

**COMPARING THE EFFECTIVENESS OF CO₂ STRIPPERS TO
REDUCE OPERATING COSTS FOR STRUVITE FORMATION**

By

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ABSTRACT

Struvite crystallization offers the potential of removing phosphorus from wastewater and recovering it in a form that can be used as a fertilizer. In 1999, the Department of Civil Engineering at the University of British Columbia (UBC) started a phosphorus recovery project. The UBC struvite group is now researching ways to reduce the operating costs of struvite production. One of the major operational costs of struvite production is the cost of caustic chemicals that is added to obtain a desired level of operative pH. The main objective of this research was to introduce two types of CO₂ strippers into the struvite crystallization process and determine their effectiveness in reducing caustic chemical use, thereby helping to reduce the operational costs of struvite production.

In this study, two CO₂ strippers were used – (i) compact media stripper and (ii) cascade stripper. The strippers were connected to two identical struvite crystallizers. The reactors were placed at the Lulu Island Wastewater Treatment Plant (LIWWTP). The strippers were tested under different operating conditions, and their effectiveness in reducing caustic use was compared.

Throughout the project, a high percentage of phosphorus removal was achieved under each condition, by both the reactors/strippers. Most of the time, the phosphorus removal rate was around 90%. The compact media stripper failed to save any amount of caustic, regardless of the operating conditions. Instead, more caustic was required once the stripper was introduced. One of the reasons was that the stripper blocked the passage of stripped off CO₂, since it was mounted on top of the clarifier. Another reason was the susceptibility of stripper's packing media to become frequently clogged, which also resulted in blocking the movement of CO₂ through the stripping tower.

On the other hand, the cascade stripper was very effective in saving caustic. The amount of caustic saved by this stripper ranged from 35% to 86%, depending on the

operating conditions. Both strippers showed very poor performance regarding ammonia stripping, with the compact media stripper being slightly better in stripping ammonia.

The harvested struvite pellets from both the reactors were composed of nearly pure struvite (94% by mass), with a small amount of calcium and traces of iron and potassium. Different operating conditions did not have any affect on the quality of harvested struvite.

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LIST OF ABBREVIATIONS AND SYMBOLS

AAS	Atomic Absorption Spectrophotometer
BNR	Biological Nutrient Removal
EBNR	Enhanced Biological Nutrient Removal
EBPR	Enhanced Biological Phosphorus Removal
ECA	External Continuous Aeration
EGA	External Gradual Aeration
FBR	Fluidized Bed Reactor
GVRD	Greater Vancouver Regional District
K_{sp}	Solubility Product
LIWWTP	Lulu Island Wastewater Treatment Plant
MAP	Magnesium Ammonium Phosphate
PAO	Phosphorus Accumulating Organism
P_s	Conditional Solubility Product
RR	Recycle Ratio
SSR	Supersaturation Ratio
UBC	University of British Columbia

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CHAPTER ONE

INTRODUCTION

1.1 Background

Phosphorus is an essential part of the nutrient cycle in nature. It is an irreplaceable element in many physiological and biochemical processes in plants and animals. Due to its high reactivity, phosphorus is never found free in nature, but it is widely distributed in many different minerals. Phosphorus compounds are present in municipal wastewater, originating from detergents as well as from metabolism processes, diffuse runoff from agricultural lands and input from the air.

Phosphorus based compounds are widely used in modern industry. The most important commercial use of phosphorus based chemicals is the production of fertilizers. Global demand for fertilizers has led to large increases in phosphate (PO_4^{3-}) production in the second half of the 20th century. Unfortunately, phosphorus is a non-renewable resource, with finite reserves globally. It is estimated that there are 7,000 million tons of phosphate rocks as P_2O_5 remaining in those reserves, that could be economically mined, and another around 11,000 million tons of phosphate rocks that cannot be processed economically at present. The human population consumes 40 million tons of phosphorus as P_2O_5 each year (Jasinski, 1999) and its demand will increase by 1.5% each year (Steen, 1998). It is predicted that this resource could be exhausted within next 100–250 years (Shu *et al.*, 2006). Hence, industry and the population, in general, are now seeking alternative, sustainable ways of recovering phosphorus from different sources.

Municipal wastewater has a great potential to become a source of phosphorus recovery. Phosphorus is generally removed from wastewater either by chemical treatment or by utilizing enhanced biological phosphorus removal (EBPR) processes, generally referred to as a biological nutrient removal (BNR) process. The BNR process is preferable in most instances, since, in addition to removal of nitrogen compounds, phosphorus removed from

wastewaters through this process remains in a bio-available form, hence making it easier for subsequent phosphorus recovery.

However, in some cases, phosphorus removal may prove to be difficult in BNR processes, since phosphorus is released back into liquid phase during the sludge handling process, especially if the process involves anaerobic digestion. It is estimated that as much as 80–90% of phosphorus removed during treatment may be released and reintroduced to the process from the digester supernatants and this can lead to potential system failure (Niedbala, 1995; Mavinic *et al.*, 1998). Under certain conditions, the elevated levels of magnesium, ammonium, and phosphate ions present in the anaerobic digester supernatant, can combine to form ‘*struvite*’ (magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Unintentional struvite accumulation is considered to be a nuisance in wastewater treatment plants. The struvite deposits are hard and often difficult to dislodge, and sometimes require replacement of encrusted parts. It causes damage to pumping systems, reduces the plant flow capacity and contributes to major plugging of piping. Therefore, until recently, a large portion of struvite research has been directed towards removal and prevention of struvite formation, rather than towards forced precipitation of it from solution.

Research shows that more than 90% of dissolved phosphorus can be removed from anaerobic digester supernatant in the form of struvite precipitation, with 50-80% of removed phosphorus recovered as harvestable struvite pellets (Battistoni *et al.*, 1997, 2001; Münch and Barr, 2001; Ueno and Fujii, 2001). Struvite has been found to be a good plant nutrient source for nitrogen and phosphorus, since it releases these nutrients slowly and has non-burning features because of its low solubility in water (Gaterell *et al.*, 2000; Shu *et al.*, 2006). In this way, struvite can actually generate revenues for wastewater treatment plants. It has been estimated that the payback period of a struvite plant processing 55,000 m³/d of waste stream could be less than five years (Shu *et al.*, 2006).

In 1999, the Department of Civil Engineering at The University of British Columbia (UBC) started a phosphorus recovery project, in collaboration with British Columbia Hydro. Initially, a “crystallizer model”, developed by the Civil Engineering Department of UBC,

was tested with synthetic wastewater at the bench-scale. After the initial bench-scale work, the crystallizer model had been modified to resolve problems associated with small reactors, and then was successfully scaled-up from the bench-scale (2.51 L) into the pilot-scale (about 90 L). The crystallizer has subsequently been tested with synthetic, and as well as with real anaerobic digester supernatant from both the Lulu Island Wastewater Treatment Plant (LIWWTP) and the City of Penticton Advanced Wastewater Treatment Plant. Studies, conducted by the UBC struvite group, show that this crystallizer process is capable of removing more than 90% of ortho-phosphate from waste stream, with more than 85% of the removed phosphorus recovered as harvestable struvite pellets (Fattah, 2004). After much research on thermodynamics and process control of struvite crystallization process, the UBC struvite group is now concentrating on finding methods to reduce operating costs of struvite precipitation.

As will be discussed in the next chapter, operational costs of struvite mainly depends on two factors - costs of chemicals to be injected in the process and energy requirements for pumping. In their study, Jaffer *et al.* (2002) showed that, compared to cost of chemicals, energy requirement costs are quite insignificant and 97% of the total chemical cost was due to the addition of caustic, in order to achieve a desirable operating pH level. Therefore, by reducing caustic use, a large fraction of struvite crystallization operational costs can be reduced. Research carried out by Battistoni *et al.* (1997, 1998, 2001) showed that the operative pH can be obtained by applying air stripping of CO₂ only, without any addition of caustic chemicals. Inspired by these findings, Zhang (2006) developed a cascade CO₂ stripper and tested it at the LIWWTP. The stripper was able to reduce 46% to 65% of caustic chemical addition, depending on the operating conditions.

1.2 Research Objectives

The objectives of this research program were designed:

- To introduce two types of CO₂ strippers into the struvite crystallization process and determine their effectiveness in reducing operating costs of struvite precipitation.
- To test the two CO₂ strippers under different conditions and compare their effectiveness in reducing caustic chemical use.
- To investigate the quality of harvested struvite.
- As a minor objective, to compare the strippers' ammonia stripping ability.

CHAPTER TWO

LITERATURE REVIEW

2.1 Phosphorus Removal From Wastewater

The technologies for phosphorus removal from wastewater started to develop back in the 1950s, in response to the problem associated with eutrophication in water bodies and the subsequent need to reduce the levels of phosphorus before discharging it to surface waters (Morse *et al.*, 1998). The current discharge limit on total phosphorus in North America ranges from 2 to 0.1 mg/L (Tchobanoglous *et al.*, 2003). Presently, several technologies are available for removing phosphorus from wastewater, in order to meet the discharge guidelines. Among those, the two most widely used technologies are chemical precipitation and biological nutrient removal (BNR).

2.1.1 Chemical phosphorus precipitation

Chemical precipitation is the oldest technology of phosphorus removal. It is a simple and reliable method, and therefore, still remains as the leading technology in removing phosphorus. The chemical precipitation of phosphorus is brought about by the addition of a divalent or trivalent metal salt to wastewater, causing precipitation of an insoluble metal phosphate that is settled out by sedimentation. The metal ions used most commonly are calcium [Ca(II)], aluminum [Al(III)] and iron [Fe(III)]. Polymers have been used together with alum and lime as flocculent aids. However, this process offers quite low phosphorus recovery as metal-bound phosphorus makes subsequent recycling difficult.

2.1.2 Biological nutrient removal

Biological phosphorus removal is achieved in the activated sludge process by utilizing the ability of phosphorus accumulating organisms (PAOs) to accumulate phosphates as polyphosphates, for their own metabolism. This enhanced biological nutrient removal

(EBNR) process also provides simultaneous nitrogen removal. Overall, phosphorus removal rates of 80-90% can be achieved through this process (Morse *et al.*, 1998). The main advantages of this technology over chemical precipitation are avoiding the use of chemicals and producing less sludge. Also, from a phosphorus recovery perspective, EBNR is better than chemical precipitation, since biologically bound phosphorus is more recyclable. On the other hand, this technology requires more complex plant configurations and operations.

2.2 Phosphorus Recovery As Struvite

2.2.1 Struvite

Magnesium ammonium phosphate (MAP) hexahydrate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), more commonly known as '*struvite*', is a mineral that is composed of magnesium, ammonium, and phosphate in equal molar concentrations. It belongs to the group of the orthophosphates. Struvite crystallizes in the orthorhombic system as white to yellowish or brownish-white, pyramidal crystals, or in platey mica-like forms. It is a soft mineral with a Mohs hardness of 1.5 to 2 and has a low specific gravity of 1.7. It is sparingly soluble in neutral and alkaline conditions, but is readily soluble in acid (Internet1).

Struvite crystals occur spontaneously in various biological media. For instance, it has been found in rotting organic material such as guano deposits and cow manure (Omar *et al.*, 1994). It has also been studied in the medical field, as it occurs as crystallites in urine and as a type of kidney stone (urolith) (Coe *et al.*, 2005); lately, it has been investigated in soil sciences, as a way to entrap nitrogen in compost (Jeong and Hwang, 2005).

In the wastewater treatment area, struvite is well known as a "scale problem". Accumulation of struvite on pipe walls and other parts of treatment plants causes plugging problems. Struvite deposits are hard, often difficult to dislodge and sometimes require replacement of encrusted parts. Struvite was first discovered in medieval sewer systems in Hamburg Germany in 1845 (Internet1). Borgerding (1972) first reported struvite as a source

of scale deposits in wastewater treatment plants, when it occurred on the walls of an anaerobic digestion system at the Hyperion wastewater treatment plant in Los Angeles in 1963. Since then, several studies have been carried out on struvite as a scaling agent (Doyle and Parsons, 2002), but most of the authors have considered struvite as a nuisance and not as a product which could be of economic interest.

2.2.2 Benefits of phosphorus recovery as struvite

Although, in most cases, unintentional struvite accumulation is known to be a serious problem in wastewater treatment plants, struvite precipitation can, in fact, serve as a process for removing and recovering phosphorus from wastewater. The interests in removing and recovering phosphorus via struvite are stated below.

➤ Since supplies of phosphorus and the quality of phosphate-bearing rock are decreasing (Shu *et al.*, 2006), people are now seeking an alternative sustainable source of phosphorus. Struvite precipitation offers an excellent sustainable way of recovering phosphorus.

➤ Struvite precipitation leads to simultaneous removal of nitrogen and phosphorus. Both of these nutrients are responsible for eutrophication.

➤ Significant reduction (8% to 31%) in sludge volume can be achieved by implementing phosphorus recovery by crystallization (Woods *et al.*, 1999).

➤ Struvite is known to be a good quality fertilizer. It represents a highly effective source of nutrients (P, N and Mg) for plants (Li and Zhao, 2003). Its low solubility in water also presents the advantage of prolonging the release of nutrients, without the danger of burning roots of crops treated (Gaterell *et al.*, 2000; Shu *et al.*, 2006). Another advantage of struvite as a fertilizer is that struvite contains low amounts of heavy metals, compare to phosphate bearing rocks that are mined and supplied to fertilizer industries (Driver *et al.*, 1999).

Several laboratory and pilot scale studies have been carried out to determine the potential of removing and recovering phosphorus as struvite. Only a few of them have been tested at full scale mainly in The Netherlands (Giesen, 1999) and Italy (Battistoni *et al.*, 2005a/b). However, to date, Japan is the only country where complete phosphorus removal and recovery, as struvite, has been implemented and the resulting production is sold to fertilizer companies (Gaterell *et al.*, 2000; Ueno and Fujii, 2001).

It should be mentioned that struvite recovery is not only confined to municipal wastewater treatment systems; other waste streams also offer prospects of struvite recovery, depending on the chemistry of these waste liquors meeting the requirements of struvite precipitation. So far, struvite has been recovered from landfill leachate, swine wastewaters, piggery effluent and animal manure (Doyle and Parsons, 2002). Research has also been carried out on the possibility of struvite precipitation from urine (Lind *et al.*, 2000; Wilsenach and van Loosdrecht, 2003; Tilley, 2006).

2.2.3 Struvite recovery technologies

The technologies used to recover phosphorus as struvite can be classified in three main categories. These are as follows:

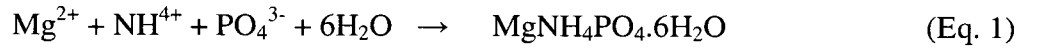
1. Selective ion exchange
2. Precipitation in a stirred reactor
3. Precipitation in fluidized bed reactors (FBR) or air-agitated reactors

Among these three processes, FBR is the most commonly used and widely investigated technology to crystallize struvite from wastewater. In FBR systems, struvite particles precipitate spontaneously from supernatants, following the addition of chemicals to reach the molar ratio of Mg:P:N to 1:1:1. Once the nucleation of the first particle starts, the growth takes place either by interaction of small struvite particles together or by contact on initial seed materials. Suspension of particles inside the reactor is maintained by either liquid flow rates (Cecchi *et al.*, 2003) or an upflow circulation of air (Suzuki *et al.*, 2002); thus, the

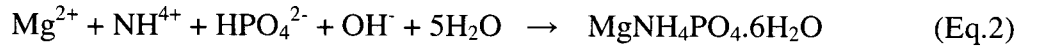
particles inside the reactor are in continuous motion, and behave like a dense fluid. In an FBR system, feed solutions enter from the bottom of the reactor and the velocity of flow decreases with increasing height of the reactor.

2.3 Struvite Chemistry

The crystallization of struvite is a highly dynamic and complex phenomenon controlled by a number of factors. The precipitation of struvite involves a number of reactions. Excluding the side reactions, the formation of struvite can be explained by the following generalized equation.



Another formula has been proposed by Shimamura *et al.* (2003). According to that formula, struvite is precipitated following the equation given below.



The difference between the above two equations is that, in the second equation, HPO_4^{2-} has been used instead of PO_4^{3-} and OH^- has been introduced. The reason for using different phosphate ion is that HPO_4^{2-} is more dominant than PO_4^{3-} in the normal operating pH of struvite formation.

2.3.1 Solubility product (K_{sp})

The solubility product (K_{sp}) is defined as the equilibrium constant of a reaction involving a precipitate and its constituent ions. The solubility product (K_{sp}) can be used to describe the rate of reaction at which struvite forms and dissolves in liquid solution. Several studies have been carried out to determine the solubility product of struvite (Buchanan *et al.*, 1994; Aage *et al.*, 1997; Ohlinger *et al.*, 1998; Bhuiyan, 2007). Unfortunately, there is no

universal agreement on the value of struvite solubility product. Andrade and Schuiling (2001) mentioned four reasons which cause this discrepancy.

- The solubility product may be derived by using approximate solution equilibrium.
- The effects of ionic strengths are often neglected.
- Mass balance and electroneutrality equations are not always used.
- Different chemical species are selected for calculations.

However, there is a general agreement on the fact that the value of the solubility product of struvite decreases with increasing pH of liquid (Ohlinger, 1999; Doyle and Parsons, 2002).

2.3.2 Conditional solubility product (P_s)

In order to avoid the complexities associated with the calculation of solubility product of struvite, the conditional solubility product (P_s) is use for practical purposes. The conditional solubility product is determined by measuring only concentrations of total magnesium, ammonium and phosphate present in solution, as shown by the following equation.

$$P_s = [Mg^{+2}]_{total} \cdot [NH_4-N]_{total} \cdot [PO_4-P]_{total} \quad (\text{Eq. 3})$$

However, calculation of the conditional solubility product takes no account of pH, ionic activity and ionic strength, and it is only accurate for a specific pH value; whereas, a solubility product can be applied at any pH (Doyle and Parsons, 2002; Adnan *et al.*, 2003a).

2.3.3 Supersaturation ratio (SSR)

The supersaturation ratio (SSR) of a solution is an indication of the potential of struvite precipitation. The SSR can be defined by the following equation.

$$SSR = P_s / P_{s-eq} \quad (\text{Eq. 4})$$

Where, P_s = Conditional solubility product of struvite in a solution,

P_{s-eq} = P_s value under the equilibrium condition.

Generally, $SSR > 1$ implies that the solution is supersaturated and precipitation of struvite is possible; $SSR = 1$ indicates that the system is in equilibrium; while $SSR < 1$ means that precipitation is not possible and the system is undersaturated. Adnan *et al.* (2003a) reported that, when the in-reactor supersaturation ratio was maintained between 1 and 5, the system's efficiency and quality of harvested product were at their best.

2.4 Parameters Of Struvite Crystallization

The mechanisms of occurrence and development of struvite crystals follow two chemical stages: (i) nucleation (crystal birth) and (ii) crystal growth (development of crystals until equilibrium is reached). Predicting or controlling these reactions is complex, since these are controlled by several physical-chemical parameters. These parameters are described below.

2.4.1 pH

The pH at which struvite may precipitate is one of the main factors influencing the crystallization process. It has been found that struvite's solubility decreases with increasing pH, until it reaches the minimum value. The pH, at which minimum solubility of struvite occurs, varies with the characteristics of wastewater. Buchanan *et al.* (1994) reported that the minimum solubility of struvite occurred at the pH of 9.0; while Ohlinger *et al.* (1998) found this value at a pH of 10.3.

A saturated condition of a solution is a prerequisite for any crystallization process. In case of struvite, the solution can be saturated either by increasing the struvite constituent ions

or by increasing the pH. Increasing the pH seems to be more preferable in running the process. The optimum operational pH value for different wastewater varies greatly depending on the characteristics of particular waste stream (Fujimoto *et al.*, 1991; Münch and Barr, 2001; Stratful *et al.*, 2001). Recommended values of pH for struvite crystallization generally ranges from 8.0 to 9.0. However, a high initial pH can be limiting in the sense that it causes the transformation of NH_4^+ ions into gaseous ammonia, thereby reducing the nitrogen concentration and affecting the molar ratio of Mg:N:P that is necessary to form struvite.

Although most of the literatures cited pH values between 8.2 and 9.0, to ensure higher (above 80%) phosphorus removals (Battistoni *et al.* 2001; Münch and Barr, 2001; Stratful *et al.* 2001; Jaffer *et al.* 2002), Adnan *et al.* (2003a) were able to achieve over 90% phosphorus removal at a pH of 7.3. Fattah (2004) also reported over 90% phosphorus removal at a pH of 7.5. Adnan *et al.* (2003a) concluded that this finding indicates that pH is not the only factor that can cause the process fluid to be supersaturated; the concentration of struvite constituent ions also plays a role.

2.4.2 Magnesium to phosphorus molar ratio

Theoretically, struvite formation requires a Mg:N:P molar ratio of 1:1:1. In most cases with municipal wastewater, magnesium is the limiting element and hence requires an external source of magnesium supplementation. Adnan *et al.* (2003b) reported that, at a fixed N:P molar ratio and a given pH value, the average phosphorus removal increased almost linearly with an increase in the Mg:P molar ratio. Katsuura (1998) also found that phosphorus removal increased with an increase in Mg:P and the increase was more pronounced at low pH values (pH at 8.0) compared to high pH values (pH at 9.0). However, Fattah (2004) reported no significant affect of the Mg:P ratio, regarding phosphorus removal and highlighted problems of keeping a constant Mg:P inside the reactor. Although, a Mg:P ratio of 1:1 is required for struvite formation, Jaffer *et al.* (2002) suggested a ratio of 1.3:1 at full scale level, in order to out-compete calcium ions present in the centrate.

2.4.3 Ammonia to phosphorus molar ratio

Municipal wastewaters usually contain higher molar concentration of ammonium ions than magnesium and phosphorus. Some studies have reported that phosphorus removal increases with increase in ammonia concentrations (Münch and Barr, 2001; Katsuura, 1998). Stratful *et al.* (2001) found that excess ammonium ion is highly beneficial for struvite precipitation and tends to form a relatively pure struvite.

2.4.4 Temperature

Temperature affects solubility and the reaction rate of struvite formation. Aage *et al.* (1997) showed an increase in the solubility product of struvite with an increase in temperature, between 10⁰C and 50⁰C. These results agreed with previous findings. Adnan *et al.* (2004) found similar results; their data showed that lower temperature was more beneficial for actual struvite formation, with the product coming out of solution more efficiently.

2.4.5 Mixing energy (or turbulence)

Mixing energy or turbulence influences struvite accumulation. In their study, Ohlinger *et al.* (1999) showed that crystal size and shape were influenced by mixing energy as they found that elongated crystals were formed in a semiquiescent environment; on the other hand, high mixing energy resulted in the formation of less elongated and more tightly formed crystals. In an addition to that, Ohlinger *et al.* (1999) demonstrated that the growth rate was also influenced by mixing energy as the lowest growth rates were found in the quiescent zone of the process, and the highest ones were found in high mixing environments. However, too much turbulence may hinder growth by increasing the collision among pellets and thereby breaking the structure (Durrant *et al.*, 1999).

2.4.6 Presence of foreign ions

The presence of ions other than Mg^{+2} , NH_4^+ and PO_4^{3-} can increase the solubility of struvite by reacting with any of these three species. Koutsoukos *et al.* (2003) showed that the presence of calcium ions affects the growth rate negatively and can lengthen the induction time. Calcium ions can also interact with phosphate, to form calcium phosphates.

2.4.7 Initial reactor seeding

Struvite precipitation requires a nucleus. Hence, the reactor has to be seeded at the start-up of the process and the operating process will eventually become self-seeding (Münch and Barr, 2001). Types of seeding materials have an impact on the reaction rate and removal efficiencies. Wang *et al.* (2006) tested three different seeding materials (quartz sand, granite and struvite pellets), and found that struvite pellets, as seeding material, produced the best performance, regarding phosphorus removal.

