO_3 to produse 5 mg/l NO_3-N,18.75 mg/l $C_6H_{12}O_6$ to produce 7.5 mg/l organic carbon (OC), 52.47 mg/l $NaHCO_3$ to produce 7.5 mg/l inorganic carbon (IC), this composition is used for each run including one cation is added to the system as summarized in table 4.2, and specific cation 660 mg/l Na^+, 25mg/l K^+, 140 mg/l Ca^{++}, 95 mg/l Mg^{++})These concentrations were employed due to being the most common in samples analyzed during characterization of (NWWTP) wastewater. Synthetic wastewater produced was sampled to be chemically characterized before any application for   studying the ammonia NH_3-N, NitrateNO_3 -N.

Table 4. 2: Composition of Synthetic wastewater. All concentration in mg/L for each run.

Run	NH_3 -N	NO_3 -N	IC	OC	Ca^{++}	Mg^{++}	K^+	Na^+
0	10	5	7.5	7.5	_	_	_	_
1	10	5	7.5	7.5	140	_	_	_
2	10	5	7.5	7.5	-	95	_	_
3	10	5	7.5	7.5	-	-	25	_
4	10	5	7.5	7.5	-	-	-	660
5	10	5	7.5	7.5	140	95	25	660

4.3 Design of batch experiment

The 12 containers containing the slurry were attached to a horizontal shaker. The shaker was operated at 40 rpm. Each single hour a sample container was removed from the shaker to be analyzed. The last container in each run was removed from the shaker after 12 hours. Each sample was analyzed for NH_3-N, NO_3-N, and for the specific added cations. **(See A-3-3)**

4.3.1 Synthetic Wastewater Runs

This experiment was repeated for the two types of soil. Throughout the whole experiment 12 containers plastic 100 ml in volume were used. In each container 40 g of soil samples less than 2-mm size fraction was added, and 60 ml of synthetic wastewater for each run consists of (NH_4^+, NO_3^-, $NaHCO_3$, and $C_6H_{12}O_6$) and specific cations, then filtrate through whatman No.1 filter paper and analyzed for NH_3-N, NO_3^--N, and specific cation. In the zero run no specific cation was presented in the synthetic wastewater, this run was classified as control run. In the first run Ca^{++} represented the cation to compete with NH_4^+ to be sorped on the effective adsorbent sites in the soil. In the second run Ca^{++}, was replaced by Mg^{++}. In the third run Mg^{++} was replaced by K^+. In the fourth run K^+ was replaced by Na^+. In the last run Na^+ was replaced by all cations were added to the synthetic wastewater. As illustrated by table 4.2

4.3.2 Secondary Treated Wastewater Runs

The previously described experiment was repeated using the same two soil types, but synthetic wastewater was replaced by Secondary Treated wastewater.

Samples collected from NGWWTP, were taken from 20 cm depth from secondary treated wstewater. A series of 3 grab samples of 1L volume were combined in a

container to form a composite sample. One liter of composite was taken in a bottle and transferred to the laboratory of Al Azhar University using ice box. Wastewater sample was analyzed for the chemical parameters as shown in table 4.3; all analysis was conducted according to the Standard Method (APHA, 1998). **(**See **A-3-7)**

Table 4. 3: Methods and Equipments used for wastewater test.

Parameter	Unit	Method	Equipment
pH		Electrometric	pH meter HI 3220
E.C	µs/cm	Electrode Method	E.C meter HI4321
TDS	mg/l	Calculation	E.C meter HI4321
			Calculation Method
Mg^{++}	mg/l	Calculation Method	
Ca^{++}	mg/l	Titrametric Method	
Na^+	mg/l	Flame Emission Photometric Method	Flame photometer Jenway PFP7
K^+	mg/l	Flame Emission Photometric Method	Flame photometer Jenway PFP7
Cl^-	mg/l	Titrametric method	
NO_3^--N	mg/l	UV Spectrophotometric Screening Method at 220nm	UV1601Spectrophotometer
NH_3-N	mg/l	Phenate Method at 640nm	UV-1601Spectrophotometer
Hardness	mg/l	Titrametric Method	

CHAPTER 5: RESULTS and DISCUSSION

5.1 Soil characterization

The results of soil physical and chemical characterization.

5.1.1 Physical characterization

Soil texture analysis for 2 samples is presented in Table 5.1.The results show that the soil used in this experiments were classified, basing on the USDA classification scheme , Soil 1 as sandy clay loam and Soil 2 loamy sand soil. Figure5.1 and figure 5.2 shows the soil classification for soil 1 and soil 2.

Table 5. 1: Soil texture analysis using the hydrometer method.

	Texture %		
	Sand	Clay	Silt
Soil 1	62	32	6
Soil2	87.28	10.72	2
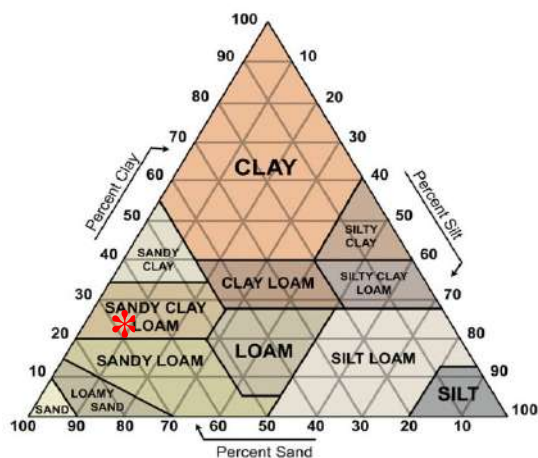
Figure 5. 2:Soil texture triangle Sandy clay loam.
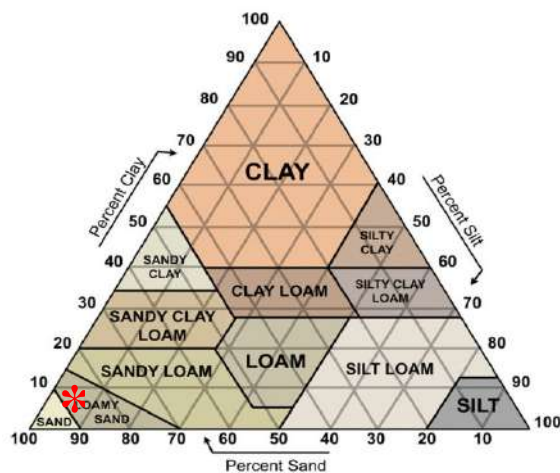
Figure 5. 1: Soil texture triangle Loamy sand.

Additionally, the key parameter of our interest is CEC. It is obvious that CEC for the

sandy clay loam was (14.34 meq/100g), and it is considered high compared to that for

loam sandy soil which was (5.84 meq/100g).

5.1.2 Chemical Characterization

Results of the chemical characterization for the sandy clay loam, and the loam sandy

soil are summarized in Table 5.2

Table 5. 2: chemical characterization for the sandy clay loam, and the loam sandy soil used for the experiment.

Parameter	Unit	Sandy clay loam	Loam sandy
pH		8.78	8
E.C	µs/cm	50.28	43.87
TDS	mg/l	24.70	22.52
Mg^{++}	mg/l	14.56	16.99
Ca^{++}	mg/l	20	18
Na^+	mg/l	64.2	49.4
K^+	mg/l	11.09	8.62
Cl^-	mg/l	106.5	35.5
CEC	meq/100mg	14.34	5.84
NO_3^--N	mg/l	3.94	1.45
$CaCO_3$	%	20.5	6.5

5.2 Wastewater characterization

Results of the chemical characterization for wastewater are summarized in Table 5.3

Table 5. 3: Chemical characterization for wastewater.

