

Chemical Pre-Precipitation
of Municipal Wastewater Treatment
using Mg^{2+}

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WASTEWATER TREATMENT USING Mg^{2+}*

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Abstract

The Masters' thesis work has been characterized by an approach to gain an insight into the municipal wastewater treatment for more efficient removal of COD and nutrients like Total Phosphorous and Total Nitrogen. The aim of this work was to evaluate a method to improve the wastewater treatment efficiency for removal of nutrients. The different objectives were to evaluate the use of magnesium chloride for the removal of COD, total Phosphorous and total Nitrogen from municipal wastewater and carry out alkaline hydrolysis of toilet paper to estimate if the toilet paper content can be reduced by natural decomposition during alkaline hydrolysis. The methodology used in this study was literature review and laboratory experiments. The study mainly focused on additional removal of COD, total Phosphorous and total Nitrogen from municipal wastewater using magnesium chloride. Several sets of experiments were carried out with different weighed samples of magnesium chloride to observe the percentage reduction of COD, total Phosphorous and total Nitrogen. Study results showed that magnesium chloride was a viable option due to its efficient removal at lower concentrations of input and economical aspects. Alkaline hydrolysis of toilet paper also revealed that the toilet paper readily dissolved in sodium hydroxide solution at a pH of 12. Therefore, it was concluded that magnesium chloride was a suitable option to achieve efficient removal of nutrients and also toilet paper dissolved faster at higher pH values. Also, due to the increase in COD while alkaline hydrolysis; it was suggested that the toilet paper from alkaline hydrolysis could be a possible option to use the carbon source for total Nitrogen removal in wastewater treatment.

Keywords: COD, total Phosphorous, total Nitrogen, removal, magnesium chloride, wastewater treatment, alkaline hydrolysis, toilet paper.

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1 Introduction

1.1 Background

Wastewater consists of many different types and discussed here is municipal wastewater. The municipal waste water has a composition of micro-organisms (pathogenic bacteria and virus), biodegradable organic materials, food wastes and agricultural wastes, other organic materials (detergents, pesticides, fat, solvents and phenols), nutrients (total Nitrogen, total Phosphorous and ammonia), metals (Hg, Pb, Cd, Cu, Ni), other inorganic materials (acids and bases). These can have a vast range of effect on the environment, posing a risk to the humans and the aquatic life (Henze et al., 2002).

The rapid urbanization and population growth in India has put an immense pressure on the future needs for water. Adding to all this, the anthropogenic activities and indiscriminate use of the natural resources have resulted in furthermore pollution of the water resources and thereby deteriorating the wastewater management. The poor sewage reticulation systems and inadequate wastewater infrastructure contribute to the high levels of COD and nutrients like Phosphorous and Nitrogen. Owing to these reasons, I decided to focus on municipal wastewater treatment due to inadequacy of proper sewerage systems.

The principle constituents of concern are the suspended solids which can lead to sludge deposits when the untreated wastewater is discharged to the end recipient. If biodegradable organics are not given appropriate treatment, then this condition can spur the development of septic conditions and there will be a problem with oxygen in the water body that receives the polluted water. Priority pollutants and refractory organics are also found in municipal wastewater that can have several toxic effects. Nutrients when discharged to the end recipient (lake) can result in undesirable aquatic life and also pollute ground water when discharged in land (Metcalf and Eddy, 2003).

Currently, chemical precipitation has become the most popular method for removal of total Organic compounds, Phosphorous and Nitrogen. Chemical precipitation has many advantages among which the increase in energy production is a significant one. Chemical precipitation results in the production of a large amount of sludge and in turn the digestion of sludge leads to an increase in the biogas. The metal salt precipitation approach to remove total Phosphorous makes the precipitate unrecoverable for the industrial processing as a fertilizer. One of the possibilities to improve the recovery of total Phosphorous is by using magnesium compound, struvite. It is magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and precipitates in an instinctive way in the wastewater treatment process and the recovered struvite can be used as a potential fertilizer (Velazquez et al., 2002).

1.2 Aims and Objectives

The primary aim of this work was to evaluate a method to improve the wastewater treatment efficiency for removal of organic compounds and nutrients.

The different objectives are:

- To evaluate the use of magnesium chloride for the removal of COD, total Phosphorous and total Nitrogen from municipal wastewater.

- To carry out alkaline hydrolysis of toilet paper to estimate if the toilet paper content can be reduced by alkaline hydrolysis and used as a carbon source for total Nitrogen removal in wastewater treatment.

1.3 System boundaries

The thesis work focuses only on COD, total Phosphorous and total Nitrogen removal. Removal of BOD and suspended solids are not a part of this study. The varying effects of pH on organic compounds and nutrients removal were also not a part of this thesis work. Also, for alkaline hydrolysis of toilet paper only sodium hydroxide solution was used.

1.4 Limitations

Due to limited time, the experiments were carried out with a constant pH value of 10. However, during the beginning of the experiments, the plan was to carry out the trials with varying pH of 9, 10 and 11, to see if the pH had any varying effect on the COD, total Phosphorous and total Nitrogen removal. The original plan was to use the software Modde in order to plan which experiments should be done. It is a program for generation and evaluation of statistical experimental designs. However, while conducting my set of experiments, the COD, Phosphorous and Nitrogen were measurements had to be conducted for each raw wastewater sample, as the 'Modde' program was very expensive. A number of experiments were showing out of range results as the dilutions had to be different with each sample of wastewater. As a result, the experiments became time consuming and the range of experiments had to be shortened. Therefore, it was not possible to use the program and the number of trials became too large and it was necessary to reduce the number of factors to test the wastewater samples. Another problem while conducting the experiments were that, the COD, total Nitrogen and total Phosphorous levels were varying in a vast range on a day-today basis and sometimes an increase in the amount of total Phosphorous and total Nitrogen was observed. The reason could be owing to that real waste water was used for all the trials and not artificial waste water; as a result it had many suspended particles and also had varying concentrations of organic compounds and nutrients. This case caused many trials to be repeated and became time consuming.

Although it was of vast interest to me to carry out the alkaline hydrolysis of toilet paper to observe if it could be used as a carbon source for total Nitrogen removal in the wastewater treatment, due to time constraints it was not possible to study exactly and provide approximate results for the same.

2 Driving forces

There were a number of driving forces that motivated me to choose this particular study as my master thesis work.

The principle constituents of concern are the suspended solids which can lead to sludge deposits when the untreated wastewater is discharged to the end recipient. If biodegradable organics are not given appropriate treatment, then this condition can spur the development of septic conditions and result in the depletion of natural oxygen resources. Nutrients when discharged to the end recipient (lake) can result in undesirable aquatic life and also pollute ground water when discharged in land (Metcalf and Eddy, 2003). Phosphorous is a vital macronutrient that incites the growth of algae and cyanobacteria and leads to eutrophication of the lakes. Therefore, it is important to remove total Phosphorous prior to the discharge of waste water into the lakes. Total Phosphorous removal must be carried out over the primary and secondary treatment of waste water.

Currently, chemical precipitation has become the most popular method for recovery of total Phosphorous. The metal salt precipitation approach to remove total Phosphorous makes the precipitate unrecoverable for the industrial processing as a fertilizer. One of the possibilities to improve the recovery of total Phosphorous is by using magnesium compound, struvite. It is magnesium ammonium phosphate hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and precipitates in an instinctive way in the wastewater treatment process and the recovered struvite can be used as a potential fertilizer (Velazquez et al., 2002). Magnesium removes 90% of the nutrients due to its high flocculation properties and is very cheap and available in plenty as a natural resource from sea water. However, the chemicals used to produce struvite, such as; magnesium oxide, total Phosphorous acid and ammonia are expensive. As an alternative, magnesium contained in sea water (bittern) can be used as a coagulant to remove nutrients from wastewater as it is cheaper and also has a higher rate of precipitation. Bittern is a reject by-product from the evaporation ponds in the sea salt production industry (Rosenzweig et al., 2007).

Magnesium is one among the most abundant positive ions available in the Sea and is becoming an important study due to its ability to remove COD, P and N from wastewater. Magnesium compounds, such as, magnesium chloride, can be used as a coagulant to remove the organic compounds. They have higher treatment efficiency and are available at lower costs owing to its availability in abundance. However, economy is a significant factor and the chemicals used in the treatment are expensive. Therefore, I stressed more on chemicals that would be abundant and cheap. Another motivation was to study if the substances from the Sea can be recovered and integrated with waste water treatment for better and efficient removal of organic compounds and nutrients. Magnesium chloride seemed to be a suitable option as magnesium ions is the fourth most abundant ion after sodium available in the Sea. Thus, I chose to study on chemical pre-precipitation of municipal wastewater using magnesium chloride for an increased removal of COD and the nutrients Total Phosphorous and Total Nitrogen.

It is of large interest today to capture as much as organic compounds from the wastewater before the biological treatment. The driving force for this is to decrease the energy consumption for the treatment and another reason is to get more biogas from a digester treating the removed sludge. Pre-precipitation and flocculation is therefore of interest today, as flocculation of the organic suspended solids facilitates

the biological treatment and also reduces the need for aeration in the aeration basin and thereby saving a lot of energy. Pre-precipitation was also of particular interest as it results in a larger amount of sludge to the digester and increases the production of biogas.

The gaseous and aqueous CO₂, carbonic acid, bicarbonate and carbonate make up the carbonate system in water and are one of the major acid-base systems in water. Water has the capacity to neutralize strong acid and base. This can be applied in municipal wastewater treatment too in nitrification and oxidation of organic matter to CO₂. This takes place in the aeration basin of the activated sludge. Toilet paper in the water can be treated by acid or alkaline hydrolysis for use as a carbon source in the denitrification (Jenkins and Snoeyink, 1980). Therefore, I decided to focus on the fate of toilet paper in the wastewater. A large amount of toilet paper is being flushed and is discharged together with waste water to the waste water treatment plants and it would be of interest to know what happens to the toilet paper during wastewater treatment. This was the reason for opting alkaline hydrolysis of toilet paper to observe if it could be used as an internal carbon source for total Nitrogen removal in the wastewater treatment.

2.1 Waste water treatment in India

The wastewater treatment in India is not very efficient. The efficiency for COD, Total Phosphorous and Total Nitrogen removal is only 63%, 41% and 40% respectively. The pH of the treated waste water usually ranges from 6 to 9. Ferric chloride is the most common chemical used in chemical precipitation. This chemical is not by far the most efficient precipitant and has some disadvantages which will be discussed later in this report. In Sweden, the average treatment efficiencies achieved by the waste water treatment plants is 93% reduction in removal of COD, 99% in BOD, 98% in Phosphorous and 93% in Nitrogen. The reasons owing to the high treatment efficiencies in Sweden with comparison to India could be due to better expertise and awareness to control the environmental quality. Economy can also be a major aspect. Another major aspect could be population. With the vast population in India, it becomes more challenging to achieve high efficiencies. Owing to these reasons, it was of interest for me to evaluate the use of magnesium chloride for efficient removal of organic compounds and nutrients from waste water.

Table 1: Average treatment efficiencies of the waste water treatment plants in India (Sharma & Dubey, 2011).

<i>Parameters</i>	<i>Concentration (mg/l)</i>		
	<i>In</i>	<i>Out</i>	<i>Eff. (%)</i>
BOD ₅ (< 40 mg/l)	19.5	6.8	60.7
BOD ₅ (< 40 mg/l)	178	32	80.7
COD	287	76	63.2
TSS	113	22.3	68.1
TN	53	29.8	39.4
NH ₄ - N	28.4	17.1	21.1
TP	8.7	4.4	40.9

3 Literature review

Efficient treatment of wastewater is gaining increasing importance and several new technologies and methods are being studied to make wastewater treatment contribute more towards sustainability. Wastewater treatment is very essential as improper treatment may have severe effects on the environment. Industrial water undergoes pretreatment prior to its discharge to the municipal wastewater treatment which consists of micro-organisms, organic and inorganic materials, heavy metals and other wastes which have been earlier mentioned under the introduction chapter. The treatment of wastewater consists of different levels.