2.5 Operating Costs For Struvite Production

Phosphorus recovery, through struvite production, offers both environmental and economical benefits. However, the success of introducing struvite crystallization processes in wastewater treatment plants will mostly depend on its economical sustainability.

Production costs of struvite mainly depend on two factors, the costs of chemicals to be injected in the process and energy requirements for pumping. In their study, Jaffer *et al.* (2002) showed that compared to cost of chemicals, the energy requirement cost is quite insignificant.

Basically, two types of chemicals are used in a struvite crystallization process –

- (i) a source of magnesium, usually magnesium chloride (MgCl_2), to obtain a suitable Mg:N:P ratio for struvite precipitation, and
- (ii) a caustic chemical, mostly sodium hydroxide (NaOH), to raise/adjust pH of wastewater so that saturated condition for struvite formation prevails in solution.

Jaffer *et al.* (2002) estimated production costs of struvite precipitation for a pilot scale project treating $400 \text{ m}^3/\text{d}$ of centrate and found that 97% of the total chemical cost was due to the addition of NaOH . This result shows that, by reducing caustic use, the overall production costs of struvite can be reduced by a large fraction. In their study at the Treviso wastewater treatment plant, Italy, Cecchi *et al.* (2003) used air stripping to raise pH and they were able to obtain a pH value of 8.5. The results demonstrated that air stripping could be an option to reduce costs associated with caustic addition, depending on the type of air stripping process.

2.6 Methods Of Raising The pH Value Of Wastewater

As mentioned in Section 2.4.1, a struvite crystallization process requires a saturated condition of solution, which can be attained either by increasing concentrations of struvite constituent ions (e.g. Mg^{2+} , NH_4^+ and PO_4^{3-}) or by increasing the solution's pH. Logically, increasing constituent ions' concentration is not feasible or desirable for running the process; hence, increasing the solution's pH value is more appropriate. Struvite is soluble in acidic condition and becomes more and more insoluble under a basic environment, until it reaches its minimum solubility (which depends on several factors). The pH required for struvite formation usually ranges in between 8.0 and 9.0 (Münch and Barr, 2001; Wang *et al.*, 2005), depending on local conditions. However, in most cases, the pH of municipal wastewater is lower than that required. Hence, it is usually necessary to raise the pH value of wastewater in order to precipitate struvite. Usually two methods are employed - these are caustic chemical addition and aeration/ CO_2 stripping.

2.6.1 Caustic chemical addition

Generally, the operating pH level of struvite precipitation is achieved and maintained by adding a caustic chemical. Usually NaOH, $\text{Mg}(\text{OH})_2$, MgO and $\text{Ca}(\text{OH})_2$ are used to raise the pH.

The addition of $\text{Mg}(\text{OH})_2$ and MgO resulted in increasing both the pH value and magnesium content of the solution. Beal *et al.* (1999) tested four caustics (NaOH, NaHCO_3 , $\text{Ca}(\text{OH})_2$ and MgO) as a pH adjuster and found MgO to be the most cost effective, based both on cost and the fact that it provided magnesium for the reaction. The MgO proved to be effective at increasing the pH of the swine waste slurry to approximately 8.5. However, due to limited solubility, it was difficult to reach a pH greater than 8.5 with MgO. To test the effect of pH above 8.5, they had to add NaOH, in addition to MgO.

A cheaper possibility for increasing the pH of wastewater is the addition of lime ($\text{Ca}(\text{OH})_2$). However, calcium addition means an excess of calcium ions for precipitation and not only forming calcium phosphate, but also calcium carbonate, thus reducing the value of the recovered product. Furthermore, lime interferes with the precipitation of struvite (Kohen and Kirchmann, 2004; Le Corre *et al.*, 2005).

The most commonly used caustic is NaOH. Adding lime introduces impurity ions in the form of Ca^{2+} . On the other hand, adding $\text{Mg}(\text{OH})_2$ and MgO means either magnesium concentration or the pH value cannot be optimized independently; moreover, these chemicals dissociates rather slowly, thus requiring longer hydraulic retention time and consequently a larger reactor. Therefore, although NaOH is relatively more expensive than the above-mentioned options, it proves to be more suitable in raising the pH of the wastewater (Huang, 2003).

The alkalinity in wastewater is generally high, thus imposing a large buffering capacity. In order to raise wastewaters' pH, this buffering capacity needs to be overcome, generally ended up in using large amount of caustic (Battistoni *et al.*, 1997). For a pilot scale

experiment, Jaffer *et al.* (2002) calculated that the daily cost of NaOH addition would be £139 or £50,735 per year. Hence, for a full scale plant, the cost required for pH adjustment by adding caustic chemicals, needs to be addressed seriously, before design and construction.

2.6.2 Aeration or CO₂ stripping

In wastewater treatment plants, struvite precipitation usually occurs at locations where CO₂ is stripped from the solution, which is linked with a corresponding increase in pH. The following equation explains how CO₂ stripping raises the pH of a solution.



Areas of high turbulence, such as pipe elbows, mixer blades, valves, and pumps are main locations of struvite deposits (Neethling and Benisch, 2004). In these locations, a reduction of partial pressure of CO₂ takes place. Hence, Loewenthal *et al.* (1994) concluded that partial pressure of CO₂ is one of the driving forces for struvite precipitation.

In their study, Pitman *et al.* (1991) demonstrated the possibility of increasing pH with aeration. This phenomenon was attributed to CO₂ stripping. In a different study, Loewenthal *et al.* (1994) showed that the partial pressure of CO₂ controls struvite precipitation inside an anaerobic digester.

Battistoni *et al.* (1997) carried out experiments on real anaerobic supernatant, to investigate struvite crystallization without adding any chemicals to raise the pH. They used two modes of air strippers, namely external gradual aeration (EGA) and external continuous aeration (ECA). The upflow rate ranged from 1.8 L/min to 5 L/min and the airflow rate was kept at 15 L/min. Air stripping increased the pH from 7.9 to 8.3-8.6. However, the EGA condition (air stripping for 56% of the total time) proved to be insufficient to obtain rapid phosphate removal, while the ECA condition gave faster phosphorus removal. They were able to obtain up to 80% of phosphorus removal, when an ECA condition was adopted.

In separate study, using anaerobic supernatant from a centrifugation station with an average pH of 7.7, Battistoni *et al.* (1998) were once again able to achieve the supersaturation pH for struvite crystallization, applying only air stripping.

In 2001, Battistoni *et al.* investigated a struvite crystallization process in a full scale plant in Treviso (Italy). The average pH of the anaerobic supernatant of the plant was 7.5. They used the air stripping of CO₂ as the only means to obtain the operative pH (pH 8.3-8.7), without any addition of chemicals. The operative pH ranged from 8.1 to 8.7 according to the airflow rate and hydraulic head employed, respectively, from 20 to 40 m³/h and from 1.7 to 2.7 m. Their results showed that, in order to obtain an operative pH ≥ 8.3 , a higher head level (2.7 m) must be used at a minimum airflow rate (10 m³/h) or lower head one (1.7 or 2.2 m) at higher airflow rate (40 m³/h). This means that higher hydraulic head can save energy, as it requires a lower airflow rate to achieve the desirable/operative pH.

Hiroyuki and Toru (2003) used 1 L bench scale reactors to demonstrate the affect of aeration on phosphorus precipitation. Along with aeration, NaOH solution was also fed continuously to increase the pH. They found that, by increasing the aeration intensity from 2.1 mg/L to 10.5 mg/L, the rate of phosphorus removal was also increased. The authors concluded that aeration influenced the quantities of CO₂ in solution, which helped in raising pH and resulted in the increased rate of phosphorus removal.

Zhang (2006) carried out an experiment using real anaerobic supernatant at the Lulu Island Wastewater treatment Plant (LIWWTP). She used a cascade stripper to increase the centrate's pH. Zhang (2006) reported a 46% to 65% reduction in caustic use (depending on operating conditions), by stripping CO₂ from the centrate, without a sacrifice in struvite production or quality.

All the above-mentioned findings indicate that air/CO₂ stripping presents an alternative solution for increasing the pH of wastewater and thereby reducing the use of caustic chemicals, for struvite precipitation; this in turn, can reduce overall production costs

of the struvite crystallization process, depending on the energy consumption used in the stripping process.

2.7 Mechanisms Of pH Increase By Stripping CO₂

Increasing the pH of water by the removal of CO₂, is a well-known reaction (Eq. 5). This reaction takes place, naturally, in aquatic environments through the uptake of CO₂ by algae. It has been shown that photosynthetic CO₂ uptake by algae can induce a pH increase up to a level of 10.5 (Kohen and Kirchmann, 2004). As described in Section 2.6.2, stripping CO₂ from wastewater, using other methods (usually stripper) than photosynthetic uptake, has the potential to increase the pH to the same high level.

The carbonate system for simple aqueous solutions can be described by the interdependent nature of six solute components, namely CO₂, H₂CO₃, HCO₃⁻, CO₃²⁻, H⁺, and OH⁻, using a set of equations given below (Stumm and Morgan, 1996).

$$[\text{H}_2\text{CO}_3^*] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] \quad (\text{Eq. 6})$$

$$[\text{H}^+][\text{HCO}_3^-] / [\text{H}_2\text{CO}_3^*] = K_1 \quad (\text{Eq. 7})$$

$$[\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-] = K_2 \quad (\text{Eq. 8})$$

$$[\text{H}^+][\text{OH}^-] = K_w \quad (\text{Eq. 9})$$

Where, K₁ and K₂ = First and second acidity constants respectively; dependent on temperature and presence of other salts in the liquid solution.

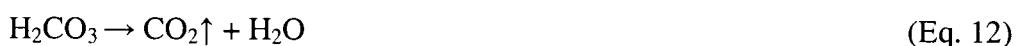
$$K_w = \text{Dissociation constant for water} = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

At neutral pH, the majority of the inorganic carbon present in water is in the form of HCO₃⁻, with the rest of the inorganic carbon present mainly as H₂CO₃* (CO₂ + H₂CO₃). The equilibrium for the reaction: H₂O + CO₂(aq) = H₂CO₃ (aq) lies rather far to the left, and the greater fraction of unionized CO₂ is present in the form of dissolved CO₂(aq) (Stumm and Morgan, 1996). Removing CO₂ from the system will induce an increase in the pH, according to the following mechanisms (Kohen and Kirchmann, 2004).

At low pH, when CO₂ is removed from the system, new CO₂ will be formed mainly by the dissociation of HCO₃⁻ to CO₂, in order to maintain the equilibrium.



At high pH, the concentration of H⁺ is low, and CO₂ is formed from HCO₃⁻ through the reaction with water.



In both cases, due to either depletion of H⁺ (Eq. 10) or generation of OH⁻ (Eq. 11), the pH value of the liquid is elevated.

2.8 Ammonia Stripping

The air stripping of ammonia from wastewater requires that the ammonia be present as a gas. Ammonium ions in wastewater exist in equilibrium with gaseous ammonia.



As the pH of the wastewater is increased above 7, the equilibrium is shifted to the left and ammonium ion is converted to ammonia, which may then be removed by air/gas stripping. However, Henry's law constant of ammonia is only 0.75 atm (mol H₂O/mol air), which makes this compound marginally strippable (Tchobanoglous, 2003). The result obtained by Musvoto *et al.* (2000) was in agreement with this fact. They compared the stripping rates of ammonia and CO₂, and found that the stripping rate for CO₂ was higher by two orders of magnitude than that for ammonia. This happens as Henry's law constant for ammonia is much lower than that for CO₂ (the dimensionless Henry's law constant for ammonia and CO₂ are 0.011 and 0.95 respectively).

The rate of ammonia stripping is influenced by pH, temperature, relative ammonia concentrations, and agitation of air-water interface. Theoretically, the greater these values are, the more efficient the stripping will be. Usually, as the temperature decreases, the amount of air required increases significantly for the same degree of removal (Tchobanoglous, 2003). Again, care should be taken as too high an air to water flow rate can result in a cooling effect (Liao *et al.*, 1995).

Cheung *et al.* (1997) investigated the effectiveness of ammonia stripping from leachate at different air flow rates (0, 1 and 5 L/min) and lime dosages (0 and 10,000 mg/L Ca(OH)_2) in aeration tanks in a laboratory. They found the ammonia removal at 20°C, after one day, was 70% for 0 L/min, 81% for 1 L/min and 90% for 5 L/min, regardless of the origin of leachate. The pH of aeration tanks was raised to above 11, by adding 10,000 mg/L Ca(OH)_2 before stripping.

Bonmatí and Flotats (2003) studied the effect of pig slurry waste type, fresh or anaerobically digested, and the effect of initial pH on ammonia air stripping from pig slurry waste at high temperature (80°C). The pH of fresh and anaerobically digested slurry was 7.5 and 8.4, respectively. For stripping purposes, the pH was adjusted using Ca(OH)_2 . An isothermal wet wall glass column was used for air stripping tests. Air was supplied by an air blower. Air and liquid flows were set at 20 and 0.266 mL/min, respectively. When fresh slurry was used, a final (after 4 h) ammonia stripping efficiency of 65, 69 and 98.8% was recorded for non-modified pH (i.e. pH=7.5), initial pH=9.5 and initial pH=11.5, respectively. On the other hand, when anaerobically digested slurry was used, final ammonia removal efficiencies above 96% were reported in all experiments, regardless of the initial pH (modified or non-modified).

In their experiment, Jaffer *et al.* (2002) found that the molar removal of ammonia exceeds the molar removal of phosphorus and the molar usage of magnesium. The removal was, in fact, greater than that needed for struvite formation. The authors believed that the surplus ammonia was being removed from the reactor by air stripping.

CHAPTER THREE

METHODS AND MATERIALS

3.1 Lulu Island Wastewater Treatment Plant

This study was carried out at the Lulu Island Wastewater Treatment Plant (LIWWTP), Richmond, BC. The LIWWTP is a secondary wastewater treatment plant that is operated by the Greater Vancouver Regional District (GVRD) of the province of British Columbia. The plant started as a primary treatment plant in 1973 and was later being upgraded to a secondary system in 1999, by the addition of a Trickling Filter/Solids Contact process. Presently, it has a flow capacity of 155 MLD and serves around 170,000 residents of Richmond. The plant consists of physical treatment that includes screening, grit removal and primary sedimentation; and biological treatment that includes trickling filter, solids contact and secondary clarification. The sludge produced is thickened by using both gravity thickener and diffused air floatation tanks. These two thickened sludge streams are mixed and then fed to the anaerobic digesters. After 32 days retention time in the digesters, the digested sludge has been reduced from ~ 4.0 % volatile solids to ~1.7 % solids. The digested sludge is then fed to centrifuges where the solids are further thickened to ~ 25 % (Internet2). The liquid centrate generated in the dewatering process was used as the inflow to the two struvite crystallizers used in this study. The characteristics of the centrate during the study period are given in the next chapter.

3.2 Materials And Equipment

3.2.1 Struvite Crystallizer

Two identical struvite crystallizers were used in this project. The reactors are referred to as the R#1 and the R#2, respectively, throughout this chapter and the next two chapters. This struvite crystallizer model was developed by the Department of Civil Engineering at the

University of British Columbia. The process consists of a reactor, an external clarifier, storage tanks for centrate, magnesium feed and caustic, pumps for feed flow, recycle flow, magnesium and pH controller. In this study, a stripper was incorporated within the system. The basic flow diagram of the crystallizer process (excluding the stripper) is shown in Figure 3.1.

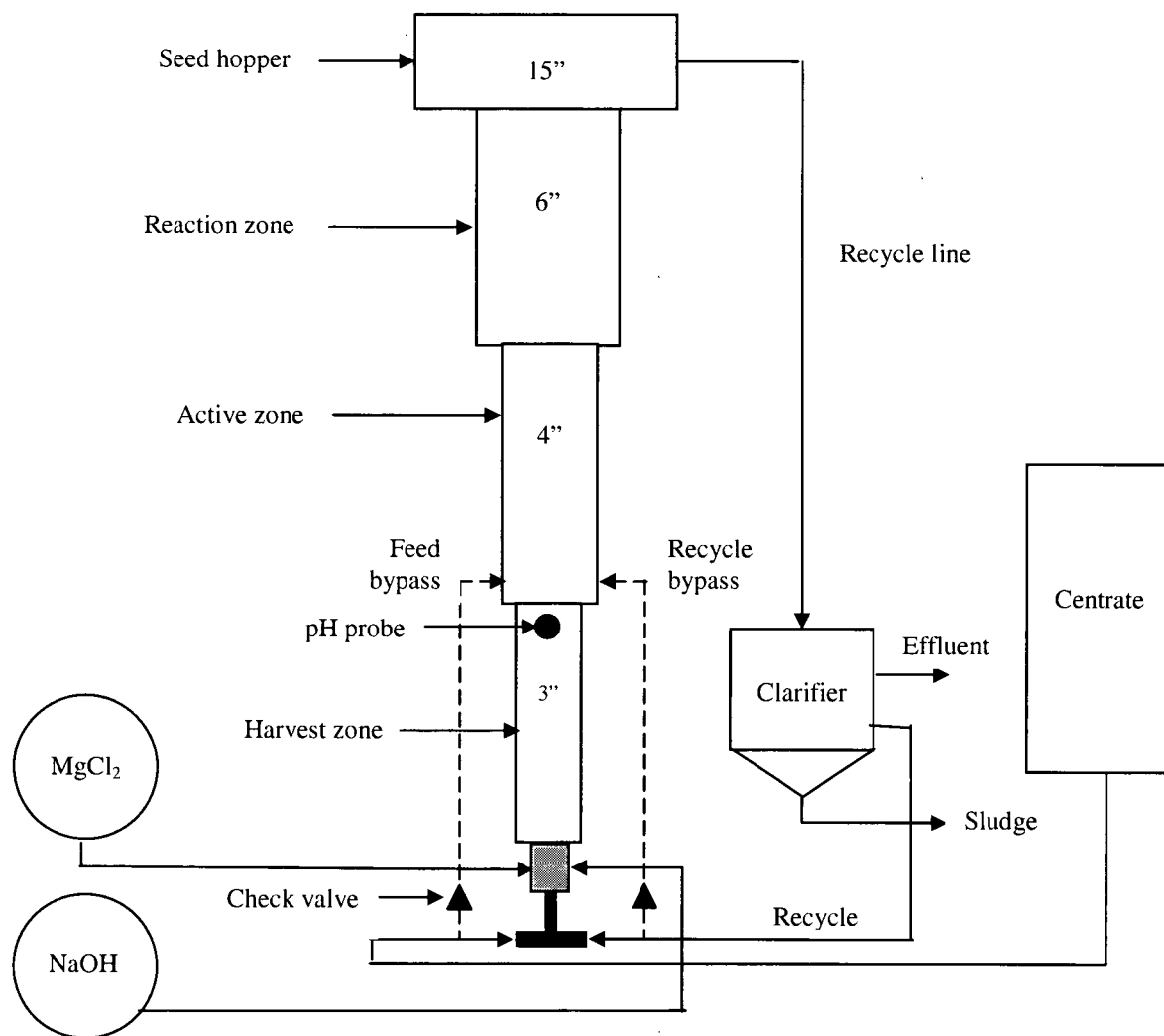


Figure 3.1: Basic flow diagram of the struvite crystallizer process

The reactor has four distinct zones, increasing in diameter from bottom to top. For a given upflow velocity, each section has a different flow rate, decreasing from bottom to top.

The dimensions of different zones are given in Table 3.1. The variation of reactor diameter with height provides a certain degree of turbulence above each transition which, in turn, ensures sufficient mixing in each zone. As pellets grow in size, they overcome higher upflow velocities and move down towards the lower sections where high turbulence enhances further crystal growth (Ohlinger, 1999). Thus, only the largest pellets in the reactor are harvested.

Table 3.1: Dimensions of the reactor

Section	Length (cm)	Diameter (cm)	Volume (L)
Harvest zone	74.9	7.6	3.42
Active zone	154.9	10.2	12.56
Reaction zone	127.0	15.2	23.17
Seed hopper	45.7	38.1	52.12
Below harvest zone	52.1	-	-

A pH probe is inserted into the top part of the harvest zone. This probe is used to control the pH controller system. The controller is capable of maintaining the pH within ± 0.1 pH units. Another pH probe is kept in the external clarifier, for countercheck.

The feed and caustic solution come from four different streams - centrate tank, recycle flow, magnesium chloride (MgCl_2) solution from the dosing pump and sodium hydroxide (NaOH) solution from the pH controller. An injection port, made of stainless steel, is built at the bottom of the harvest zone, in order to provide complete mixing of the feed constituents before entering the reactor.

A more detailed description of the reactor is provided by Fattah (2004).

Chemicals, Storage Tanks And Pumps

As stated previously, centrate from the LIWWTP was used in this study. At the beginning of the project, the centrate was stored in two 5600 L capacity holding tanks. On many occasions, the plant failed to provide sufficient amount of centrate on a regular basis, due to operational problems. As a result, the reactors had reverted to recycle mode

frequently, thus hampering the struvite crystallization process. Later on, another tank of the same capacity was installed, to provide more storage for centrate.

The supplementary magnesium feed for this project was made from commercial grade magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). The solution was stored in a 1400 L capacity holding tank. A Master Flex dosing pump was used to pump the solution to the injection ports of the reactors.

The struvite crystallization process is highly dependent on pH. The formation of struvite is associated with a subsequent drop in the pH of the system; hence, it is necessary to return the pH to the required value. In this project, the pH was adjusted using a caustic solution. The caustic was made from NaOH and was stored in a 120 L tank. A carbon dioxide (CO_2) trap was used to strip off CO_2 from the air, before the air entered the caustic tank.

The pH of the system was monitored and controlled by the pH probe inserted into the top of the harvest zone. This pH meter and the pH meter connected to the external clarifier were regularly calibrated by the two point method, using standard buffer solutions of pH 7.0 and pH 10.0.

The set up of the study area is shown in Figure 3.2.

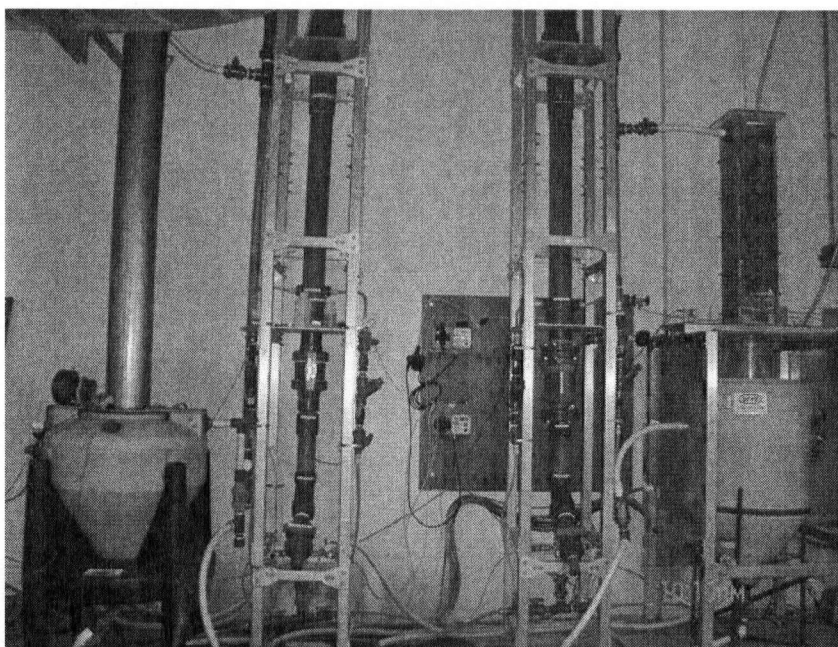


Figure 3.2: The set up of struvite crystallizers (with strippers) at the LIWWTP

3.1.1 Compact Media Stripper

Two strippers were used in this project. One of the strippers was a compacted media type of stripper. This stripper was connected with the R#1. The compact media stripper was developed by Ostara Nutrient Recovery Technologies Inc., Canada.