Parameter	Unit	Period 1	Period 2
NH_3-N	mg/l	63	42.5
NO_3-N	mg/l	11.9	9.6
Na^+	mg/l	617	549
K^+	mg/l	23.5	28
Ca^{++}	mg/l	124	132
Mg^{++}	mg/l	86	66.5

The total number of samples were used and   the parameters which analyzed for it,

In addition to the needed volume for each measurement are summarized in table 5.4.

Table 5. 4: Statistical summaries of the properties monitored during the experiment.

Parameter	Needed volume for each measurement (mL)	Dilution factor	Total No. of samples
NH_3 -N	5	5	168
NO_3^- -N	5	10	168
Mg^{++}			72
Ca^{++}	5	5	72
Na^+	5	5	72
K^+	5	5	72

Total measurement	624

The variations in NH_3 and NO_3^- in the presence of major cations as a function of time in different soil type are discussed in the next sections.

5.3 Sandy clay loam soil

During each run a notable behavior was observed, concerning the concentration of NH_3. There was a significant drop in NH_3 concentration immediately as the synthetic wastewater contacted the soil. It was reported to be zero time. However, to avoid the decalcification of the plot it was removed from the figures. These values are reported in table 5.5.

Table 5. 5: The concentration for ammonia and nitrate at initial and zero time in each run.

		Concentration mg/l			
Run No.	Cation present	Initial NH_3	zero time	Initial NO_3^-	zero time
1	None	8.68	3.97	3.97	8.03
2	Ca^{++}	9.54	1.79	5	8.48
3	Mg^{++}	9.60	2.45	4.19	8.55
4	K^+	9.86	6.37	3.97	7.49
5	Na^+	9.86	2.41	3.7	7.32
6	$Ca^{++}, Mg^{++}, K^+, Na^+$	10.37	3.58	4.38	7.5

The increase in NO_3^- concentration can be contributed to the Nitrification of NH_3 in the synthetic wastewater, which confirmed that the nitrification process was fast in the system. The two subsequent steps conversion of NH_3 to NO_2^- by Nitrosomanse and

NO_2^- to NO_3^- by Nitrobacter comprising the process of nitrification are faster and rarely limit the rate of production of nitrate (Smith, 1982).

Figure 5.3 shows that there was sudden drop in ammonia concentration in synthetic wastewater from 8.08 mg/l to 0.36 mg/l after 12 hours. Based on this the removal of NH_3 from the system was reported to be (95.8%) at the end of experimental time. This reduction can be contributed to both the biochemical nitrification of NH_3 as well as the sorption of NH_3 to the active sites of soil. The initial concentration of NO_3^- during this run was 3.97 mg/l.

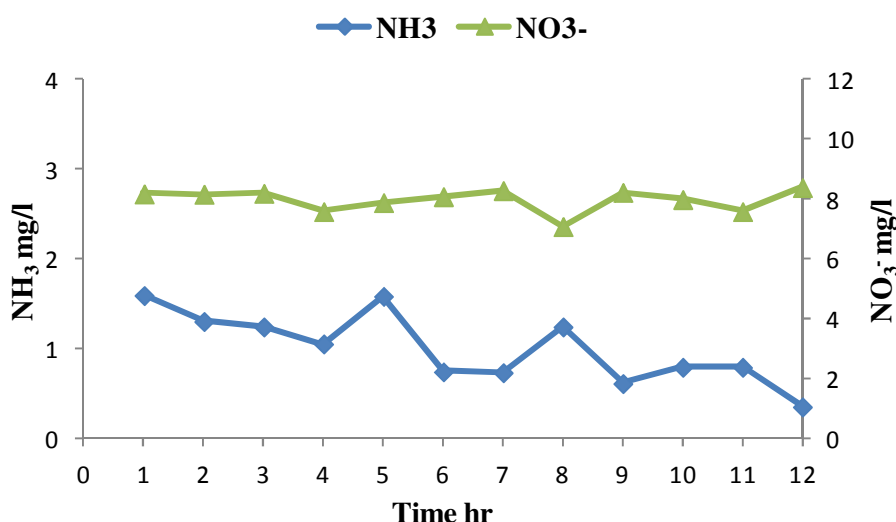**Figure 5. 3: Concentration of ammonia and nitrate in the synthetic wastewater at different contact times in Sandy clay loam soil in the absence of all cations.**

This level of NO_3^- was increased up to 8.03 mg/l as the synthetic wastewater contacted the soil. This can be considering as a strong evidence of our hypothesis of nitrification of NH_3. At the end of the experiment the NO_3^- concentration was reported

to be 8.4 mg/l after 12 hours. However, during the experiment time as shown in figure 5.3 the variation in NO_3^- concentration was insignificant. However, there was an obvious decreasing trend in NH_3 concentration. The main contribution of this was due to the exchange capacity of the soil, leading to continues reduction in the NH_3 in the soil solution. Besides, that it is not clear if the activated sites of the soil were occupied by NH_3 after 12 hours. In other words, there was more rome in the soil for more NH_3 to be exchange.

Figure 5.4 reveals the effect of Ca^{++} ion on the concentration of ammonia when added to the synthatic wastewater. As previously mentioned, the initial concentration of NH_3 which was 9.54 mg/l was decreased to 1.79 mg/l as well as the NO_3^- concentration was decreased also rapidly during this time. The NH_3 behaviour during the experimental time as shown in figure 5.4 is similar to the synthatic wastewater in the absence of Ca^{++}, both decreased with time. However, the concentration of NH_3 in the synthatic wastewater in the presence of Ca^{++} is considered high all the time compared to NH_3 concentration in the synthatic wastewater without Ca^{++}. The Ca^{++} concentration which was 140 mg/l in the synthatic wastewater competed NH_3 on the active site of the soil. It is very clear that most of the active sites were occupied by Ca^{++} rather than NH_3. This led to more appear in the soil solution less to be exchanged with the soil, as shown clearly in figure 5.4. At the end of the experiment the NH_3 removal was reported to be 87.52% which less than 95%. The NO_3^- level was reported to be 8.1mg/l at the end of experiment. However, for the time passing of experiment and as shown in figure 5.4 the difference in NO_3^- level was irrelevant. On other hand, there was an apparent falling movement in NH_3 level. The major reson of this is due to the exchange capacity of the soil, leading to continuous decreas in the NH_3 in the

soil solution. In addition it is not understable if the activated sites in the soil was occubied by NH_3 after 12 hours.

The decreasing trend for both curves are another strong evidence for the reduction of NH_3 from the soil solution and it may contributed to exchange of the cations.

Figure 5. 4: Effect of Ca^{++} on the ammonia and nitrate concentration in synthetic wastewater at different contact times in Sandy clay loam soil.

