Determining The Viability of Struvite Precipitation as an Alternative Method for Phosphate Ion Removal and Recovery from Wastewater.

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Abstract:

One of the largest problems facing the Baltic Sea as well as other water bodies across the world is eutrophication due to the addition of excess nutrients. The specific nutrient being dealt with in this work is phosphorus in the form of phosphate. Whether the reason it enters water bodies is due to effluent untreated wastewater or phosphate leeching at nonpoint sources, the precipitation of a compound struvite should be considered as a method of reducing the amount of phosphate entering or leaching into the hydrosphere.

Initially the benefits of using struvite are qualitatively discussed as a motivation to implementing struvite precipitation as a method for phosphate removal. It is mentioned that since struvite is an excellent fertilizer with a low solubility product that synthesis of this compound from wastewater would be an effective method of recovering phosphate and effectively reusing it, and thus reducing the amount of phosphate mining; preserving the dwindling global phosphorus stocks. Additionally the current methods of phosphate precipitation are compared to use of struvite precipitation. This comparison questions whether the benefits of recycling the phosphate as a fertilizer, which prevent phosphate from entering via non-point sources, outweigh the fact that struvite is to a degree more soluble than the other currently used methods, meaning that less phosphate is percipitated. The primary research question of this work then becomes:

"Can the concentration of phosphate ions in effluent water be decreased through synthesis of struvite, to a level that is in accordance with the Helsinki Commission's latest regulations on wastewater treatment?"

The Helsinki Commission's regulations are chosen as they largely pertain to the Baltic Sea, which has been one of the water bodies most affected by eutrophication, thus implying that these stringent rules would be beneficial for other countries and their respective water bodies.

The second half of the work primarily focuses on the practical method of precipitating phosphate from water using struvite. The experiments are conducted under laboratory conditions, so it is noted that these results, while informative, cannot be used to as

basis for predicting how the process will fair under real life conditions (though they are a good indication of the potential of this method). Furthermore early trials reveal that precipitating may not be as simple as other methods of phosphate removal; requiring pH monitoring, the creation of buffer solutions, as well as the use of more advanced chemical procedures such as titration. These observations and realizations also question the commercial viability of this procedure. However the final results show that with a reduction of over 99% the method seems to work very effectively under laboratory conditions suggests that there is certainly a large possibility that this method of phosphate precipitation could be an effective measure to recover more phosphate and overall be a step in a more sustainable future.

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1. Introduction

1.1. Struvite & Sewage Chemistry

I initially became interested in the topic area of sewage chemistry when I discovered the problem eutrophication in the Baltic Sea.[1] This phenomenon has severely affected the biodiversity of this region due to the presence of excess nutrients in its brackish waters. Concerned, I began to research which chemicals and conditions caused eutrophication in Baltic Region.

I discovered that while the primary cause of eutrophication in many freshwater bodies is due to the addition of nutrients through insufficiently treated or completely untreated effluent wastewater, this is not the case in the Baltic Sea, as The Helsinki Commission has implemented stringent wastewater handling measures that monitor nutrient levels in recycled water. [2] While The Helsinki Commission has successfully decreased the nutrient flow into the Baltic from this front, it has still not effectively tackled the main cause of nutrient loading in the Baltic: agricultural runoff & soli leaching

Agricultural runoff & soil leaching are the predominant gateways of nutrient inflow into the Baltic Sea. Unlike wastewater, these two sources of excess nutrients are much more difficult to monitor and regulate, as nutrients in these case enter water bodies through non-point sources.[3, 4] Although nutrient loading occurs naturally, currently the amount of nutrients entering the natural

[1] "Eutrophication of the Baltic Sea" The Baltic Sea Portal *http://www.itameriportaali.fi/en/tietoa/rehevoityminen/en_GB/rehevoityminen_itameri/* [Web Access: August 2nd 2012]
[2] "Municipal Wastewater Treatment" Helsinki Commission: Baltic Marine Environment Protections Commission. (2007). http://www.helcom.fi/Recommendations/en_GB/rec28E_5/ [Web Access: September 20th 2012]
[3] Non-point Source: there is no specific point(s) where agricultural runoff occurs.
[4] "Threat of eutrophication the Baltic Ecoregion." World Wild Life Fund for Nature. http://wwf.panda.org/what_we_do/where_we_work/baltic/threats/eutrophication/ [Web Access September 30th 2012]

water bodies has been immoderately supplemented by human activity, such as agriculture. The nutrient rich fertilizers used in these professions have exacerbated the low amount of naturally occurring eutrophication, worsening its effect on the environment.

As there are many different nutrients and several types of aquatic biomes on Earth I decided to specify my research to one nutrient in one environment. I chose to focus on the effect of phosphate on the Baltic Sea. This combination seemed intriguing as the Baltic Sea seems to be inherently prone to eutrophication [5] and phosphate related eutrophication is exclusively caused through various types runoff, as the phosphate cycle contains no gaseous stages (as opposed to, for instance the nitrogen cycle) [6]. Phosphate was also selected as the nutrient as it has been recently discovered that the abundance of natural phosphorous is not as plentiful as previously thought, meaning that its conservation is essential.