The stripper was designed for a maximum hydraulic loading rate of 30 L/min. It consists of a circular stripping tower, a supporting plate for the packing material at the lower part, a liquid distributor system located above the packing material and a fan at the bottom of the stripping tower. The rate of air provided by the fan is fixed. The total height of the stripping tower is 180 cm, of which 120 cm was packed with the packing material. One inch diameter hollow plastic balls were used as packing material.

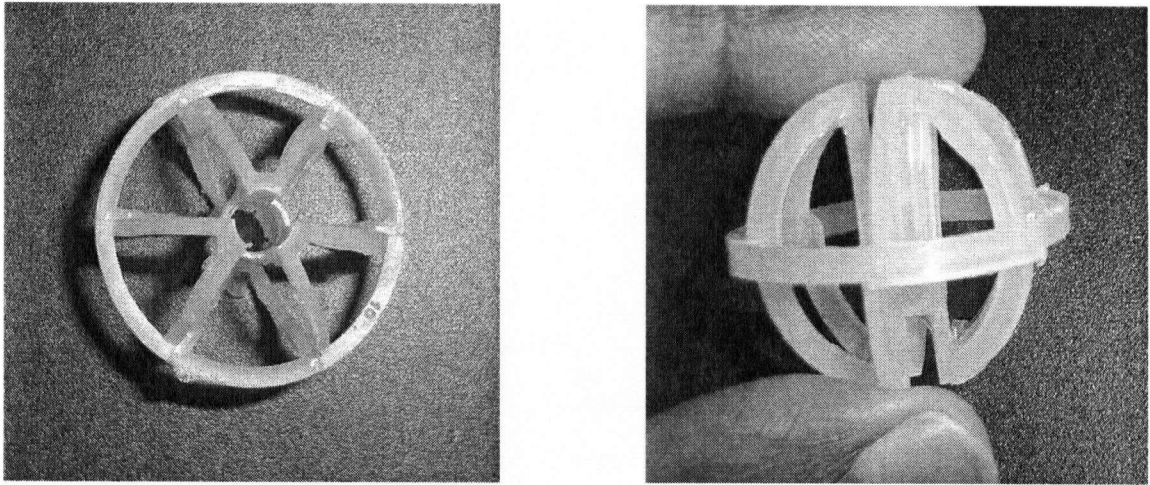


Figure 3.3: Packing material of the compact media stripper

At the beginning of the project, the plastic balls were simply put inside the stripping tower, in-between the liquid distributor and the supporting plate. However, clogging was observed after 3 weeks of running the stripper and as a result, the performance of the stripper decreased. This led to a modification in the arrangement of the packing materials. From that point, the packing materials were hung inside the tower from the liquid distributor system, with the help of strings.

The basic principle of air/ CO_2 stripping is the mass of gas transferred from the liquid phase to the gas phase. This transfer is accomplished by contacting the liquid containing the gas that is to be stripped off with another gas, usually air, which does not contain the gas or contains at a lower amount than the liquid initially (Tchobanoglous, 2003). To achieve a high rate of removal, it is required to provide enough air/water contact time and enough specific surface area. The hollow plastic ball packing media provide both the conditions for the stripper. In addition, a certain degree of turbulence is generated while water passes through the packing media, which, in turn, enhances the stripping rate. The schematic of the stripping tower is illustrated in Figure 3.4.

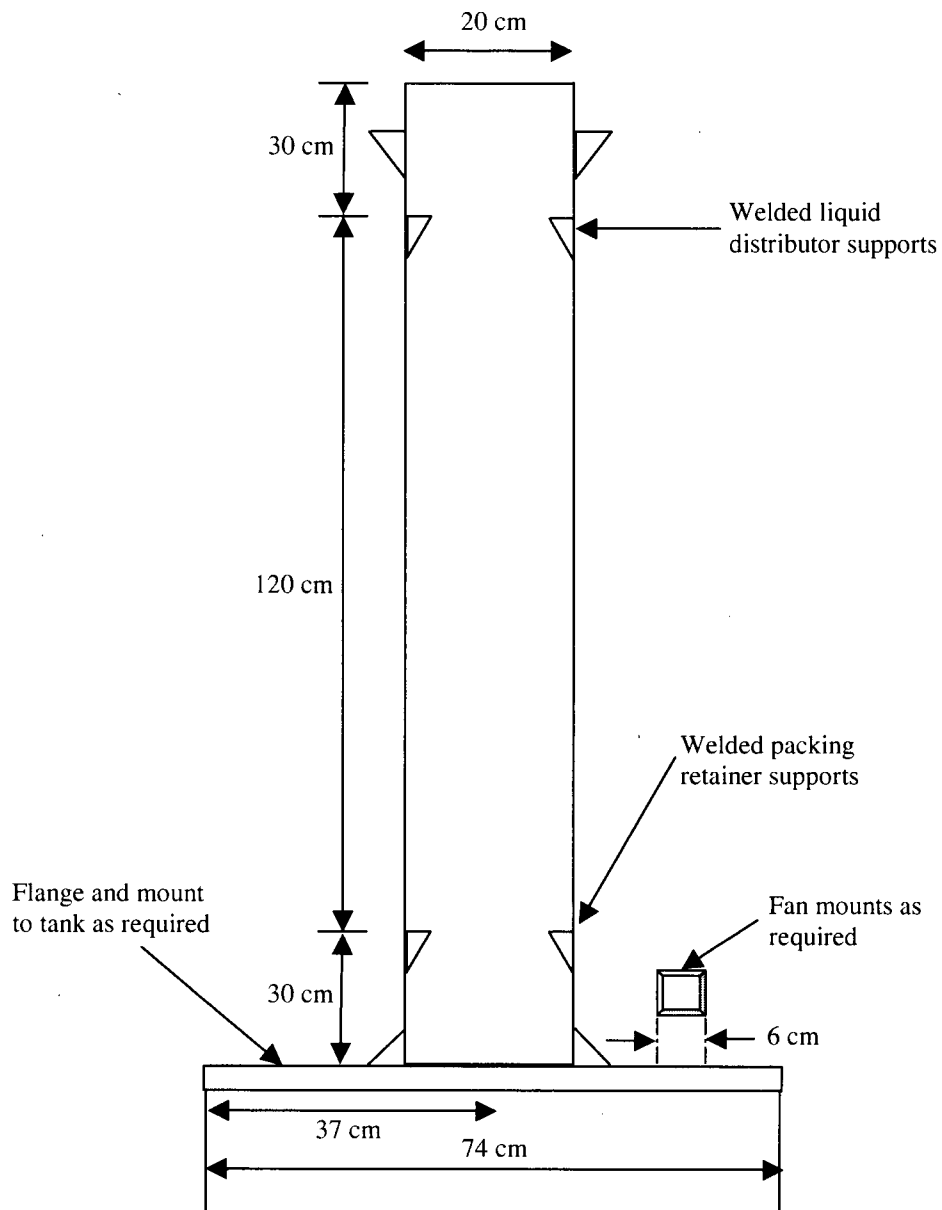


Figure 3.4: Compact media stripper

The stripping tower is mounted on top of the external clarifier. It blocks the top of the clarifier entirely and thereby makes the whole stripper system almost a sealed vessel, except for the 20 cm diameter opening at the top of the stripping tower. This had a negative impact on the stripper's efficiency, which will be discussed in the next chapter.

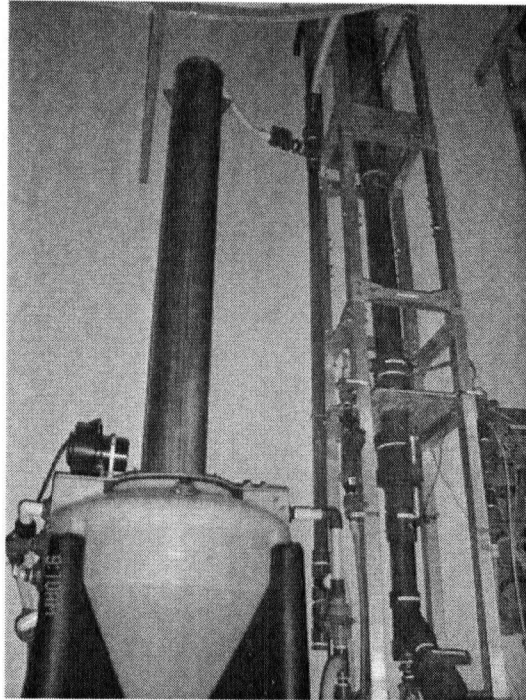


Figure 3.5: Compact media stripper connected to the R#1 at the LIWWTP

3.2.3 *Cascade Stripper*

The second type of stripper used in this project was a cascade stripper. This stripper was connected with the R#2. The cascade stripper was developed by Zhang (2006) as a part of her M.A.Sc. research carried out in the Department of Civil Engineering, UBC. The reasons that led Zhang (2006) to develop an external cascade stripper were as follows:

- This kind of stripper does not have plugging problems
- It is easy to build and operate
- It is easy to clean, which in turn lowers the maintenance costs

The cascade stripper was designed for a maximum hydraulic loading rate of 20 L/min. As mentioned previously, the basic principle of air stripping is gas transfer and hence, the primary guidelines for the design of the cascade stripper were as follows:

➤ To provide enough specific surface area. This was achieved by adjusting the baffle angle of the stripper. For the stripper, the baffle angle was fixed at 10 degrees.

➤ To provide enough air/water contact time. This was achieved by placing reasonable number of baffles. The maximum number of baffles that can be placed in this stripper is 20. For this project, a total of 10 baffles was selected to be placed in the stripper.

The baffle was designed to have an effective surface area of $15 \times 15 \text{ cm}^2$. The detailed design of the baffle is shown in Figure 3.6.

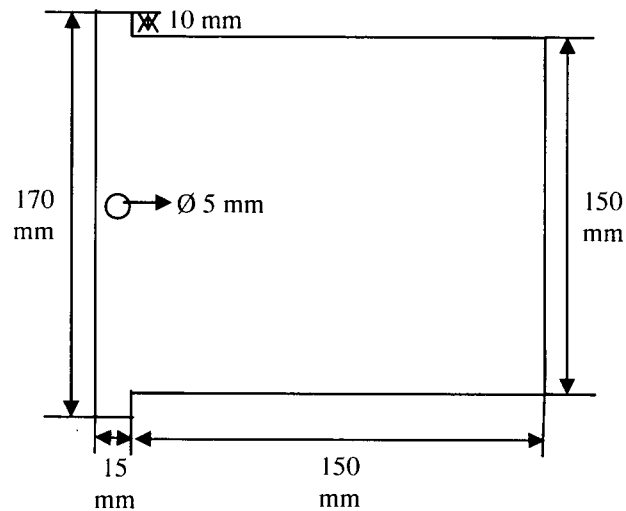


Figure 3.6: Detailed design of the baffle

The cascade stripper was made of plexiglass. The dimensions of the stripper and the front view are shown in Figure 3.7.

Dimensions of the stripper

Total height	:	107 cm
External dimension	:	20 cm × 20 cm
Internal dimension	:	19 cm × 19 cm

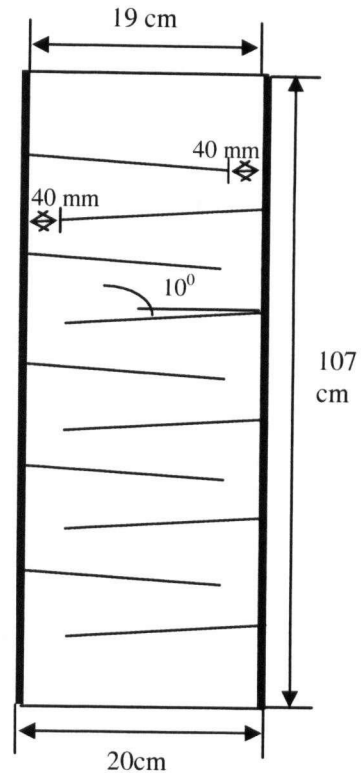


Figure 3.7: Front view of the cascade stripper

The cascade stripper was incorporated into the crystallizer system just before the external clarifier. The stripper substituted almost 1/3 of the reactor downpipe. The flow from the seed hopper first passed through the stripper and then it entered the clarifier.

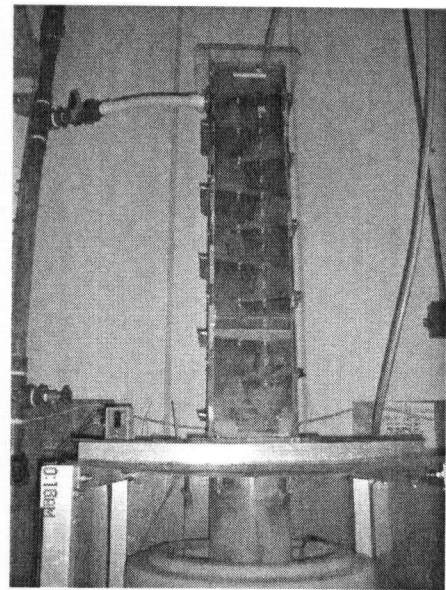
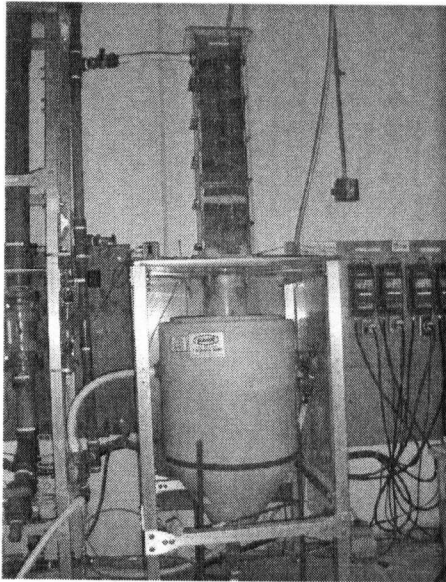


Figure 3.8: Cascade stripper connected to the R#2 at the LIWWTP

In her study, Zhang (2006) tested the cascade stripper without an external air supply at the LIWWTP. However, in this project the stripper was run under both air and without air supply conditions, and its efficiency in saving caustic under different conditions was measured. The air was supplied through an airflow meter from the top of the stripper. The maximum airflow rate provided by the flow meter was 107.5 L/min. While running without external air supply, the top surface of the stripper was kept open. With the introduction of the airflow meter, the top surface of the stripper was covered with a plexiglass lid.

3.3 Experimental Design

The project was originally planned to test one reactor with one of the stripper and use the other reactor as a control, under different conditions and then switch the case and control; then, repeat the same procedure for the second stripper. However, due to time limitation, as well as previous data obtained, this plan was modified and both the reactors were run with strippers. The efficiency of the strippers was determined by comparing the amount of caustic saved by each of them. Before making any comparison between the strippers' efficiency, we had to make certain that the two reactors, with which the strippers were connected, performed identically, so that a direct comparison could be made between the strippers' performance. Therefore, at the beginning of the study, both the reactors were run in parallel without strippers. The reactors were tested under four different conditions. These are tabulated in Table 3.2. The conditions were the same for both the reactors.

Table 3.2: Test condition (for both reactors)

	Stripper	Air	Recycle Ratio	Upflow velocity (cm/min)
Run #1	×	×	6	400
Run #2	√	√	6	400
Run #3	√	×	6	400
Run #4	√	√	9	450

Throughout the course of the study, the operating conditions were selected using the Potts' Crystallizer Model (Potts, 2002). From known values of centrate's magnesium, ammonia and phosphate concentrations, temperature, conductivity, upflow velocity, feeding/recycle rates, and recycle ratio, this model can calculate the amount of MgCl_2 to be added into the reactor to obtain a desired Mg:P ratio and the operating pH, for a desired reactor supersaturation ratio. The model also predicts the effluent concentrations of the three main species of interest (magnesium, ammonia and phosphate). Being a continuation of the previous study conducted at the LIWWTP, the centrate characteristics obtained by Zhang (2006) were used to determine the preliminary operating conditions. However, struvite formation is a highly dynamic process and change in any of the parameters will have a significant affect on the process. Hence, for each run afterwards, the most recent data were used for selecting operating conditions, as the centrate characteristics fluctuated continuously. The characteristics of the centrate during the project period is given in Table 4.1 and shown graphically in Figures 4.1 to 4.3.

Several parameters were monitored and recorded each day. These include grab samples of centrate and effluents for determining Mg^{2+} , NH_4^+ and PO_4^{3-} concentrations; pH, temperature and conductivity of the centrate and effluents; feed and recycle flows were measured daily and adjusted (if required); caustic samples from both tanks were collected and amount of caustic used by the strippers were recorded; a sample from the magnesium feed tank, whenever new feed was prepared; and CO_2 samples from seed hoppers and effluents.

3.4 Sample Collection, Storage And Preservation

Grab samples of centrate and effluents were collected from the centrate tank and effluent flows, respectively. For magnesium feed, the sample was collected from the magnesium storage tank, whenever new feed was prepared. The pH, temperature and conductivity of the samples were recorded on-site, using a Horiba D54 portable meter.

For measurement of ions, the samples were pre-filtered through 1.25 μm glass fibre filter papers and final filtration was done by using 0.45 microns membrane filter papers (Standard Methods). For the NH_4^+ and PO_4^{3-} test, one drop of 5% v/v sulfuric acid was added to 2 mL of filtered sample to lower the pH below 2. Five drops of 50% nitric acid was added to 15 mL of filtered sample to preserve the metal samples. The samples were kept at 4°C until analysis.

Caustic samples were collected from the two caustic tanks each day. The volume of caustic used by the two strippers was recorded daily.

The samples for CO_2 measurement were collected from the seed hopper and effluent flow. Sample bottles were filled to the brim of the bottles and then the lids were closed tightly, to prevent pick-up of CO_2 from the air. The dissolved CO_2 of the samples was measured immediately up on arriving at the Environmental Engineering Laboratory, UBC.

3.5 Analytical Methods

All analyses were carried out in the Environmental Engineering Laboratory, UBC.

3.5.1 Magnesium

Magnesium analysis was performed by the flame atomic absorption spectrophotometry using a Varian Inc. SpectrAA220 Fast Sequential Atomic Absorption Spectrophotometer (AAS). Instrument operational parameter details are given in Appendix A.

The samples were digested with nitric acid before running into the AAS. This was done to reduce dissolve organic matters that interferes with analysis. For digestion, 2 mL 50% nitric acid was added to 10 mL of sample. Digestion was carried out on a hot plate until the sample volume was reduced to approximately 1 mL and the color of the sample got cleared. The sample was then brought back to original 10 mL by adding distilled water. Dilution of the sample was carried out, if needed.

3.5.2 Ortho-phosphate and ammonia

Ortho-phosphate and ammonia samples were analyzed using flow injection analysis on a Lachat QuickChem 8000 instrument. Instrument operational parameters are provided in Appendix A.

3.5.3 Calcium, aluminum, iron and potassium

Calcium, aluminum, iron and potassium analyses were undertaken to get the composition of the harvested struvite pellets. All analyses were done by atomic absorption spectrophotometry, using the same instrument as for the magnesium described earlier. Instrument operational parameter details are given in Appendix A.

3.5.4 Caustic analysis

Caustic solutions were made from NaOH pellets. Caustic samples were collected everyday from the two caustic tanks and were analyzed for the sodium ion present in the sample. The sodium ion present in the sample gave the indication of the amount of hydroxide ion present in the solution, as one mole of sodium ion reacts with one mole of hydroxide ion, to produce one mole of NaOH.

The caustic solution was prepared at the project site, using hot water supplied at the LIWWTP. The reason for using hot water instead of cold water was that the hot water at the LIWWTP contained lesser amount of suspended solids than the cold water. The hot water sample was collected whenever a new solution was made and was analyzed for sodium ion. The sodium concentration, obtained from the water sample, was deducted from the concentration obtained from the caustic solution sample, to obtain the actual amount of sodium ion associated with the hydroxide ion in the caustic solution. This analysis gave the concentration of the caustic solution. The volume of the caustic used by the reactors was recorded daily. From the daily volume usage and the concentration of the solution, the mass of caustic used each day by the reactors was determined.

Sodium analysis was done by the atomic absorption spectrophotometry, using the same instrument as mentioned previously. Instrument operational parameter details are given in Appendix A.

3.5.5 Dissolved CO₂

Concentration of dissolved gaseous CO₂ in liquid solution was measured by the Accumet Gas-Sensing Combination ISE. The electrode was connected with a meter that gave millivolt output. The direct calibration technique was used for measuring purposes, as it requires only one meter reading for measurement.

The calibration curve was prepared using a series of sodium bicarbonate (NaHCO₃) standards namely 10⁻⁴ M, 5×10⁻⁴ M, 10⁻³ M, 5×10⁻³ M, 10⁻² M, 5×10⁻² M. The calibration curve is given in Appendix B. A buffer solution was added to the standard just before measurement in order to convert all carbonates and bicarbonates to carbon dioxide. The concentration of dissolved CO₂ in samples was determined by comparison to the standards. Since it was intended to get only the amount of dissolved CO₂ in liquid solution and not the bicarbonates and carbonates, no buffer solution was added to the samples. Standard and sample volume used for each measurement was 75 mL. Final results were adjusted for temperature effect.

3.6 Pellet Quality Determination

The quality of harvested pellets was determined by checking the composition of the pellets obtained from different runs performed during the study period. Grab samples of the harvested pellets were randomly chosen for analysis. For the test, 0.5 g of struvite was dissolved in 50 mL of 50% nitric acid and then 50 mL of distilled water was added to the sample. Samples were analyzed for magnesium, ammonia, ortho-phosphate, calcium, aluminum, iron and potassium.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Centrate Characteristics

The study was carried out at the Lulu Island Wastewater Treatment Plant (LIWWTP) from 22 August 2006 to 13 December 2006. Centrate samples were collected six days a week. Summary of centrate characteristics during the study period is given in Table 4.1 and shown graphically in Figures 4.1 to 4.3.