As shown in figure 5.5, It can be obtained in the presence of Mg^{++} ion in synthatic wastewater the concentration of ammonia decreasing continued constantly in the 12 hour reached 1.88 mg/l. The NH_3 movement is parallel to the NO_3^- movement in the lack of Mg^{++} and both decreased with time. Nevertheless the concentration of NH_3 in the synthatic wastewater in the existence of Mg^{++} all of the time comparing to NH_3 concentration in the synthatic wastewater alone. The Mg^{++} concentration was 95 mg/l in the synthatic wastewater competed NH_3 on the active sites. It was very apperent that the majority of the active sites were occupied by Mg^{++} more than NH_3. This led more NH_3 to emerge in the soil solution less to be sorped on soil, as shown clearly in figure.5.5. After 12 hours the NH_3 removal was reported to be 80% and less than the NH_3 removal in the synthatic wastewater alone. It is smaller than the NH_3 removal in

the presence of Ca^{++} which was 87.5%. This indicats that the Mg^{++} was more competitive for NH_3 than Ca^{++}. In the first two hours the NO_3^- concentration decreased to 8.38 mg/l, then at the next two hurs increased to 10.17mg/l, at the end of the experiment it was reached 7.66 mg/l. However, for the period of experiment and as shown by figure 5.5 the difference in NO_3^- level was unrelated. However there was a visible declining movement in NH_3 level. The main payment of this was due to the exchange capacity of the soil, leading to continuose decrease in the NH_3 in the soil solution. In addition it is not understable if the activated sites in the soil was occubied by NH_3 at the end of time.
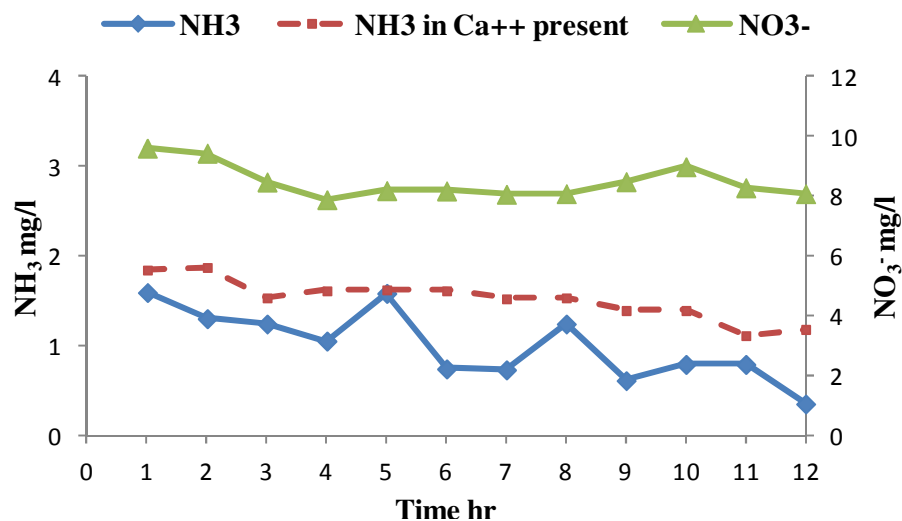
**Figure 5. 5: Effect of Mg^{++} on the ammonia and nitrate concentration
in synthetic wastewater at different contact times in Sandy clay loam
soil.**

Figure 5.6 shows the for NH$_3$ cocentration after K$^+$ addition to synthatic wastewate, NH$_3$ is highly decerased from initial concentraion 9.8 mg/l to 1.27 mg/l at the last hour of experiment. The NH$_3$ behaviour is similar to the NO$_3^-$ behaviour in the lack of K$^+$, both decreased with time. The concentration of NH$_3$ in the synthatic wastewater in the presence of K$^+$ was high all of the time compared to NH$_3$ cocentration in the synthatic wastewater wihout K$^+$. The K$^+$ concentration was 25 mg/l in the synthatic wastewater competed NH$_3$ on the active sites of the soil. It was clear that most of the active sites were occupied by K$^+$ more than NH$_3$. This resulted in the more NH$_3$ to arise in the soil solution minimal to be exchanged with soil, as shown clearly in figure 5.6 the removal of ammonia in the presence of K$^+$ was 85.7% and it is smaller than the removal of ammonia in synthetic wastewater alone 95%. The NO$_3^-$ concentration increased to 7.25 mg/l during the period of the experiment (12 hours). However, during the experiment and as shown in figure 5.6 the variation in NO$_3^-$ concentration

was insignificant. However, there was an obvious decreasing trend in NH_3 concentration. The main cotribution of this decreas in concentration was due to the exchange capacity of the soil, leading to continuose reduction in the NH_3 in the soil solution.
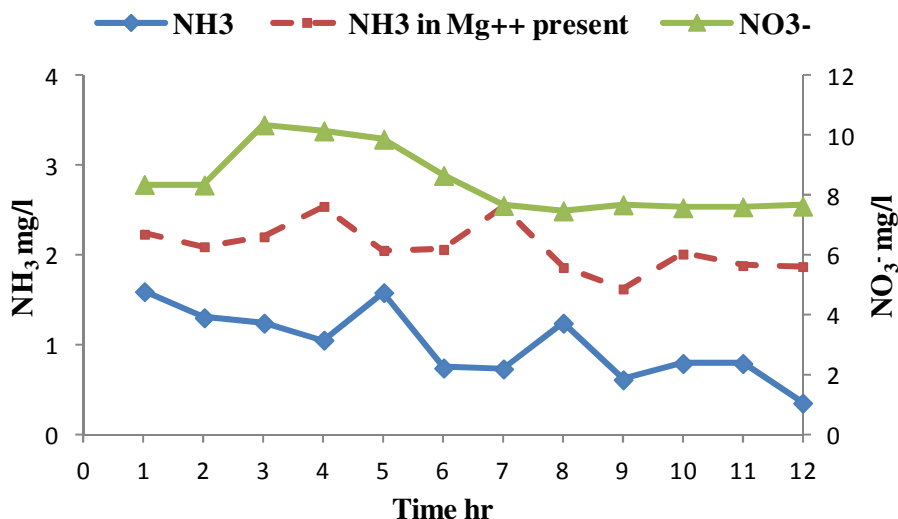

Figure 5. 6: Effect of K^+ on the ammonia and nitrate concentration in synthetic wastewater at different contact times in Sandy clay loam soil.

Figure 5.7 results show a significant decreased of the initial concentration 9.86 mg/l to the 2.02 mg/l for the rest of the experiment. The concentration of NH_3 in the synthetic wastewater in the presence of Na^+ is considered high all the time comparing to NH_3 concentration in the synthetic wastewater without Na^+. The Na^+ concentration was 660 mg/l in the synthetic wastewater competed the NH_3 on the active site of the soil. It was very clear that most of the active sites were occupied by Na^+ rather than NH_3. This led to be more appear in the soil solution less to be exchanged with the soil, as shown clearly in figure 5.7. It is important to note the low amount of ammonia removal efficiency from synthatic wastewater in the presence of Na^+ which was reached to 79.5 mg/l at the end of the experiment. The NO_3^- concentration increased in the first hour to 6.49 mg/l then decreased constantly in the rest of time. Helfferich,

(1962) has given the following selectivity sequence or lyotrophic series, which described the relative strength of various cations adsorption, Na^+ was the least to be sorped in this series, but unexpected behaviour for the sorption of Na^+ in this study, it was sorped more than other cations , the reason for is cotributed to significant high concentration of Na^+ in the sample. The same response was previously reported by Jellali et al., (2010), Chen et al., (2002) found that increasing the concentration of Na^+ ion in solution significantly reduced the ammonia sorption. (Huang et al., 2009) found that Na^+ the largest effect on the removal of ammonium followed by K^+, Ca^{++},and Mg^{++} .

El-Shahawy and Ghazi, (1983), El-Shinnawi,(1981), El-Shahawy and Amer, (1984) found that nitrogen transformations in soil are governed by various environmental factors including moisture, salinity and organic matter.

Bouwer and Idelovitch, (1987) indicats that under certain conditions, the level of Na^+, Ca^{++}, and Mg^{++} in treated effluents can adversely affect soil structure and worsen the soil infiltration and tillage characteristics. Na^+ when present in high concentration relative to Ca^{++} and Mg^{++} can cause dispersion of soil aggregates leading to reduce infiltration and permeability the degree to which the various concentration of Na^+ may affect soil structure is related not only to concentration of Ca^{++} and Mg^{++} but also to the salinity of effluent.