During my continued research on phosphate ions, I discovered that it enters water bodies through its dissolution into groundwater, meaning that it can easily flow back into natural aquatic environments. The high solubility of phosphate posed an interesting challenge. Would it be possible to synthesize a highly insoluble phosphate-based compound that could also act as an effective phosphate-based fertilizer? If possible, eliminate the problem of excess phosphate through agricultural runoff. Keeping this in mind, I stumbled upon white insoluble crystalline compound struvite (ammonium magnesium

[5] "30 years Protecting the Baltic Sea" Helcom. http://www.helcom.fi/stc/files/Publications/OtherPublications/30_years_jubilee.pdf [Web Access September 30th 2012]
[6] "Phosphorus Cycle" Environmental Literacy Council http://www.enviroliteracy.org/article.php/480.html [Web Access September 30th 2012]

phosphate). While usually considered a nuisance due to build up sewage pipes, [7] its qualities have warranted its investigation as an insoluble phosphate-based plant fertilizer. Results from experimental testing show that its potency as a slow release fertilizer is comparable to that of the commercial fertilizer monocalcium diphosphate (super phosphate).[8] This suggests that struvite could be simultaneously synthesized from wastewater, eliminating phosphate ions and also used as an insoluble fertilizer to reduce agricultural runoff.

1.2. Defining the Scope of the Experiment

Since the fertilizing capabilities of struvite are already well documented, the research question should rather focus on struvite synthesis from wastewater.

The principle issue that then needs to be considered is whether the precipitation of phosphate via the formation of struvite reduces the concentration of phosphate ions in effluent [9] water to the extent its phosphate levels comply with the regulations set by the Helsinki Commission Recommendations (latest regulations adopted on the 15.11.2007). Another key concern is whether the conditions required are too difficult to replicated with the available school laboratory equipment. One last query that would need to be addressed is whether the method of the chosen method of struvite synthesis, is viable on an industrial level. While I cannot conduct this

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[7] "Struvite Control in Wastewater". General Chemical http://www.generalchemical.com/assets/pdf/Struvite_Control_in_Wastewater.pdf [Web Access: August 10th 2012]

[8] Miso, Analiza. " Executive Summary". SSWM. http://www.sswm.info/category/implementation-tools/reuse-and-recharge/hardware/reuse-urine-and-faeces-agriculture/fertili [Web Access: February 2nd 2013]
Barak, Philip & Stafford, Alysa. (2006). "Struvite: A Recovered And Recycled Phosphorus Fertilizer". [Print]

[9] Effluent Water: water that is recycled into natural water bodies after it has been treated.

experiment on commercial level, I can qualitatively approach this problem and analyse this potential problem using my knowledge from this small-scale experiment.

1.3. The Research Question

Using my preliminary research the following research question was created:

"Can the concentration of phosphate ions in effluent water be decreased through synthesis of struvite, to a level that is in accordance with the Helsinki Commission's latest regulations on wastewater treatment?"

2. Hypothesis

Unlike many of the compounds created through current phosphate precipitation methods, the synthesis of struvite to remove phosphate from water is more complex, requiring both ammonium and magnesium ions. The resulting intricacy of this method will likely mean that considerable amounts experimentation and trials are needed to determine a procedure that effectively reduces the phosphate ion concentration. Although I am certain that struvite insolubility will reduce the presence of phosphate ions in water when it is synthesized, it whether an effective method can be found or created in school-laboratory circumstance that also decreases the presence of phosphate ions in the effluent water to love enough levels that comply with the Helsinki Commissions regulations

3. Background Information

3.1. The Role of Phosphorus in Nature & Agriculture

Phosphorous is a vital element essential for the existence of life on Earth. Occurring frequently in the form of insoluble phosphate compounds, of

which many play an active role in the function of an organism. [10] For instance phosphates are present in the phosphate-sugar backbone of deoxyribonucleic acid (DNA), which allows for sequences of amino acids to be replicated. They are also present in adenosine triphosphate (ATP), which is used to release energy in various metabolic reactions.[11] As phosphates play many important roles in the function of many organisms, it is often scares in most environments, meaning that it is usually the limiting nutrient in organism growth.[12] For this exact reason, phosphate-based fertilizers are heavily used in agriculture, ensuring that phosphorus is never the limiting nutrient for the plants. Although large amounts of phosphates are added to the soil, around 56-71% of it is removed "when seeds, grain, fleshy fruit crops are harvested" (Bradley).[13] This indicates that fertilizers need to be added constantly to maintain high phosphate levels in the soil. This sustainability of agriculture could be increased by using struvite formed from recycled waster water instead of fertilizers created from virgin phosphorus.[14] [15]

3.2. Depletion of Global Phosphorus Stocks

Although phosphorus is the 12th most abundant element on Earth, phosphorus reserve depletion is becoming an increasingly critical issue.[16] While it was initially predicted that global stocks would last at least for another 345 years, many scientists now believe that all accessible could be depleted in "50 to

[10] Keely, Brendan (2000) Phosphorus. *Chemistry Review Volume 10, Number 2* (p.16-17) [Print]
[11] Allot Andrew. (2007) Biology for the IB Diploma (2nd ed.) Oxford: Oxford University Press. Print]
[12] Keely, Brendan (2000) Phosphorus. *Chemistry Review Volume 10, Number 2* (p.16-17) [Print]
[13] Bradley, David. (2010). Phosphorus Footprint, *InfoChem issue 10* (p.1) [Print]
[14] Virgin phosphorus: phosphorus that is originally found within Earth and is initially obtained through various means (mining).
[15] Barak, Philip & Stafford, Alysa. (2006). "Struvite: A Recovered And Recycled Phosphorus Fertilizer". [Print]
[16] Keely, Brendan (2000) Phosphorus. *Chemistry Review Volume 10, Number 2* (p.16-17) [Print]