Table 4.1: Characteristics of Centrate (22 Aug – 13 Dec, 2006)

	pH	Temp (°C)	Cond (mS)	Mg (mg/L)	PO ₄ -P (mg/L)	NH ₃ -N (mg/L)	Molar Ratio	
							Mg:P	N:P
Minimum	7.2	15.3	4.11	4.11	42.6	500	0.01	18
Maximum	8.1	34	12.48	17.44	100	916	0.39	36
Average	7.6	25	7.01	9.79	77.75	782	0.17	23

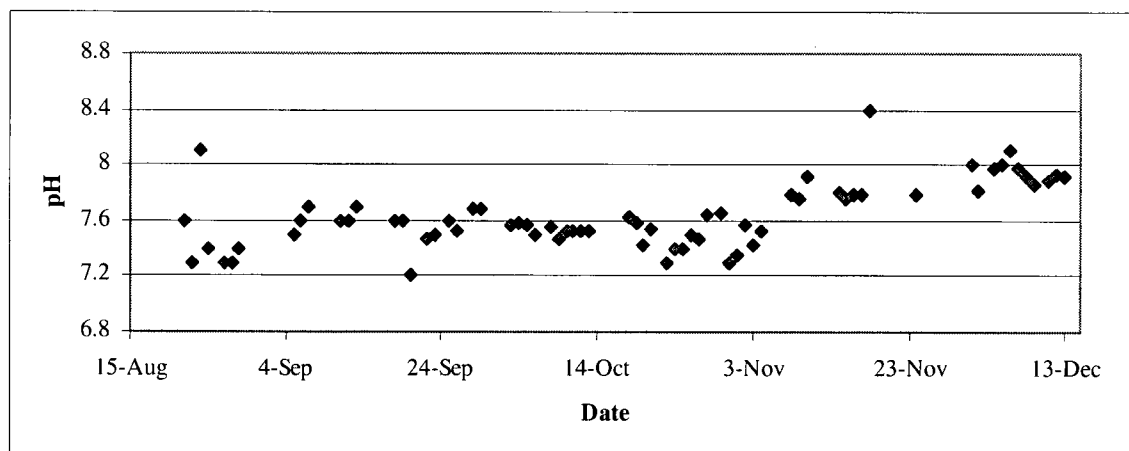


Figure 4.1: pH of centrate (22 Aug – 13 Dec, 2006)

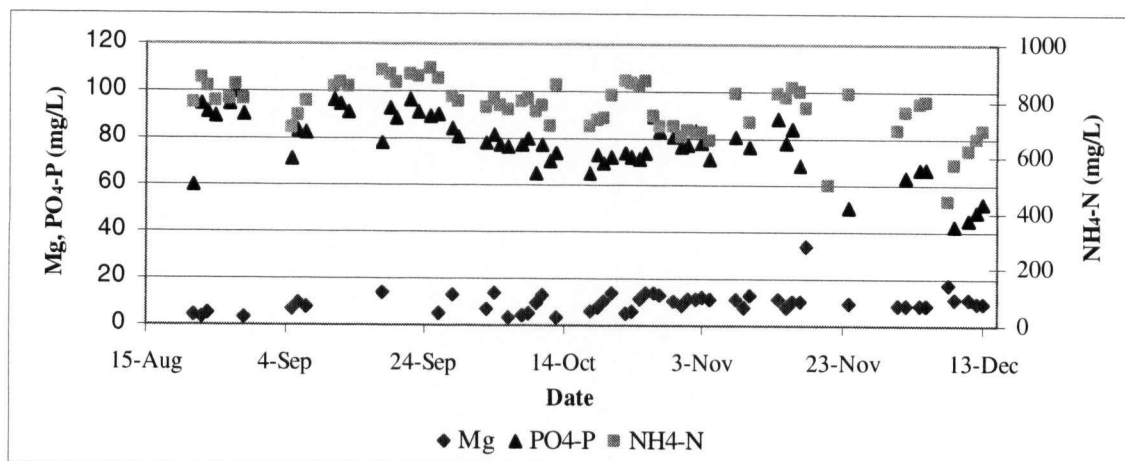


Figure 4.2: Magnesium, phosphate and ammonia concentration in centrate (22 Aug – 13 Dec, 2006)

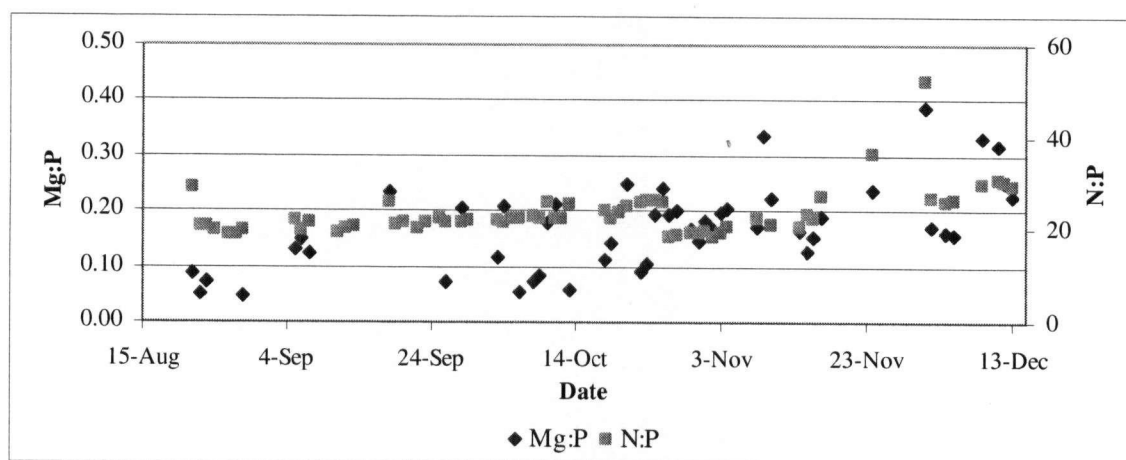


Figure 4.3: Mg:P and N:P ratio of centrate (22 Aug – 13 Dec, 2006)

As expected, the magnesium quantity in the centrate was the limiting factor for struvite crystallization. The molar ratio of Mg:P was always below 1, which is required for struvite precipitation. Hence, magnesium feed was injected into the reactors, to raise the Mg:P ratio.

The average supersaturation ratio (SSR) of centrate during the study period was 0.96. This value was calculated using the Pott's Crystallizer Model (Potts, 2002). The average values given in Table 4.1 were used as inputs in the model. A minimum SSR of 1 is required for struvite crystallization. As mentioned in Chapter 2, the SSR can be raised by increasing

the solution's pH (more preferable option). In this study, this was done by injecting NaOH solution and by using strippers to strip CO₂ from centrate. However, struvite formation inside the centrate inflow pipes was noticed on some occasions. This can be explained by the fact that, during those particular cases, centrate was saturated with respect to struvite constituent ions (i.e. Mg²⁺, NH₄⁺ and PO₄³⁻).

4.2 Performance Of The Reactors (Without Stripper)

The two struvite crystallizers used in this project were identical in size and shape. Both were seeded with 1L of struvite at the beginning of the study. It was assumed that both would perform in almost an identical manner. Reactors were run from 25 September to 6 October, without strippers, to check whether the above stated assumption was correct. The operating conditions during this run are given in Table 4.2.

Table 4.2: Operating conditions (25 Sep-6 Oct, 2006)

Total feed	:	2.61 L/min
Centrate flow	:	2.53 L/min
Mg feed flow	:	80 mL/min
Recycle ratio	:	6
Recycle flow	:	15.63 L/min
Total flow	:	18.24 L/min
pH	:	8.1
Harvest zone upflow velocity	:	400 cm/min

In this run, the removal rates achieved for magnesium, ammonia and phosphorus were 69%, 88% and 7% respectively in the R#1; and 66%, 90% and 10% respectively, in the R#2. The difference in removal rates for magnesium and phosphorus were within 4%. For ammonia, except for one day, the difference was around 13%, although the absolute removals, for both, were relatively low. The results are shown graphically in Figures 4.4 to 4.6.

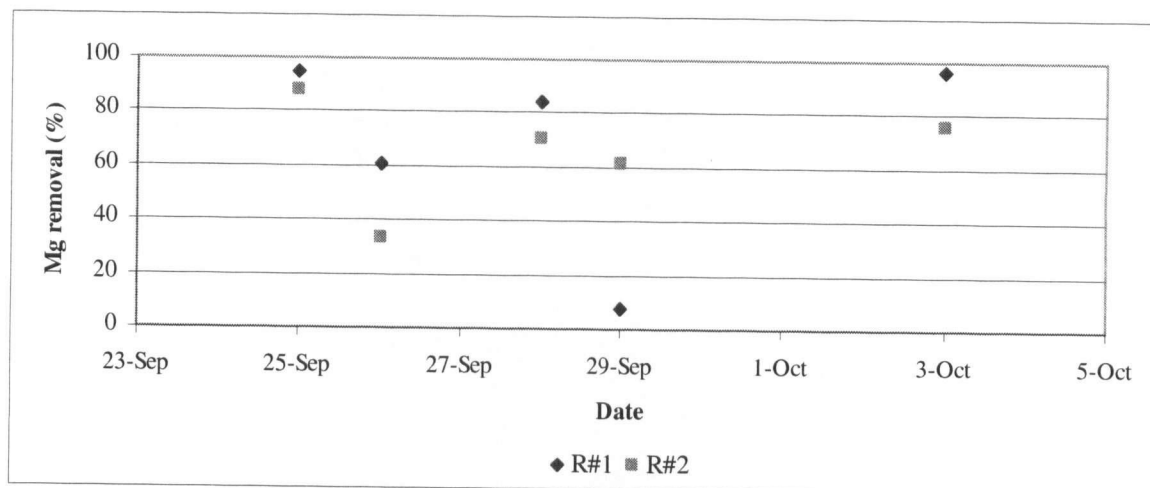


Figure 4.4: Magnesium removal rates in R#1 and R#2 (25 Sep-6 Oct, 2006)

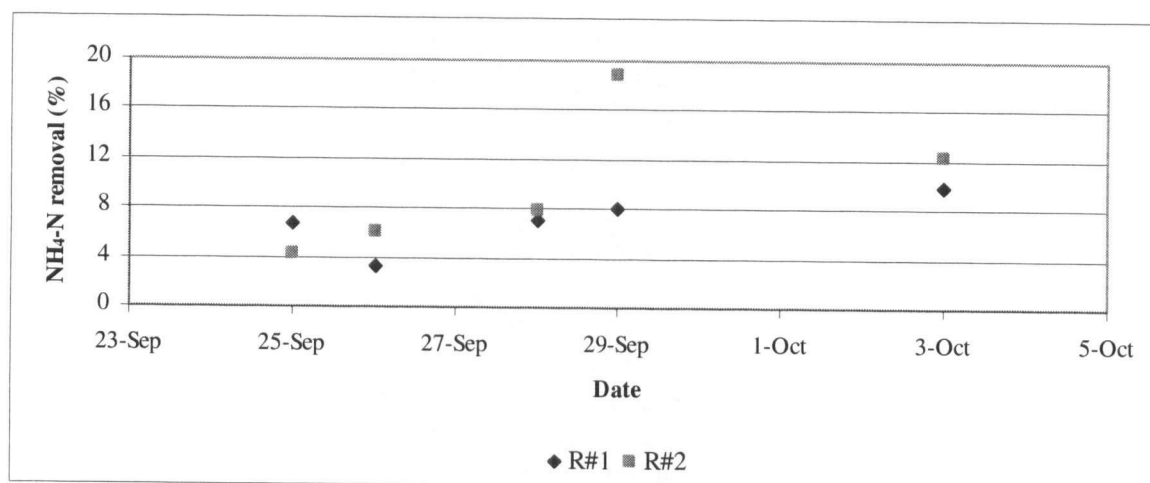


Figure 4.5: Ammonia removal rates in R#1 and R#2 (25 Sep-6 Oct, 2006)

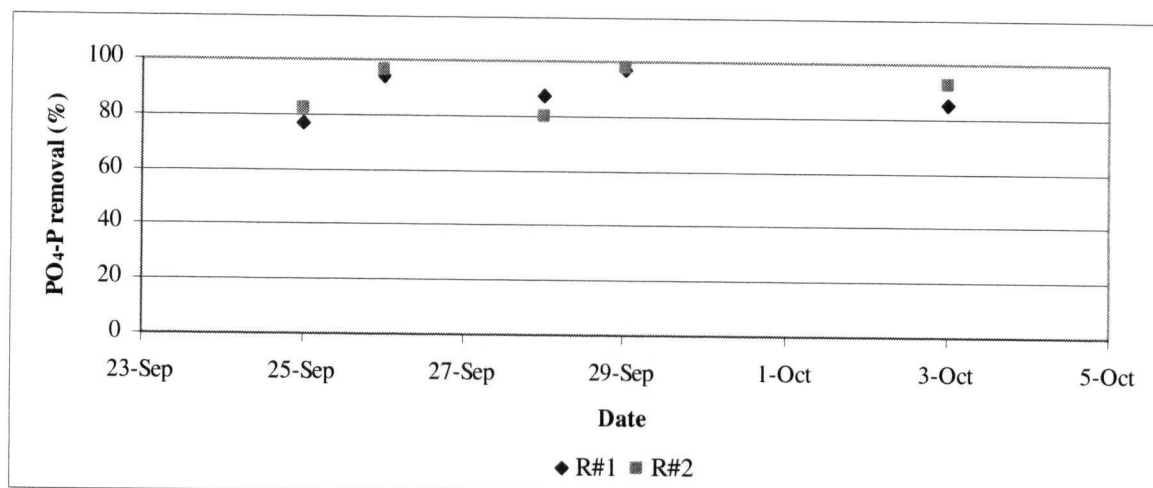


Figure 4.6: Phosphorus removal rates in R#1 and R#2 (25 Sep-6 Oct, 2006)

Except for one day, more caustic had been used by the R#1 than the R#2, during this period. The average difference of caustic used by the two reactors was 91%. On the other hand, the average pH increase was 0.65 for both reactors. The R#1 needed an average 2.35 kg/d of caustic to raise the pH value, while an average 1.23 kg/d of caustic was used by the R#2, to achieve the same amount of pH increase. During this period, both reactors were removing almost the same amount of molar phosphorus from the inflow, while the R#1 was using around 91% more molar caustic than the R#2. The daily caustic use profiles are shown in Figures 4.7 to 4.9.

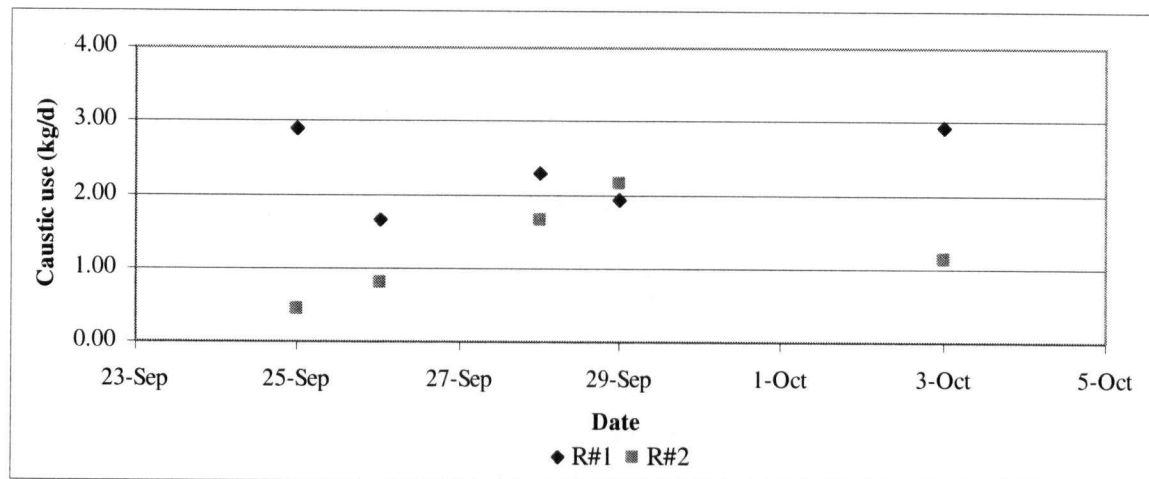


Figure 4.7: Daily caustic use in R#1 and R#2 (25 Sep-6 Oct, 2006)

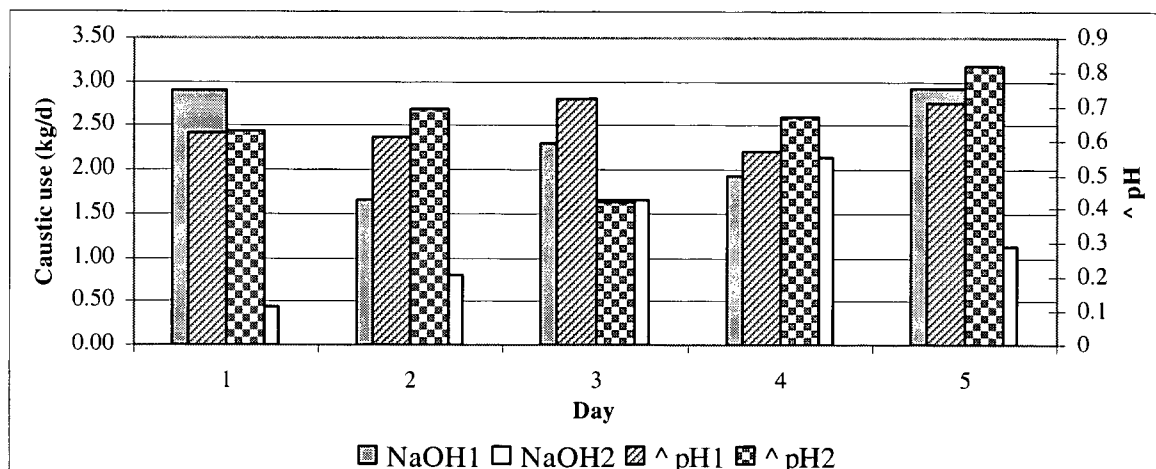


Figure 4.8: Caustic use and pH increase in R#1 and R#2 (25 Sep-6 Oct, 2006)

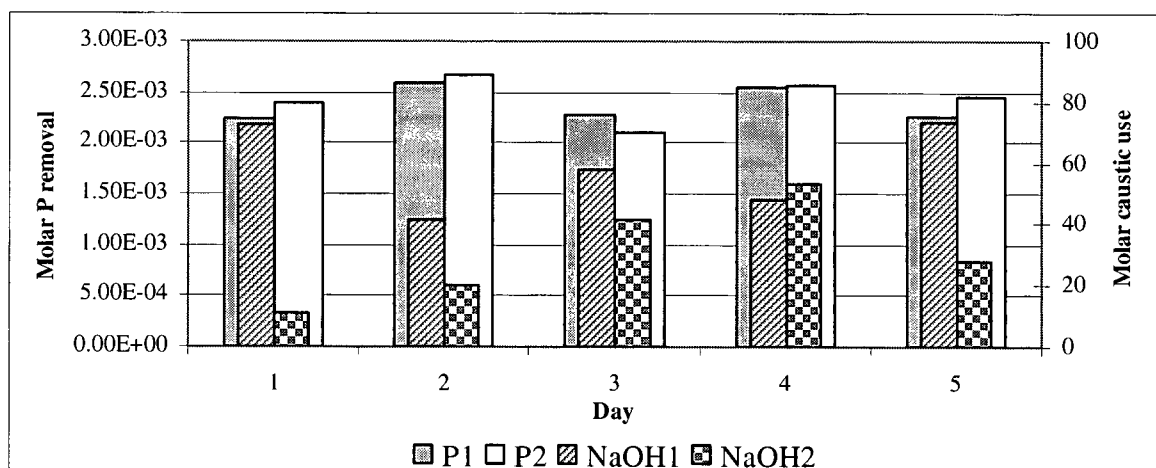


Figure 4.9: Molar P removal and caustic use in R#1 and R#2 (25 Sep-6 Oct, 2006)

It can be concluded from this phase that both reactors performed almost identically, in the removal of magnesium, ammonia and phosphorus from the centrate. The major difference was observed in the case of caustic use, where the R#1 was consistently using more caustic than the R#2 to increase the pH to the same level and remove almost the same amount of phosphorus. This difference might arise due to several reasons.

Firstly, it was very hard to keep the centrate and recycle flows constant to the set point. The flows fluctuated everyday and the amount of fluctuation varied in-between the two reactors. Change in flows will have an effect on the supersaturation ratio, thereby effecting

the struvite production rate; this, in turn, will have an impact on caustic use. In order to minimize this effect, data having more than $\pm 15\%$ fluctuation in flows from the set point had been discarded, for analytical purposes.

Secondly, both strippers were already connected to the respective reactors (compact media stripper with the R#1 and cascade stripper with the R#2) during the whole test period. Flow was going directly from the seed hopper to the clarifier, by bypassing the strippers. As mentioned previously, the compact media stripper was installed directly over the clarifier #1, thereby totally blocking the top of the clarifier. On the other hand, the top of the clarifier #2 was open as the cascade stripper was installed about 1 ft above the top surface; as a result, stripped off CO_2 could escape through this opening. As the compact media stripper sealed the R#1 system, stripped off CO_2 eventually dissolved back into the liquid stream. As a result of this, recycle flow from the clarifier #1 carried a solution saturated with CO_2 to the R#1. The removal rates of CO_2 during this period by the two reactors support the above stated fact. Only 9% CO_2 removal was observed in the R#1; on the other hand, a 16% CO_2 removal rate was achieved by the R#2. The difference between the CO_2 removal rates also had an impact on caustic use by the two reactors.

It would be better if the experiment could be re-run without placing strippers above clarifiers i.e. keeping top surface of both clarifiers open to the environment. However, due to a shortage of on-site research time, the experiment could not be repeated.

Summary of the results

- Both reactors basically performed identically, as assumed at the beginning, and hence, performances obtained from the two strippers would be directly comparable to each other.

- The only major difference observed was in case of daily caustic usage which was basically related to the way the compact media stripper was designed (i.e. sealing the crystallizer system). This was one of the major disadvantages of the compact media stripper design.

4.3 Performance Of The Strippers

The performance of the strippers was tested under three different conditions. The Pott's Crystallizer Model (Potts, 2002) was used to set the preliminary operating conditions. All parameters, other than the recycle ratio, air flow and upflow velocity, remained constant during each testing period.

4.3.1 Run No. 1

This first, full test was carried out from 13 to 18 November. In this case, the strippers were run with air. The compact media stripper had a built-in fan mounted at the top of the clarifier. The fan provided a fixed airflow for ventilation. On the other hand, the airflow rate could be varied in the cascade stripper, with the help of the airflow meter. Due to shortage of time at the site (Christmas shut down at the plant), it was decided to run the cascade stripper with the maximum airflow provided by the flow meter, which was 107.5 L/min. The operating conditions for this run are given in Table 4.3.

Table 4.3: Operating conditions for Run No. 1 (13-18 Nov, 2006)

Parameter	Compact media stripper	Cascade stripper
Total feed	2.61 L/min	2.61 L/min
Centrate flow	2.51 L/min	2.51 L/min
Mg feed flow	100 mL/min	100 mL/min
Recycle ratio	6	6
Recycle flow	15.63 L/min	15.63 L/min
Total flow	18.24 L/min	18.24 L/min
pH	8.1	8.1
Harvest zone upflow velocity	400 cm/min	400 cm/min
Air	Yes	107.5 L/min

Nutrient removal

During this test period, 90% phosphorus removal was achieved by both reactors. The average removal rate of ammonia was 6% and 5% in the R#1 and R#2, respectively. Magnesium removal rate was almost 74% in the R#1. In the R#2, except for the last day, this rate was around 75%. On that day, only 22% of Mg removal was achieved. The results are shown in Figures 4.10 to 4.12.