3.1 Effects of COD, Phosphorous and Nitrogen

The sewage discharged finally after the wastewater treatment might still have its effects on the aquatic environment. The sewage has unavoidable toxins which mainly affects the aquatic environment. If the wastewater is not treated well, then the sewage that is finally discharged to the recipient (Sea) will have a high density of suspended solids that would cloud the water and suffocate the aquatic species and clog the animal's gill. These particles are very rich in fecal matter and serve as an energy source for the bacteria which multiply to larger populations before they leave the human body. These bacteria consume the organic components and the large number of bacterial growth leads to depletion in oxygen in the aquatic environment due to respiration (Frid and Dobson, 2002).

Elements like Phosphorous can cause eutrophication. Phosphorous is a significant element providing nutrition to plants and animals. Phosphorous in the form of phosphates is present in natural waters. These phosphates form insoluble compounds with calcium and other salts and settles as sediments in the bottom. Therefore, the available concentration of Phosphorous is less in natural waters. It is also a limiting factor for the growth of algae and other organisms. However, when Phosphorous increases and becomes excessive, it breaks this limiting factor and initiates a rapid growth of micro organisms. This problem is termed as eutrophication (Carpenter et al., 1998).

In eutrophication, the formally deficient nutrients reach the surface of the water. Centuries ago, eutrophication was occurring as a natural process and took several centuries to transform natural water bodies into a dry land. Nowadays, due to rapid urbanization and anthropogenical activities, eutrophication has been greatly accelerated. A number of researches have been conducted where it was observed that almost 54% of the lakes in Asia and 53% of the lakes in Europe are eutrophic. Thus, this problem is of utmost significance (Carpenter et al., 1998). Several negative impacts have been observed in the case of eutrophication. Some of them have been listed below:

- Proliferation of toxic blooms
- Water pollution owing to change in color, transparency, odor, taste and sometimes treatment problems in the water.
- Loss of biodiversity
- Oxygen depletion which is in return harmful to the aquatic life

Therefore, it is of great significance to achieve very good efficiency in Phosphorous removal during the treatment of wastewater. This saves an enormous amount of non-renewable Phosphorous and prevents wastewater pollution and eutrophication (Carpenter et al., 1998).

Nitrogen present in natural waters gives rise to algal blooms caused by cyanobacteria namely *Nodularia* and *Aphanizomenon*. These species are capable of fixing atmospheric Nitrogen and can be toxic. It hampers recreational activities as the blooms last for a long period of time and these are potentially toxic accumulations. The growth of these blooms is regulated by the availability of Nitrogen and Phosphorous in the Sea. These are released from the sediments when there is a reduction of oxidized iron compounds (Figure 1). The prime cause for this reduction of oxygen is due to the lack of vertical mixing in winter (Kiriiki et al., 2001).

Although the hydrographical and meteorological factors control the outcome of blooms, the intensity of the blooms can also be affected by anthropogenic eutrophication. When the nutrients load like Phosphorous and Nitrogen increases, the biomass production and sedimentation also increases. The decomposition of this material requires increased oxygen consumption, thereby resulting in reduced oxidized iron compounds and thus promoting the growth of cyanobacteria (Kiriiki et al., 2001). The figure below shows the conceptual model for Nitrogen in the Gulf of Finland. The elemental cycle of Nitrogen is displayed in the figure. The two types of phytoplankton are represented, the Nitrogen fixing which cyanobacteria and the other which is non-Nitrogen fixing. Phosphorous and Nitrogen assimilates in the phytoplankton biomass and there is subsequent release into dissolved nutrients present in the Sea. Excess release Phosphorous and Nitrogen settles as sedimenting fraction in the bottom of the Sea (Kiriiki et al., 2001).

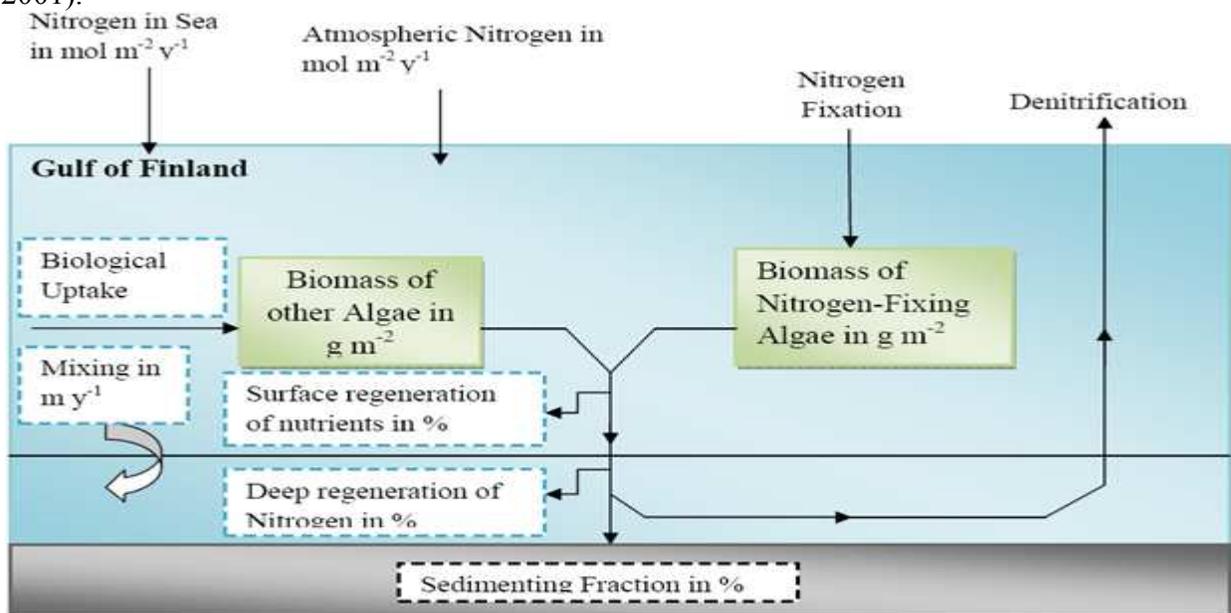


Figure 1: Nitrogen fixation

The growth of the blooms is affected by the availability of Phosphorous in the Sea. After the algal cells die, they settle at the bottom as detritus Nitrogen and Phosphorous and forms the sedimenting fraction in the Ocean belt. However, the rate of Phosphorous regeneration is approximately twice that of Nitrogen regeneration. Denitrification is included in the sediment of detritus Nitrogen. Below the mixing layer there is no algal growth and interaction with dissolved nutrients (Kiriiki et al., 2001).

Due to the above stated effects, efficient removal of COD, Phosphorous and Nitrogen is necessary. However, some general methods can be followed to decrease the amount of COD, Phosphorous and Nitrogen entering into the environment from inland human activity.

- Reduced emission from the primary sources. Eg. Wastewater treatment and agriculture.
- Decrease phosphate input to the material flow. Eg: sewage and detergents
- Removal of COD, Phosphorous and Nitrogen at wastewater treatment by introducing additional removal capacity

3.2 Municipal waste water treatment

Municipal waste water also contains Industrial wastewater that undergoes pretreatment prior to its discharge to the municipal wastewater treatment which consists of micro-organisms, organic and inorganic materials, heavy metals and other wastes which have been earlier mentioned under the introduction chapter. The treatment of wastewater consists of different levels.

3.2.1 Preliminary treatment

Preliminary treatment takes place first where materials such as, grit, sticks, floatables and grease and other large particles are removed which generally cause operational and maintenance problems during the treatment operations (George et al., 2003). Various unit operations such as, screening, grit routings and grinding is used for removal of large particles as they cause damage to the processes (Peavy et al., 1985). Filtration of large particles such as logs, sticks, leaves, stumps, bones, plastics, bottle caps, rocks, heavy debris is prevented from entering the wastewater treatment processes by using screens. The amount of coarse particles to be removed depends on various factors such as opening of the screen, wastewater flow, the characteristics of the municipality, etc. The screenings have 10 to 20% of dry solids and 70 to 95% of volatile solids (Vesilind P.A., 2003).

There are different screens used in the treatment plants today. Bar screens have a width ranging from 38 mm to 150 mm. A coarse screen or step screen is also used for waste water treatment. The coarse screen is built up of sloping parallel rods with an opening of 10 – 20 mm. whereas the step screen has movable lamellae. These are easier to maintain as they have higher self cleaning efficiency due to the movable lamellae. Large suspended particles are removed. As an alternative, drum screens are also being used with 1 – 5 mm widths. Mechanical screens have screen opening of width 6 to 38 mm and are set 0 to 30° vertical. These screens have reduced labor costs and have better screening capture and flow conditions and are more efficient in handling large quantities of debris. The chain or the cable driven screens have a chain or cable to move the rake teeth through screen opening. In these screens the deposits might get jammed with the trash which is a disadvantage. The continuous self-cleaning screens have a belt made of plastic or stainless steel and are pulled through the wastewater so that screening is provided along the entire screen length. Due to the continuous action of the screen, larger amount of solids are removed and prevents the build of deposits in the unit. But these are prone to clogging when there are very high flow conditions (Vesilind P.A., 2003).

3.2.2 Primary treatment

At the primary treatment, removal of suspended solids and organic matter takes place by mechanical methods or by addition of chemicals. The effluent from preliminary treatment is treated here by retaining it in a settling tank for few hours for the suspended solids and organic

matter to settle down or float to the surface. A scraper collects the settled matter from the bottom of the settling tank, thereby reducing the waste load (Peavy et al., 1985).

In primary treatment, sedimentation takes place in a rectangular or circular basin and the water flow is horizontal or vertical. The flow velocity is decreased so that the heavier particles sink to the bottom. Flotation is also another primary treatment method where the density differences between the particles and surrounding liquid is utilized. In this, tiny air bubbles are attached to the sludge particles. This sludge-air aggregate produced has a lower density than the surrounding liquid and therefore rises to the top of the surface and is removed by means of a scraper (Persson&Nilson, 2005).

3.2.3 Secondary treatment

In the secondary level the biodegradable organic matter, suspended solids and nutrients are removed by many common methods such as, biological treatment, chemical treatment, chemical oxidation, etc. The effluent after primary and advanced primary levels of treatment consists of 40% to 50% of organic matter and suspended solids.

3.2.3.1 BOD removal

The dissolved organics is removed by biological treatment. Microorganisms feed on the organics and are then converted to biomass and removed as sludge. This is carried out by fixed film, suspended growth by biofilms and sewage lagoon systems (Hassanzadeh, 2005).

The suspended biofilms are of interest due to its high efficiency in wastewater treatment. They are simple, reliable and are stable as their natural immobilization allows a good rate of biomass retention and accumulation, thereby ruling out the need of having solid-separation devices. The biofilms create an internal unique microenvironment by adsorbing the corrosive release of Fe^{2+} ions and other toxins and they also trigger a physiological change in the bacteria (WEF, 1998).