100 years" (Bradley). [17] This shift in figures can be partially attributed to the overuse of phosphates in fertilizers to increase the yield of crops in agriculture. Phosphate shortages would have global ramifications, such as food-related famines. Although several solutions, such as genetically modified crops less reliant of phosphorus, have been proposed, these proposals carry their own risks, and will likely remain unimplemented until the full ramification of their use is known. The next best solution to this problem is phosphate recycling. While the used of struvite from wastewater as a fertiliser, would not completely solve this problems, it would certainly alleviate the agricultural stain on global phosphorus stocks.

3.3. Outlining the Terms Nutrient Loading & Eutrophication

Nutrient loading is the process where nutrients enter water bodies through various natural or artificial methods. As mentioned in the introduction, the addition of excess nutrients in the water bodies can cause eutrophication. The main symptom of eutrophication is increased hypoxia in water. These hypoxic conditions are caused by the decomposition of microorganism by aerobically oxidising bacteria found on the benthic level which use deplete dissolved oxygen. On a small scale this has a very minimal effect on the ecosystem, but when large amounts of nutrients are loaded into the water bodies, the ramification are greatly amplified. After the resultant large increase in the populations of the photosynthesizing organisms, much of the population quickly die as most of the loaded nutrients have been exhausted. The dead microorganisms fall to the bottom of the water body and are then decomposed by the bacteria, which deplete dissolved oxygen and cause

[17] Bradley, David. (2010). Phosphorus Footprint, InfoChem issue 10 (p.1) [Print]

hypoxia. This often results in the distress & death of immobile aerobically respiring organisms. As agricultural runoff introduces the largest amount of nutrients to the Baltic Sea, the benefits of using an insoluble phosphate based fertilizer are apparent. [18]

3.4. Current Methods of Phosphate Precipitation

Nowadays, the vast majority of all nutrients in wastewater are precipitated through various procedures that leave only trace amounts of nutrients in effluent water. The most widely used global methods for phosphate precipitation requires metallic ions; three of the most commonly used ions in phosphate precipitation and their products are compared against struvite in the following table.

Ions used for precipitation	Phosphate compound formed	Solubility product of the compound (K_{sp}) at around 25°C	Known use of the compound
Calcium (Ca^{2+})	$Ca_{10}(PO_4)_6 \cdot (OH)_2$	$1.0 \cdot 10^{-26}$	A Few Medical Uses
Iron (Fe^{3+})	$FePO_4$	$1.3 \cdot 10^{-22}$	Pesticides & coating on Industrial Metal Surfaces
Aluminium (Al^{3+})	$AlPO_4$	$6.3 \cdot 10^{-19}$	Various Structural & Catalytic Properties
Ammonium (NH_4^+) Magnesium (Mg^{2+})	$NH_4MgPO_4 \cdot 6H_2O$	$11.65 \cdot 10^{-14}$	Fertilizer

Table 1: shows some of the qualities of metallic ions used for phosphate precipitation compared to the same qualities of struvite.[19] [20] [21] [22] [23]

[18] "Eutrophication of the Baltic Sea" The Baltic Sea Portal. http://www.itameriportaali.fi/en/tietoa/rehevoityminen/en_GB/rehevoityminen_itameri/ [Web Access: August 2nd 2012]

[19] "Solubility Product Constants near 25ºC" The University of Rhode Island. http://bilbo.chm.uri.edu/CHM112/tables/KspTable.htm [Web Access: September 12th 2012]

While the products of these precipitations vary in solubility, the general trend is that they are all very insoluble. Although calcium, iron, and aluminium phosphate compounds have a few uses, these compounds are not considered terribly valuable, either because they are naturally abundant or easily synthesized through other means. This means that though the products of these reactions are highly insoluble and very effectively remove phosphate ions from water, they are nonetheless considered waste and are usually discarded. This means that the metallic ions do not recycle any phosphate from the water, which when considering the current state of global phosphate reserves, makes struvite seem like a more appealing candidate for phosphate removal, as although it has the lowest solubility product it could also decrease dependency on virgin phosphorus.

3.5. Helsinki Commission: Baltic Sea Waste Water Regulations

The Helsinki Commission has established different requirements depending on how many people use a municipal sewage plant. The data has been complied in the following table.