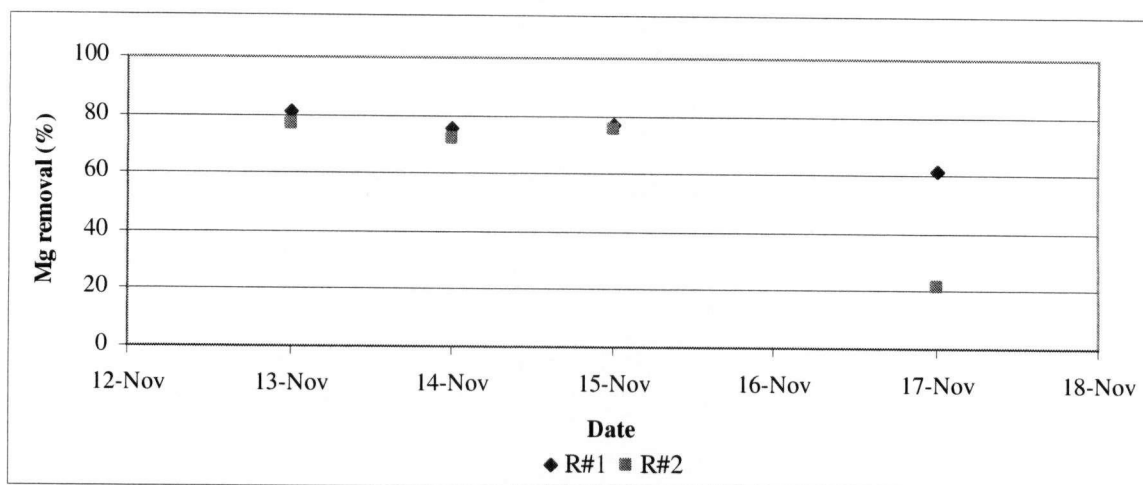


Figure 4.10: Magnesium removal rates in R#1 and R#2 (13-18 Nov, 2006)

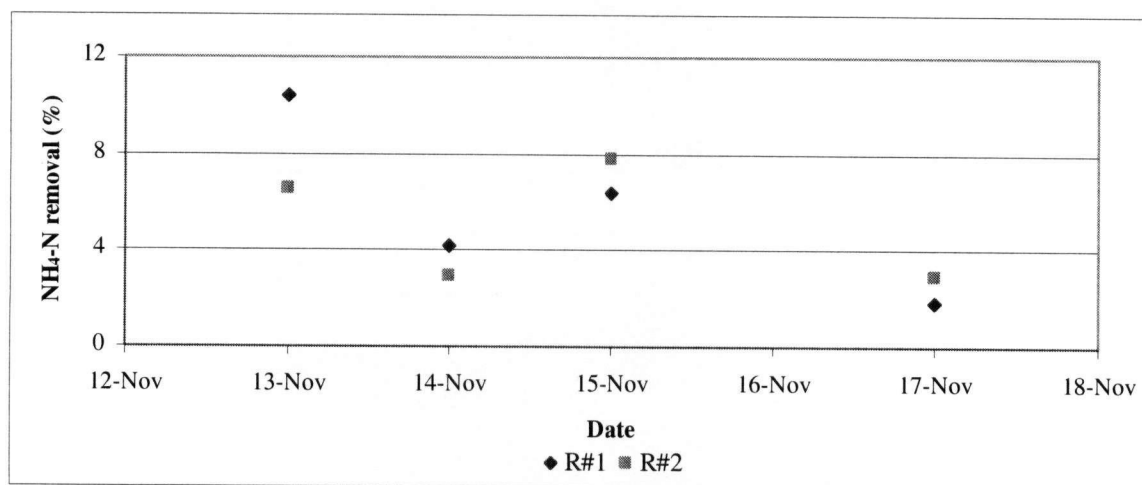


Figure 4.11: Ammonia removal rates in R#1 and R#2 (13-18 Nov, 2006)

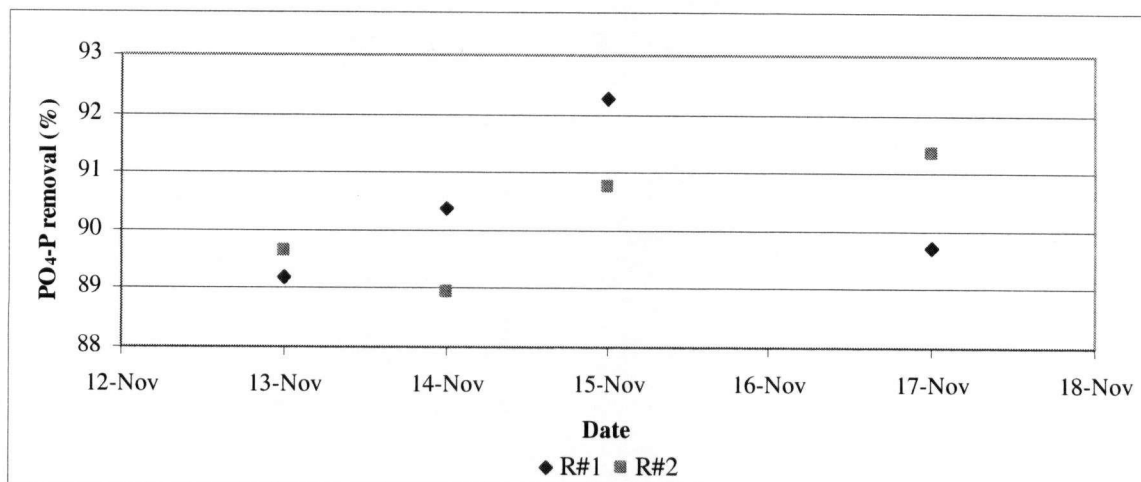


Figure 4.12: Phosphorus removal rates in R#1 and R#2 (13-18 Nov, 2006)

Caustic use

Throughout the test period, the amount of caustic used by the R#2 was consistently lower than that was used by the R#1. On an average, the R#2 was using 0.84 kg/d of caustic, whereas in case of the R#1, this amount was 1.41 kg/d. It should be noted that almost the same amount of molar phosphorus had been removed by both the reactors during this period. The results are shown graphically in Figures 4.13 and 4.14.

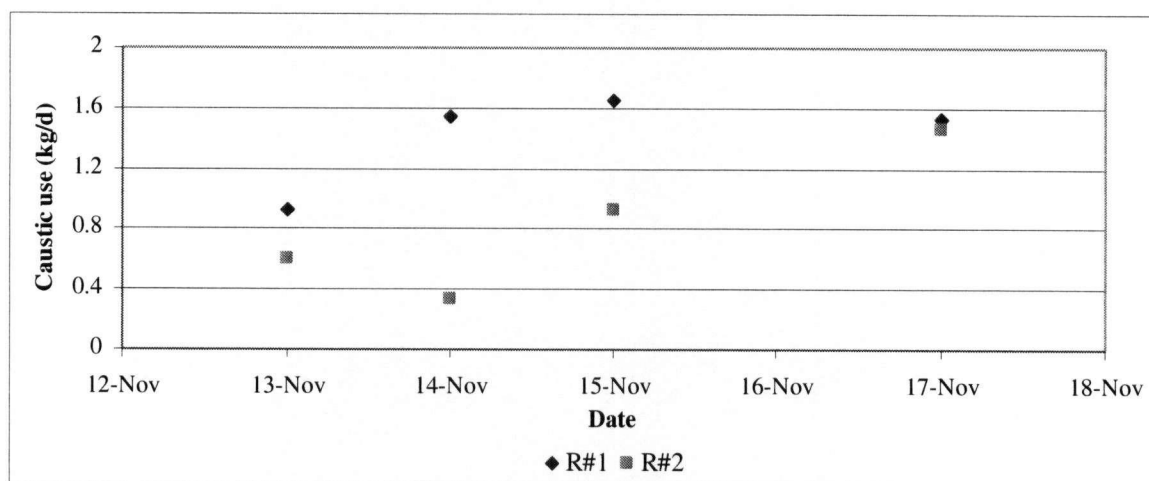


Figure 4.13: Daily caustic use in R#1 and R#2 (13-18 Nov, 2006)

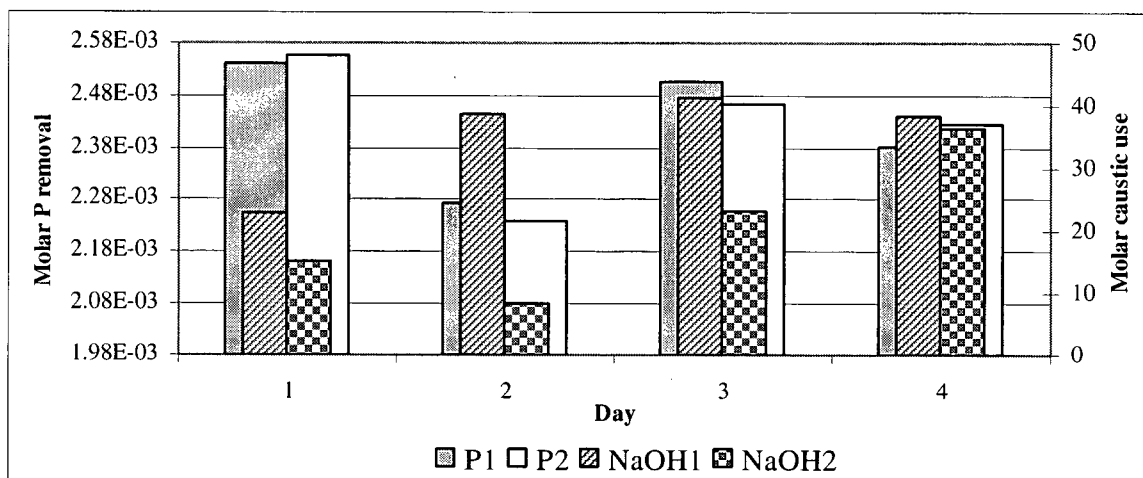


Figure 4.14: Molar P removal and caustic use in R#1 and R#2 (13-18 Nov, 2006)

Comparing these results with the results obtained by running the reactors without strippers, it can be seen that, by introducing the cascade stripper into the system, a 46% savings in caustic use was achieved. On the other hand, the compact media stripper failed to save any caustic; in fact, around 15% extra caustic was used daily by the R#1 during this period. As mentioned earlier, the compact media stripper blocked the top of the clarifier #1 and turned the whole crystallizer system into a sealed vessel. The stripped off CO_2 had very little open space to escape from the system. To make things worse, throughout the study period, it was found that the compact media stripper was prone to clogging. These two factors raised the amount of daily caustic used by the stripper.

It should be mentioned that the results obtained by the R#2 system, without a stripper, are being used all the time for comparison. It was already discussed in Section 4.2 that, during that run, the compact media stripper was placed on top of the external clarifier permanently which, in turn, gave a biased result regarding caustic use. Except for caustic use, other results obtained (i.e. nutrient removal) were almost identical for both reactors, confirming the assumption of the two reactors being identical in performance. Based on this fact, it can be said that the R#1 probably would have used the same amount of caustic as the R#2, if the top of the clarifier was not blocked by the compact media stripper. Hence, the amount of caustic (average 1.23 kg/d) used by the R#2 (when the reactors were tested without the strippers) is used for comparison purposes.

Carbon dioxide stripping

Three days of CO₂ stripping data were available for this run. The cascade stripper proved to be more effective in stripping CO₂, than the compact media stripper. Throughout this run, the cascade stripper removed more CO₂ from the system, thus lowering the daily requirement of caustic. The overall CO₂ removal rate for the R#1 was 11%, and was 20% for the R#2. The results are shown graphically in Figure 4.15.

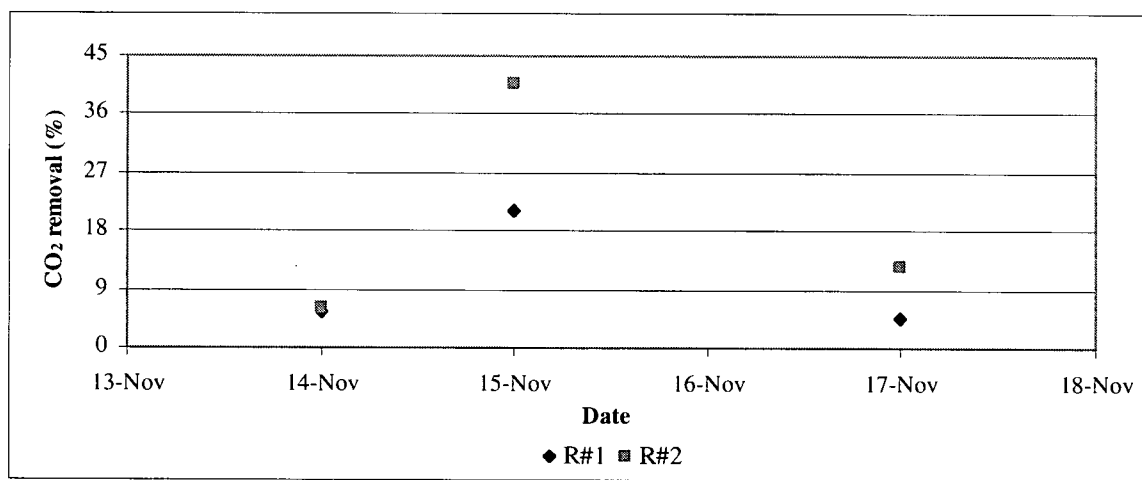


Figure 4.15: CO₂ removal in R#1 and R#2 (13-18 Nov, 2006)

Ammonia stripping

Theoretically, the formation of struvite requires a molar ratio of Mg:N:P of 1:1:1. During some days, the molar removal of ammonia exceeded that of magnesium and phosphorus. The removal of this extra amount of ammonia from the system might be achieved through stripping. Figure 4.16 shows this extra amount of molar removal of ammonia by the two reactors and Figure 4.17 shows the percent removal of ammonia through stripping.

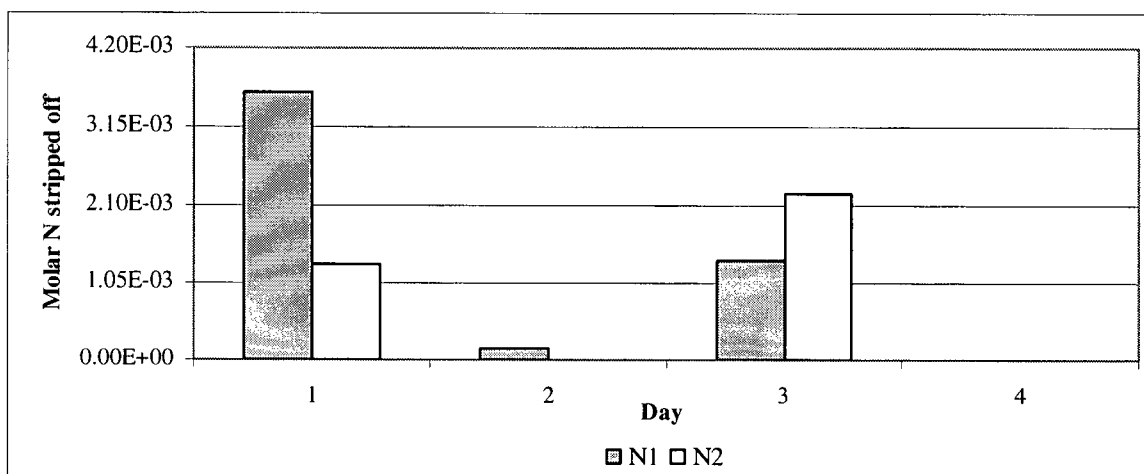


Figure 4.16: Ammonia stripping in R#1 and R#2 (13-18 Nov, 2006)

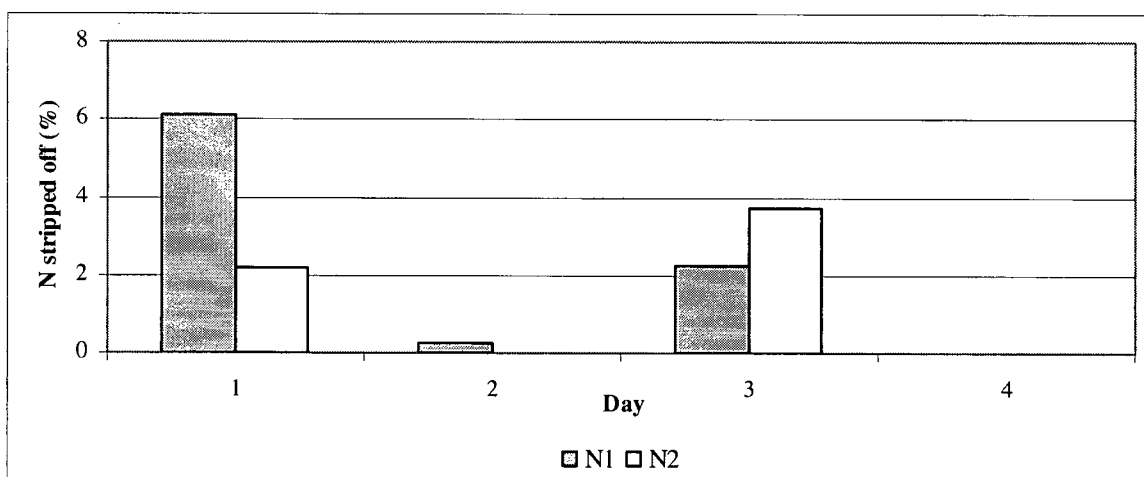


Figure 4.17: Ammonia stripping in R#1 and R#2 (13-18 Nov, 2006)

The compact media stripper seemed to be slightly better in the case of ammonia stripping, than the cascade stripper. During this period, an extra 2% ammonia was removed by the R#1, while the R#2 removed 1% of extra ammonia. Statistically, this difference is probably not significant. However, the higher amount of caustic usage by the R#1 could be related to the removal of ammonia, since the pH of the system would decrease.

Summary of results

- 90% phosphorus removal was obtained by both reactors.
- The cascade stripper (R#2) consistently used lesser amount of caustic than the compact media stripper (R#1). The average difference between the usage rates was around 68%.
- 46% of caustic was saved by the cascade stripper. On the other hand, the compact media stripper failed to save any caustic; rather it used an extra 13% caustic.
- A higher amount of CO₂ was stripped by the cascade stripper. The compact media stripper seemed to work better in the case of ammonia removal. Both of these factors played a role in case of the caustic use pattern by the two reactors.

4.3.2 Run No. 2

This test was conducted from 20 November to 1 December. In this case, the strippers were run without an external air supply. The other operating parameters remained the same as in the first run. The operating conditions for Run No. 2 are given in Table 4.4.

Table 4.4: Operating conditions for Run No. 2 (20 Nov -1 Dec, 2006)

Parameter	Compact media stripper	Cascade stripper
Total feed	2.61 L/min	2.61 L/min
Centrate flow	2.51 L/min	2.51 L/min
Mg feed flow	100 mL/min	100 mL/min
Recycle ratio	6	6
Recycle flow	15.63 L/min	15.63 L/min
Total flow	18.24 L/min	18.24 L/min
pH	8.1	8.1
Harvest zone upflow velocity	400 cm/min	400 cm/min
Air	No	No

Nutrient removal

Both reactors were able to remove around 90% of phosphorus during this period. However, significant differences were noticed in the case of both magnesium and ammonia removal rates. Compared to the previous run, the magnesium removal rates dropped from 74% to 46% in case of the R#1, while for the R#2 this rate dropped from 62% to 39%. On the other hand, the ammonia removal rate increased in both reactors. The ammonia removal rate was around 18% in the R#1 and around 15% in the R#2, compared to 6% and 5%, respectively. All of these results are shown in Figures 4.18 to 4.20.

Due to some operational problems, the reactors were set to recycle mode from 24 to 29 November and restarted on 30 November 2006. A milky-white, kind of material was found at the bottom of the (both) clarifiers. It was suspected this material to be some form of residual magnesium, although no formal analysis was done on this material. The clarifiers were cleared before restarting the reactors. Six days of continuous recycle mode might have some affect on the performance of the crystallizers.

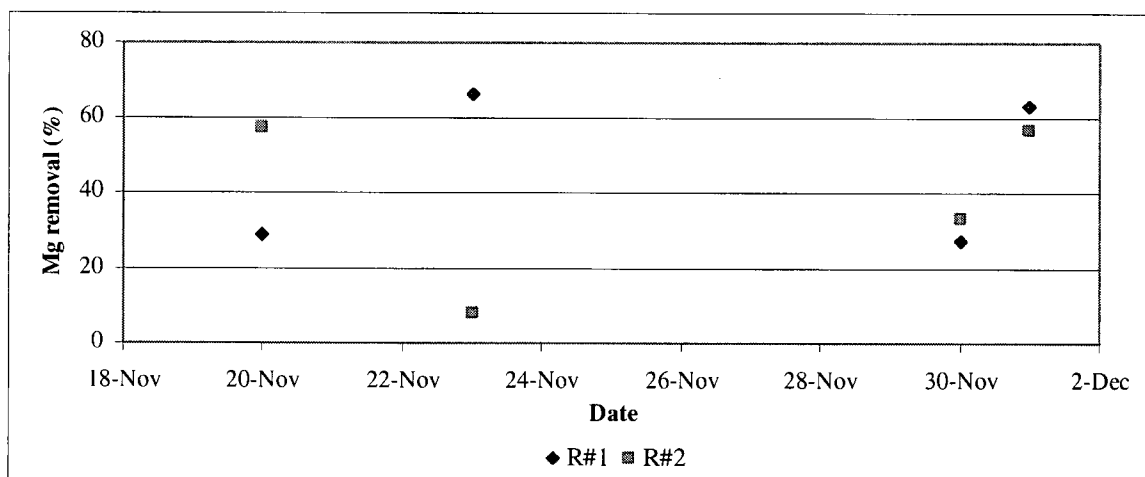


Figure 4.18: Magnesium removal rates in R#1 and R#2 (20 Nov -1 Dec, 2006)

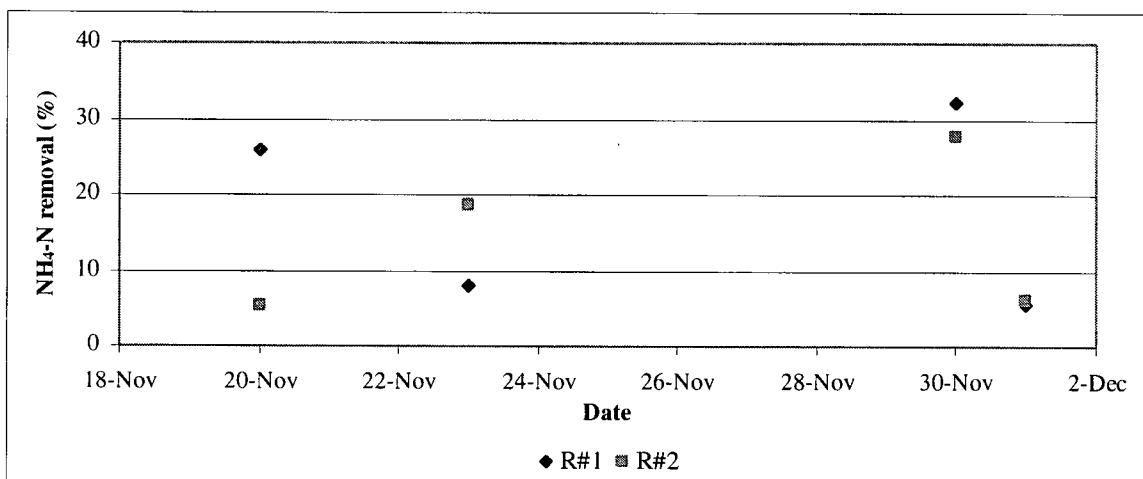


Figure 4.19: Ammonia removal rates in R#1 and R#2 (20 Nov -1 Dec, 2006)

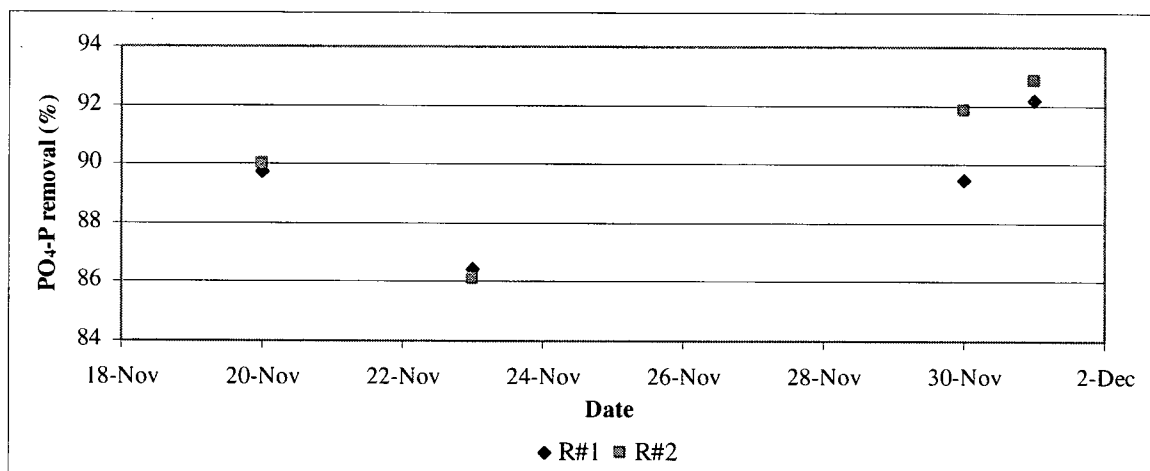


Figure 4.20: Phosphorus removal rates in R#1 and R#2 (20 Nov -1 Dec, 2006)

Caustic use

As expected, without an external air supply, the caustic use rate increased in both reactors. Again, the cascade media stripper used lesser amounts of caustic than the compact media stripper. The average difference of daily use rate between these two strippers was around 66%. The molar caustic used per mole of phosphorus removed showed the same trend as previous runs. The results are shown in Figures 4.21 and 4.22.