The moving-bed biofilm reactor consisted of Kaldnes rings. This was invented by a Norwegian company KaldnesMiljoteknologi. The reactor consisted of small cylindrical polyethylene carrier elements in aerated and non-aerated basins to support the biofilm growth in the reactor. These cylinders are usually 10 mm in diameter and 7 mm in height and have a cross inside the cylinder and have longitudinal fins outside the cylinder. The packing of these rings are circulated by air agitation or mixers and these rings fill upto 25-50% of the reactor volume. These reactors possess an advantage of not requiring any return of the activated sludge. Finally, a clarifier is used to settle the sludge. However, the disadvantage is that the cylinder packaging's need to be cleaned and therefore requires periodic drainage of the aeration, thereby discouraging the use of a fine bubble aeration equipment (Rusten et al., 1998).

The fixed film system has materials made of rock, sand or plastic and the microorganisms grow on them. The microorganisms grow and form a film and absorb nutrients as the wastewater passes through them. In the suspended growth systems, the microorganisms are mixed in wastewater and also grow in quantity by absorbing the nutrients and are later removed as sludge, whereas in the sewage lagoon system the wastewater is naturally degraded by retaining in a shallow earthen basin for a long period of time where oxygen is provided by artificial means (Hassanzadeh, 2005).

3.2.3.2 Nutrients removal:

Nutrients are vital constituents essential for the growth of plants, animals and human beings. A majority of the nutrients is used in agriculture in the form of fertilizers and are absorbed by the plants or transported the adjacent water body by agricultural runoff. The most commonly found nutrients in wastewater are total Nitrogen (N) and total Phosphorous (P) compounds and it is important to treat them as they may cause eutrophication when present in excess.

Chemical precipitation is induced by adding a chemical to promote and aid the precipitation process. It is a unit process in which a settleable solid is formed by the chemical joining of two or more inorganic dissolved species and of these species is removed. The conceptual framework of precipitation is represented in Figure 2. In induced precipitation, the chemicals are added to the pollutant to be precipitated to enhance the precipitation. The particles that are formed are then removed from the source using particle separation method, such as sedimentation (Sincero, 2002).

Precipitation can be induced during waste water treatment in different stages. They are direct precipitation, pre-precipitation, pre-dosage, simultaneous precipitation and post-precipitation. In direct precipitation the chemicals are added in the flocculation stage to roughly treated water and the sludge is removed. There is no biological treatment in direct precipitation. In pre-precipitation chemicals are added before primary settling and then undergoes biological treatment. In pre-dosage the chemicals are added before primary settling and in simultaneous precipitation added before or in the biological stage. Therefore, biological and chemical treatment occurs at the same stage. In post precipitation chemicals are added after the biological treatment (Persson&Nilson, 2005).

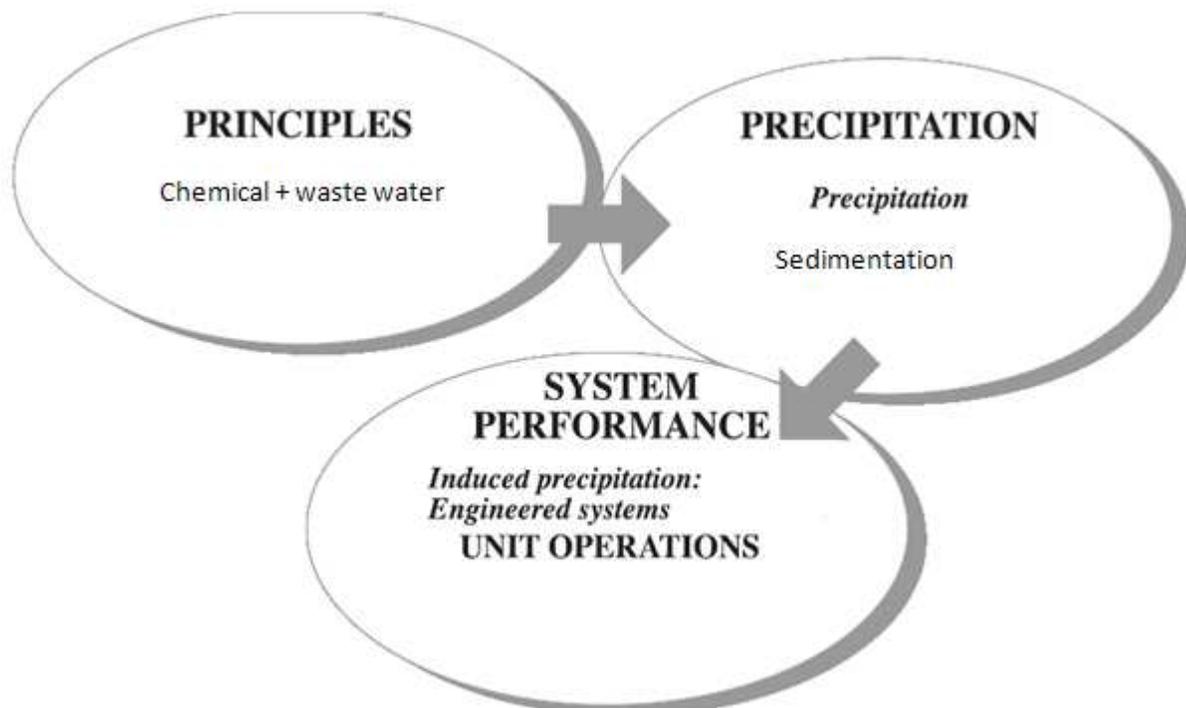
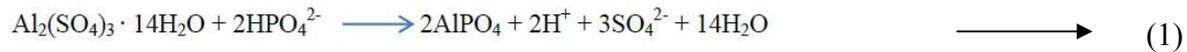


Figure 2: conceptual framework for precipitation

Precipitation by metal-salts addition to a biological process has become one among the effective methods for organic compounds and total Phosphorous removal today. Aluminum and ferric cations are usually added as aluminum sulfate and ferric chloride and used in precipitation for the removal of total Phosphorous and thereby removed as AlPO_4 and FePO_4 in the sludge. These ions are added prior to primary sedimentation. These cations precipitate with the orthophosphate anion in wastewater at neutral pH values ($\text{pH} = 7$) and can be added directly to the wastewater (Rittman and Carty, 2001).

The reactions are represented as follows:

Aluminum sulfate:



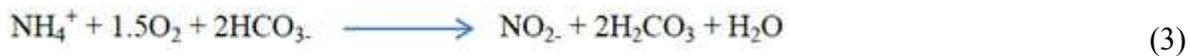
Ferric chloride:



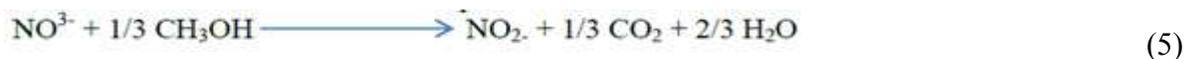
The pH also plays a key role in precipitation, higher the pH greater is the fraction of total Phosphorous (PO_4^{3-} : precipitating cation) removed. But, aluminum and iron results in the reduction of pH value. The optimum pH value is 5.5 to 6 for aluminum and 5 for iron. However, lower pH is required for obtaining greater fractions of Al^{3+} and Fe^{3+} (precipitating anion) and due to this opposing trend of pH for the precipitating cation and anion; an optimal pH exists (George et al., 2003).

Biological Nitrogen removal

Biological treatment is mostly carried out to improve the waste water to reduce total Nitrogen compounds. The waste water treatment plants in Sweden with Sea as the recipient are obliged to reduce the amount of ammonium and total Nitrogen compounds. In wastewater treatment, the most common technology used is biological nitrification and denitrification. Biological nitrification is an aerobic autotrophic process. In this *nitrosomonas* consume ammonia as the energy source and the ammonium is oxidized to nitrite (Eq. 1). Then, nitrite is oxidized to nitrate by the *nitrobacter* (Eq. 2) and the biological nitrification goes on until there is a requirement for the removal of ammonia without the complete removal of total Nitrogen (George et al., 2003).



In biological denitrification, the heterotrophic bacteria consume oxygen from nitrite and nitrate and transform the nitrite to total Nitrogen gas (Eq. 3 and 4). Methanol is provided as a supplement carbon source in the reaction and is performed in an anoxic environment.



The bacteria in nitrification and denitrification processes are affected by the pH value and have an optimum range of 6.8 to 8.0. The level of dissolved oxygen (DO) also plays a significant role as it drives the rate of nitrifier growth and promotes the growth of *nitrosomonas* and *nitrobacter* in the nitrification process. A high concentration of dissolved oxygen might inhibit the denitrification process as it is carried out in anoxic environment (Hassanzadeh, 2005). The most important and efficient method for total Nitrogen removal is nitrification combined with denitrification and both the reactions have different demands with concern to the environmental condition. If the denitrification stage is placed before the nitrification, then it is possible to use the organic content of the incoming waste water as an internal carbon source. This process solution is termed as pre-anoxic denitrification. If the denitrification is placed after the nitrification stage it is called post-anoxic denitrification (Persson, 2005).

Biological Phosphorous removal:

Bacteria known as phosphate accumulating organisms (PAOs) concentrate the phosphate in Poly-P granules when they are cycled between the aerobic and anaerobic conditions in wastewater. The granules serve as a reserve that facilitate the bacteria to take up the acetate under aerobic conditions and store as poly- β -hydroxybutyrate (PHB) and polyhydroxyalkanoic acids (PHA) and soluble phosphate is released in the process. The PHAs, in turn, provide energy to the bacteria for their growth under the aerobic conditions (Grady et al., 1999).

The simplest process has two bioreactors in series and contains an anaerobic-aerobic sequence and is also known as the Phoredox process as termed by Barnard (Figure 3). Barnard reasoned that the anaerobic zone is placed first in the sequence so as to take advantage of the electrons available in the raw wastewater and allows the PAOs to interact with the autotrophs and heterotrophs (Barnard, 1976). The phosphate is released and the concentration of phosphates increases in the anaerobic zone. The released phosphate is assimilated and stored as PHAs and PHB in the bacteria cells and removed in the activated sludge process (Eugene and Weiner, 2000).

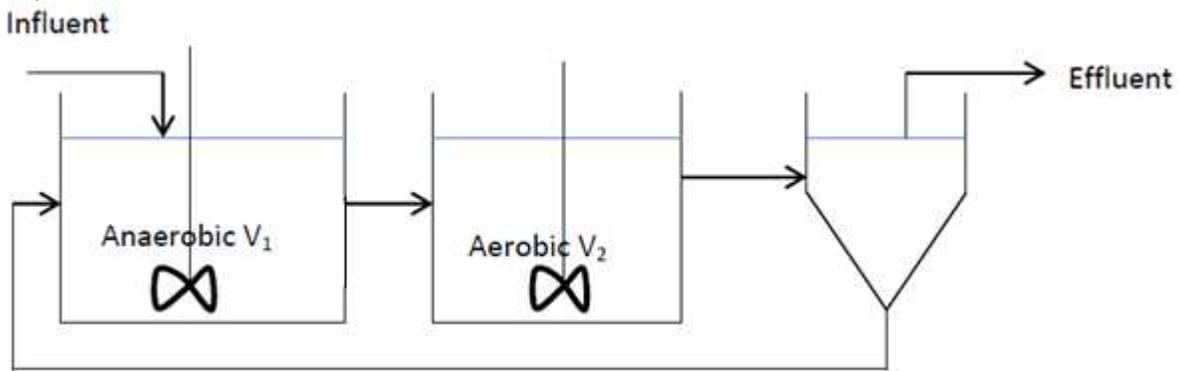


Figure 3: biological removal of total Phosphorous

3.2.4 Tertiary treatment and sludge handling

The tertiary level of treatment is involved by granular medium filtration or micro screens and the residual suspended solids are removed. Disinfection is also carried out in this level or in the secondary level of treatment. The total Nitrogen and total Phosphorous is removed to an acceptable level by advanced treatment (Peavy et al., 1985). Finally, in the tertiary treatment of

wastewater treatment, the dissolved and suspended material after the biological treatment is removed and after which the wastewater can be sent for reuse or be discharged (George et al., 2003).