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[20] Aage, H.K., Andersen, B.L., Biota a., & Jensen I. (1997) "The solubility of struvite" https://akkrt.metapress.com/content/p02p525112301832/resource-secured/?target=fulltext.pdf&sid=wwtl4dyegs5pi4xs304fkezc&sh=www.akademiai.com [Web Access: September 12th 2012]

[21] Campelo, J. M., Jaraba, M., Luna, D., Luque, R., Marinas J.M., & Romero A.A. "Structural and Catalutic Properties of Amorphous Mesoporous $AlPO_4$ Materials prepared in the presence of 2,4-Pentanedione and 2,5-Hevanedione as Aluminium Chelating Agents. http://www.docstoc.com/docs/26711756/Structural-and-Catalytic-Properties-of-%20Amorphous-Mesoporous-AlPO4- [Web Access: September 30th 2012]

[22] wiseGEEK. "What is Iron Phosphate?" http://www.wisegeek.com/what-is-iron-phosphate.htm [Web Access: September 30th 2012]

[23] Sopyan, I., Mel, M., Ramesh, S., & Khalid K.A.. (2006) Porous hydroxyapatite for artificial bone applications. http://iopscience.iop.org/1468-6996/8/1-2/A21/pdf/1468-6996_8_1-2_A21.pdf [Web Access: September 30th 2012]

Number of people a municipal sewage plant services	Reduction of phosphorus by percentage (%)	Maximum Concentration of phosphorus in effluent water (mg L^{-1})
300 - 2000	70%	2 mg L^{-1}
2001 – 10,000	80%	1 mg L^{-1}
10001 – 100,000	90%	0.5 mg L^{-1}
> 100,000	90%	0.5 mg L^{-1}

Table 2: shows the phosphorous requirement that the Helsinki Commission imposes depending on the number of people a sewage plant services. [24]

It is important to note that only one of the two phosphorus related columns must be fulfilled. The commission makes an exception if any municipal water plant that can show that it has reduced the phosphorus concentration by 90% in its treated water. If a water plant shows this 90%, it does not have to observe the other specific requirements shown in the table.

4. General Theory Behind Struvite Synthesis

4.1. The Reaction Mechanisms of Struvite Precipitation

Struvite is formed when PO_4^{3-} ions is attracted to the oppositely charged Mg^{2+} and NH_4^+ ions. This reaction would be an ideal situation, however since struvite synthesis most commonly occurs in solution, phosphate would likely be speciated and magnesium and phosphate ions would likely occur in a compound. These conditions clearly complicate the procedure and increase the possibility for other reactions t occur and inhibit the formations of struvite. This makes it difficult to estimate how the reactants will interact with one

[24] "Municipal Wastewater Treatment" (2007) Helsinki Commission: Baltic Marine Environmental Protections Commission. http://www.helcom.fi/Recommendations/en_GB/rec28E_5/ [Web Access: September 20th 2012]

another and how the other effects such as pH would affect these reactions (detailed in Sections 4.3 & 4.4).

4.2. The Reactants Used for This Experiment

Throughout this experiment the following reactants were used due to their availability in the laboratory: magnesium chloride ($MgCl_2$), potassium hydrogen phosphate (K_2HPO_4), ammonium (NH_4^+), and ammonia (NH_3).

$$K_2HPO_{4(aq)} + MgCl_{2(aq)} + NH^+_{4(aq)} \rightarrow NH_4MgPO_{4(aq)} + 2K^+_{(aq)} + 2Cl^-_{(aq)} + H_3O^+_{(aq)}$$

Figure 1: shows the chemical equation of the reactions between most of the reactants used through the duration of this investigation. Ammonia is not contained in this equation as it serves a different purposed later on.

In addition to that, the same concentration of K_2HPO_4 was used in every experiment. Since As 6 grams of K_2HPO_4, the molarity of the solution was:

$$n = \frac{m}{Mr}$$

$$n(K_2HPO_4 \cdot 3H_2O) = \frac{6\ g}{228\ gmol^{-1}}$$

$$n = 0.0263\ mol$$

$$c = \frac{n}{V}$$

$$c = \frac{0.0263}{1L}$$

$$c = 0.0263\ mol \cdot L^{-1}$$

Figure 2: shows the formulas used to calculate the molarity of the solution in terms of the potassium hydrogen chloride. An online periodic table was used for calculate it relative formula mass for the equation.

The reactants react on a 1:1:1 ratio, as seen in the equation in Figure 1, and therefore the amount of the other reactants used in the experiment would be 0.0263 mol, if not otherwise specified.

4.3. The Solubility Product of Magnesium Hydroxide in Water

One of the first observations made during the initial trials was that a compound prematurely precipitated when magnesium chloride was added to the phosphate solution. It was deduced that the compound was magnesium hydroxide. Knowing that magnesium hydroxide is a popular antacid, I varied the pH of the solution and verified that the more acidic the pH was made the less precipitate remained. In order to prevent the premature precipitation of this compound I determined the minimum pH of precipitation of magnesium hydroxide at 0.0263 mol/L using the solubility product of magnesium hydroxide.

$$K_{sp}\left[MgOH_2\right] = 1.8 \cdot 10^{-11}$$
$$\left[Mg^{2+}\right]\left[OH^-\right]^2 = 1.8 \cdot 10^{-11}$$
$$\left[Mg^{2+}\right]\left[OH^-\right]^2 = \frac{1.8 \cdot 10^{-11}}{c\left(Mg^{2+}\right)}$$
$$\left[OH^-\right] = \sqrt{\frac{1.8 \cdot 10^{-11}}{0.0263}}$$
$$\left[OH^-\right] = 2.6161 \cdot 10^{-11}$$
$$pOH = 4.5823$$
$$14 = pH + pOH$$
$$pH = 14 - 4.5823$$
$$pH \approx 9.42$$

Figure 3: shows the calculations used to determine the minimum pH of magnesium hydroxide precipitation when the concentration of magnesium in the solution was 0.0263 mol L^{-1}. [25]

These calculations show that so long as the pH is below 9.42 magnesium hydroxide should not precipitate.

