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# Investigating the feasibility of recovering urea from human urine

Department of Civil Engineering

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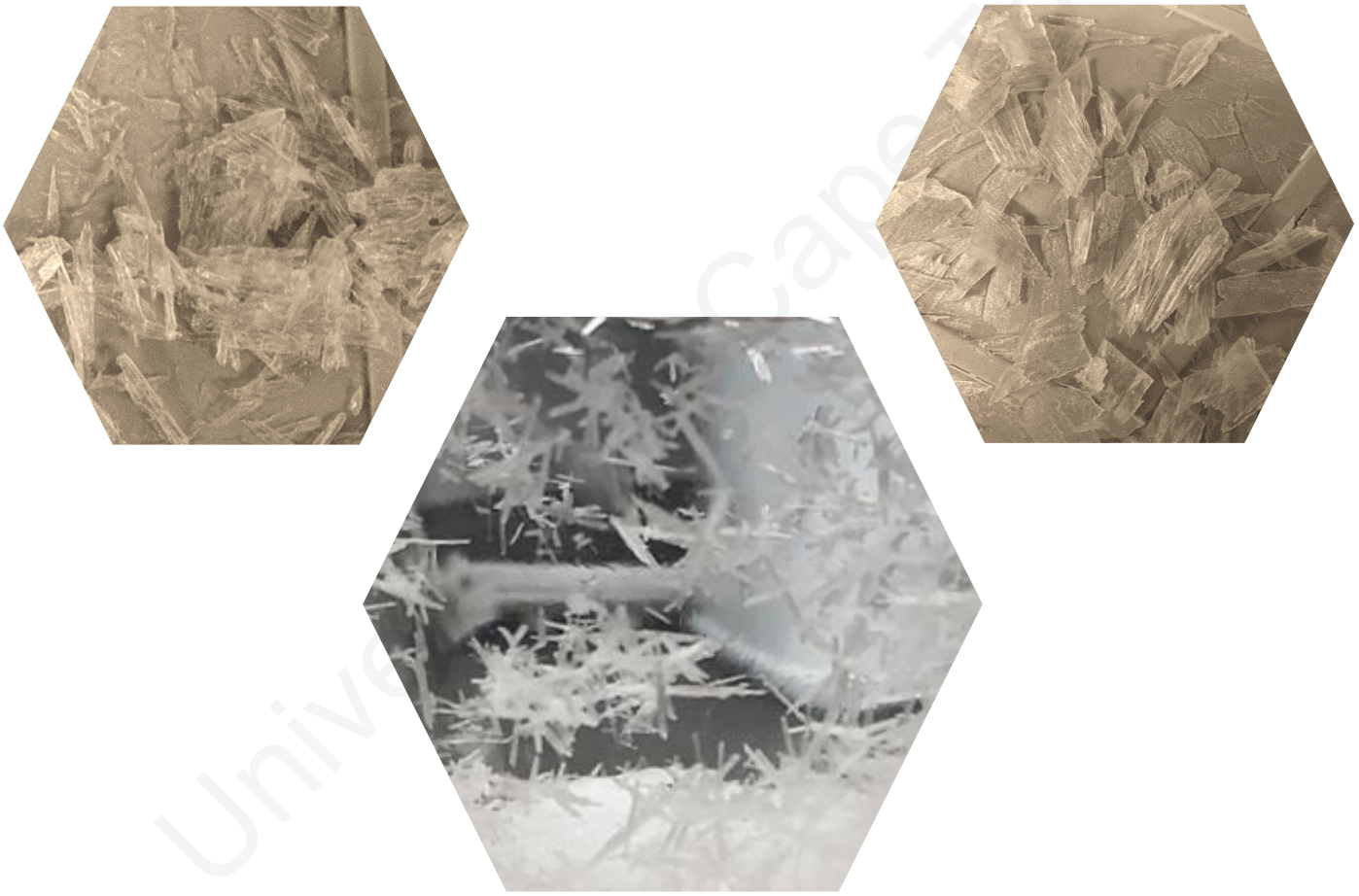



Dissertation submitted in fulfilment of the requirements for the degree:

MSc. Civil Engineering

# Declaration

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# Abstract


## Background

Urea is the most frequently used fertilizer by farmers globally and accounts for more than 50% of nitrogen-based fertilizer. It is produced indirectly through an energy intensive process known as the Haber-Bosch process. This process is often considered the most important invention in modern history because it contributed to the exponential growth in human population by providing food security. However, the process consumes 1 – 2% of the world's energy and contributes significantly to greenhouse emissions.

The growth in human population has brought with it a multitude of challenges including waste management, resource depletion, greenhouse gas emissions and water scarcity. All these challenges are addressed in isolation and the synergistic benefits of integrating their solutions are not often realized. One way to integrate the solutions is to create a paradigm shift where 'wastes', particularly human urine, are recognized as valuable resources, used to create value-added products.