The concentrated solids from the wastewater treatment need to be treated prior to disposal. These may contain hazardous components and is essential to stabilize them to prevent the diffusion into the environment. The sludge is thickened by a thickener to reduce the volume and then undergoes biological degradation by aerobic or anaerobic digestion. This is carried out to degrade the organic material and the stabilized sludge is incinerated, land-filled or used as a fertilizer (Mancl, 1996).

Before the stabilization, the sludge is thickened by a gravity/sedimentation thickener or flotation thickener. These thickeners are equipped with agitators and sludge rakes. By careful agitation the sludge is thickened and the clear water phase is separated. The flotation thickener consumes lot of energy but is very efficient in providing sludge of thicker concentration (Persson, 2005).

The different stages in the wastewater treatment produce sludge that requires appropriate treatment. However, the amount of sludge that is produced varies between the different stages. It is of vital importance to stabilize and dewater the sludge obtained from municipal waste water treatment. The sludge is stabilized to eliminate the biologically degradable matter and disease generating pathogenic organisms. It is essential to dewater the sludge because the sludge obtained from sedimentation has very high moisture content and making it necessary to reduce the high moisture content for reduction in transportation and disposal costs (Sperling, 2007).

The most common option for the disposal of municipal sludge is use as capping material on the landfills or as a filling material and soil conditioner. While choosing a suitable option for disposal, the risks and effects on ground water, infection and organic poisons in the sludge must be considered. The aerobic and anaerobic sludge stabilization does not result in complete die-off of the pathogens and can prove to be toxic. If there is difficulty in disposing the sludge, then incineration is considered as a suitable alternative.

3.2.4.1 Thickening:

The sludge obtained from municipal waste water treatment is high in organic material and thereby making it necessary to undergo sludge stabilization. Inorganic sludge cannot be stabilized. Stabilization is mainly carried out in three ways:

- *Biological stabilization:* This is the most common method for stabilization of municipal waste water sludge. It undergoes anaerobic degradation in a digestion chamber and biogas is produced as a by-product which can be utilized for heating purpose. The aerobic biological stabilization is carried out in an aerated basin for a long period of time of about 15 – 20 days at +15°C. The micro-organisms produce a stable sludge.
- *Chemical stabilization:* In this lime is added to increase the pH above 11 and the micro-organisms in the sludge are inhibited and the degradation process is stopped to reduce the sanitary risks. The metals in sludge also bond more tightly due to the addition of lime and

prevent leaching. However, this is expensive and results in an increase in the amount of sludge.

- *Thermal stabilization:* Pasteurization is one of the methods where the sludge is heated to 70°C for 20 – 30 minutes and the micro-organisms are inhibited due to the high temperature and the degradation stops. Drying at high temperatures and incineration are other methods that are carried out in thermal stabilization. However, to carry out incineration, it is important to achieve a high degree of dewatering of the sludge (Persson, 2005).

3.2.4.2 Sludge dewatering:

Centrifugation, filtration, vacuum filters, pressing are some of the most widely used methods for sludge dewatering. Vacuum filters were used in the past but were very energy consuming and did not provide satisfactory results. These days pressing and centrifuges are very common. The centrifuges and belt presses (Figure 4) yield proportional results, that is, higher the dry matter of the incoming sludge, higher is the dry content of the outgoing sludge. A centrifuge provides 25 – 27% sludge concentration whereas belt press can provide up to 30%. Chamber filter press is the most common choice. The reject water from this can be recycled (Persson, 2005).

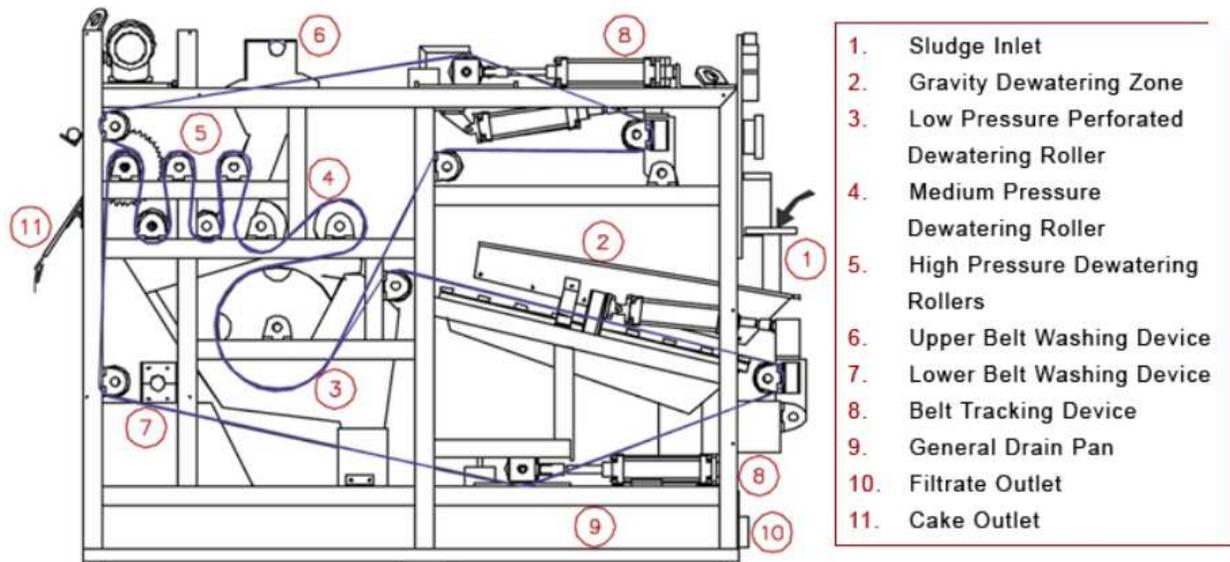


Figure 4: components of belt press – sludge dewatering

Source: Google images

3.2.5 Advanced primary treatment

Chemical precipitation is a major part of the advanced primary treatment. It is carried out for efficient removal of organic compounds and nutrients.

3.2.5.1 Chemical precipitation with magnesium

The efficiency of nutrients removal by additions of magnesium compounds was studied in primary treatment. To find out the nutrient removal efficiency in the raw wastewater and the feasibility of magnesium ammonium phosphate (MAP) recycling in wastewater treatment, the

postulations of combining MAP and nitrification-denitrification process, and MAP and partial nitritation - anammox process were carried out by experimental works in the laboratory. It was found that 92-97 % of Phosphorous and 57 % of Nitrogen was removed from raw wastewater by magnesium addition at pH10 to pH10.5. The thesis work revealed that recycling of MAP by nitrification-denitrification and partial nitritation - anammox processes were also feasible. In MAP and nitrification -denitrification process, the released ammonium was mostly oxidized to nitrate in nitrification phase and ready for denitrification. Based on presented results on MAP and partial nitritation - anammox process, it was found that the released ammonium was consumed by anammox bacteria (Liang, 2009).

Sources for magnesium:

Magnesium ions are the fourth most abundant positive ion in Sea water (Table 2). Therefore, due to the availability of magnesium ions in abundance, they can be a very viable option in the use of chemical precipitation.

Table 2: List of salt ions that make up 99.9% of the Sea water

Source: <http://www.seafriends.org.nz/oceano/seawater.htm#composition>

chemical ion	valence	concentration ppm, mg/kg	part of salinity %	molecular weight	mmol/kg
Chloride Cl	-1	19345	55.03	35.453	546
Sodium Na	+1	10752	30.59	22.990	468
Sulfate SO4	-2	2701	7.68	96.062	28.1
Magnesium Mg	+2	1295	3.68	24.305	53.3
Calcium Ca	+2	416	1.18	40.078	10.4
Potassium K	+1	390	1.11	39.098	9.97
Bicarbonate HCO3	-1	145	0.41	61.016	2.34
Bromide Br	-1	66	0.19	79.904	0.83
Borate BO3	-3	27	0.08	58.808	0.46
Strontium Sr	+2	13	0.04	87.620	0.091
Fluoride F	-1	1	0.003	18.998	0.068

Magnesium chloride is obtained as a by-product from solar sea salt. The numerous physical and chemical properties of salt make it possible to have determined 14,000 known uses. Magnesium chloride is produced from the natural evaporation of Sea water or brine. The seawater is stored in large earthen concentration ponds called condensers where natural evaporation takes place. When the sea water enters these condensers, it has a concentration of 3.5% sodium chloride. The climatic conditions, that is the Sun and Wind provide energy for the evaporation and increase the salt concentration to 25.8%. At this point crystallization is achieved. Calcium carbonate crystallizes first as the water concentrates (Salt Institute, 2011).

The brine is moved through a series of condensers with increasing saline concentration and the calcium carbonate is removed from the final salt product. After the concentration of the brine reaches a favorable crystallization level, the brine is moved to the crystallization pond. As the salt crystallization continues, the concentration increases and proper brine control during the crystallization process results in a salt with purity of 99.7% sodium chloride. Then the crystallization pond is highly concentrated magnesium brine. This magnesium brine is called “bitterns” and is drained off the crystallization pond. This is a very rich source of magnesium chloride which can be used in chemical precipitation during waste water treatment (Salt Institute, 2011).

The sodium magnesium chloride occurs as the mineral bischofite in nature in evaporate deposits. It is known as magnesium chloride hexahydrate and is a white crystalline salt. It is one among the last components that is provided from the natural evaporation of solar sea salt and it has 30 – 35 wt% magnesium chloride in solution. However, magnesium chloride can also be prepared synthetically by the reaction of hydrochloric acid with magnesium containing materials. The bittern obtained after the precipitation of sodium chloride is pumped to a shallow solar evaporation pond to concentrate the bittern. Magnesium and potassium salts are precipitated and impure magnesium chloride is obtained as the final product. Further evaporation produces crystallized magnesium chloride hexahydrate (Bengtson, 1999).

In this study magnesium chloride is used in chemical precipitation. Apart from this, bitterns and magnesium chloride have various other uses. Some of them have been listed below:

- Suppressant for dust on dirty roads, construction sites, unpaved parking lots etc as it has the capacity to absorb moisture.
- Corrosion inhibitor on steel surface.
- To melt ice on road surface
- It is used in several other industries for many industrial applications (Wilson et al., 1995).

3.3 Henriksdal Waste Water Treatment Plant

Discussed below is an example of a typical municipal waste water treatment plant.

The Henriksdal waste water treatment plant, serves Stockholm, Huddinge, Haninge, Nacka and Tyresö, and is one of the largest and most modern wastewater treatment plants in Europe. It was opened in 1941, and had the capacity for low-grade treatment of scarcely 150 000 m³ of waste water per day. The plant was extended in 1953, to double its capacity. It was further extended to include chemical and biological treatment. The most recent expansion programme, lasted from 1992 until 1997, was undertaken to reduce the total Nitrogen emissions by at least 50% and to also improve phosphorus treatment. Henriksdal is an underground treatment plant and is considered to be one of the world’s largest underground treatment plants. Its area covers approx. 300 000 m², and has approx. a length of 18 kilometres of tunnels. The basin block completely lies inside chambers that are blasted into the rock. The mechanical treatment, control Center building, sludge tanks, upper parts of the sludge thickeners, digesters, gas holder, gas collection plant and gas storage are included in the surface facilities. The ventilation chimney is 80 meters in height and 7 meters in width. Sludge treatment takes place in a separate facility at Sickla, which is located about two km from Henriksdal. The treatment plant is situated 2

kilometers from Slussen on the boundary between Stockholm and Nacka (Stockholm Vatten, 2004).