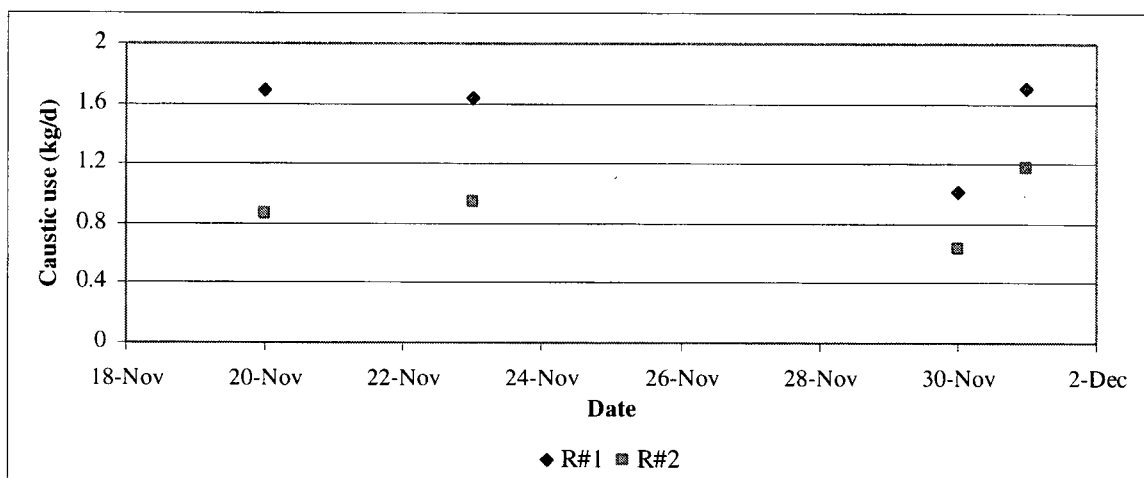


Figure 4.21: Daily caustic use in R#1 and R#2 (20 Nov -1 Dec, 2006)

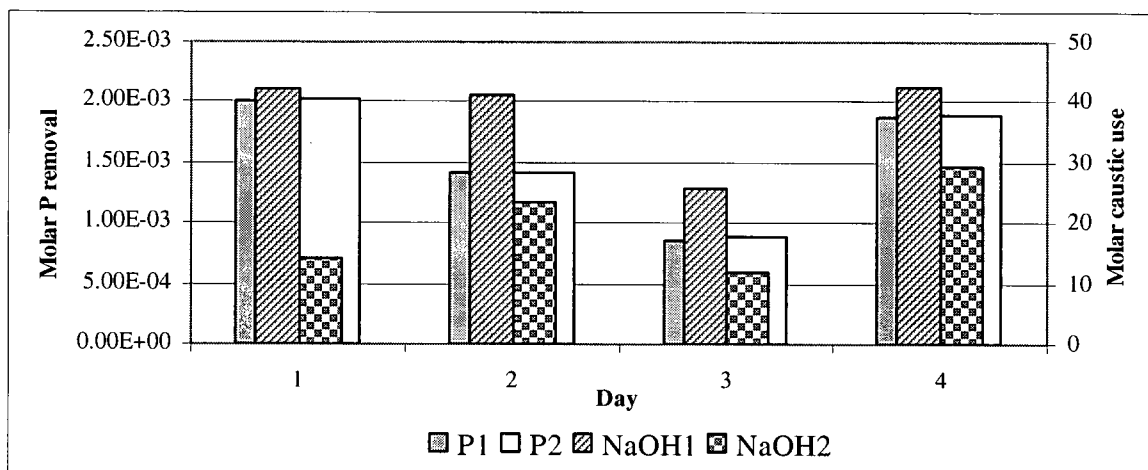


Figure 4.22: Molar P removal and caustic use in R#1 and R#2 (20 Nov -1 Dec, 2006)

During this period, the cascade media stripper saved an average 35% of caustic chemical used, compared to 46% in the previous run. On the other hand, the compact media stripper used an extra 23% of caustic, on a daily basis.

Carbon dioxide stripping

Without an external air supply, the CO₂ removal rate was expected to decrease. Surprisingly, a slightly higher amount of CO₂ removal was achieved by the compact media stripper. The average CO₂ removal rate for the R#1 was around 14% during this test, whereas this amount was only about 11% in the previous run with the air supply. On the other hand,

the CO₂ removal rate for the R#2 decreased slightly, from 20% to 17%. The CO₂ removal rate during this run is shown in Figure 4.23.

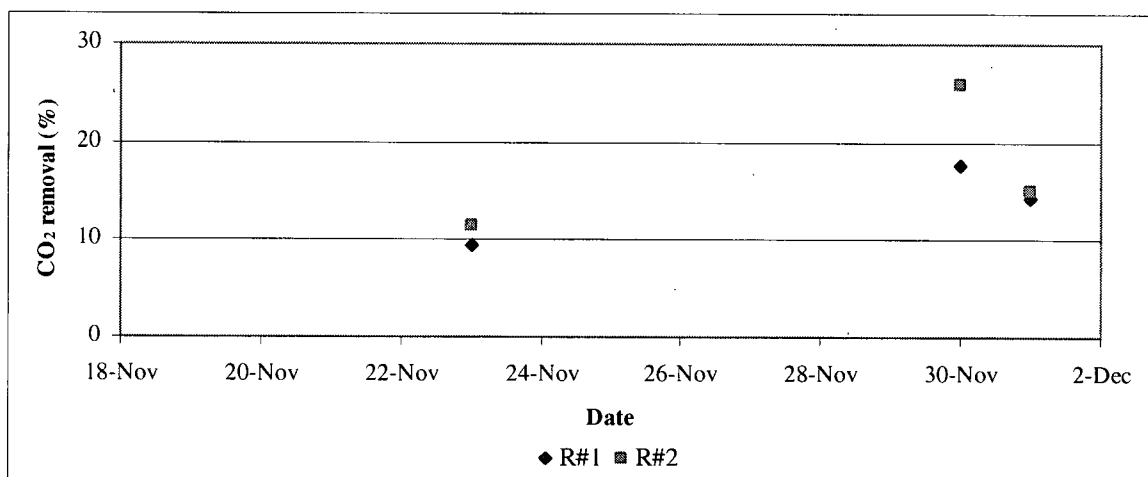


Figure 4.23: CO₂ removal in R#1 and R#2 (20 Nov -1 Dec, 2006)

As already mentioned, the clarifiers were cleared before restarting the reactors. While cleaning the clarifier #1, water was passed through the stripping tower of the compact media stripper and this seemed to clear the clogging of the packing media. As a result, the stripped off CO₂ more easily escaped from the system than in the previous run. The result shown in Figure 4.23 illustrates this point; on 23 November, the removal rate was less than 10%, whereas the highest removal (18%) was achieved on 30 November.

Ammonia stripping

The ammonia removal rate increased significantly for both reactors during this run. The average amount of ammonia being removed/stripped off, after fulfilling the theoretical requirement of struvite formation, was 9% and 7% for the R#1 and R#2, respectively. In the previous run, with an external air supply, this amount was 2% and 1% for the R#1 and R#2, respectively. The highest amount of stripping was achieved on day 3, which corresponds to 30 November. The results are shown in Figures 4.24 and 4.25. These results were quite unexpected, since without an external air supply, ammonia stripping was likely to decrease. Further study is needed to explain this result.

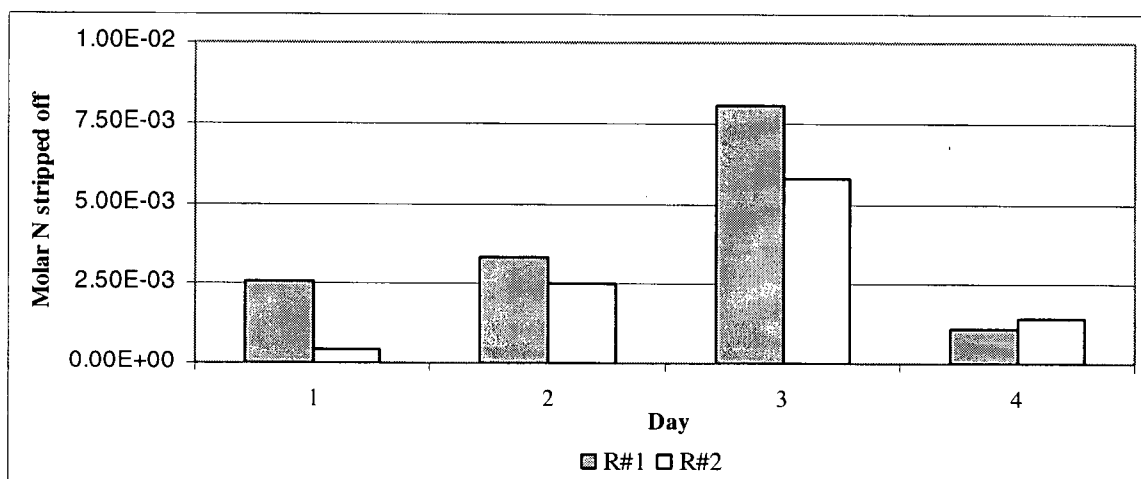


Figure 4.24: Ammonia stripping in R#1 and R#2 (20 Nov -1 Dec, 2006)

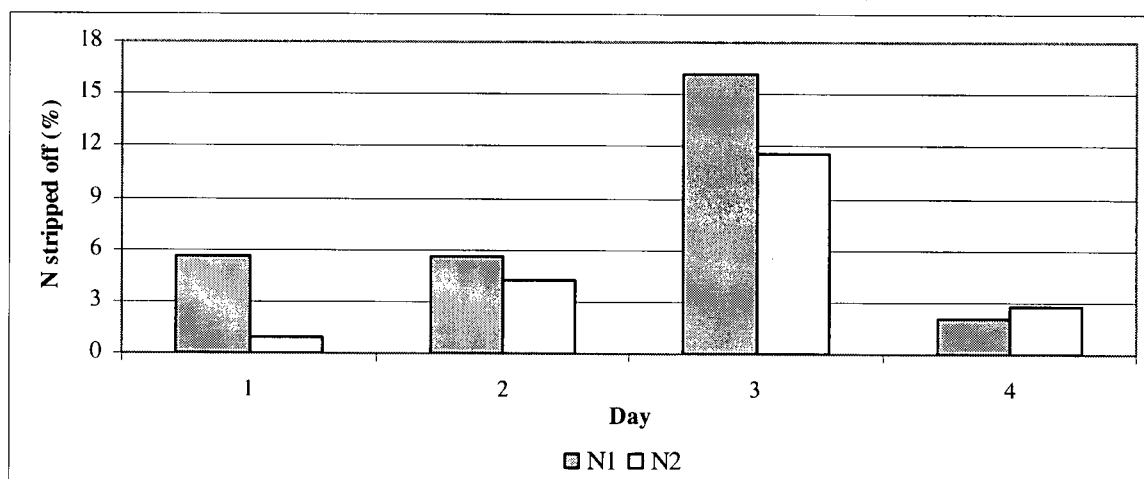


Figure 4.25: Ammonia stripping in R#1 and R#2 (20 Nov -1 Dec, 2006)

Summary of results

- The average phosphorus removal rate was 90% in both reactors.
- The reactors were run in a recycle mode from 23 to 30 November, which might have affected magnesium and ammonia removal rates.
- The strippers performed less effectively without an external air supply. During this time, 35% caustic was saved by the cascade stripper, while the compact media stripper used an extra 25% caustic.

➤ The carbon dioxide stripping rate was better in the compact media stripper than the cascade stripper. The stripping tower was cleaned on 30 November, possibly contributing to better CO₂ stripping by the compact media stripper.

➤ A higher ammonia removal/stripping rate was achieved by both the reactors than the previous run, where external air was supplied. This surprising result requires further investigation and explanation.

4.3.3 Run No. 3

This run was carried out from 4 to 12 December. In this test, the recycle ratio and the upflow velocity were set to 9 and 450 cm/min, respectively. The external air supply was resumed. The operating conditions for this run are given in Table 4.5.

Table 4.5: Operating conditions for Run No. 3 (4-12 Dec, 2006)

Parameter	Compact media stripper	Cascade stripper
Total feed	2.02 L/min	2.02 L/min
Centrate flow	1.94L/min	1.94 L/min
Mg feed flow	80 mL/min	80 mL/min
Recycle ratio	9	9
Recycle flow	17.98 L/min	17.98 L/min
Total flow	20 L/min	20 L/min
pH	8.1	8.1
Harvest zone upflow velocity	450 cm/min	450 cm/min
Air	Yes	107.5 L/min

Nutrient removal

In this run, the R#1 was able to remove an average 89% of phosphorus. The R#2 system was slightly better in removing phosphorus, achieving an average 92% during this test period. Both reactors showed improvement in magnesium removal, compared to the

previous run. The magnesium removal rate for the R#1 averaged 55% and for the R#2 unit, it was 42%. However, the ammonia removal rate decreased in both the reactors; in this run, the ammonia removal rate averaged 9% and 8% in the R#1 and R#2, respectively, whereas it was 18% and 15% for R#1 and R#2, respectively, in the previous run without an external air supply. The results are shown in Figures 4.26 to 4.28.

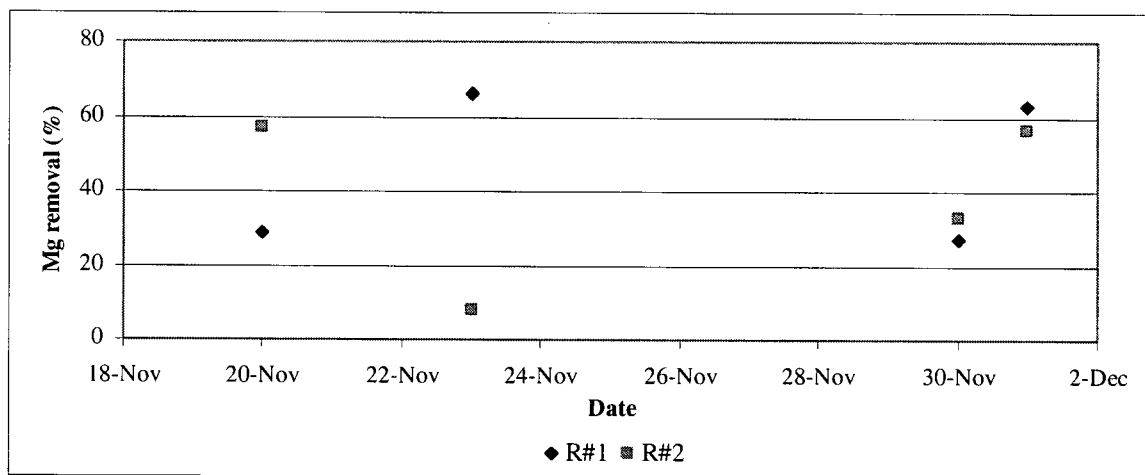


Figure 4.26: Magnesium removal rates in R#1 and R#2 (4-12 Dec, 2006)

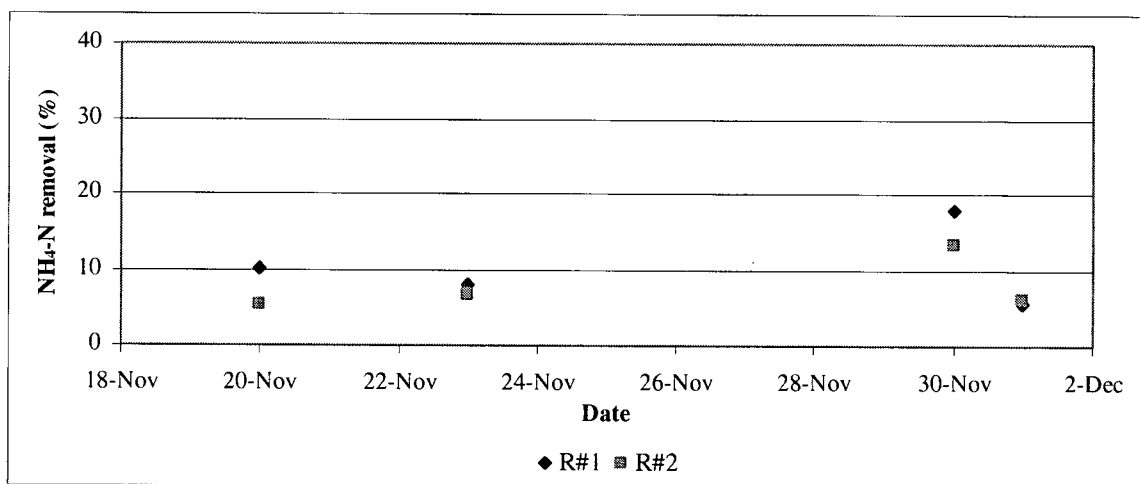


Figure 4.27: Ammonia removal rates in R#1 and R#2 (4-12 Dec, 2006)

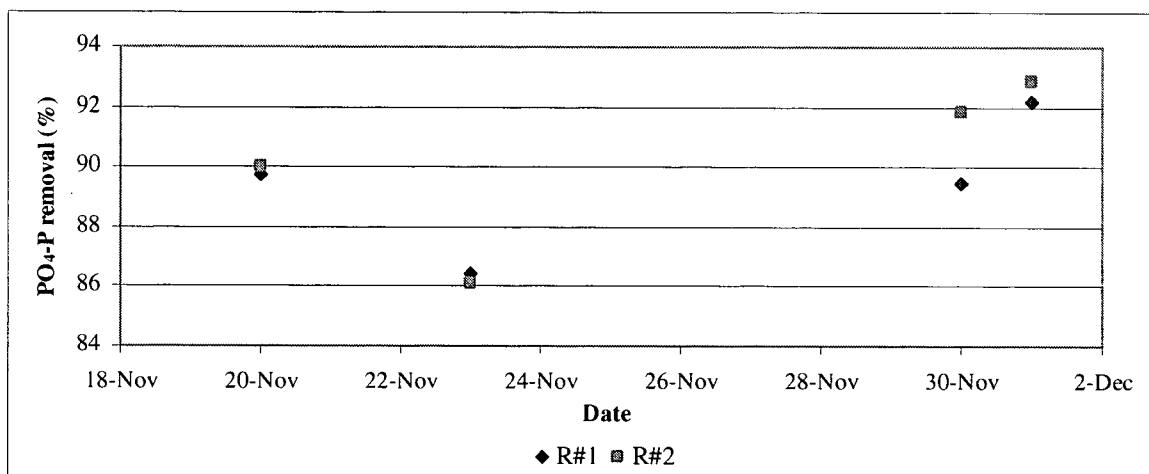


Figure 4.28: Phosphorus removal rates in R#1 and R#2 (4-12 Dec, 2006)

Caustic use

The higher recycle ratio and upflow velocity proved to have positive impacts on the performance of the strippers, regarding daily caustic use. The R#1 used an average 1.35 kg/d of caustic during this time. The improvement was more pronounced in case of the R#2, where the average caustic used during this run was only 0.66 kg/d. Both reactors were removing almost same amount of molar phosphorus from the system. Like all previous runs, the R#2 used less molar caustic to remove the same amount of molar phosphorus, compared to the R#1. The results are given in Figures 4.29 and 4.30.

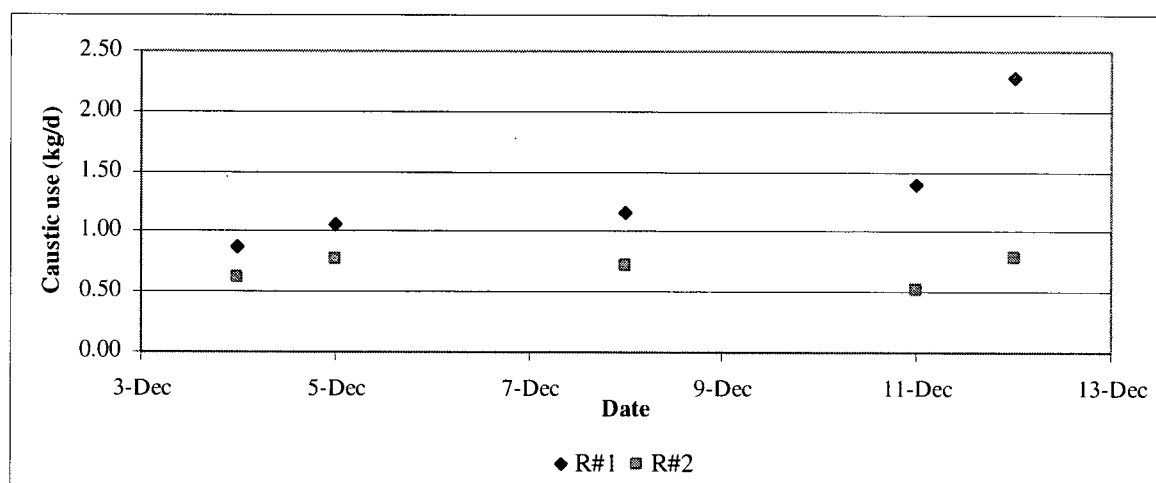


Figure 4.29: Daily caustic use in R#1 and R#2 (4-12 Dec, 2006)

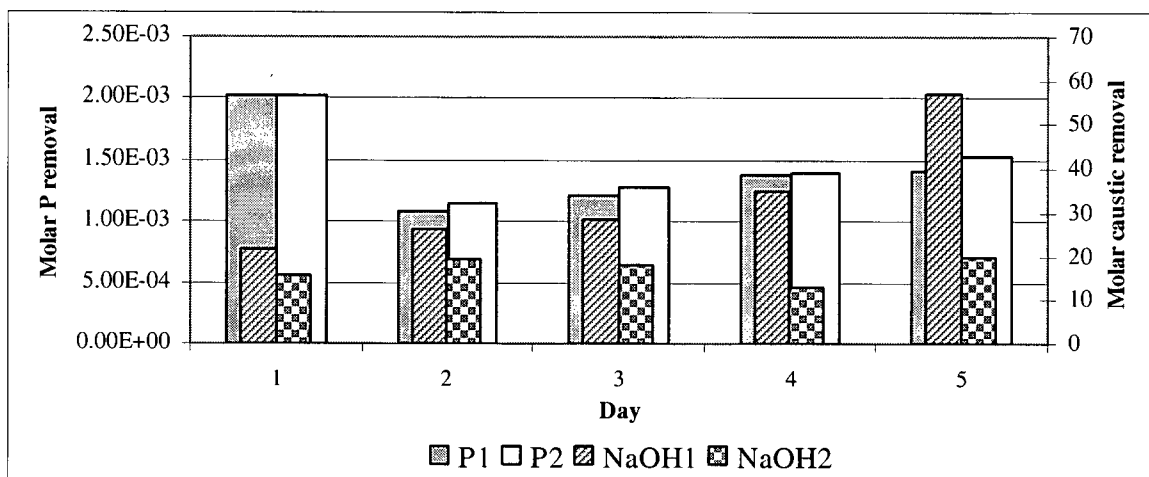


Figure 4.30: Molar P removal and caustic use in R#1 and R#2 (4-12 Dec, 2006)

Comparing these results with the results obtained by running the reactors without the strippers, showed that the amount of caustic saved by the cascade stripper alone, during this test, was 86%. On the other hand, the compact media stripper again failed to save any caustic; instead, it used an extra 10% caustic. However, this stripper also showed an improvement under higher recycle ratio and upflow velocity; in the previous two runs, it used an extra 15% (with external air supply) and 23% (without external air supply) caustic.

The caustic use pattern of the R#1 showed a gradual increase in usage rate over time. This was an indication of “clogging” of the packing media in the compact media stripper. It was mentioned earlier that the stripping tower was cleaned on 30 November; therefore, it was relatively clean when this run was started on 4 December and resulted in better, overall performance. However, the performance again decreased as clogging started to occur.