4.4. The Speciation of Phosphoric Acid with Changing pH

The pH of the solution in which the reaction occurs not only plays a significant role in the precipitation of undesired compound, but also in the

[25] "Selected Solubility Products and Formation Constants at 25ºC" California State University. http://www.csudh.edu/oliver/chemdata/data-ksp.htm [Web Access: September 12th 2012]

synthesis of struvite. Specifically pH affects the speciation of phosphoric acid and vice versa. In non-laboratory settings, optimal conditions occur rarely, predominantly in the elbows of sewage pipes, [26] which accounts for the low amount of struvite produced naturally in the elbows of sewage pipes, where the pH is increased due to degassing, thus causing the speciation of phosphoric acid into a more desirable form. Producing struvite on a large scale requires maintaining an ideal environment so to form the purest and highest yields of struvite. A graph showing phosphoric acid speciation with differing pH is shown below.

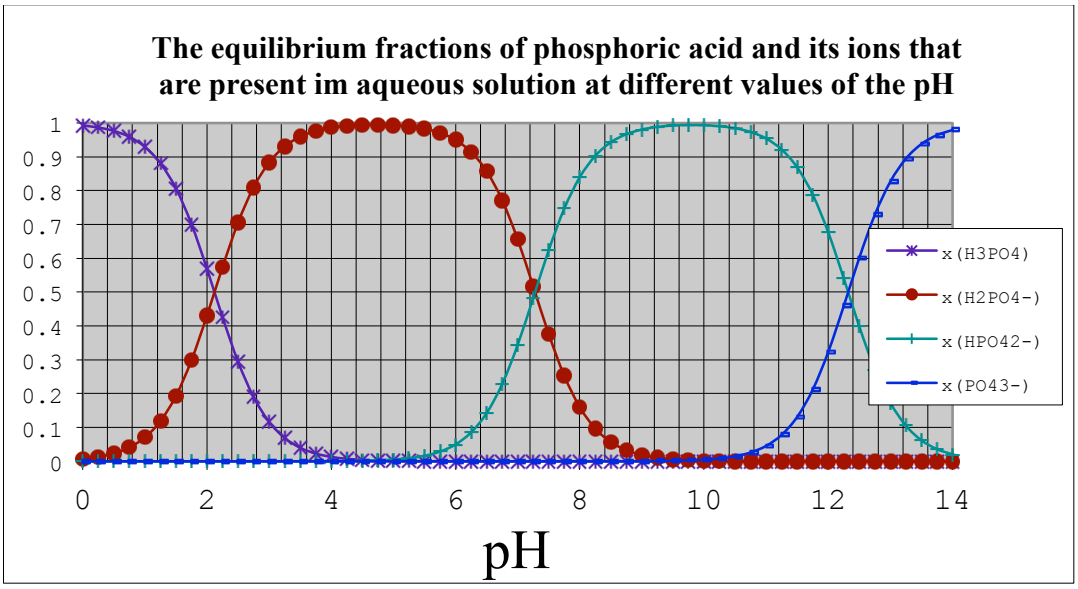

Figure 4: shows a graph demonstrates the general trend and ratio of phosphoric acid speciation with changing pH. [27]

As the species of phosphoric acid has an effect on the pH of a solution, the effect of 0.0263 moles of K_2HPO_4 needs to be calculated to determine the conditions it creates. Since HPO_4^{2-} is released by the dissociating of K_2HPO_4

[26] "Struvite Control in Wastewater" General Chemical. http://www.generalchemical.com/assets/pdf/Struvite_Control_in_Wastewater.pdf [Web Access: August10th 2012]

[27] Näsäkkälä, Elina (1999). "Introducing Simulations Models in Chemistry Classrooms. A study in a Finnish Senior Secondary School with an International Baccalaureate Section" (p.165). Helsinki: Departments of Teacher Education, University of Helsinki. [Print]

in water at pH values above pH=7 the following equilibrium equation must be considered in the opposite direction for this experiment.

$$HPO^{2-}_{4(aq)} + H_2O^- \rightleftarrows H_2PO^-_{2(aq)} + OH^-_{(aq)}$$

$$0.0263 \rightleftarrows x + x \quad \text{(concentrations and equilibrium)}$$

$$0.0263 - x \rightleftarrows x + x \quad \text{(concentrations and equilibrium)}$$

Figure 5: shows the amount equilibrium reaction that will be calculated.

Using a literary value for the acid dissociation constant (noted as K_a in these calculations) of $H_2PO^-_2$, the base dissociation constant of $H_2PO^-_2$ (K_b in the calculations) was found and then subsequently the pH at equilibrium was determined.

$$K_a = 6.3 \cdot 10^{-8}$$

$$1.00 \cdot 10^{-14} = K_a \cdot K_b$$

$$K_b = \frac{1.00 \cdot 10^{-14}}{6.3 \cdot 10^{-8}}$$

$$K_b \approx 1.6 \cdot 10^{-7}$$

$$K_b = \frac{\left[H_2PO^-_2\right] \cdot \left[OH^-\right]}{\left[HPO^{2-}_4\right]}$$

$$1.6 \cdot 10^{-7} = \frac{x \cdot x}{0.0263 - x}$$

$$x^2 - 1.6 \cdot 10^{-7} \cdot (0.0263 - x) = 0$$

$$x^2 - 3.9 \cdot 10^{-9} + 1.6 \cdot 10^{-7} x = 0$$

$$x \approx 6.4 \cdot 10^{-5}$$

$$\left[OH\right] \approx 6.4 \cdot 10^{-5}$$

$$\left[pOH\right] \approx 4.1938$$

$$14 = pH + pOH$$

$$pH = 14 - 4.1938$$

$$pH \approx 9.81$$

Figure 6: shows the calculations done in order to obtain the value at which pH the solution after the potassium hydrogen phosphate was added. [28]