Al-Falih and Wainwright, (1996) reported that the nitrfication rate in soil decreased with increasing cocentration of salts in the soil, as result, the largest effect of salts on ammoium nitrification was observed at higher levels indicating the sensitivity of nitrification to salt concentration.

Kielen et al, (1996) found that negative effect of sodium degraded soil structure, crust formation reduces the infiltration rate of irrigation water into the soil. The water will

enter the soil at slow rate, and leave water standing for along time on the soil surface. During this period, soil aeration will be greatly reduced, thereby significantly inhibtinting or decreasing in nitrification process.
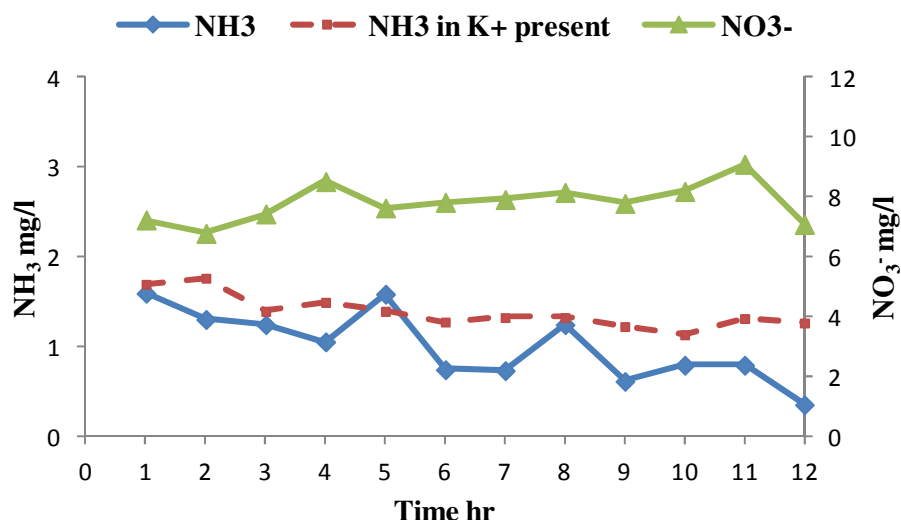

Figure 5. 7: Effect of Na$^+$ on the ammonia and nitrate concentration in synthetic wastewater at different contact times in Sandy clay loam soil.

Figure 5.8 shows that in the presence of Ca^{++}, Mg^{++}, K$^+$, Na$^+$ ion in synthatic wastewater the concentration of ammonia decreasing continued constantly in the 12 hour reached 3.22 mg/l. The NH$_3$ movement is parallel to the NO$_3^-$ movement in the lack of Ca^{++}, Mg^{++}, K$^+$, Na$^+$, both decreased with time. Nevertheless the concentration of NH$_3$ in the synthatic wastewater in the existence of Ca^{++}, Mg^{++}, K$^+$, Na$^+$ measured advanced all time compared to NH$_3$ concentration in the synthatic wastewater alone. The Ca^{++}, Mg^{++}, K$^+$, Na$^+$ concentration were 140 mg/l, 95 mg/l, 25 mg/l, 660 mg/l in the synthatic wastewater competed NH$_3$ on the active sites. It was very apperent that the majority of the active sites were occupied by Ca^{++}, Mg^{++}, K$^+$, Na$^+$ more than NH$_3$. This led more NH$_3$ to emerge in the soil solution less to be sorped on soil, as shown clearly in figure. 5.8. After 12 hours the NH$_3$ removal was reported to be 67.8% less than the NH$_3$ removal in the synthatic wastewater alone. The NO$_3^-$ concentration

increased to 7.33 mg/l at the end of the experiment. However, in the period of experiment as shown in figure 5.8, the difference in NO_3^- level was unrelated. However there was on visible declining movement in NH_3 level. The main payment of this was due to the exchange capacity of the soil, leading to continuose decrease in the NH_3 in the soil solution.
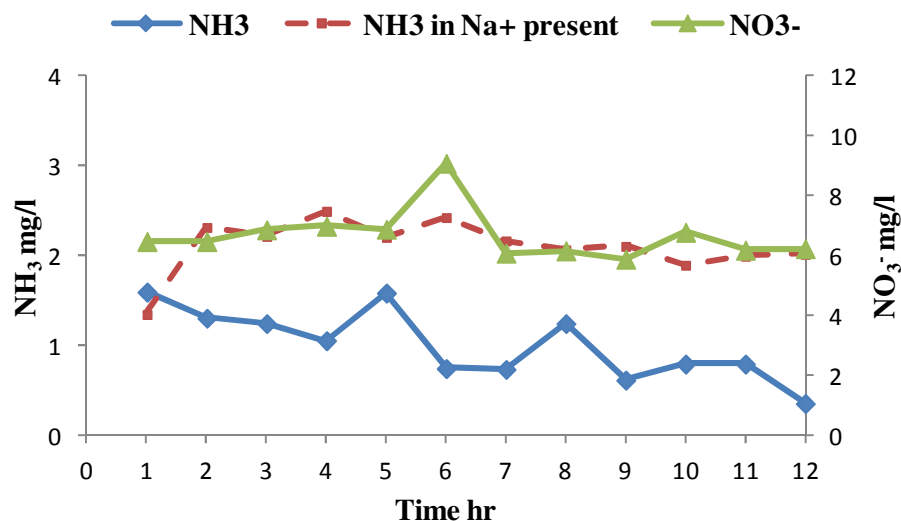

Figure 5. 8: Effects of cations on the ammonia and nitrate concentration in synthetic wastewater at different contact times in Sandy clay loam soil.

5.4 Loamy sand soil

The NH_3 and NO_3^- concentration at initial and at zero time, values are reported in table5.6.

Table 5. 6: The concentration for ammonia and nitrate at initial and zero time in each run.

Run No.	Cation present	Concentration mg/l			
		Initial NH_3	zero time	Initial NO_3^-	zero time
1	None	9.4	7.11	5	12.6
2	Ca^{++}	8.65	6.3	5.4	10.5
3	Mg^{++}	8.22	6.73	4.54	9.61
4	K^+	9	6.2	5	11.9
5	Na^+	9.5	5.9	4.8	10.4
6	$Ca^{++}, Mg^{++}, K^+, Na^+$	9.2	2.4	4.48	10.3

During each run a remarkable behavior was observed on the NH_3 concentration, there was a significant drop in NH_3 concentration after two hours as the synthetic wastewater contacted the soil. That means the loamy sand soil with low CEC (4.48 meq/100gm), needs long time to allowed ammonia removal.

It is clear that from in figure 5.9, the nitrification process in the Loamy sand soil considered the domenant mechanism for NH_3 removal from the soil solution.