Figure 5 represents the wastewater treatment at Henriksdal wastewater treatment plant. It has a step screen to capture the suspended particles from the incoming waste water. It has a slot width of 3/6 mm and has an installation angle of 40° - 53°. It is easy to maintain and is able to handle big screening volumes. It has a self cleaning effect due to movable lamellae and has a high operational reliability (Hans Huber AG, 2005).

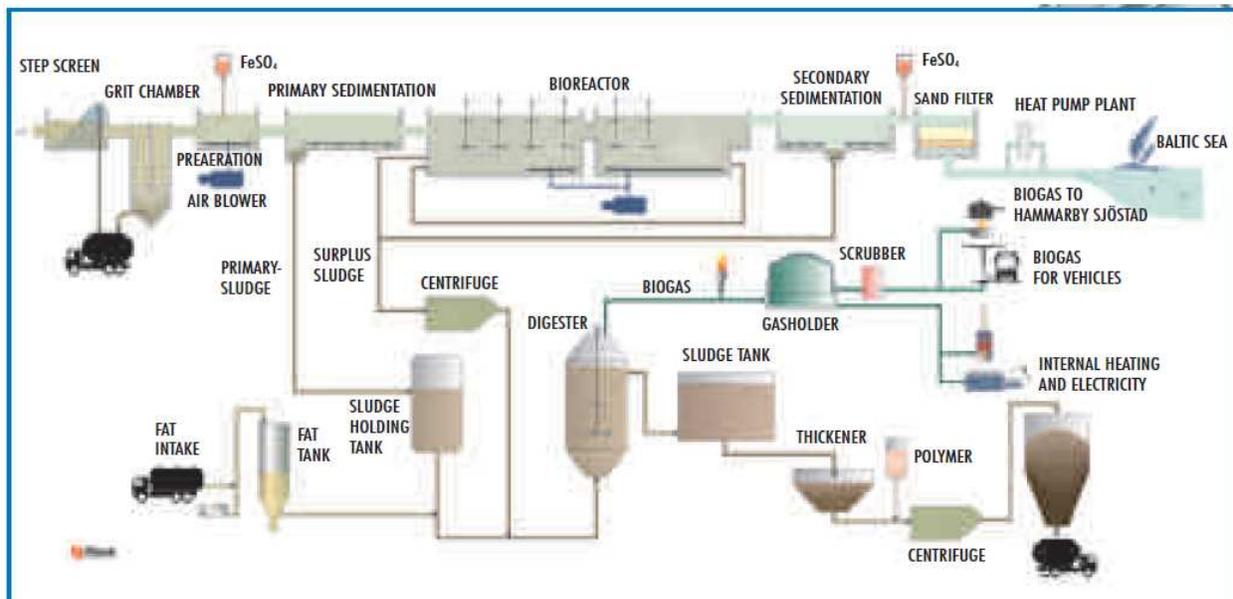


Figure 5: Henriksdal Waste Water Treatment Plant

Source: <http://www.stockholmvatten.se/>

The raw waste water then goes to the grit chamber where the inorganic particles are removed to prevent damage to the pumps and also avoid their accumulations in the sludge digestors. Here the smaller but relatively heavier particles are sorted out and ferrous sulfate is added to induce chemical precipitation of total Phosphorous. Then, the water is aerated in the pre-aeration tank to mix the ferrous sulfate well. Most of the total Phosphorous is removed as ferrous sulfate causes the total Phosphorous to precipitate as solid particles and settle in the bottom of the primary sedimentation tank. This sludge is taken to the sludge holding tank for sludge treatment (Hans Huber AG, 2005).

Next, in the bioreactor phase (anaerobic tank) the nitrate rich waste water is mixed with the active sludge containing microorganisms. These microorganisms convert the nitrate total Nitrogen into total Nitrogen gas and are ventilated out. In the bioreactor phase (aerobic tank) air is added and the microorganisms are nourished by the residual organic matter in the waste water. Here the total Nitrogen is converted from ammonium total Nitrogen to nitrate total Nitrogen and the nitrate rich water is pumped over to the anaerobic tanks (Myllymaa, 1998).

The waste water flow is very slow in the secondary sedimentation tank and the sludge containing microorganisms and total Phosphorous settles to the bottom. The waste water almost becomes

free from solid pollutants in the secondary sedimentation tank. A part of the sludge is returned to the anaerobic tank to maintain favorable micro organisms' culture and the excess sludge is led to the mud thickening phase (Myllymaa, 1998).

The waste water after the secondary sedimentation goes to a deep-bed sand filter that consists of expanded clay and sand and the flow rate is under 10 m/h. The biological process continues in the filter and again ferrous sulfate is added to remove any remaining total Phosphorous. The heat stored in the treated water which is about +15°C is recovered by means of heat pumps and is used for Stockholm's district heating network (Myllymaa, 1998).

Finally, the treated water is discharged via a discharge pipe which is in Lake Saltsjo, a part of the Baltic Sea. The discharge depth is about 30 meters and the waste water level rises up to 10 – 15 meters and then forms an outgoing current (Myllymaa, 1998).

The sludge obtained first goes to mud thickening phase where excess mud from the secondary sedimentation is fed to the mud thickening and the rest of the sludge goes to centrifuge to reduce the volume of the sludge or is sent to the aeration tank. However, in the centrifuge only 5% of the sludge volume is reduced. Then a part of the organic content of the sludge is degraded in the digester and the biogas formed is collected in the gasholders. The biogas formed is used as fuel in the waste water treatment plants' boilers and thereby is self-sufficient in meeting its heating requirements. Sometimes the biogas is also used to produce electricity and as fuel for cars in Bromma. Then, the water content of the sludge is reduced again by sludge dewatering and after this polymer is added to the sludge for further thickening and dewatering. Finally, the dry sludge is stored in silos and is used to improve soil if its metal content has allowable limits (Myllymaa, 1998). Nowadays, it is used as capping material in mining sites as it has a lot of metal content resulting in a poor sludge quality.

3.4 Alkaline hydrolysis

The alkaline degradation of cellulose in wastewater can be used as a carbon source in denitrification. Many researchers have established basic principles on alkaline degradation of cellulose. Nef and Nef (1907, 1910) discovered the tautomerism of aldoses and ketoses with enediols and proposed that these reactions took place in two main steps: (i) isomerization of monosaccharide with loss of water to a α -dicarbonyl intermediate. (ii) production of acidic degradation products by benzilic acid type rearrangement. Evans and Hockett (1931) proposed a mechanism supported upon the alkaline degradation of maltose. The mechanism put forward that a (1, 4)-linked disaccharide experiences reverse aldol condensation to yield many smaller components which further undergo alkaline degradation to give saccharinic, lactic and other acids.

The degradation of periodate-oxidised cellulose using NaOH at the room temperature when observed showed that oxidized cellulose was degraded to acidic products of lower molecular weights. The Nef-Isbell mechanism for alkaline degradation of glucose involves the production of enediol in the first step through keto-enol tautomerism. This reaction is followed by the production of an enediol anion through deprotonation by hydroxide ions. After this the anion isomerization takes place which results in a mixture of equilibrium intermediate anions (Corbett, 1959).

Cellulose degradation

End-wise degradation / peeling

Under temperatures below 170°C the glycosidic(1,4)- linkages are alkali stable between β -D-Glucose units in cellulose. However, a fair amount of reduction in molecular weight is observed when the cellulose is boiled in dilute NaOH at temperatures below 170°C without oxygen. The suggestions were that these reduction or losses were due to the dissolution of the short chain material that were detached from the reducing ends of the cellulose molecules and this is known as peeling or also as unzipping (Davidson, 1934).

In cellulose degradation the D-glucoisosaccharinic acids is released by the elimination of β -alkoxy-carbonyl which is the elimination of rest of the cellulose chain. This leads to a new deprotonated end group that undergoes further alkaline degradation. Calcium ions can be utilized to improve the yield by catalyzing the production. Also it was found that the alkaline earth metals resulted in a higher loss of molecular weight due to the peeling and more acid production in comparison with alkali metal ions when there was a low concentration of the alkaline earth metals (Zideman, 1980).

Termination

A stopping reaction causes the stabilization of the cellulose and the principle of this reaction is applied by modifying the cellulose end groups so as to produce alkali stable cellulose derivatives (Procter and Wiekenkamp, 1969). However, some reducing end groups can continue in a fully alkaline stabilized hydrocellulose due to the inaccessibility with respect to the alkali. Therefore, with high weight losses due to the alkaline hydrolysis, the degree of polymerization remains constant or even increases slightly (Johansson and Samuelson, 1975).

Alkaline scission

When the cellulose is heated above temperatures at 170°C there is a reduction in molecular weight and decrease in the degree of polymerization and this is due to the random alkaline scission of the glycosidic linkages. The scission does not depend on the presence of molecular oxygen and results in grater loss in molecular weight than in comparison with alkaline degradation at lower temperatures. This is because scission is followed by peeling from any of the new reducing end group that is produced by the scission process. But at higher temperatures the termination stabilization has a greater effect than the termination stabilization at lower temperatures (Richards, 1971).

Aerobic / oxidative alkaline degradation

In alkaline degradation, anaerobic conditions prevail for long times. However, there are some short period of time during and after resaturation where the aerobic conditions prevail. For thereduction of the degree of polymerization in wood pulp to manufacture viscose rayon the oxidation of alkali cellulose by atmospheric molecular oxygen has been used. In this autoxidation process the carbonyl-containing oxidized celluloses known as the oxycelluloses are formed in the first step and is subsequently degraded by the alkali. Ketone, aldehyde and carboxyl groups are the main functional groups formed (Klemm et al., 1998).

Researchers O'Meara and Richards (1958) confirmed that β -alkoxycarbonyl elimination was the main reaction causing alkaline degradation by applying Isbell's theory to periodateoxycellulose. Glycolic acid and 2,4-dihydroxybutanoic acids were found in large proportions as the degradation products from the alkaline degradation. Thus, any resulting oxidized cellulose that does not have carbonyl groups in the end group is alkali labile and complete scission of the cellulose molecule under mild conditions is anticipated at any molecule that has a carbonyl group to a reducing end group and has a stabilizing effect (Lai, 1991).

4 Experiments description

Experiments were done to study the aims of this thesis work which were to evaluate the use of magnesium chloride for the removal of COD, total Total Phosphorous and total Total Nitrogen from municipal wastewater and to use toilet paper from alkaline hydrolysis as a carbon source for denitrification in wastewater treatment.

All the experiments were carried out at Hammarby Sjöstadsværk located on top of the Henriksdal wastewater treatment plant and is owned by the Stockholm Vatten company. This facility belongs to and is also operated by IVL Swedish Environmental Research Institute and the Royal Institute of Technology {KTH} (Hammarby Sjöstadsværk, 2010).

4.1 Chemical precipitation using magnesium chloride

The materials required and the method carried out for the experiment of chemical precipitation using magnesium chloride is described in this section.

4.1.1 Materials

The chemicals used in this experiment are listed in Table 3.

Table 3: Chemicals used in experiment – chemical precipitation using magnesium chloride

SNo	Chemical name	Chemical formula	Assay
1.	Magnesium chloride	$MgCl_2 \cdot 6H_2O$	$\geq 99\%$
2.	Sodium hydroxide	NaOH	$\geq 99\%$

All apparatus, glass ware, filter papers, magnetic stirrers were provided by the Industrial Ecology Department, KTH. The analytical instruments were provided at Hammarby Sjöstadsværk laboratory.