The pH of the solution after 0.0263 moles of K_2HPO_4 results in a higher pH than the minimum pH required for the precipitation of magnesium hydroxide, meaning that if $MgCl_2$ was added before any precaution had been taken to lower the pH, the preliminary precipitation of Magnesium Hydroxide would definitely occur.

4.5. Similar Particle Size Substitution

In addition to the effect of pH on the synthesis of struvite, certain ions present in the solution can affect the formation struvite. For instance potassium from K_2HPO_4 has the same charge as ammonium and both the ion and molecule share a similar radius. Due to these qualities potassium occasionally substitute the ammonium in struvite. Luckily though this substitution has no known effect on the precipitation of phosphate from water. [29]

5. Initial Trials

5.1. Experimentation with the Reactants

During the beginning of the investigation, while familiarizing myself with the reactants, I conducted a few trial experiments to understand the different approaches one could attempt to synthesis struvite. In these primary trials I discovered that a substance would prematurely precipitate after the magnesium chloride was added to the phosphate solution (before the ammonium was added). I assumed that the substance was magnesium hydroxide as it would counteract an increase in pH and then dissolve, but was

[28] "K_a and pK_a for Polyprotic Acids" Upper Canada District School Board. http://www2.ucdsb.on.ca/tiss/stretton/database/polyprotic_acids.htm [Web Access: September 12th 2012]

[29] Fritz, James S. & Schenk, George H. (1969) "Quantitative Analytical Chemistry (3rd ed.). Boston: Allyn and Bacon, INC. [Print]

otherwise a highly insoluble white powder, which is consistent with its description.

5.2. Recorded Data & Verification of the Precipitate

The data recorded from three initial trials are shown below.

Trials	Gram Amount of $MgCl_2$ added to solution. (±0.1g)	Cloudiness of the Solution	Recorded pH after $MgCl_2$ addition (±0.001 units)	Millilitres of Concentrated HCl used to titrate the solution. (±1mL)
1	5.0	Mildly Cloudy	7.231	8
2	5.0	Mildly Cloudy	7.402	7
3	10.0	Very Cloudy	6.029	20

Table 3: shows the trends observed in the initial trails with changing amounts of magnesium chloride added.

The predominant difference between trials 1 & 2, when compared to 3 is the amount of magnesium chloride added to the solution. The clear trend is that the more magnesium chloride added the lower the pH becomes. The decrease in pH can be attributed either to an increase in hydroxide ion concentrations or a decrease in oxonium ion concentrations. Theoretically both of the following reactions could have occurred to cause a decrease in pH.

$$Mg^{2+}_{(aq)} + 4H_2O \rightarrow Mg(OH)_{2\,(s)} + 2H_3O^{+}_{(aq)}$$
$$3Mg^{2+}_{(aq)} + 2HPO^{2-}_{4(aq)} + 2H_2O \rightarrow Mg_3(PO_4)_{2\,(s)} + 2H_3O^{+}_{(aq)}$$

Figure 7: compares the two potential chemical equation that causes the premature precipitation.

There is however one observation that singles out magnesium hydroxide as the premature precipitate. The presence of phosphate is not required for the

synthesis of magnesium hydroxide, which is seen in the chemical equation. All that is required is the minimum pH for precipitation. On the other hand the latter of the two equations is dependent on the amount of phosphate. Considering that the concentration of magnesium present is almost twice the solution's concentration of hydrogen phosphate (5 grams of magnesium chloride per litre = 0.0525 $molL^{-1}$) increasing the magnesium chloride would not have any further effect as all the pH would have been reacted when 5 grams of magnesium chloride was added. Therefore the insoluble precipitate according to the experimental data must be magnesium hydroxide as it is the only alternative that follows the trends of the results. [30]

6. The Final Experiment

6.1. Further Research on Struvite Precipitation

After the conducting the initial trials, I realized that struvite synthesis is a process that has to be carefully manoeuvred, so not to upset the delicate balance of conditions, which can only be maintained through more sophisticated techniques. As I continued to research for possible procedures, I came across Vogel's method for struvite synthesis. I decided that since this method had accounted for many of the issues that arose from the initial trials, it would be potent solution that would result in lower phosphate concentration after the synthesis of struvite.

6.2. Procedure of Struvite Synthesis Based on Vogel's Method of Struvite Synthesis

[30] "Magnesium Hydroxide" Chemical Land 21. http://www.chemicalland21.com/industrialchem/inorganic/MAGNESIUM%20HYDROXIDE.htm [Web Access: September 4th 2012]

The procedure for Struvite Synthesis used in the final experiment is based on Vogel's and the University of Helsinki's methods.[31] In addition to this experiment method, I also sought out to find whether the addition of excess Magnesium Chloride or Ammonia would reduce phosphate levels the most.[32] [33] [34]

Initially a 1-litre solution of Hydrogen Phosphate with a molarity of 0.0263 mol L^{-1} litres was created. Then a volume 0.6 L was taken from solution and equally distributed into three flasks. An additional 0.1 litre sample was taken and added to another flask. Meaning there were a total four flasks containing either 200 to 100 ml of Hydrogen Phosphate Solution. The theoretical amount of phosphate presence in grams for each volume has been calculated below.