The evidences for this can be summarised as follow:

The concentration of NO_3^- in the all runs with the loamy sand soil was higher than the NO_3^- concentration in all runs with the Sandy clay loam soil. However, the NH_3 level in the Sandy clay loam soil was higher than the loamy sand soil.
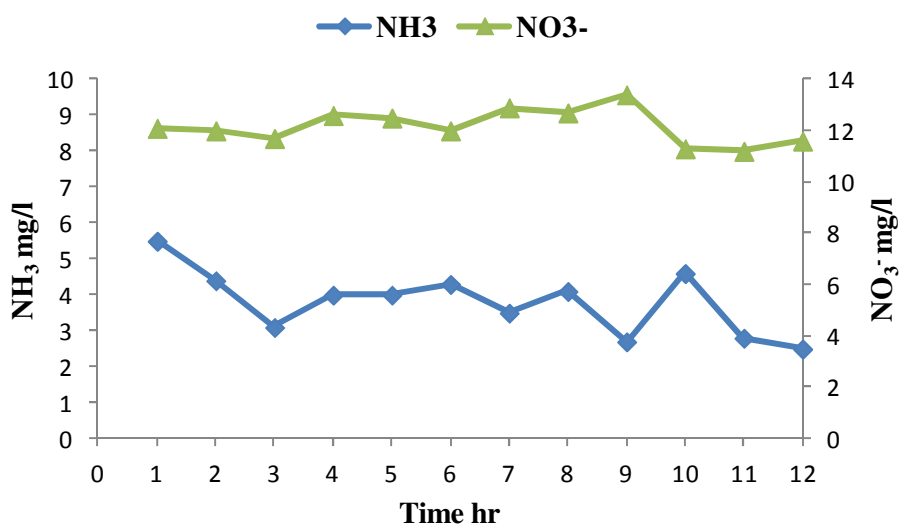
Figure 5. 9: Concentration of ammonia and nitrate in synthetic wastewater at different contact times in loamy sand soil.
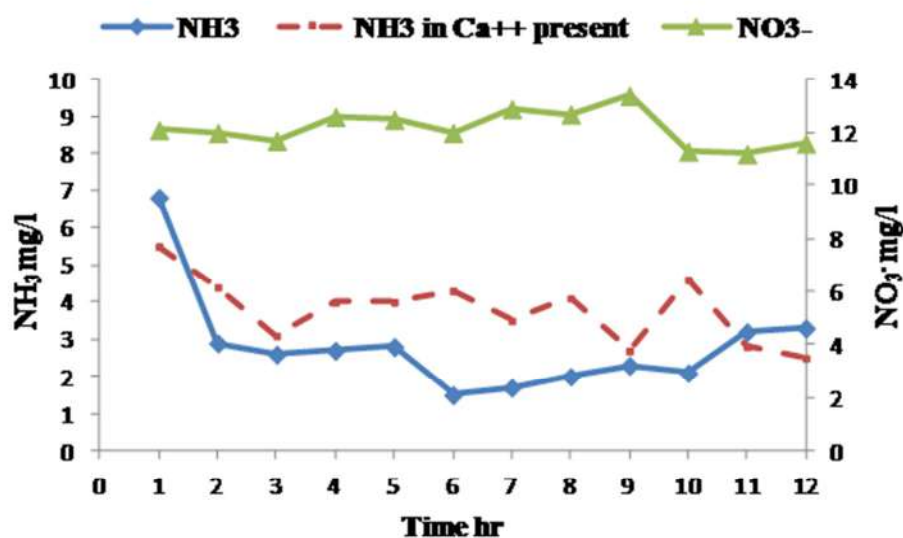
Figure 5. 10: Effect of Ca^{++} on ammonia and nitrate concentration in synthetic wastewater at different contact times in soil loamy sand.
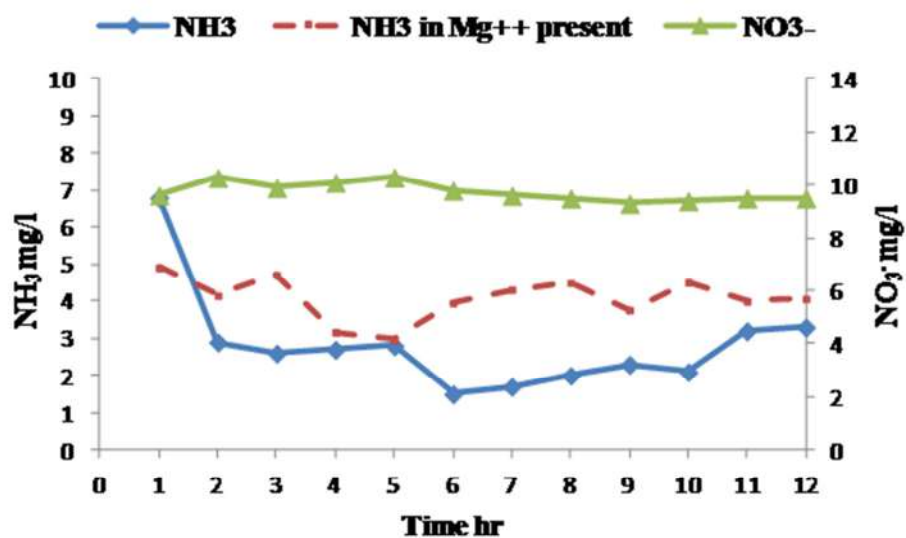
Figure 5. 11: Effect of Mg^{++} on ammonia and nitrate concentration in synthetic wastewater at different contact times in loamy sand soil.
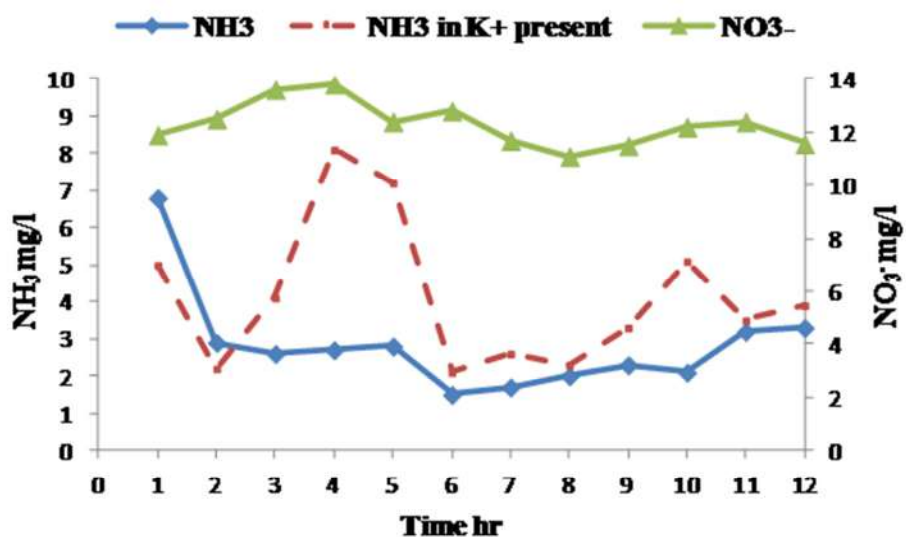
Figure 5. 12: Effect of K^{+} on ammonia and nitrate concentration in synthetic wastewater at different contact times in loamy sand soil.
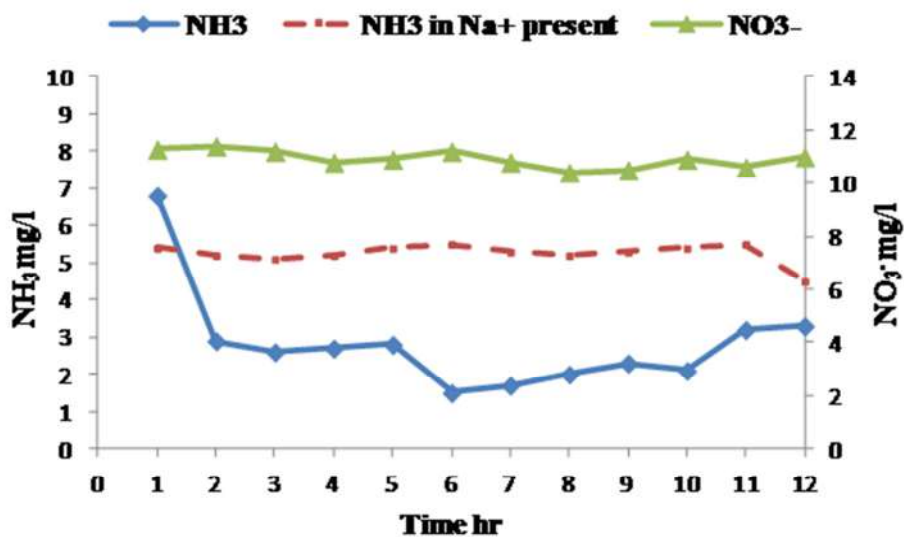
Figure 5. 13: Effect of Na$^+$ on ammonia and nitrate concentration in synthetic wastewater at different contact times in loamy sand soil.
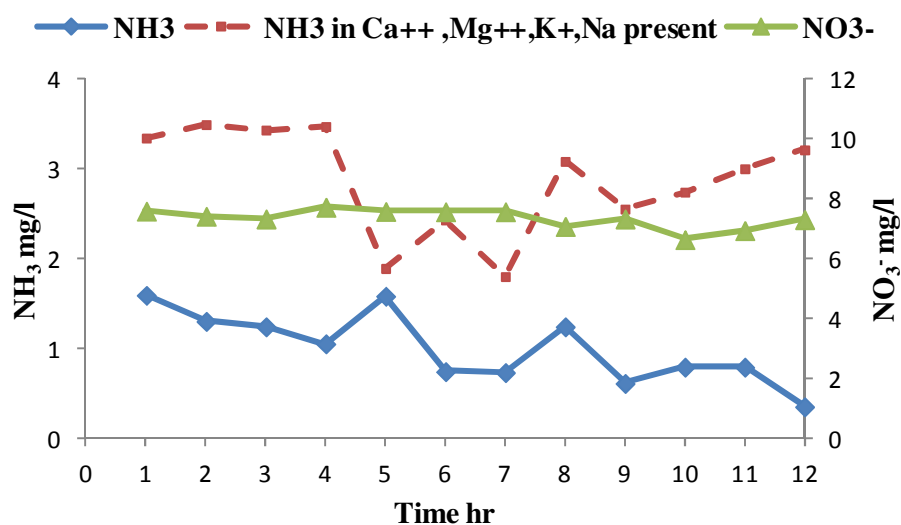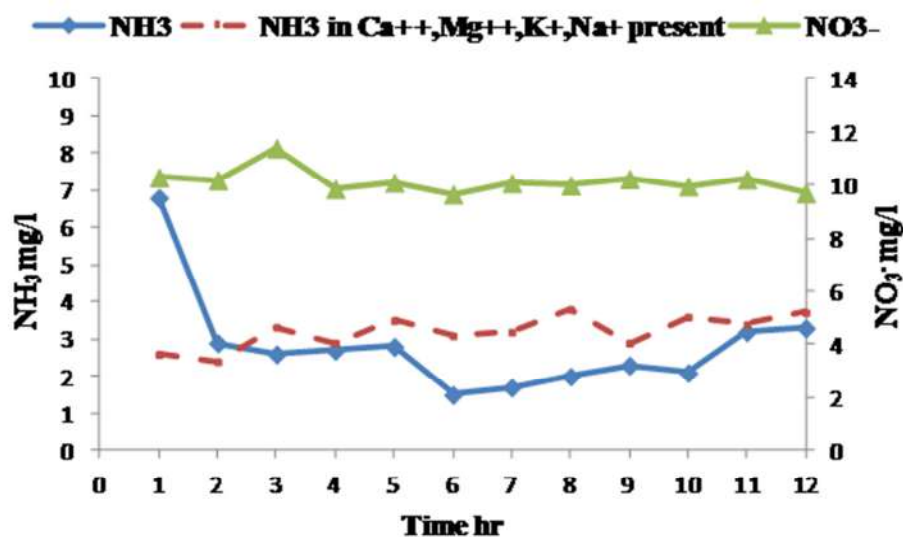