4.1.2 Method

Several trials were carried out to find out the optimal range of magnesium chloride to be used in mg/l of the wastewater for effective and efficient removal of COD, total Phosphorous and total Nitrogen.

4.1.2.1 Chemical pre-precipitation with $MgCl_2$

1 liter of the raw wastewater sample was taken and weighed sample of magnesium chloride ($MgCl_2$) was added to it. Five different samples of varying concentrations from 25 mg to 45 mg of magnesium chloride were chosen to study the varying effect on the removal of COD, total Phosphorous and total Nitrogen from municipal waste water. The pH was adjusted to 10 by adding sodium hydroxide solution (NaOH). Stirring was carried out for 30 minutes using magnetic stirrers at 20 rpm and then the sample was allowed to settle for 60 minutes.

4.1.2.2 Measuring COD

Principle

The oxidizable substances react with potassium dichromate sulphate with silver sulphate as a catalyst to obtain reduction of Cr^{6+} ions.

The concentration of COD in all the experiments was checked using the HACH LANGE Cuvette tests (Figure 6). Two types of Cuvettes with different measuring ranges were used. For high concentrations of COD where the raw wastewater sample was used to determine the COD tests 150-1000 mg/L range of COD was used. For the wastewater sample after pre-precipitation with $MgCl_2$ 15-150 mg/L range of COD was used.



Figure 6: COD HACH-LANGE Cuvettes

The sample was diluted if needed. The dilution rates were calculated based upon the COD concentration of the raw wastewater. For experiments with raw wastewater COD concentration of 300 – 400 mg/L the dilution rate was usually 80 ml or 70 ml of treated wastewater sample to make a solution in a 100 ml volumetric standard flask. For 15-150 mg/L range Cuvettes it results in 95 – 170 mg/L of final range that covers a range of all expected values. In case the final result is in a specific narrow diapason, a smaller dilution rate is taken to minimize the number of out-of-range measurements and also the total number of trials.

For the dilution, necessary volume of the sample wastewater (V_{sample}) was taken in a pipette and transferred to a volumetric flask (V_{flask}) of certain volume and then diluted with distilled water to the specific volume. The dilution rate (DR) was calculated as follows

$$DR = \frac{V_{\text{sample}}}{V_{\text{flask}}}$$

Once the dilutions are ready, then for the COD measurement, the HACH LANGE Cuvette is taken and then shaken well till the substances present in the Cuvette dissolve. Then 2 ml of the sample solution is added and the Cuvette is shaken again. After this, the Cuvette is placed in the

thermostat for 2 hours in 148°C. After this, the Cuvette is removed and cooled to 20°C and kept in the Dr. LANGE spectrophotometer to get the reading of COD.

The COD of the incoming waste water and the treated waste water are listed in Table 4.

Table 4: Treatment efficiency of COD removal using magnesium chloride

Parameter	[Mg ²⁺] in mg	COD In (mg/L)	COD Out (mg/L)		Efficiency(% reduction)	
			Trial 1	Trial 2	Trial 1	Trial 2
COD	25	240	156	144	35	40
	30	240	153	151	36.25	37.1
	35	660	98.9	106	85.01	83.9
	40	660	137	122	79.2	81.5
	45	240	86.7	89	63.8	62.9

After measuring all the samples, the result was multiplied on the dilution rate to obtain the actual concentration of COD in the probe.

$$C_{actual} = C_{meas} \cdot DR$$

To calculate the percentage reduction in COD the following equation was used

$$\% \text{ reduction} = [(A - B) / A] * 100$$

Where;

A is the COD measurement of the raw wastewater

B is the COD measurement of the treated wastewater.

4.1.2.3 Measuring Total Phosphorous

Principle

The phosphate ions react with molybdate and antimony ions in an acidic solution to form an antimonylphosphomolybdate complex, which is reduced by ascorbic acid to phosphomolybdenum blue.

The concentration of total Phosphorous in all the experiments was checked using the HACH LANGE Cuvette tests (Figure 7). For total Phosphorous tests 0.05-1.50 mg/L range was used.



Figure 7: Cuvettes for total Phosphorous

The sample was diluted as the range was less. The dilution rates were calculated based upon the total Phosphorous concentration of the raw wastewater. For experiments with raw wastewater and treated wastewater for concentration of 0.6 – 1.4 mg/L the dilution rate was usually 10 ml of the raw wastewater or treated wastewater sample to make a solution in a 100 ml volumetric standard flask. For 0.05-1.50 mg/L range Cuvettes it results in 0.6 – 1.4 mg/L of final range that covers a range of all expected values. In case the final result is in a specific narrow diapason, a smaller dilution rate is taken to minimize the number of out-of-range measurements and also the total number of trials.

For the dilution, necessary volume of the sample wastewater (V_{sample}) was taken in a pipette and transferred to a volumetric flask (V_{flask}) of certain volume and then diluted with distilled water to the specific volume. The dilution rate (DR) was calculated as follows

$$DR = \frac{V_{\text{sample}}}{V_{\text{flask}}}$$

Once the dilutions were ready, then for the total Phosphorous measurement, the HACH LANGE Cuvette was taken and the foil from the DosiCap was removed carefully. The DosiCap was unscrewed and 2 ml of the sample was pipetted into the Cuvette. Then, the DosiCap was screwed back but now had the **fluting** at the top and shaken firmly and heated in the thermostat for 60 minutes at 100°C. After this, the Cuvette was taken out from the thermostat and allowed to cool to 20°C. Then, 0.2 ml of reagent **B** was pipetted into the Cuvette and was screwed with a grey DosiCap **C** and shaken for 10 minutes and kept in the Dr. LANGE spectrophotometer to get the reading of nutrient Total Phosphorous (Figure 8).



Figure 8: Dr. LANGE spectrophotometer

The total Phosphorous of the incoming waste water and the treated waste water are listed in Table 5.

Table5: Treatment efficiency of total Phosphorous removal using magnesium chloride.

Parameter	[Mg ²⁺] in mg	Total Phosphorous In (mg/L)	Total Phosphorous Out (mg/L)		Efficiency(% reduction)	
			Trial 1	Trial 2	Trial 1	Trial 2
Total Phosphorous	25	2.15	1.11	0.947	48.4	55.9
	30	2.15	1.08	1.16	49.8	46.04
	35	0.866	0.708	0.658	18.24	24.02
	40	0.866	0.766	0.796	11.6	8.08
	45	2.15	1.14	1.18	46.9	44.8

After measuring all the samples, the result was multiplied on the dilution rate to obtain the actual concentration of total Phosphorous in the probe.

$$C_{actual} = C_{meas} \cdot DR$$

To calculate the percentage reduction in total Phosphorous the following equation was used

$$\% \text{ reduction} = [(A - B) / A] * 100$$

Where;

A is the total Phosphorous measurement of the raw wastewater

B is the total Phosphorous measurement of the treated wastewater.

4.1.2.4 Measuring Total Nitrogen

Principle

Inorganic and organically bound total Nitrogen is oxidized by digesting with peroxodisulphate to nitrate. Nitrate ions react in a sulphur and total Phosphorous solution with 2,6-dimethylphenol to nitrophenol.

The concentration of total Nitrogen in all the experiments was checked using the HACH LANGE Cuvette tests (Figure 9). For total Nitrogen tests 5-40 mg/L range was used.



Figure 9: Cuvettes and reagents for total Nitrogen test

The sample was diluted as the range was less. The dilution rates were calculated based upon the total Nitrogen concentration of the raw wastewater. For experiments with raw wastewater and treated wastewater for concentration of 12 – 49 mg/L the dilution rate was usually 50 ml of the raw wastewater or treated wastewater sample to make a solution in a 100 ml volumetric standard flask. For 5-40 mg/L range Cuvettes it results in 12 – 49 mg/L of final range that covers a range of all expected values. In case the final result is in a specific narrow diapason, a smaller dilution rate is taken to minimize the number of out-of-range measurements and also the total number of trials.

For the dilution, necessary volume of the sample wastewater (V_{sample}) was taken in a pipette and transferred to a volumetric flask (V_{flask}) of certain volume and then diluted with distilled water to the specific volume. The dilution rate (DR) was calculated as follows

$$DR = \frac{V_{\text{sample}}}{V_{\text{flask}}}$$

Once the dilutions were ready, then for the total Nitrogen measurement, the sampling bottle available in the Cuvette box was taken and 0.5 ml of the wastewater sample was pipetted with 2 ml of solution **A** and 1 tablet **B** was also added and kept for heating in the thermostat for 60 minutes at 100°C. After this, the sampling bottle was taken out from the thermostat and allowed to cool to 20°C and a microcap **C** was added and shaken firmly. Then, 0.5 ml of the solution

from the sampling bottle was pipetted into the HACH LANGE Cuvette and shaken well and kept aside for 15 minutes. After this, the reading was taken for total Nitrogen using the Dr. LANGE spectrophotometer.

The total Nitrogen of the incoming waste water and the treated waste water are listed in Table 6.

Table 6: Treatment efficiency of total Nitrogen removal using magnesium chloride.

Parameter	[Mg ²⁺] in mg	Total Nitrogen In (mg/L)	Total Nitrogen Out (mg/L)		Efficiency(% reduction)	
			Trial 1	Trial 2	Trial 1	Trial 2
Total Nitrogen	25	38.2	26.2	27.1	31.4	29.05
	30	38.2	25.2	26.8	34	29.8
	35	15.9	13.8	15.1	13.2	5.03
	40	15.9	12.9	12.5	18.9	22.1
	45	38.2	22.9	23.1	40	39.2

After measuring all the samples, the result was multiplied on the dilution rate to obtain the actual concentration of total Nitrogen in the probe.

$$C_{actual} = C_{meas.} \cdot DR$$

To calculate the percentage reduction in total Nitrogen the following equation was used

$$\% \text{ reduction} = [(A - B) / A] * 100$$

Where;

A is the total Nitrogen measurement of the raw wastewater

B is the total Nitrogen measurement of the treated wastewater.

4.2 Alkaline hydrolysis

The materials required and the method carried out for the experiment of alkaline hydrolysis is described in this section

4.2.1 Materials

The chemicals used in this experiment are listed in Table 7 given below.

Table 7: Chemicals used in experiment – alkaline hydrolysis

S.No	Chemical name	Chemical formula	Assay
1.	Toilet paper		
2.	Sodium hydroxide	NaOH	≥ 99 %

All apparatus, glass ware, filter papers, magnetic stirrers were provided by the Industrial Ecology Department, KTH.

4.2.2 Method

Only one trial was carried out to carry out the alkaline hydrolysis of toilet paper. The experiment was carried out to know the fate of toilet paper in wastewater and to estimate if it could be reduced by natural decomposition. For this experiment, 5 grams of toilet paper was weighed and dissolved in 500 ml of distilled water which was adjusted to a pH of 12 using NaOH. The solution was stirred vigorously and covered with plastic and aluminum foil and kept aside for 24 hours. After this, the solution was filtered using the vacuum filter and the toilet paper sample was kept in a aluminum foil dish and heated in an oven at 100°C for 24 hours. The filtrate solution was used to measure COD using the HACH LANGE Cuvette test and the reading was taken using the Dr. LANGE spectrophotometer.

5 Results

5.1 Chemical pre-precipitation with MgCl₂

The results of chemical pre-precipitation with MgCl₂ for efficient removal of COD and nutrients like Phosphorous and Nitrogen are discussed below.

5.1.1 COD removal

As was mentioned above, the COD concentrations were measured using the Dr. LANGE spectrophotometer. The COD concentrations were measured for 5 different samples of raw wastewater with varying concentrations of magnesium chloride within a range of 25 mg/L – 45 mg/L of MgCl₂. However, two trials were conducted for each sample of MgCl₂ to estimate this optimum range of weighed samples of magnesium chloride. The results of the COD concentration obtained are shown in Figure 10.