	At 200 ml	**At 100 ml**
Concentration of Potassium Hydrogen phosphate (g L^{-1})	6.00	6.00
Moles of Hydrogen Phosphate (mol)	0.0053	0.0026
Mass of Phosphate Present (g)	~0.50	~0.25
Mass of Phosphate present in milligrams (ml)	~500	~250

Table 4: Shows the varying figures pertaining to the amounts of phosphate present in different volumes of water.

In both Vogel's and The University of Helsinki's methods additional precautions and conditions were created, shown in the table below, to yield the highest amount of struvite. The substances that created these conditions,

[31] The University of Helsinki's method on struvite synthesis gives a more precise account on how to synthesize struvite from a phosphate solution using more precise measurements and some of the same chemicals that were to be used.
[32] Vogel, Arthur I. (1961). "Inorganic Analysis Including Elementary Instrumental Analysis (p.574-575) (3rd ed.) London: Longmans. [Print]
[33] Hämäläinen, R., Korvenranta, J., & Näsäkkälä, M. (2000) "Inorganic Chemistry Basis II (p.29-30). Helsinki: Department Chemistry: Inorganic Chemistry Laboratory, University of Helsinki. [Print]
[34] The apparatus used in this experiment can be found the in Appendix.

where in essence added to the solution to prevent the premature precipitation of magnesium hydroxide.

	Sample A	Sample B	Sample C	Sample D
Volume of solution (L)	0.2	0.2	0.2	0.1
Volume of Concentrated HCl added (mL) ±0.1 mL	12.0	12.0	12.0	6.0
Ph of Solution after HCl addition	2.562	2.522	2.452	0.339
Moles of Magnesium ions added	0.0084	0.0084	0.0053	0.0053
Volume of Magnesia Mixture [35] used (mL) ±0.1 mL	20.0	20.0	12.4	12.4

Table 5: shows the substances added to the solution, to allow for the highest yield of struvite. [36]

After these precautions had been taken, the solution was continuously stirred as it was slowly titrated with ammonia until the buffer point of pH= 9.25 [37] was reached. As I was also investigating the effect of ammonia on the yield of struvite, more ammonia was added to samples C & D seen in the following table.

[35] Magnesia Mixture is the buffer solution of ammonia and ammonium chloride, which is created, with addition of magnesium chloride to ammonia.
[36] As can be inferred from the data from Table 5, Samples A & B investigated the effect of excess magnesium Chloride while Samples C & D investigated the effect of adding an additional specific amount of ammonia after the buffer point of the solution had been reached.
[37] "Buffer Solutions" Chem Guide. http://www.chemguide.co.uk/physical/acidbaseeqia/buffers.html [Web Access: September 30th 2012]

	Sample A	Sample B	Sample C	Sample D
Volume of Ammonia used till buffer point reached	3.8	3.6	3.4	9.0
Volume of Ammonia Added After the buffer point	-	-	10.0	10.0

Table 6: shows the amount of ammonia added to the different samples. A dash indicates that no further ammonia was added.

Afterwards the samples were allowed to settle for at least 30 minutes, then the whit precipitate was removed from the solution via vacuum filtration.

Then the phosphate concentrations of the remaining solutions were determined. This was done by taking a 10-millilitre sample of the solutions and reacting it with the provided phosphate reagent PhosVer3, which coloured the water. A spectrophotometer was used to determine the colour of the solution and thus the concentration or phosphate in samples of solution after precipitation. [38]

6.3. Final Results & Discussion

The results obtained from the final experiment (shown below) were surprising. The phosphate levels in the solution after precipitation were unexpectedly low when considering all the complication encountered in the initial trials.

[38] Hach Company (2010). "Spectrophotometer handbook (Method 8048 was used). [Print]

Struvite Synthesis and Phosphate Precipitation a Procedure based off Vogel's Methods.				
	Precipitation with the use of excess magnesium		Precipitation with the use of excess ammonia	
	Sample A	Sample B	Sample C	Sample D
Theoretical concentration of phosphate before procedure (mg/L)	2500	2500	2500	2500
Experimental concentration of phosphate after procedure (mg/L)	1.62	1.71	1.44	1.14
Percentage of Remaining Phosphate	0.648%	0.684%	0.576%	0.456%
Average of Percentages in terms of excess substance used	0.666%		0.516%	

Table 7: shows various values, given in terms of litres, related to how effective struvite synthesis precipitated phosphate from water.

It was also intriguing that even though 6 g L^{-1} of K_2HPO_4 solution was used, which is more than Vogel's suggested amount of 5 g L^{-1}, the experiment still

shows that very low amounts of phosphate remained in solution.[39] This suggests that struvite precipitation could effectively remove phosphate ions from a wider range of phosphate ion concentrations, than previously thought.