Figure 5. 14: Effects of cations on ammonia and nitrate concentration in synthetic wastewater at different contact times in loamy sand soil.

At the end of the experiment time the removal effeciency of the loamy sand soil for NH$_3$ was reported to be 71.1%, 50.6%, 57%, 45.3% in the presence of Ca^{++}, Mg^{++}, K$^+$, Na$^+$, respectively.

Besides the presence of competetive cations during the loamy sand soil runs decreased the sorption of NH_3 on the soil, and increased in the NH_3 level significantly in synthatic wastewater as shown in figures 5.10 throug 5.14

Although, the NO_3^- concentrations remained within the same level as the first run.

Figure 5.15 shows the compersion between the effect of the same cations on the behaviour of NH_3 in the Sandy clay loam soil and the Loamy sand soil, the result showed that the NH_3 concentration in the solution with all cations in the Loamy sand soil was higher than the NH_3 concentration with all cations in the Sandy clay loam.
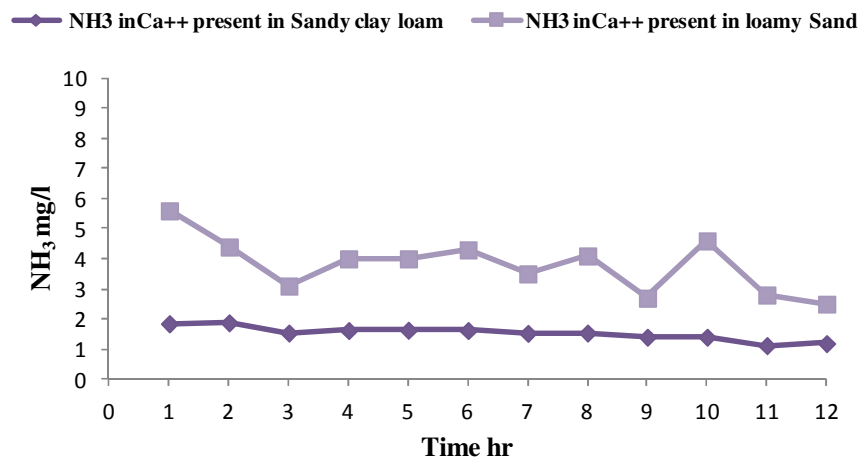
(A)
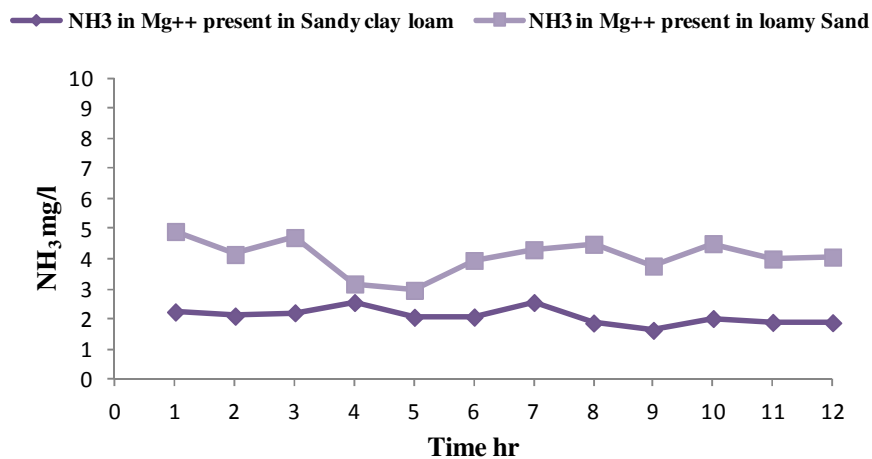
(B)
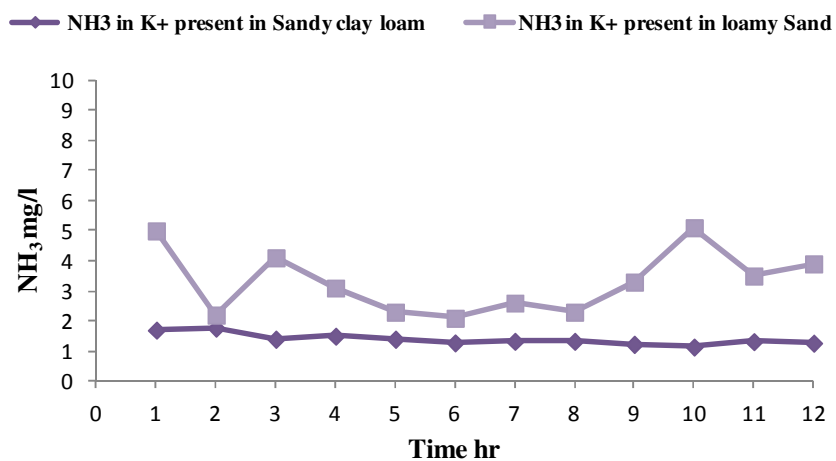
(C)
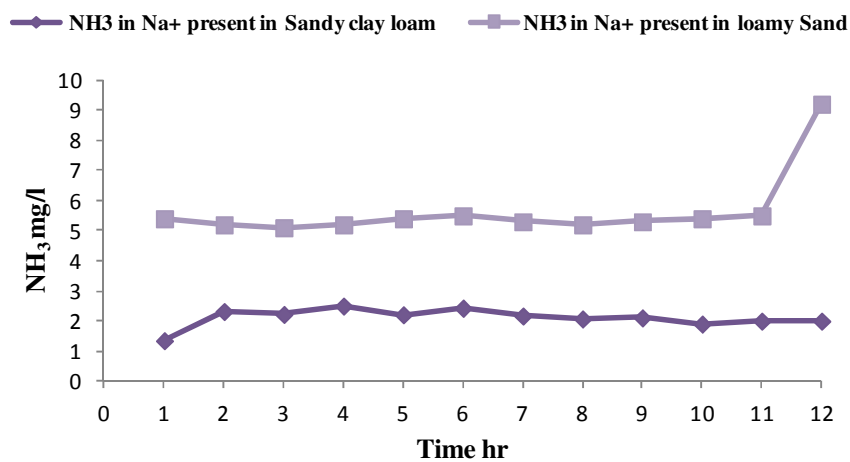
(D)