Carbon dioxide stripping

Under a higher recycle ratio and upflow velocity, both strippers performed better than the previous two runs, in stripping CO_2 . The average CO_2 stripping rates achieved by the R#1 and R#2 were 14% and 21%, respectively. The higher the amount of CO_2 stripping, the less caustic was used by the reactors. This result is shown in Figure 4.31.

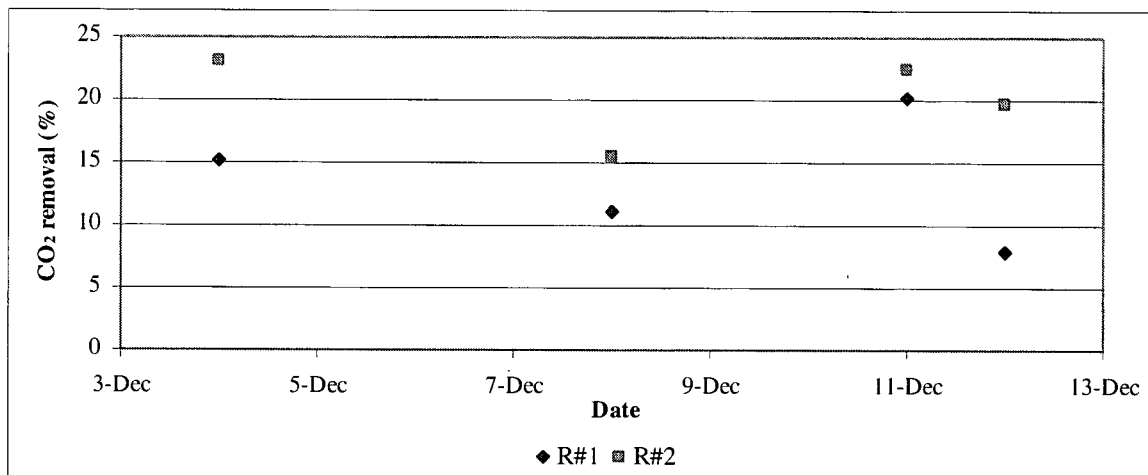


Figure 4.31: CO₂ removal in R#1 and R#2 (4-12 Dec, 2006)

Ammonia stripping

The amount of ammonia removal, after fulfilling the requirement of theoretical struvite formation, decreased somewhat, relative to the previous run, when the strippers were run without an external air supply. The average ammonia stripping achieved by the R#1 and R#2 was 6% and 5%, respectively; in the previous run, this was 9% and 7% for the R#1 and R#2, respectively. Once again, the compact media stripper was slightly better in stripping ammonia than the cascade stripper, although the difference was almost negligible. The results are shown in Figures 4.32 and 4.33.

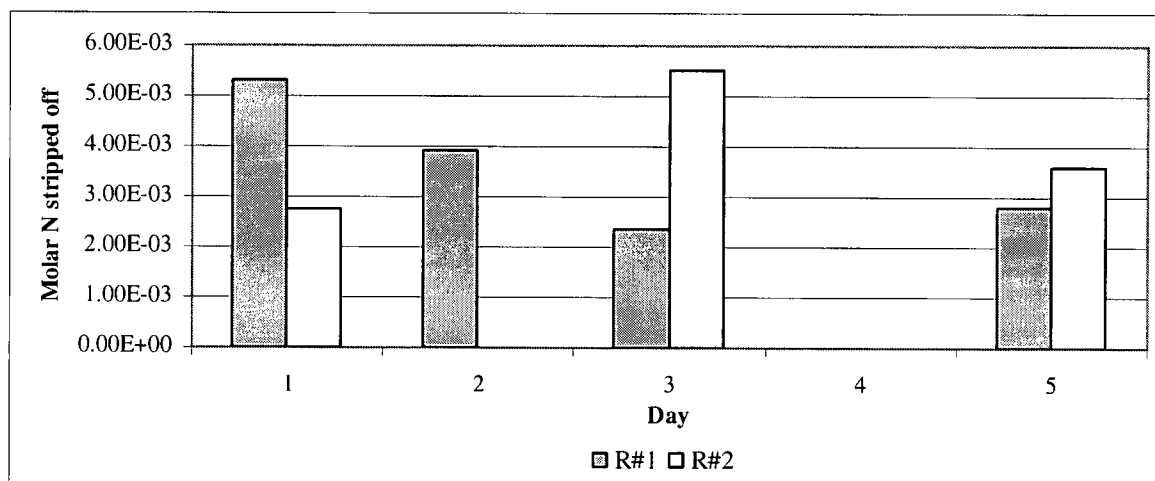


Figure 4.32: Ammonia stripping in R#1 and R#2 (4-12 Dec, 2006)

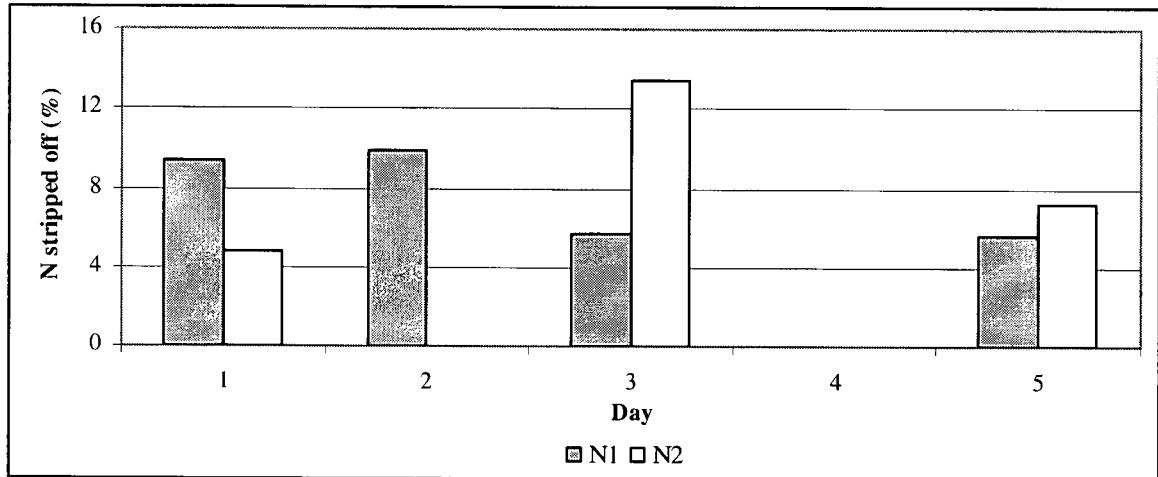


Figure 4.33: Ammonia stripping in R#1 and R#2 (4-12 Dec, 2006)

Summary of results

- The average phosphorus removal was 89% and 92% for the R#1 and R#2, respectively.
- A higher recycle ratio and upflow velocity had a positive effect, regarding caustic use. During this run, the cascade stripper saved around 86% of caustic usage.
- Although the overall performance of the compact media stripper improved under this condition, it still could not save any caustic. The stripper suffered from frequent clogging, thus affecting its performance.
- CO₂ stripping improved under this condition. However, ammonia removal decreased somewhat, compare to the previous run, when the strippers were run without an external air supply.

4.4 Comparison Of Stripper Performance

During the course of this study, a total four experiments were conducted – one without strippers and rest with strippers under different conditions. The first experiment was

carried out to check whether the two reactors used in this study were similar, regarding overall performance, so that direct a comparison could be made between the two. The results showed that they were very similar and hence, all comparisons between two strippers' performances were done directly. Major findings from all the experiments are summarized in Table 4.6.

Table 4.6: Summary of findings from four tests

	Without Stripper	1 st Run [*]		2 nd Run [§]		3 rd Run ^ψ	
		Compact media stripper	Cascade stripper	Compact media stripper	Cascade stripper	Compact media stripper	Cascade stripper
P removal (%)	90	90	90	90	90	88	92
Caustic use (kg/d)	1.23	1.41	0.84	1.51	0.91	1.35	0.66
Caustic savings^θ (%)	-	0 (-15)	46	0 (-23)	35	0 (-10)	86
CO₂ stripping (%)	-	11	20	14	17	14	21
NH₃-N stripping (%)	-	2	1	9	7	6	5
[*] : With air, Recycle ratio (RR) = 6, Upflow velocity = 400 cm/min [§] : Without air, RR = 6, Upflow velocity = 400 cm/min ^ψ : With air, RR = 9, Upflow velocity = 450 cm/min ^θ : Caustic savings were calculated comparing the results of the runs (1 st , 2 nd and 3 rd) to the “without stripper” condition test. Negative values indicate extra amount of caustic usage.							

Throughout this project, a high percentage of phosphorus removal was achieved under each condition, by both reactors. Overall, the removal rate was around 90%.

The compact media stripper failed to save any amount of caustic; rather, extra caustic was required all of the time, since the compact media stripper was incorporated into the system. This resulted from lack of proper ventilation. The stripper was mounted directly above the clarifier, leaving only a small opening at the top of the stripping tower for the stripped off CO_2 to escape from the system. The stripped CO_2 had to move upward through the packing media to reach to the top. However, the fact that the packing media was prone to clogging easily and frequently, made this CO_2 movement through it even harder. As a result, a part of the stripped off CO_2 probably dissolved back into the liquid stream that was carried back to the reactor, through the recycle flow. This process went on repeatedly, thereby putting an additional CO_2 load into the system to be stripped.

The compact media stripper was slightly better in stripping ammonia than the cascade stripper. The stripping of ammonia is associated with lowering the pH in the system. Thus, ammonia stripping, together with circulation of stripped off CO_2 into the reactor, resulted in more caustic being utilized, in order to raise the pH of the system, for improved performance.

The cascade stripper proved to be effective in saving caustic usage. The amount of caustic saved by this stripper ranged from 35% (without an external air supply) to 86% (with air, higher recycle ratio and upflow velocity). In the previous study done at the LIWWTP by Zhang (2006), the reduction in caustic addition ranged from 46% to 65%. Even though Zhang (2006) never used any external air supply, she was able to obtain a higher amount of caustic savings than the present study, where only 35% caustic was saved when the stripper was run without an external air supply (the amount was 46% with an external air supply at the recycle ratio of 6.0). However, it should be noted that the operating pH during the previous study was lower (7.9 and 8.0) than the current study, where the operative pH was maintained at 8.1 all the time. The higher caustic saving was achieved by Zhang (2006) because a lower pH (7.9) was employed for operation. Hence, it can be concluded that, with a lower operating pH (if conditions satisfy all criteria of struvite formation and recovery), the

cascade stripper will be more effective in saving caustic; thus, a lower cost of struvite production can be expected.

In this study, the highest amount of caustic was saved by the cascade stripper, when the reactor was running with a higher recycle ratio (9.0). This result was expected, as the pH of the effluent is higher than the inflow; when this effluent is recycled back to the reactor at a higher amount, it resulted in raising the overall in-reactor pH, and hence, reduces the need for caustic addition. On the other hand, to get a higher recycle ratio, the centrate flow has to be reduced, in order to satisfy the maximum hydraulic loading rate of the stripper/reactor. The system will run with a higher recycle flow that ultimately will reduce the in-reactor phosphorus level, as the effluent contains a lower amount of phosphorus than the centrate/inflow. This might have a detrimental effect on the phosphorus removal and recovery process. An overall cost-benefit analysis is called for

As expected, better results regarding caustic saving were obtained when the cascade stripper was run with an external air supply. Due to a shortage of on-site research time, tests were performed with only one airflow rate (107.5 L/min). It is likely that, with a higher airflow rate, the stripping efficiency will increase, resulting in further reduction in caustic addition. However, it should be noted that the supply of external air will result in additional operating costs. Thus, there may be a trade off between saving caustic, by increasing the external air supply rate and stripping more CO₂, and vice versa.

The cascade stripper did not work well, regarding stripping ammonia. The ammonia stripping ranged from 1% to 7%. In some days, there was no stripping at all. This low amount of ammonia stripping, in fact, contributed to reducing caustic addition. Hence, it is a matter of choice between whether we want additional ammonia removal/stripping from the centrate, or want savings from caustic addition.

4.5 Quality Of Harvested Struvite

The quality of harvested struvite was determined by measuring its composition and purity. For this purpose, apart from the regular species of struvite (i.e. magnesium, ammonia and phosphorus), four other elements, namely calcium, aluminum, iron and potassium, were tested. Grab samples were chosen randomly from each experiment carried out on the two reactors. The summary of the analyses is given in Table 4.7. Detailed analyses are given in Appendix C.

Table 4.7: Summary of struvite pellet composition

		Theoretical value (mg)			Actual value (mg)			Purity (%)
		Mg	N	P	Mg	N	P	
1 st Run [*]	R#1	49	28.6	63	48.5	28.5	62.7	99
	R#2				48.2	27.9	60.1	95
2 nd Run [§]	R#1				48.5	27.4	59.3	94
	R#2				46.9	26.8	59	93
3 rd Run ^ψ	R#1				48.5	28	60.3	95
	R#2				44.9	25.4	57.7	89
* : With air, Recycle ratio (RR) = 6, Upflow velocity = 400 cm/min								
§ : Without air, RR = 6, Upflow velocity = 400 cm/min								
ψ : With air, RR = 9, Upflow velocity = 450 cm/min								

The results show that the harvested pellets from both reactors were composed of, on average, 94% pure struvite (by mass). Previous analysis of struvite pellets grown at the LIWWTP was, on average, found to be 96% pure struvite (Fattah, 2004); thus, both results are quite similar. One thing to be noted - the different operating conditions did not seem to have any affect on the quality of harvested struvite.

The impurity content of the harvested struvite pellets are given in Table 4.8. The previous two studies at the LIWWTP found potassium to be present below detection limit in the struvite (Huang 2003; Fattah, 2004). However, this time, the potassium level was

detectable; rather aluminum was found to be below the detection level. It can be seen that the impurity ions were present in a very small quantity, relative to magnesium. Hence, there were few or almost no phosphate salts of impurity ions.

Table 4.8: Impurity contents of struvite pellet

		Content by mass (mg)			Content by mass (%)		
		Ca	Fe	K	Ca	Fe	K
1st Run[*]	R#1	0.90	0.69	0.16	0.18	0.14	0.03
	R#2	1.10	0.60	0.18	0.22	0.12	0.04
2nd Run[§]	R#1	0.85	0.62	0.13	0.17	0.12	0.03
	R#2	0.82	0.73	0.13	0.16	0.15	0.03
3rd Run^ψ	R#1	0.82	0.50	0.12	0.16	0.10	0.02
	R#2	0.51	0.48	0.10	0.10	0.10	0.02
*		: With air, Recycle ratio (RR) = 6, Upflow velocity = 400 cm/min					
§		: Without air, RR = 6, Upflow velocity = 400 cm/min					
ψ		: With air, RR = 9, Upflow velocity = 450 cm/min					

4.6 Operational Problems

During this project, several operational problems arose while running the crystallizer systems at the LIWWTP. This section describes the problems faced and the ways the problems were mitigated and minimized.

4.6.1 Clogging of the compact media stripper

From the very beginning of this study, the major problem that was faced in operating the compact media stripper was its susceptibility to clogging. The stripping tower of the compact media stripper was packed with one inch, hollow plastic balls, which were used to provide a larger specific surface area and sufficient air/water contact time for the passing liquid stream (in order to achieve better CO₂ stripping). At the beginning of this study, the

plastic balls were simply put inside the stripping tower in between the liquid distributor and the supporting plate.

After three weeks of use, it was noticed that the stripper's performance was decreasing. It started to use more caustic than it previously needed. The amount of caustic requirement increased over the course of operating time. This probably happened due to clogging of the packing materials. The stripping tower was connected to the external clarifier with a series of bolts. In order to check the condition inside of the stripping tower, it was dismantled from the top of the clarifier on 27 September. It was found that the packing materials were severely plugged due to formation of struvite encrustation and suspended material on the walls. This layer left almost no space for the stripped CO_2 to escape from the system, consequently affecting the stripper's performance.

Hot water was passed through the tower to clean the packing media; but it did not work. After that all the plastic balls were taken out from the tower, cleaning was attempted by using a garden hose. This attempt also failed. This demonstrated how difficult it was to clean the packing material once it got plugged. Hence, it was decided to change the arrangement of the packing materials inside the tower, to make it somewhat easier to clean and maintain. This resulted in hanging the packing media with the help of a string from the liquid distributor inside the stripping tower; also, the old supporting plate was replaced by a new plate with more open space. These changes in arrangement are illustrated in Figures 4.34 to 4.36.

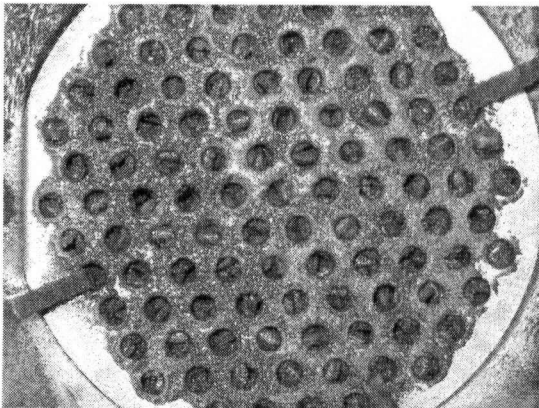


Figure 4.34: Old supporting plate

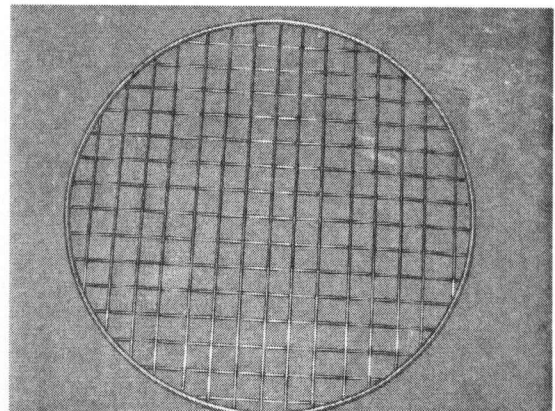


Figure 4.35: New supporting plate

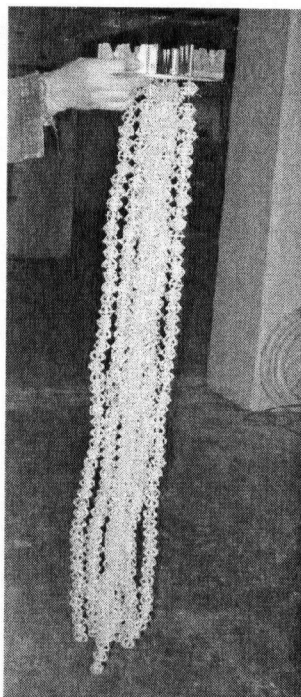


Figure 4.36: Hanging packing materials

Even after these changes were made, the clogging problem returned and remained until to the end of the study. The compact media stripper required thorough cleaning at least once a month. However, the change in arrangement of packing material made it easier to clean, since it could be cleaned by only taking out the liquid distributor from top of the tower.

4.6.2 pH controller problem

The struvite crystallization process is highly pH dependent, and in this study, the pH of the system was maintained by adding caustic and stripping CO_2 . The pH controller setup was used to adjust in-reactor pH to the set point, by controlling the caustic addition. During mid-October, it was observed that the daily caustic use rate, for both reactors, was gradually increasing. But, as the strippers were running without an external air supply at that moment, this increased amount of caustic use was linked with the no-air supply condition (as under no-air condition, the caustic use rate was expected to raise). The air was restarted from 23 October. Still, there was no sign of improvement regarding caustic use.

The research team started searching for the reason for this unusual behavior and discovered that both the pH controllers were broken. The controllers kept pumping caustic even when the in-reactor pH was right on the set point. In order to solve this problem, the broken controllers were replaced with two new controllers on 10 November. Since it was not known when this problem started, all data collected during 8 October to 10 November were discarded.

4.6.3 Flow fluctuation

As mentioned previously, it was very hard to keep flows, especially feed and recycle flows, constant to the set point. Variation in the flow of one of the components will have an effect on in-reactor supersaturation ratio and, thereby, on the performance of the reactor. Centrate was provided once a day from the treatment plant and stored in the storage tanks. From the storage tanks, it was supplied continuously to the reactors. As a result of this intermittent filling of storage tanks and continuous feeding of reactors, there was a significant drop in pump head that resulted in fluctuation of flow. In order to minimize this problem, all flows were measured and readjusted (if necessary) by adjusting the pump speed daily. To minimize this effect, data having more than $\pm 15\%$ variation from the set point were discarded in this study. Another solution was to minimize the variation of centrate head in the holding tank, which was not possible in this pilot-scale study. However, in a full-scale operation, it is expected that this problem would be minimal, with the use of online flow controllers.

4.6.4 Plugging of tubing

Plugging of tubing was another reason that caused a change in flows. The centrate and recycle flow tubing were often clogged with suspended solids and struvite. Occasionally, the encrusted layer broke off from tubing walls and clogged the pump and other ports. This problem was solved by tapping the clogged portion with the handle of screwdriver. This process dislodged the accumulated layer, into smaller pieces, and allowed normal flow to be resumed. Hot water was passed through the tubing (especially the one that carried the centrate to reactor) at least once a week. This process softened the encrusted layer, making it

easier to wash away. Tubing was always disconnected from the reactors while running hot water through it.

4.6.5 Reactor fouling

The reactor walls were often coated with a layer of struvite. Like the cleaning process of tubing, the handle of screwdriver was used to tap off the layer from the reactor walls. Care has to be taken in removing the encrusted layer, as the material may drop to the bottom of the reactor and plug the injection port. Usually, cleaning was undertaken right before harvesting.

The most susceptible place for struvite encrustation within reactor is the injection port, as the highest local supersaturation ratio existed there. The injection port was always cleaned whenever struvite was harvested. Cleaning was done by scraping off the struvite with a screwdriver. The caustic and magnesium entrances were cleaned with a thin wire.

4.6.6 Centrate supply

Due to some operational problems at the treatment plant, the LIWWTP was unable to supply sufficient centrate regularly. As a result of this, the reactors were often set to recycle mode. This hampered the reactors performance. At the beginning of the study, two storage tanks were used to hold centrate. A third tank was installed at the beginning of October in order to increase storage capacity and to use that extra volume of centrate in case the plant failed to provide centrate.

4.6.7 Suspended solids

Occasionally, the solids content of the centrate was quite high (700 mg/L). Since the residence time of the centrate in the storage tank was low, some solids made their way into the reactor, resulting in solids accumulation in the tubing. This also caused clogging in the compact media stripper, thereby affecting the performance of the stripper. The solids also accumulated at the bottom of the storage tanks. Thus, it was necessary to flush the tanks at

least once every 45 days. In a full-scale operation, it is recommended to install a sedimentation tank between the centrifuge and the reactor, to reduce the amount of suspended solids in the inflow, thereby reducing the plugging problem.

CHAPTER FIVE

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

Based on the results obtained from this study on the effectiveness of introducing a CO₂ stripper into the struvite crystallization process, the following conclusions can be drawn:

➤ The performances of the two struvite crystallizers (when running without CO₂ strippers) were identical. Essentially, the same amount of magnesium, ammonia and phosphorus removal was achieved by the two reactors, while running in parallel. Hence, the results obtained from the two reactors, when running with strippers, would be directly comparable. Throughout the project, a high percentage of phosphorus removal was achieved under each condition by both the reactors. Most of the time, the phosphorus removal rate was around 90%.

➤ The compact media stripper failed to save any amount of caustic, regardless of the operating conditions. Instead, more caustic was required when the stripper was introduced. One of the reasons was that this stripper blocked the passage of stripped CO₂, since it was mounted on top of the clarifier. Another reason was the susceptibility of the stripper's packing media to become frequently clogged, which also resulted in blocking the movement of the CO₂ through the stripping tower. It was also found to be difficult to clean and maintain the compact media stripper.