Additionally the experiment shows that there is a marginally significant difference between using excess magnesium and ammonia in the effectiveness of precipitating struvite.[40] When using excess ammonia, in amounts according to the University of Helsinki's method, there was 23% less phosphate remaining. While it cannot be definitively stated that additional ammonia increases the yield of struvite based on four trials, such an outcome is intuitive as the addition of excess magnesium would decrease the minimum pH of magnesium hydroxide precipitation, meaning that more of it would precipitate rather than struvite.

Another noteworthy observation was the differences between the way Samples C & D were conducted and the resulting differences in the remaining phosphate concentrations. While both samples followed the general guidelines given in Vogel's method, Sample D used half the amount of reactants of the other samples (in the same ratios) and also followed the Helsinki University procedure more strictly. These differences resulted in slightly lower levels of remaining phosphate in the solutions. While this observation could be due to either of the changes or random error. This observation does hint at the possibility that equal of phosphate concentrations may be precipitated more easily when relatively low masses or amounts of phosphate are present, when compared to relatively high amounts. This

[39] Vogel Arthur I (1961). Inorganic Analysis Including Elementary Instrumental Analysis (p.574-575) (3rd ed.) London: Longmans. [Print]

[40] The addition of extra magnesium was achieved by increasing the amount of magnesia mixture used in a specific solution.

questions whether this method could truly be used in a commercial setting where the relative amounts of phosphate are much higher than in this experiment.[41]

7. Conclusion

When considering the results and their analysis, it becomes apparent that struvite synthesis is an effective method for phosphate removal. This is a safe assumption, as although very small gram amounts were used when conducting this trial, the reduction in phosphate concentrations were over 90%, which complies with the guidelines set by the Helsinki Commission for phosphate ion concentration reductions. Nn the context of this experiment, this method could at least be thought effective in cases where the phosphate levels does not exceed the concentration of 2.5 g L^{-1}. This single result would clearly have to be verified through further testing, however this result does seem reliable as this method of struvite synthesis was thoroughly investigated and well understood

One of the key oversight in this conclusion is that is assumes that struvite precipitation would occur in a solution of distilled water, where very few impurities exist that could inhibit this process. While phosphate precipitation could occur at the very end of the wastewater treatment process, after all the other nutrients and impurities have been removed, the water at the point would still not be as pure as the distilled water used in this laboratory experiment. However, not even this assumption can be taken for granted, as there is no guarantee that phosphate removal does not occur at the beginning of the process, where substances are present and could react

[41] Considering the context of this experiment the last point means to signify that while the concentration of phosphate in each solution was 2.5 g L^{-1}, only 0.5 and 0.25 grams were precipitated, which if taking this concern into consideration may not make the results obtained directly applicable to the precipitation of 2.5g of phosphate from a litre of water.

with the reactants, thus decreasing the amount of phosphate ions removed form the water.

Another limitation of this experiment is that fact that very few repeats were done, meaning that obtained results cannot be considered completely reliable. However considering the fact that this work was mainly investigative, this is not a weakness of the work as its main purpose of this it was to analyse the trends of the struvite formation while also to determining its plausibility in industrial settings.

While this experiment was not conducted in commercial settings, certain aspects of the experiment could be considered to be suitable and plausible for real world use. From the perspective of the Helsinki Commission, this experiment does suggest that struvite synthesis to reduce phosphate ion concentrations is a viable alternative to currently used methods as it reduces the amount of ions so significantly. However when considering the methods, certain procedures such as titration may not be replicable on a large scale. This means that further experimentation on a larger or industrial scale would be need to be conducted to verify if the intricate methods and specific produces and equipment used in this experiment could be translated into the real life situation of commercial waste water treatment or whether suitable modification to this procedure could be invented to allow for this method to work as effectively in large-scale wastewater treatment

In addition to verifying this procedures effectiveness in a commercial setting, the arising questions associated with this method of phosphate removal should also be answers through further experimentation. In addition to testing the purity of the struvite formed to verify the low phosphate levels, additional testing should be conducted that also determines how effective this method is in widely varying

phosphate ions concentrations as well as whether the relative gram amount of phosphate dissolved immensely affects the remaining phosphate concentration.

Overall this experiment has given insight into the potential of struvite as a means to reduce phosphate concentration in wastewater. While it has not investigated all aspects of this field, this investigation is a step in direction of using struvite.

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9. Appendix: Apparatus Used in the Final Experiment

This appendix contains a list of the apparatus used for the final experiment as well as in some cases how they were used. Many of the same apparatus was used in the initial trails as well.

Apparatus List:

- Digital Analytical Balances (0.1g & 0.01g accuracies)
- Glass Funnel
- 500 mL Beaker
- 1 L Volumetric Flask
- 250 mL Erlenmeyer Flasks
- Buchner Funnel (for vacuum filtration)
- Sidearm Flask (for vacuum filtration)
- Hose (for vacuum filtration)
- Aspirator (for vacuum filtration)
- 50 mL Burette (for ammonia titration)
- pH Meter
- Clamp Stand & Clamps
- Vacuum Assisted Volumetric Pipettes
    - 1 mL pipette
    - 5 mL pipette
    - 10 mL pipette
    - 20 mL pipette
    - Micro pipette (for measuring 0.1 mL values)
- Magnetic Stirrer & Stir Bar
- Spectrophotometer (with included 10 mL vile & phosphate reagent)