Human urine contains the key nutrients used in agriculture, nitrogen (N), phosphorous (P) and potassium, (K), of which N is the most dominant nutrient. Most of the N present in human urine is in the form of urea. Therefore, the aim of this work was to investigate the feasibility of recovering and purifying urea crystals from human urine using a novel ethanol evaporation and recrystallization process. This would be achieved by exploiting human urine for its N content to produce urea crystals in a sustainable way. In this investigation, it was hypothesized that urea can be recovered from urine by evaporating the water from it and dissolving the remaining solids in ethanol to purify the product. The impurities would then be isolated via filtration, resulting in a urea-ethanol solution that can be evaporated to isolate purer urea crystals. This is because most inorganic compounds found in urine are insoluble in ethanol while urea is highly soluble.

The successful recovery of urea from human urine could potentially supplement the fertilizers produced from the Haber-Bosch process and address resource depletion. Challenges with waste management could also be addressed by introducing source separation of urine and faeces so that urine can be recycled for urea production. Because urine contains the highest nutrient load entering wastewater treatment plants (WWTPs), removing it from the wastewater flow could render the treatment process more energy efficient.

Urea is a versatile product with uses spanning across different industries including agriculture, chemical, aviation, and automotive. Therefore, the success of this study has the potential to sustain urea production by manufacturing it in a responsible manner by utilizing a 'waste' stream as a key input.

## Methodology

Three objectives were investigated to recover urea from human urine using the solubility differences of urea and impurities in water and ethanol. The first objective involved conducting a series of thermodynamic simulations on five different urine compositions obtained from

literature. The results of these simulations informed the conditions and parameters for the physical experiments that followed. Water removal from urine was simulated to determine at which point urea and other impurities would form. The simulation also predicted the potential yield and purity of the urea product. Thereafter, the addition of an intermediate filtration step at 99% and 95% water removal as a purification step was modelled to investigate whether the purity of urea improved.

Following that, the solubility of pure urea in ethanol was simulated to determine the volume of ethanol required to dissolve and maximize the yield of urea. Physical experiments were then conducted to validate the results of the model. To improve the volume estimate of ethanol, the impact of the urine composition on the solubility of urea in ethanol was also investigated. From these results, the solubility of one of the compositions was chosen as a standard to conduct all physical experiments.

The second objective involved recovering urea from different types of urine by operating within the parameters set by the thermodynamic model. Urea was recovered from a synthetic urine stream containing urea and inorganics (SI), a synthetic urine stream containing urea, organics, and inorganics (SO) and finally, a real urine stream (RU). The yields and purities of the three different experiments were compared and interrogated. In a final experiment, the solubility of urea in ethanol was investigated and compared to the thermodynamic model prediction. The model did not have the necessary database to model organics, other than urea. Therefore, another experiment was conducted to confirm the solubility of ethanol in urine containing organics.

The final objective was the conceptual design of a small-scale urea recovery unit treating 1 $m^3$ of urine per day. This was done to estimate the power requirements of such a system and the potential urea yield recovered per day. Finally, the profitability of the procedure was investigated by exploring different urea-based products.

**Key findings**

Thermodynamic modelling revealed that the point of crystallization of urea from urine was above approximately 99% water removal. Therefore, complete water removal was necessary to obtain the optimum amount of urea. An intermediate filtration step at 95% (58% purity) only improved the purity by 5% (from a purity of 53% at 100% water removed), while intermediate filtration at 99% (71% purity) improved the purity by 17%. An improvement of 5% was found to be insignificant relative to the final purity that could be achieved. In addition, intermediate filtration at 99% would not be practically feasible for the small volumes used in this study (1 L). Therefore, 100% water removal was used for these experiments. Based on this, a yield and purity of 100% and 53% was predicted by the model.

The solubility of pure urea in ethanol was determined to be 40.98 g $L^{-1}$ at 22°C, which was the average temperature in the laboratory. However, the impact of the urine composition on the solubility of urea in ethanol resulted in a higher solubility (50.05 g $L^{-1}$). This value was therefore used for all physical experiments that followed and resulted in an ethanol volume requirement of ~232 mL.

After complete water removal, yields of 91%, 84% and 93% and purities of 41%, 41%, and 43% were achieved for urea recovery from SO, SI and RU, respectively, which was lower that what the simulation predicted. After ethanol evaporation, yields decreased to 88%, 77% and 67% while the purities increased to 91%, 76% and 76% for SI, SO and RU, respectively. This demonstrated that the addition of ethanol improved the purity, but at a reduced yield. The loss in yield was likely due to a gradual decrease in pH during water removal, and prolonged evaporation times during ethanol evaporation, which could have resulted in enzymatic urea hydrolysis and loss of nitrogen as ammonia gas.

To improve the solubility measurement, a physical experiment was conducted and revealed that the actual solubility of a typical urine stream containing organics is 56.7 g $L^{-1}$, demonstrating that the solubility increases with the presence of organics. Therefore, future work should use this higher solubility instead to further maximize the yield and purity.

The conceptual design of a small-scale urea recovery system treating 1 $m^3$ of urine per day had an estimated system power requirement of 8.4 kW $m^{-3}$. The potential recovery of urea per day was 15.61 kg (67% yield) at a purity of 76%. The system could be improved to recover 20.5 kg at 88% yield and 91% purity if the measures for improving the purity and yield are incorporated in the design. These measures include the selective removal of dissolved ions from the urea-ethanol solution via ion-exchange, increasing the temperature to speed up the evaporation process, and adding an intermediate filtration step at 99% water removal.