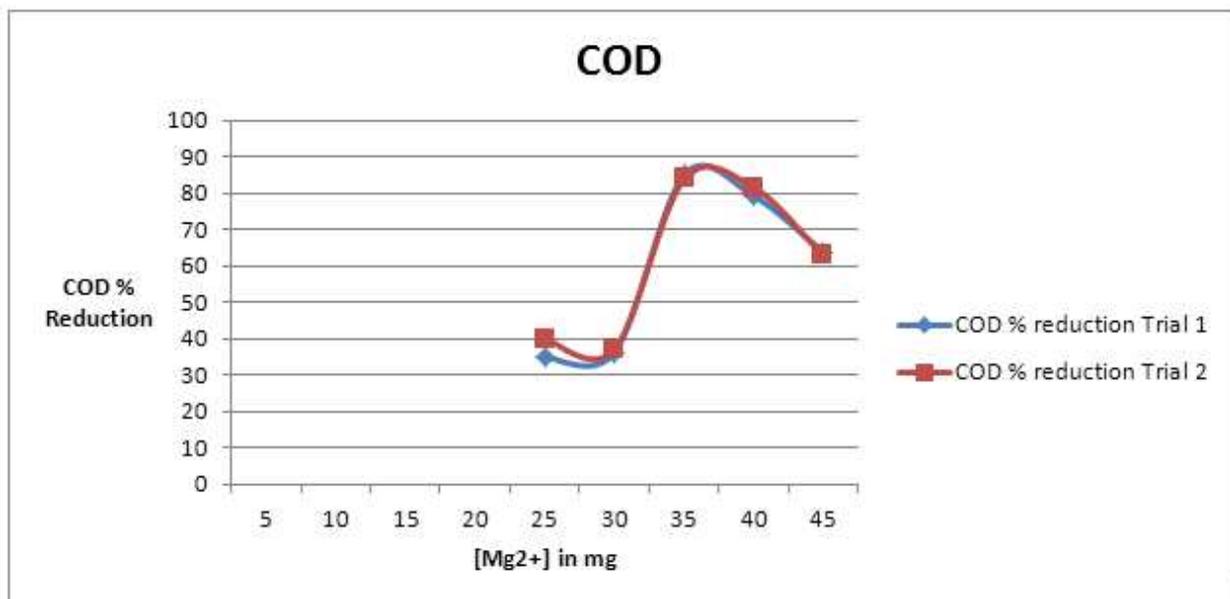


Figure 10: Percentage COD reduction Vs Mg²⁺ concentration

The above figure shows that when the wastewater sample was treated with 25 mg/L of MgCl₂, the reduction in COD concentration was the least when compared to other samples and was between 35% - 40%. A maximum amount of 80 % COD reduction was observed when the wastewater sample was treated with 35 – 40 mg/L of MgCl₂. After this, there was again a decrease in the % COD reduction.

5.1.2 Phosphorous removal

As was mentioned above, the Phosphorous concentrations were measured using the Dr. LANGE spectrophotometer. The Phosphorous concentrations were measured for 5 different samples of raw wastewater with varying concentrations of magnesium chloride within a range of 25 mg/L – 45 mg/L of MgCl₂. However, two trials were conducted for each sample of MgCl₂ to estimate this optimum range of weighed samples of magnesium chloride. The results of the Phosphorous concentration obtained are shown in Figure 11.

Figure 11 shows that when the wastewater sample was treated with 25 and 30 mg/L of $MgCl_2$, the reduction in Phosphorous concentration was maximum and ranging between 45 – 55 % reduction. The % reduction of Phosphorous was minimum when the wastewater sample was treated with 35 and 40 mg/L of $MgCl_2$. After this, again an increase in the % Phosphorous reduction was observed.

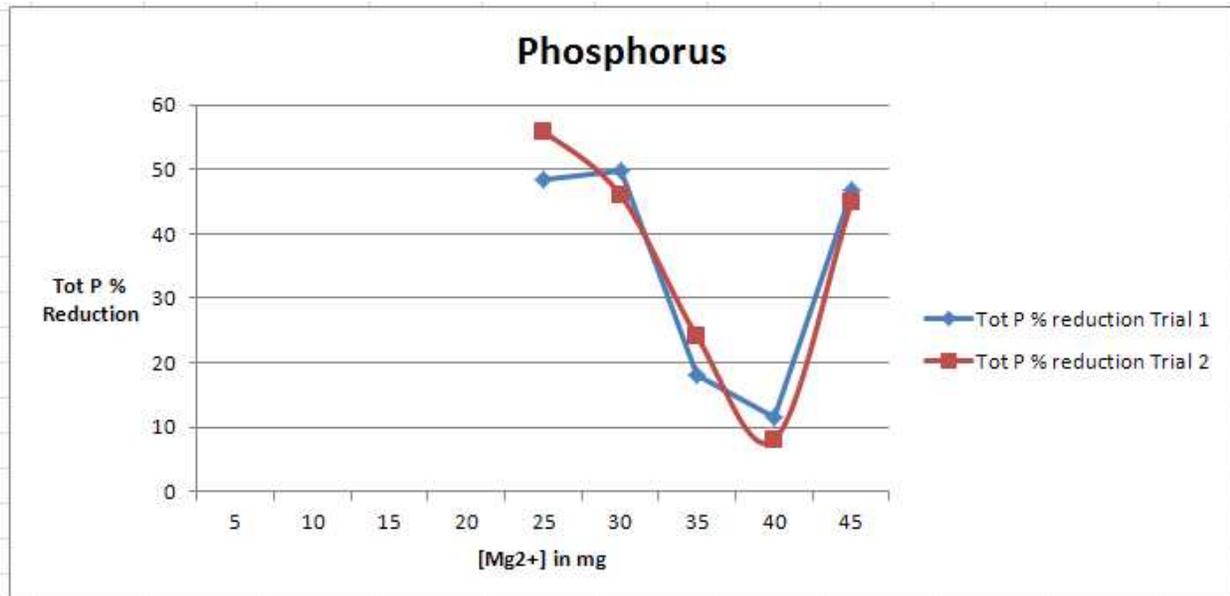


Figure 11: Percentage Phosphorous reduction Vs Mg^{2+} concentration

5.1.3 Nitrogen removal

As was mentioned above, the Nitrogen concentrations were measured using the Dr. LANGE spectrophotometer. The Nitrogen concentrations were measured for 5 different samples of raw wastewater with varying concentrations of magnesium chloride within a range of 25 mg/L – 45 mg/L of $MgCl_2$. However, two trials were conducted for each sample of $MgCl_2$ to estimate this optimum range of weighed samples of magnesium chloride. The results of the Nitrogen concentration obtained are shown in Figure 12.

Figure 12 shows that when the wastewater sample was treated with 25 and 30 mg/L of $MgCl_2$, the reductions in Nitrogen concentration were ranging between 25 – 35 % reductions. The % reduction of Nitrogen was lowest when the wastewater sample was treated with 35 and 40 mg/L of $MgCl_2$. After this, again an increase in the % Nitrogen reduction was observed and had the maximum of 40 % of Nitrogen reduction.

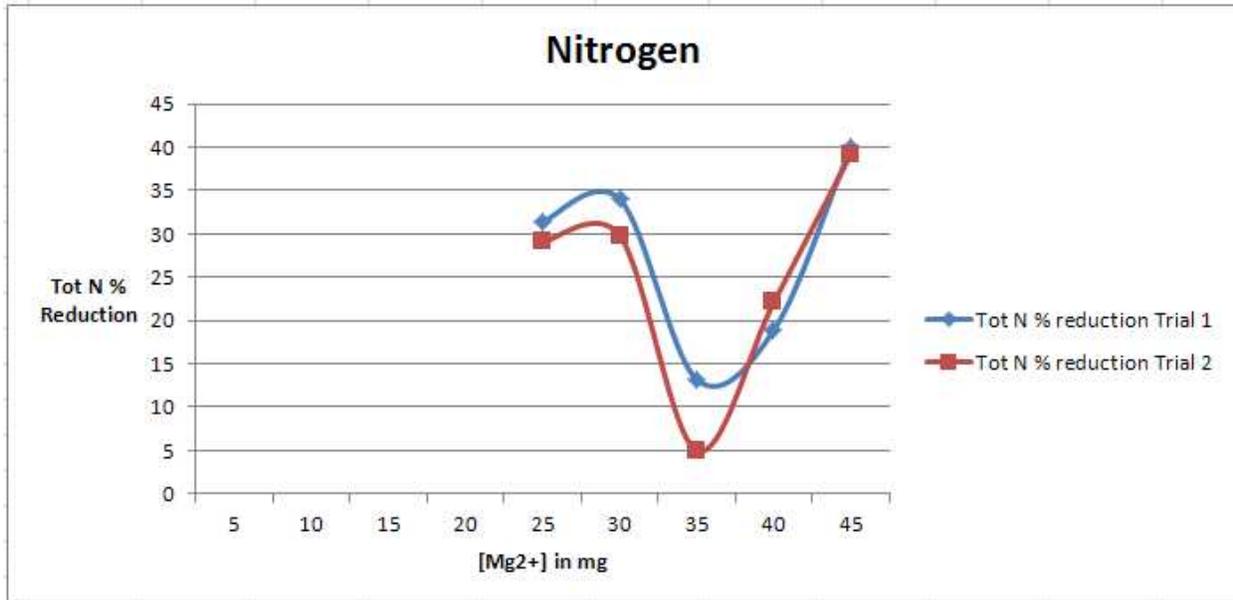


Figure 12: Percentage Nitrogen reduction Vs Mg^{2+} concentration

5.2 Alkaline hydrolysis

As was mentioned above in the experiments description part, the COD concentration was measured using the Dr. LANGE spectrophotometer. The COD concentration was measured for one sample where 5 grams of toilet paper was dissolved in a solution of NaOH made up to 500 ml with a pH of 12. The COD of the unfiltered sample measured 168 mg/L.

From the results, we can also observe that the COD is higher in the unfiltered sample, that is, the sample with the toilet paper. This is due to the breakdown of the cellulose to glycolic and 2,4-dihydroxybutanoic acids. Therefore, the hydrolysis of toilet paper can be used as an internal source for carbon in denitrification for Nitrogen removal in waste water treatment. Also, the toilet paper in the sodium hydroxide solution after 24 hours was filtered using the vacuum filter. The filtered toilet paper sample was kept in an aluminum foil dish and heated in the oven for 24 hours at 105°C. The sample was weighed and it was observed that the weight of the toilet paper had decreased from 5.000 grams to 4.658 grams.

6 Discussion

6.1 Results discussion

First of all, magnesium chloride was efficient in removal of COD. It had achieved 80% efficiency in the COD reduction when the wastewater sample was treated with 35 – 40 mg/L of magnesium chloride. However, the Nitrogen reduction was observed to be about 35% when the sample was treated with 35 – 40 mg of $MgCl_2$. The maximum reduction in Nitrogen was observed when the wastewater sample was treated with 45 mg/L of magnesium chloride. In the case of Phosphorous, the reduction was the least and about 10% when the wastewater sample was treated with 35 – 40 mg of magnesium chloride. A maximum of 45 – 55% reduction in Phosphorous was obtained when the wastewater sample was treated with 25 – 30 mg of magnesium chloride.

It was difficult to achieve the maximum reductions for COD, Phosphorous and Nitrogen with the same amount of magnesium chloride. Averages of both the trials were taken in order to get a graph where it is possible to compare the reductions of COD, total Nitrogen and total Phosphorous.