➤ The cascade stripper, on the other hand, was very effective in saving caustic. The amount of caustic saved by the stripper ranged from 35% (without external air supply) to 86% (with air, higher recycle ratio and upflow velocity). In a previous study, Zhang (2006) was able to obtain a higher amount (46% to 65%) of caustic savings, without an external air supply, but at an operating pH of 7.9 and 8.0. The operating pH of the current study was 8.1, higher than that used by Zhang (2006). It is believed that, with a lower operating pH (if

conditions satisfy all criteria of struvite formation), the cascade stripper will be more effective in saving caustic.

➤ The cascade stripper was more effective in saving caustic with higher recycle ratio and an external air supply. Unlike the compact media stripper, the cascade stripper never had any plugging problem and it was easy to clean and maintain. Both strippers showed very poor performance regarding ammonia stripping, with the compact media stripper slightly better in stripping ammonia.

➤ The harvested struvite pellets from both reactors were composed of nearly pure struvite (94% by mass), with a small amount of calcium and traces of iron and potassium. Different operating conditions did not have any affect on the quality of struvite.

5.2 Recommendations

Based on the experience gained from this study on the effectiveness of introducing a CO₂ stripper into the struvite crystallization process, the following recommendations are made.

➤ In order to achieve better efficiency, it is recommended that the centrate should pass through the stripper first. In this way, the inflow to the reactor (from the stripper) will carry a lesser amount of CO₂, which would result in having an inflow with a higher pH value.

➤ A higher airflow rate could be used in strippers, since aeration increases CO₂ stripping efficiency and thereby raises the pH value of wastewater. However, before applying a higher airflow, it is recommended to do a cost-benefit evaluation, since this would the increase energy consumption of the process.

➤ Instead of air, other gases (e.g. pure oxygen, nitrogen gas, CO₂ free air) could be used for aeration which, as it was found, could raise the pH of wastewater around 10.3

(Cohen and Kirchmann, 2004). However, it should be noted that these gases are more expensive than that of air.

- The reactor (with stripper) should be tested under different pH values. The (both) strippers are believed to perform better with a lower operating pH.

- The strippers should be tested under different recycle ratios, as improvement was noticed, in case of both strippers, when the recycle ratio was increased.

- The compact media stripper should run with applying the stripper's maximum hydraulic loading capacity. A higher amount of liquid flow has a better probability to reduce the plugging of packing media.

- Further study on the strippers' efficiency regarding ammonia stripping is also recommended, and incorporated into a cost-benefit evaluation.

- In a full-scale operation, it is recommended to install a sedimentation tank between the centrifuge and the reactor, to reduce the amount of suspended solids in the inflow, thereby reducing the plugging problem.

CHAPTER SIX

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APPENDIX A

INSTRUMENT OPERATIONAL PARAMETERS

FLAME ATOMIC ABSORPTION SPECTROPHOTOMETER

Element Analyzed	Magnesium	Calcium	Iron
Concentration Units	mg/L	mg/L	mg/L
Instrument Mode	Absorbance	Absorbance	Absorbance
Sampling Mode	Autonormal	Autonormal	Autonormal
Calibration Mode	Concentration	Concentration	Concentration
Measurement Mode	Integrate	Integrate	Integrate
Replicates Standard	3	3	3
Replicates Sample	3	3	3
Wavelength	202.6 nm	422.7 nm	248.3 nm
Range	0-100 mg/L	0-60 mg/L	0.06-15 mg/L
Flame Type	N ₂ O/C ₂ H ₂	N ₂ O/C ₂ H ₂	N ₂ O/C ₂ H ₂
Calibration Algorithm	New Rational	New Rational	New Rational
Lamp Current	4.0 mA	10 mA	5.0 mA

FLAME ATOMIC ABSORPTION SPECTROPHOTOMETER

Element Analyzed	Aluminum	Potassium	Sodium
Concentration Units	mg/L	mg/L	mg/L
Instrument Mode	Absorbance	Absorbance	Emission
Sampling Mode	Autonormal	Autonormal	Autonormal
Calibration Mode	Concentration	Concentration	Concentration
Measurement Mode	Integrate	Integrate	Integrate
Replicates Standard	3	3	3
Replicates Sample	3	3	3
Wavelength	309.3 nm	766.5 nm	
Range	0-20 mg/L	0.03-2 mg/L	
Flame Type	N ₂ O/C ₂ H ₂	N ₂ O/C ₂ H ₂	N ₂ O/C ₂ H ₂
Calibration Algorithm	New Rational	New Rational	New Rational
Lamp Current	10 mA	5.0 mA	

FLOW INJECTION ANALYSIS

Ion Analyzed	PO₄-P	NH₃-N
Concentration Units	mg/L	mg/L
Range	0-100 mg/L	0-100 mg/L
Temperature	63°C	63°C
Method	Ammonium Molybdate	Phenate
Reference	1	2

1. LaChat Instrument Methods Manual for QuickChem[®] Automated Ion Analyzer (1990). QuickChem method number 10-115-01-1Z.
2. APHA, AWWA, WPCF (1995). Method 4500-NH₃-F. Phenate Method. In Standard Methods for the Examination of Water and Wastewater, 19th Edition. American Public Health Association, Washington, DC.

APPENDIX B

OPERATIONAL DATA

CENTRATE

Date	pH	Temp (°C)	Cond. (mS)	Mg (mg/L)	PO ₄ -P (mg/L)	NH ₃ -N (mg/L)	Molar Ratio Mg:P N:P	
22-Aug	7.6	31.8	8.17	4.14	60.3	791	0.09	29
23-Aug	7.3	30.5	7.19	7.75	95.2	879	0.10	20
24-Aug	8.1	28.9	6.7	5.19	91.5	848	0.01	21
25-Aug	7.4	30.7	6.2	6.76	89.8	797	0.10	20
27-Aug	7.3	29.8	7.03	8.71	95.1	804	0.12	18
28-Aug	7.3	34	7.7	7.12	100	854	0.09	19
29-Aug	7.4	32	6.18	6.43	90.2	804	0.09	20
5-Sep	7.5	31	6.16	7.23	71	705	0.13	22
6-Sep	7.6	25.3	6.16	5.27	83.4	746	0.08	20
7-Sep	7.7	29.5	6.79	7.98	82.3	796	0.12	21
11-Sep	7.6	25.9	6.9	12.01	96.6	850	0.16	19
12-Sep	7.6	26.5	6.7	10.22	94.4	861	0.14	20
13-Sep	7.7	23.1	6.6	10.56	91.6	849	0.15	21
18-Sep	7.6	25.8	7.29	14.27	78.1	916	0.23	26
19-Sep	7.6	33	7.19	13.42	92.9	888	0.18	21
20-Sep	7.2	27	7.2	11.3	88.8	863	0.16	21
22-Sep	7.5	31	7.19	9.33	96.8	891	0.12	20
23-Sep	7.5	27	7.15	7.01	91.6	881	0.10	21
25-Sep	7.5	27	6.9	5.3	90.4	878	0.07	21
26-Sep	7.6	29.6	7.2	9.38	85.8	838	0.14	22
28-Sep	7.7	32.1	7.5	13.45	81.1	797	0.21	22
29-Sep	7.6	29.6	7.4	12.1	81.6	800	0.19	22
3-Oct	7.6	26	7.36	13.48	82	802	0.21	22
5-Oct	7.6	24.7	7.15	9.56	77.1	785	0.16	23
6-Oct	7.5	28.4	7.17	5.9	76.6	769	0.10	22
8-Oct	7.6	24.5	7.22	8.5	77.1	796	0.14	23
9-Oct	7.5	28.2	6.44	8.32	80.2	846	0.13	23
10-Oct	7.5	22.1	7.66	9.2	85.3	762	0.14	20
11-Oct	7.5	26	7.21	12.92	77.8	783	0.21	22
12-Oct	7.5	27.2	6.93	8.89	70.6	708	0.16	22
13-Oct	7.5	25.4	7.04	8.22	73.8	852	0.14	26
18-Oct	7.6	23.2	6.46	5.74	75.3	712	0.10	21

CENTRATE

Date	pH	Temp (°C)	Cond. (mS)	Mg (mg/L)	PO ₄ -P (mg/L)	NH ₃ -N (mg/L)	Molar Ratio	
							Mg:P	N:P
19-Oct	7.6	24.6	6.55	8.22	73	734	0.14	22
20-Oct	7.4	25.4	7.02	10.86	89.5	768	0.15	19
21-Oct	7.5	24.4	6.21	14.04	72	817	0.25	25
23-Oct	7.3	26	7.23	7.38	74	870	0.13	26
24-Oct	7.4	25	7.76	8.98	72.3	860	0.16	26
25-Oct	7.4	26	6.11	10.98	76.7	854	0.18	25
26-Oct	7.5	26	7.11	13.9	84	869	0.21	23
27-Oct	7.5	26.3	7.27	13.56	89.4	746	0.19	18
28-Oct	7.6	24.5	7.39	13.21	83.7	713	0.20	19
30-Oct	7.7	22.8	7.25	10.76	81	787	0.17	21
31-Oct	7.3	21.4	6.32	8.84	76.8	671	0.15	19
1-Nov	7.4	23.6	7.3	11.16	77.7	694	0.18	20
2-Nov	7.6	21.4	7.05	11.08	83.2	688	0.17	18
3-Nov	7.4	28.1	7.03	12.08	78.2	688	0.20	19
4-Nov	7.5	22.9	6.62	11.4	70.9	658	0.20	21
8-Nov	7.8	23.8	7.33	10.9	81.2	823	0.17	22
9-Nov	7.8	20.7	6.57	7.86	77.8	729	0.13	21
10-Nov	7.9	21.2	6.95	13.4	76.8	724	0.22	21
13-Nov	7.8	26.3	7.62	11.5	88.3	826	0.17	21
14-Nov	7.8	23	7.44	7.93	78	814	0.13	23
15-Nov	7.8	24.9	7.22	10.15	84.1	845	0.15	22
16-Nov	7.8	23.8	7.04	10.12	68.3	834	0.19	27
17-Nov	8.1	21	7.4	11.23	82.2	775	0.17	21
20-Nov	8.0	21	7.33	10.69	69.3	634	0.20	20
23-Nov	7.8	24	7.16	9.45	50.6	827	0.24	36
30-Nov	8.0	19.3	6.83	9	42.6	698	0.27	36
1-Dec	7.8	25.6	7.15	8.58	63.1	760	0.17	27
4-Dec	8	16.3	6.99	8.31	67.3	799	0.16	26
5-Dec	8.1	15.3	12.48	13.65	38.2	553	0.39	32
8-Dec	7.9	17.1	5.09	11.09	42.6	575	0.33	30
11-Dec	7.9	18.9	5.99	9.64	49	670	0.25	30
12-Dec	7.9	19.9	5.68	9.36	52.6	696	0.23	29
13-Dec	7.4	19.1	5.3	11.14	54.9	680	0.26	27

MAGNESIUM FEED

Date	Concentration (mg/L)	Conductivity (mS/cm)
18-Aug	2276	17.81
22-Aug	1956	16.69
25-Aug	2072	16.93
27-Aug	2443	18.48
28-Aug	2470	17.5
29-Aug	2471	18.88
5-Sep	2443	17.95
6-Sep	2140	18
7-Sep	2250	18.11
18-Sep	2422.5	17.43
20-Sep	2362.5	17.51
26-Sep	2357.5	19.7
29-Sep	2207.5	20.3
3-Oct	2122.5	19.58
10-Oct	2480	19.4
11-Oct	2447.5	18.2
19-Oct	2050	17.79
26-Oct	2207.5	18.23
27-Oct	2170	17.96
7-Nov	2026	19.3
8-Nov	1846	17.58
16-Nov	1688	17.58
17-Nov	1774	17.33
30-Nov	1754	16.11
1-Dec	1732	15.63
11-Dec	2147	17.56
12-Dec	2150	18.3

REACTOR #1

Flows							
Date	Centrate (L/min)	Mg Feed (L/min)	Total Feed (L/min)	Recycle (L/min)	Total (L/min)	RR	Mg Inflow to Reactor (L/min)
25-Sep	1.92	0.08	2	13.36	15.36	6.7	99.39
26-Sep	2.42	0.08	2.5	15.5	18	6.2	84.52
28-Sep	2.42	0.08	2.5	15.5	18	6.2	83.66
29-Sep	2.47	0.08	2.55	15.5	18.05	6.1	80.98
3-Oct	3.52	0.08	3.6	16.8	20.4	4.7	60.35
13-Nov	2.51	0.1	2.61	14.49	17.1	5.6	81.79
14-Nov	2.2	0.1	2.3	16	18.3	7.0	87.85
15-Nov	2.2	0.1	2.3	15.4	17.7	6.7	89.97
17-Nov	2.51	0.1	2.61	15.63	18.24	6.0	78.77
20-Nov	2.51	0.1	2.61	15.63	18.24	6.0	78.25
23-Nov	2.51	0.1	2.61	15.63	18.24	6.0	77.06
30-Nov	2.51	0.1	2.61	15.63	18.24	6.0	75.02
1-Dec	2.6	0.1	2.7	14.4	17.1	5.3	72.41
4-Dec	1.42	0.08	1.5	17.1	18.6	11.4	100.24
5-Dec	1.97	0.08	2.05	18.47	20.52	9.0	80.71
8-Dec	1.87	0.08	1.95	19.35	21.3	9.9	81.69
11-Dec	2.67	0.08	2.75	17.65	20.4	6.4	59.75
12-Dec	2.52	0.08	2.6	16.9	19.5	6.5	75.22

REACTOR #1

Effluent						
Date	pH	T (°C)	Cond. (mS/cm)	Mg (mg/L)	PO ₄ -P (mg/L)	NH ₃ -N (mg/L)
25-Sep	8.15	26	6.9	5.53	21	819
26-Sep	8.22	26	7.53	33.22	5.3	810
28-Sep	8.4	29.3	7.27	13.3	10.5	741
29-Sep	8.2	25	7.76	74.88	2.71	736
3-Oct	8.29	26	7.13	2.4	12.3	723
13-Nov	8.29	21.5	7.13	15.24	9.56	740
14-Nov	8.3	28	6.88	21.78	7.51	780
15-Nov	8.41	21.8	6.73	20.49	6.49	791
17-Nov	8.42	21	7.04	30.21	8.45	761
20-Nov	8.51	21	7.21	55.88	7.11	570
23-Nov	8.44	17.2	7.26	26.22	6.87	761
30-Nov	8.49	15.4	5.18	54.42	3.13	573
1-Dec	8.45	22.5	7.09	26.97	4.95	718
4-Dec	8.42	15.2	7.04	44.4	4.57	696
5-Dec	8.45	14.7	5.25	16.86	4.47	483
8-Dec	8.48	16.4	5.33	44.44	4.89	525
11-Dec	8.46	18.2	5.94	32.52	6.26	652
12-Dec	8.25	19.2	5.8	38.49	9.03	637

REACTOR #1

Caustic use				
Date	Na (g/L)	NaOH (g/L)	Caustic use (L/d)	Caustic use (kg/d)
25-Sep	19.42	33.77	86	2.91
26-Sep	28.1	48.87	34	1.66
28-Sep	30.04	52.24	44	2.30
29-Sep	37.04	64.42	30	1.93
3-Oct	40.11	69.76	42	2.93
13-Nov	26.52	46.12	20	0.92
14-Nov	23.52	40.90	38	1.55
15-Nov	22.08	38.40	43	1.65
17-Nov	28.44	49.46	31	1.53
20-Nov	27.72	48.21	35	1.69
23-Nov	28.48	49.53	33	1.63
30-Nov	32.44	56.42	18	1.02
1-Dec	30.6	53.22	32	1.70
4-Dec	33.16	57.67	15	0.87
5-Dec	31.72	55.17	19	1.05
8-Dec	36.64	63.72	18	1.15
11-Dec	24.32	42.30	33	1.40
12-Dec	24.8	43.13	53	2.29

REACTOR #1

Dissolved CO₂		
Date	Concentration (ppm as CO₂)	
	Inflow to stripper	Outflow from stripper
14-Nov	14.62	13.8
15-Nov	20.75	16.34
17-Nov	20.75	19.77
23-Nov	45.65	41.38
30-Nov	48.38	39.78
1-Dec	44.5	38.1
4-Dec	57	48.38
8-Dec	53.27	47.29
11-Dec	50.5	40.35
12-Dec	51.37	47.32

REACTOR #2

Date	Flows						Mg Inflow to Reactor (L/min)
	Centrate (L/min)	Mg Feed (L/min)	Total Feed (L/min)	Recycle (L/min)	Total (L/min)	RR	
25-Sep	2.37	0.08	2.45	15.55	18	6.3	82.11
26-Sep	2.37	0.08	2.45	15.55	18	6.3	86.05
28-Sep	2.47	0.08	2.55	15.65	18.2	6.1	82.28
29-Sep	2.47	0.08	2.55	15.65	18.2	6.1	80.98
3-Oct	2.62	0.08	2.7	18.9	21.6	7.0	75.97
13-Nov	2.2	0.1	2.3	13.3	15.6	5.8	91.26
14-Nov	2.2	0.1	2.3	14.8	17.1	6.4	87.85
15-Nov	2.2	0.1	2.3	15.7	18	6.8	89.97
17-Nov	2.1	0.1	2.2	15.5	17.7	7.0	92.00
20-Nov	2.51	0.1	2.61	15.63	18.24	6.0	78.25
23-Nov	2.31	0.1	2.41	15.5	17.91	6.4	82.67
30-Nov	2.74	0.1	2.84	15.85	18.69	5.6	69.67
1-Dec	2.6	0.1	2.7	15.69	18.39	5.8	72.41
4-Dec	1.97	0.08	2.05	18.47	20.52	9.0	75.58
5-Dec	1.97	0.08	2.05	18.47	20.52	9.0	80.71
8-Dec	1.82	0.08	1.9	17.6	19.5	9.3	83.55
11-Dec	1.92	0.08	2	15.95	17.95	8.0	78.54
12-Dec	1.82	0.08	1.9	20.7	22.6	10.9	99.49

REACTOR #2

Date	pH	Effluent				
		T (°C)	Cond (mS/cm)	Mg (mg/L)	PO ₄ -P (mg/L)	NH ₃ -N (mg/L)
25-Sep	8.16	26	7.11	10	16.2	841
26-Sep	8.3	26	7.81	57.55	3.32	787
28-Sep	8.1	29.3	7.39	24.18	16.1	734
29-Sep	8.3	24.3	8.48	31.23	1.95	649
3-Oct	8.4	25.1	7	18.3	5.85	703
13-Nov	8.2	22.7	7	21.03	9.14	772
14-Nov	8.1	25	7.34	24.33	8.62	790
15-Nov	8.28	21.4	7.11	22.08	7.78	779
17-Nov	8.46	21	7.13	72	7.11	752
20-Nov	8.46	21	8	33.68	6.9	600
23-Nov	8.48	19.1	7.5	76	7.04	772
30-Nov	8.36	16	8.09	46.8	2.42	605
1-Dec	8.3	22.8	7.14	31.65	4.49	713
4-Dec	8.42	15.8	6.98	34.29	4.42	732
5-Dec	8.54	16.3	8.61	53.7	2.47	545
8-Dec	8.23	16.2	8.47	51	2.96	221
11-Dec	8.22	20	6.14	52.60	5.94	653
12-Dec	8.31	20.3	5.94	49.13	5.13	624

REACTOR #2

Caustic use				
Date	Na (g/L)	NaOH (g/L)	Caustic use (L/d)	Caustic use (kg/d)
25-Sep	15.36	26.71	16	0.43
26-Sep	15.56	27.06	30	0.81
28-Sep	15.32	26.64	62	1.65
29-Sep	28	48.70	44	2.14
3-Oct	21.52	37.43	30	1.12
13-Nov	19.32	33.60	18	0.61
14-Nov	24.12	41.95	8	0.34
15-Nov	24.32	42.30	22	0.93
17-Nov	20.48	35.62	41	1.46
20-Nov	25.08	43.62	20	0.87
23-Nov	27	46.96	20	0.94
30-Nov	28.1	48.85	13	0.64
1-Dec	26.96	46.89	25	1.17
4-Dec	27.32	47.51	13	0.62
5-Dec	25.97	45.17	17	0.77
8-Dec	22.91	39.85	18	0.47
11-Dec	22.83	39.70	13	0.52
12-Dec	22.64	39.37	20	0.79

REACTOR #2

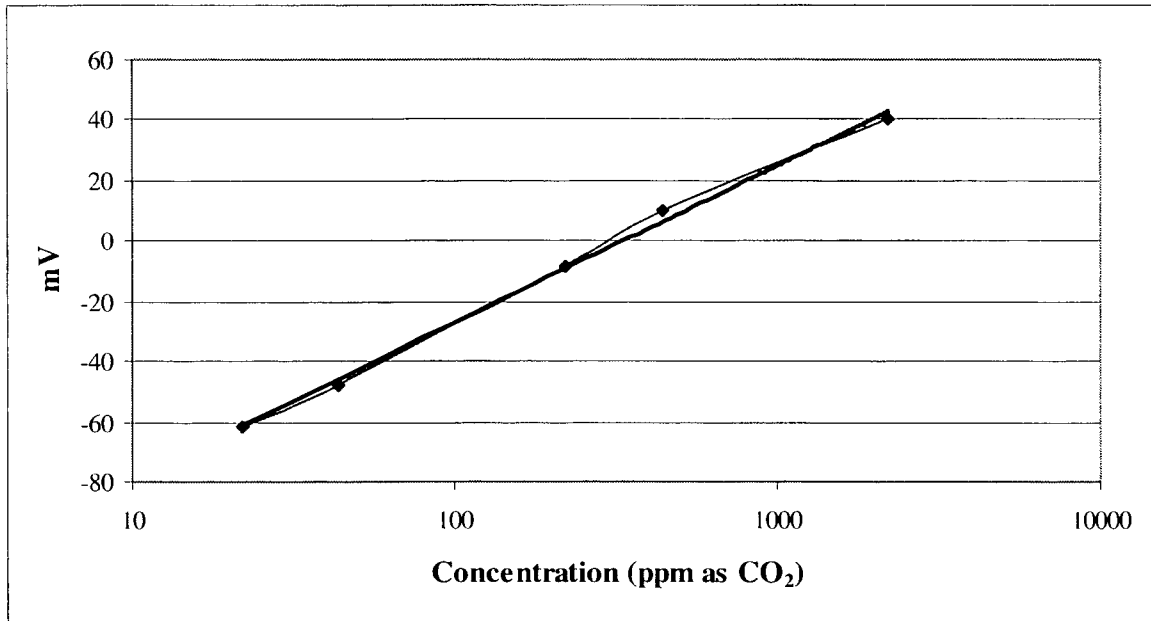
Dissolved CO₂		
Date	Concentration (ppm as CO₂)	
	Inflow to stripper	Outflow from stripper
14-Nov	23	21.6
15-Nov	28.68	17
17-Nov	18.66	16.34
23-Nov	44.95	39.81
30-Nov	48.38	35.84
1-Dec	44.5	37.82
4-Dec	50	38.5
8-Dec	53.4	45.12
11-Dec	73.72	57.13
12-Dec	65.23	52.42

APPENDIX C **CHEMICAL ANALYSIS OF STRUVITE PELLETS**

Sample		Mg (mg/L)	N (mg/L)	P (mg/L)	Ca (mg/L)	Al (mg/L)	Fe (mg/L)	K (mg/L)
1st Run *	R#1	485	285	627	9	0	6.9	1.6
	R#2	482	279	601	11	0	6	1.8
2nd Run §	R#1	485	274	593	8.5	0	6.2	1.3
	R#2	469	268	590	8.2	0	7.3	1.3
3rd Run ψ	R#1	485	280	603	8.2	0	5	1.2
	R#2	449	254	577	5.1	0	4.8	1
* : With air, Recycle ratio (RR) = 6, Upflow velocity = 400 cm/min § : Without air, RR = 6, Upflow velocity = 400 cm/min ψ : With air, RR = 9, Upflow velocity = 450 cm/min								

APPENDIX D

CO₂ CALIBRATION CURVE



$$y = 22.564\ln(x) - 130.93$$

$$R^2 = 0.99$$