Figure 5. 15 (A, B, C and D) : Effects of cations on the ammonia concentration in synthetic wastewater at different contact times in Sandy clay loam soil and in loamy sand soil.

5.5 Secondary Treated Wastewater

The results of experiments to determine the effect of Sandy clay loam soil and Loamy sand soil in the NH_3 removal efficiency by using secondary treated wastewater in contact time from 1 hour to 12 hour,
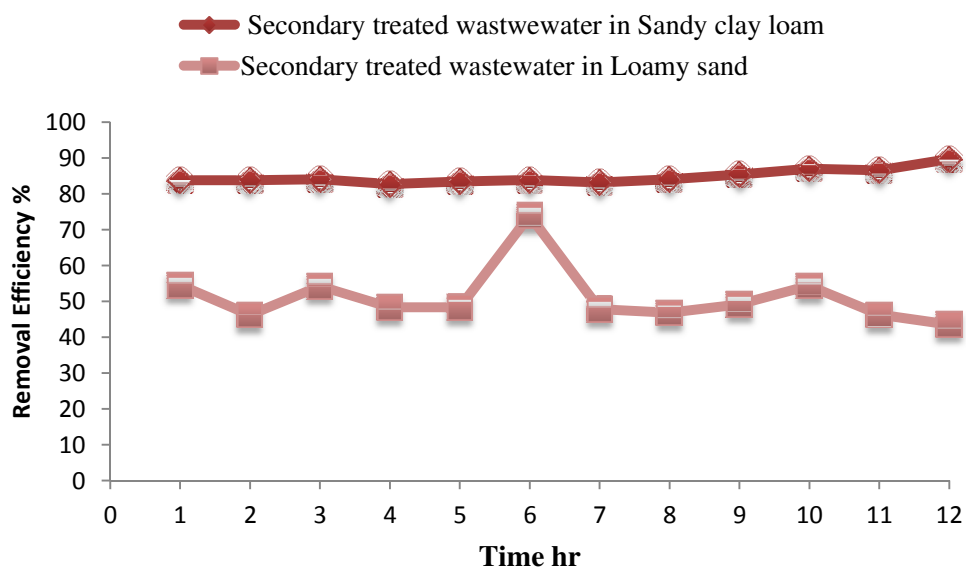
Figure 5. 16: The Removal Efficiency of ammonia concentration in secondary treated wastewater at different contact times in loamy sand soil and in Sandy clay loam soil.

Figure 5.16 shows that, the NH_3 removal efficiency increased in Sandy clay loam soil and reached 89.69%. This is means that a high sorption for NH_3 in the particles of Sandy clay loam soil was achived and decreasing of NH_3 concentration in the secondary treated wastewater was observed. Comparing with NH_3 removal efficiency in Loamy sand soil which reached to 43.5%.

CHAPATER 6: CONCLUSIONS & RECOMMENDATIONS

6.1 CONCLUSIONS

Some conclusions can be drawn on this review:

- The decreasing in the NH_3 concentration with the increasing in the NO_3^- concentration indicates there was a significant nitrification process in the first hours of experimental, However, during the last hours of experimental, the NH_3 was continued to decreased with stable increase in NO_3^-, was a result of sorption process.

- The nitrogen removal process such as nitrification and sorption can be affected by the presence of major cations with difference concentration.

- The higher concentration of specific cations Na^+ as a result of this study, is consrdered the largest one effect on the behavior of NH_3 other than the other types of cations.

- The soil type affected on the behavior of NH_3 with present of cations, it was found that the main dominate removal mechanism for NH_3 in the Sandy clay loam soil was sorption, However, Nitrification process was observed to be the main mechanism for NH_3 removal in the Loamy sand soil.

6.2 RECOMMENDATIONS

The main recommendation for this can be summarized as follow:

1. Since the main mechanism for NH_3 removal in sandy clay loam soil was reported to be ion exchange, it is recommended to increase the drying time during SAT operation, to avoid NH_3 accumulation in the soil.

2. However, since the main process for NH_3 removal in loamy sand soil was nitrification, it is recommended for SAT system to be operated with long wetting time. By which the hydraulic of the system will be increased.

3. A selective removal or decresing in concentration for Na^+ in the secondary treated wastewater is needed since, and from current experiments Na^+ was found to have the major effect on NH_3 sorption mechanism and nitrification conversion.

4. More investigation are needed to measure the significnce of both NH_3 nitrification and NH_3 sorption mechanism in each local soil, since it is clear that one mechanism could be dominant in a soil, and other mechanism could be dominant in other type of soil.

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Annexes

A-1 Runs Results of Sandy Clay Loam Soil

Table (1) : Concentraion of NH_3 and NO_3^- using Sandy clay loam in the absence of all cations.