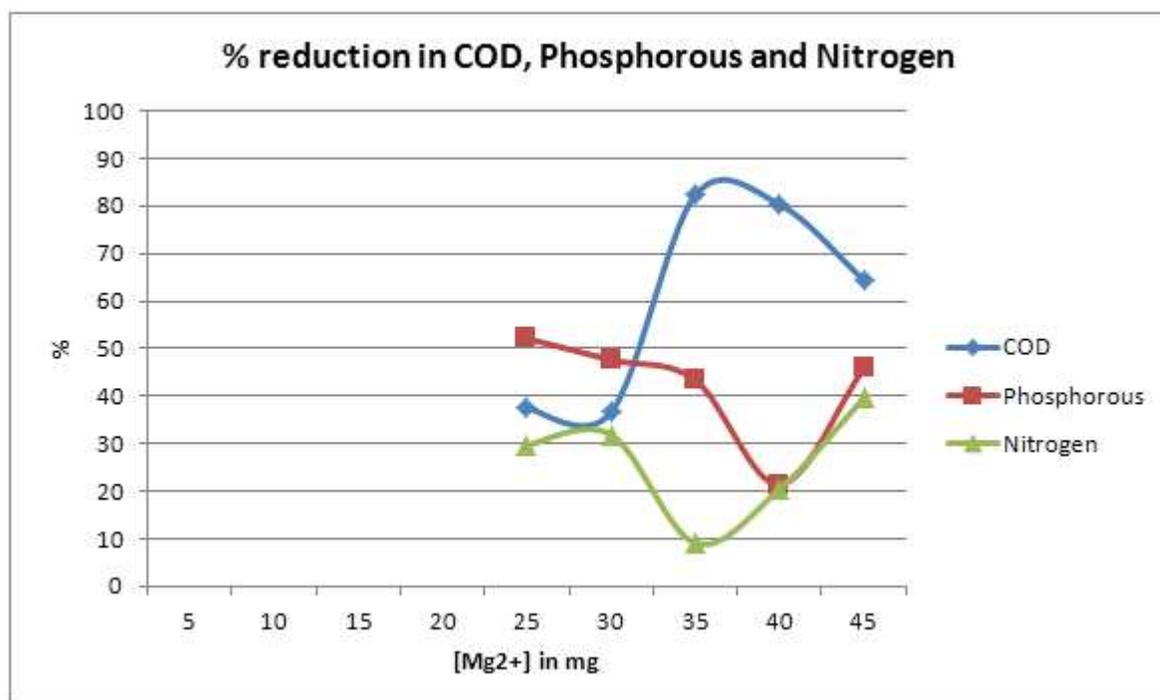


Figure 13: Comparison of COD, Phosphorous and Nitrogen reductions.

It can be observed from the graph that to achieve effective reductions in COD, Phosphorous and Nitrogen, the suitable amount of magnesium chloride to be added to the wastewater sample can be 30 – 35 mg. At this amount of the weighed sample of $MgCl_2$, the reductions are observed to be more efficient when compared to other values. Also, the reductions in Phosphorous and Nitrogen are lesser when Mg^{2+} concentrations are from 30 – 40 mg. The reason could be that real waste water was used. The suspended particles in the waste water can also be a major reason. pH could also be the reason according to literature studies. However, the varying effect of pH could not be

studied during this thesis work. The stirring that occurs when magnesium chloride is added to the waste water can also be another reason as this might bring a change in the suspended particles in the waste water.

The high percentage of COD removal obtained could result in lot of biogas and also lesser oxygen consumption in the biological stage. It will also facilitate nitrification. The nitrates and phosphates bound to the organic compounds also require higher removal efficiency. Higher removal of these nutrients is most desirable when the sludge is utilized for fertilization purposes. The nutrients can be recycled from the effluent of the biogas digester and higher removal of the nutrients like Phosphorous and Nitrogen will ensure a richer quality of sludge that is more suitable for agriculture and aquaculture.

Another focus of interest could be that chemical precipitation is mostly preferred as suitable option after biological treatment. This is known as post precipitation and is the traditional option. This way more organic compound enters the active sludge process and it would require more energy as more oxygenation would be required (Janssen et al., 2002). However, in this thesis work chemical pre precipitation was carried out where magnesium chloride is added before primary settling and then undergoes the biological treatment. Many studies show that pre precipitation is more energy saving. The reason is that, as the organic compounds are mostly captured, then lesser amount of organic compounds enters the activated sludge process (ASP), the BOD-reduction would require lesser oxygen and thereby reducing the power consumption that would be required by the aerators. Studies have also revealed that when pre-precipitation is carried out, the amount of BOD is cut down to third of the actual amount that would enter if post precipitation was carried out (Karlsson & Tovar, 2007).

Also, an experiment was carried out to observe if the suspended particles present in the waste water affect the COD. To carry out this experiment, the COD of the raw waste water was first measured and it had a range of 452 mg/L. Later, the COD was measured for the filtered sample of the waste water where a range of 121.5 mg/L was observed. The results show that the percentage reduction in COD of 73% was achieved. From this experiment it can be observed that the suspended particles in the waste water have a major impact on the COD reduction.

Ferric chloride is one among the most commonly used chemicals in waste water treatment. But these ions tend to form strong complexes with pyrophosphates which need to be separated later by adsorption thereby increasing the cost. Also the precipitation is pH and temperature dependent when Ferric chloride is used as the precipitant and it may cause staining of equipment due to iron carry over. When compared to aluminum salts, they are lower in cost and also produce sludge with excellent dewatering properties. On the other hand, aluminum salts are the most effective precipitants because Phosphorous is not released even during storage or digestion and also produce a low sludge volume. There is requirement for pH adjustment and it also has a flexible point of addition. However, these are the most expensive precipitants and also capable of inhibiting the nitrification in biological treatment (Yeoman et al., 1987).

In comparison to other salts, magnesium chloride is very cheap owing to its abundant production. The cost of raw bittern varies from 16 – 53 US\$/ ton, depending on location. The magnesium chloride made from the bittern by further treatment and costs 0.32 US\$/ kg. These prices have

been stable over many years in the market. Ferrous sulfate which is another widely used chemical for wastewater treatment costs 0.4 US\$/ kg. Chemicals like calcium chloride is priced about 0.41US\$/ kg and aluminum sulfate at 1.2 US\$/ kg. Therefore, magnesium chloride can be viewed as a viable option in chemical precipitation (Aral et al., 2004).

Alkaline hydrolysis of toilet paper with sodium hydroxide gave highest reading in COD with 168 mg/L. The decomposition was the highest when the toilet paper was treated with sodium hydroxide. So, it can be noticed that the toilet paper dissolutes at higher pH ranges of 10 – 12. Also the toilet paper gets collected while the raw wastewater goes the screening in primary treatment. This can be a nuisance and hamper the treatment. As such high COD was measured after the alkaline hydrolysis and also previous studies showed that the cellulose breaks down to glycolic acid and 2,4-dihydroxybutanoic acids were formed. The main functional groups formed after alkaline hydrolysis was aldehyde, ketone and carboxyl groups. Therefore, continued studies could yield desirable results where the formations and reactions occurring could be used as a carbon source in denitrification stage for Nitrogen removal in wastewater treatment.

6.2 Results accuracy

There were several errors that were observed while carrying out the experiments, such as:

- Method error
- Human error
- Dilution error
- Miscalculation
- Measuring equipment error, etc.

The measuring error was the most frequent error while conducting the experiments. The weighing machine only showed an approximate value which was changing each time the same sample was reweighed. However, the change was very minute ± 0.0005 mg and would have had only a negligible effect on the results. Dilution errors also occurred sometimes, when extra volume was added by mistake. However, their influence on the results was less than 0.05%. The miscalculation and human errors were negligible. In general, the results obtained were reliable. This fact can be explained as every experiment had 2 trials in parallel and yielded similar values. The waste water was also a problem as real waste water was used. This had a varying effect on the results owing to the suspended particles present in the waste water and caused a large problem with the result accuracy since the concentration of different compounds and especially the amount of solids were very varying.

6.3 Discussion of previous studies

This master's thesis work used the report by Mi Liang as a starting point. However, the studies are quite different and the methodology and results followed were completely varied. This study had focused mainly on Phosphorous and Nitrogen removal.

In the thesis work by Mi Liang, 3 batch experiments were conducted and 'Modde' model was used for experimental design. It is a program for generation and evaluation of statistical experimental designs. The measurements never went out of range due to this program. However,

while conducting my set of experiments, the COD, Phosphorous and Nitrogen were measurements had to be conducted for each raw wastewater sample, as the 'Modde' program was very expensive. A number of experiments were showing out of range results as the dilutions had to be different with each sample of wastewater. As a result, the experiments became time consuming and the range of experiments had to be shortened. Therefore, the effects of varying pH on COD, Phosphorous and Nitrogen removal could not be studied.

7 Conclusion

After the experiments were performed, it could be concluded that at smaller amounts of concentration of magnesium chloride has a great potential for efficient removal of COD, Phosphorous and Nitrogen. It displayed very good results at concentrations between 30 – 35 mg/L of magnesium chloride when added to the wastewater sample. Taking into account the efficiency of the method at higher concentrations of magnesium chloride samples, several steps may be needed for higher COD, Nitrogen and phosphorus removal. Chemical precipitation with magnesium chloride can be used in pre-precipitation rather than the traditional option of adding chemicals during post-precipitation.

As mentioned earlier, magnesium chloride is cheap and available in plenty. Solar sea salt can be considered a very rich resource for magnesium chloride. These reasons can make it an economically feasible and profitable option. However, biological methods using enzymes can also be considered as a viable option for desirable removal of COD, Phosphorous and Nitrogen. Various studies are being carried out in this regard.

Alkaline hydrolysis of toilet paper using sodium hydroxide also yielded good results which can be seen as an option to naturally decompose toilet paper in wastewater. However, sodium hydroxide being a very expensive chemical, this option can be expensive. But, it was also observed that when the pH was adjusted to 12, the toilet paper readily dissolved. So, the toilet paper present in the wastewater could be naturally dissolved at some point of treatment when subjected to varying pH values. Also, as a high COD was measured after the alkaline hydrolysis and also previous studies showed that the cellulose breaks down to glycolic acid and 2,4-dihydroxybutanoic acids were formed. The main functional groups formed after alkaline hydrolysis was aldehyde, ketone and carboxyl groups. Therefore, it might be a good option to have continued studies to gain an insight that could yield desirable results where the formations and reactions occurring during alkaline hydrolysis could be used as a carbon source for Nitrogen removal in wastewater treatment.

8 Future studies and prospects

There would be a number of studies that would be of interest related to this thesis work. Some of them are listed here:

- Does pre-precipitation influence the chemical composition of the sludge?
- Is the chemical composition of the sludge changed when MgCl_2 is used in pre-precipitation?
- Can energy efficiency of the sludge be improved due to chemical pre-precipitation?
- Is it economically viable when compared to other chemicals such as FeSO_4 or FeO_3 ?

I come from India, where authority stakeholders hold supreme power in making decisions with concern to the environmental quality. The academy and public stakeholders have less importance. Therefore, it would be a very challenging and ambitious task for me to implement this thesis work in reality. In India solar salt production industry has a huge market and produces 99.5% purity from solar salts. However, aluminum and iron salts seem to be the most commonly used chemicals in India. Magnesium salts are always present in sea salts. It can have a ratio of 1.5 units of magnesium chloride to 1 unit of magnesium sulfate. Sambhar Lake, in Rajasthan (India) is the main producer of solar sea salts in India. Therefore, the magnesium salts can be used as a biggest source for chemical precipitation in wastewater treatment plants.

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