Time (hr)	NH_3 (mg/l)	NO_3^- (mg/l)
1	1.6	8.19
2	1.3	8.18
3	1.25	8.21
4	1.06	7.6
5	1.59	7.9
6	.75	8.1
7	.74	8.3
8	1.25	7.1
9	0.62	8.24
10	0.8	8
11	0.8	7.6
12	0.36	8.4

Table (2) : Concentraion of NH_3 and NO_3^- using Sandy clay loam in the presence of Ca^{++}

Time (hr)	NH_3 (mg/l) in Ca^{++} present	NO_3^- (mg/l)
1	1.85	9.62
2	1.88	9.45
3	1.54	8.49
4	1.62	7.90
5	1.63	8.2
6	1.62	8.19
7	1.53	8.08
8	1.54	8.1
9	1.4	8.5
10	1.4	9
11	1.12	8.3
12	1.19	8.1

Table (3) : Concentraion of NH₃ and NO₃⁻ using Sandy clay loam in the presence of Mg⁺⁺

Time (hr)	NH$_3$ (mg/l) in Mg^{++} present	NO$_3^-$ (mg/l)
1	2.24	8.38
2	2.10	8.36
3	2.21	10.37
4	2.55	10.17
5	2.06	9.89
6	2.07	8.68
7	2.55	7.68
8	1.87	7.5
9	1.63	7.7
10	2.02	7.6
11	1.89	7.63
12	1.88	7.66

Table (4) : Concentraion of NH₃ and NO₃⁻ using Sandy clay loam in the presence of K⁺.

Time (hr)	NH$_3$ (mg/l) in K$^+$ present	NO$_3^-$ (mg/l)
1	1.7	7.25
2	1.77	6.8
3	1.4	7.45
4	1.5	8.53
5	1.4	7.65
6	1.28	7.84
7	1.33	7.93
8	1.33	8.17
9	1.23	7.8
10	1.14	8.2
11	1.32	9.11
12	1.27	7.10

Table (5) : Concentraion of NH$_3$ and NO$_3^-$ using Sandy clay loam in the presence of Na$^+$.

Time (hr)	NH$_3$ (mg/l) in Na$^+$ present	NO$_3^-$ (mg/l)
1	1.35	6.49
2	2.32	6.49
3	2.22	6.88
4	2.50	7
5	2.21	6.9
6	2.43	9.1
7	2.17	6.1
8	2.07	6.18
9	2.11	5.9
10	1.9	6.8
11	2	6.2
12	2.02	6.25

Table (6) : Concentraion of NH$_3$ and NO$_3^-$ using Sandy clay loam in the presence of Ca^{++}, Mg^{++}, K$^+$, Na$^+$

Time (hr)	NH$_3$ (mg/l) in Ca^{++},Mg^{++}, K$^+$, Na$^+$ present	NO$_3^-$ (mg/l)
1	3.35	7.61
2	3.50	7.44
3	3.44	7.35
4	3.48	7.74
5	1.90	7.60
6	2.44	7.59
7	1.81	7.59
8	3.09	7.1
9	2.56	7.35
10	2.75	6.66
11	3.01	6.96
12	3.22	7.33

Table (7) : Concentraion of NH$_3$ and NO$_3^-$ using Sandy clay loam using secondary treated wastewater.

Time (hr)	NH$_3$ (mg/l) in secondary treated wastewater	NO$_3^-$ (mg/l)
1	10.8	7.4
2	10.8	7.1
3	10.6	7.09
4	11.2	7
5	11	7.6
6	10.7	6.6
7	11.2	6.3
8	10.6	6.4
9	9.7	6.6
10	8.65	6.6
11	8.94	6.5
12	6.85	7.1

A-2 Runs Results of Loamy Sand Soil

Table (1) : Concentraion of NH_3 and NO_3^- using Loamy sand soil in the absence of all cations.

Time (hr)	NH_3 (mg/l)	NO_3^- (mg/l)
1	6.8	13.4
2	2.9	15
3	2.6	16.3
4	2.7	14.5
5	2.8	15.5
6	1.5	17.3
7	1.7	14.3
8	2	13.9
9	2.3	11.5
10	2.1	13
11	3.2	12.4
12	3.3	11

Table (2) : Concentraion of NH_3 and NO_3^- using Loamy sand soil in the presence of Ca^{++}.

Time (hr)	NH_3 (mg/l) in Ca^{++} present	NO_3^- (mg/l)
1	5.5	12.1
2	4.4	12
3	3.1	11.7
4	4	12.6
5	4	12.5
6	4.3	12
7	3.5	12.9
8	4.1	12.7
9	2.7	13.4
10	4.6	11.3
11	2.8	11.2
12	2.5	11.6

Table (3) : Concentraion of NH₃ and NO₃⁻ using Loamy sand soil in the presence of Mg⁺⁺

Time (hr)	NH$_3$ (mg/l) in Mg^{++} present	NO$_3^-$ (mg/l)
1	4.91	9.61
2	4.15	10.28
3	4.71	9.9
4	3.17	10.1
5	2.96	10.3
6	3.95	9.8
7	4.31	9.6
8	4.49	9.5
9	3.76	9.3
10	4.51	9.4
11	4	9.5
12	4.06	9.5

Table (4) : Concentraion of NH₃ and NO₃⁻ using Loamy sand soil in the presence of K⁺.

Time (hr)	NH$_3$ (mg/l) in K$^+$ present	NO$_3^-$ (mg/l)
1	5	11.9
2	2.2	12.5
3	4.1	13.6
4	8.1	13.8
5	7.2	12.4
6	2.1	12.8
7	2.6	11.7
8	2.3	11.1
9	3.3	11.5
10	5.1	12.2
11	3.5	12.4
12	3.9	11.57

Table (5) : Concentraion of NH_3 and NO_3^- using Loamy sand soil in the presence of Na^+.

Time (hr)	NH_3 (mg/l) in Na^+ present	NO_3^- (mg/l)
1	5.4	11.28
2	5.2	11.4
3	5.1	11.3
4	5.2	10.8
5	5.4	10.9
6	5.5	11.2
7	5.3	10.8
8	5.2	10.4
9	5.3	10.5
10	5.4	10.9
11	5.5	10.6
12	9.2	11

Table (6) : Concentraion of NH_3 and NO_3^- using Loamy sand soil in the presence of all cations.

Time (hr)	NH_3 (mg/l) in Ca^{++},Mg^{++},K^+,Na^+ present	NO_3^- (mg/l)
1	2.6	10.3
2	2.4	10.2
3	3.32	11.4
4	2.9	9.86
5	3.5	10.1
6	3.1	9.66
7	3.2	10.09
8	3.8	10
9	2.9	10.24
10	3.6	9.96
11	3.4	10.23
12	3.72	9.71

Table (7) : Concentraion of NH$_3$ and NO$_3^-$ using Loamy sand soil using secondary treated wastewater.

Time (hr)	NH$_3$ (mg/l) in Secondary treated wastewater	NO$_3^-$ (mg/l)
1	31.6	10.8
2	27.3	10.1
3	32.3	9.72
4	27.4	9.4
5	31.0	9.69
6	15.6	9.8
7	31.3	9.7
8	31.9	10.09
9	22.6	9.8
10	30.5	10.1
11	27.4	9.8
12	32.2	8.8

A-3 Activites Images

A-3-1 Hydrometr Analysis

A-3 Activites Images

A-3-2 Soil Water Extracts prepration

A-3-3 Samples Shaking

A-3-4 NH$_3^+$, NO$_3^-$ Measurment

A-3-5 Na$^+$, K$^+$ Measurment

A-3-5 Ca^{++}, Mg^{++}, Hardness Measurment

A-3-6 Wastewater Samples

A-3-7 Samples