Finally, through the analysis of different urea markets, the profitability of the procedure developed in this study was determined. It was concluded that a niche urea-rich liquid fertilizer would be the most valuable end-product to produce by redissolving the urea crystals in reclaimed water from the process. However, due to the small market of niche liquid fertilizers (~10% in the Cape Town region) it can only be produced in low volumes. Therefore, it was recommended that the remainder be used for diesel engine fluid production. The estimated profit per day (1 $m^3$ of urine) from the production of 20 L of niche liquid urea fertilizer, 11.5 kg of solid calcium phosphate fertilizer and 44.6 L of diesel engine fluid was R3110.

## Conclusion and outlook

This investigation demonstrated that the recovery of urea from human urine is achievable using the solubility differences in water and ethanol. All research objectives were fulfilled and the study described various opportunities for future work. This research developed an innovative method for recovering urea from human urine to potentially supplement the energy intensive Haber-Bosch process and discussed the possibility of producing alternative high-value products from human urine.

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# 1. Introduction

## 1.1 Background/ motivation

The rapid growth in the world's population has become an increasing threat to waste management systems and water security. The city of Cape Town's overburdened sewage plants (Chua, 2019) has shown the effect that a rapidly growing metropolis has on water resources. South Africa is faced with massive infrastructure maintenance and upgrading backlogs in the sanitation industry (Sikosana et al., 2017). The untreated wastewater often finds its way into the sea, polluting freshwater and affecting marine life (Chua, 2019). The conventional design and operation of these plants is based on the paradigm that human excreta are 'wastes' meant for disposal (Simha et al., 2018a). Consequently, there is a need to advance ways of decreasing the waste entering these plants to decrease the strain on our water supply.

In municipal wastewater, urine accounts for the majority of recoverable nutrients with approximately 80% of nitrogen (N), 50% phosphorous (P) and 70% potassium (K) (Jiang et al., 2017). This makes the recovery of nutrients from human urine a promising pre-treatment of wastewater. Comparatively, human faeces carry a significantly lower nutrient load (Ganrot, 2005). Furthermore, humans produce roughly 1.4 L of urine per day, compared to 140 g of faeces excreted per day (Larsen et al., 2009). Separating these streams at the source could render wastewater treatment more energy efficient (Larsen et al., 2009), ensuring clean and treated water is disposed into freshwater bodies. This source separation of urine and faeces has been achieved through various studies which introduced urine-separating sanitation solutions to isolate human urine from faeces (Menter, 2016; Münch & Winker, 2011; Simha & Ganesapillai, 2017).

Climate change and, subsequently, increased water scarcity resulted in Cape Town becoming the world's first major city to face the threat of a drought (Browdie, 2019). This resulted in severe water restrictions being imposed on the city and various water saving measures were introduced. Accordingly, researchers at the University of Cape Town (UCT) designed waterless, fertilizer-producing urinals to significantly reduce the amount of water used for flushing (Chipako & Randall, 2019; Flanagan & Randall, 2018). These waterless urinals were designed to simultaneously collect and treat urine on-site. This small-scale source separation initiated various urine-related research topics, including the focus of this dissertation: the recovery of urea crystals from human urine.

Urea is produced by many living organisms; however, it is manufactured industrially as a synthetic fertilizer. Synthetic urea is used as a soil additive in agriculture and accounts for more than 50% of global nitrogen-based fertilizer (Glibert et al., 2006). Its allure among farmers is due to it being easily transportable at room temperature (Nexant, 2019) and its low per unit cost of fertilizer application (Simha et al., 2018a). Its price per kilogram as of the end of February 2021, was R4.88 (IndexMundi, 2021). This is because it has twice the N content of the alternative ammonium sulphate fertilizer (Simha et al., 2018a).

However, synthetic urea production is energy intensive because it is produce indirectly by the Haber-Bosch process (Glibert et al., 2006). The process is responsible for the current human

population ‘explosion’ because it allowed farmers to produce more food and made it possible for agriculture to support a larger population (Briney, 2019). Global urea consumption continues to increase. It is estimated to have totalled 173 million tons in 2018, with fertilizer usage accounting for about 80% of this (Nexant, 2019). This is a significant contrast to the approximate 60 million metric tons produced in 2005 (Glibert et al., 2006).

Ammonia synthesis via the Haber-Bosch process requires high operating temperatures (185 - 190°C) and pressures (180 - 200 atm) to produce the amount of ammonia necessary to satisfy the growing global demand (Alper & Yuksel Orhan, 2017). This high energy input in the Haber-Bosch process represents approximately 2% of the global energy consumption (Sutton et al., 2013). This contributes to the climate change challenges posed by the demands of a rapidly growing population.

The agricultural sector is fertilizer intensive and irrigation-based (Zosfia Ganrot, 2005), whilst conventional sanitation uses energy intensive wastewater treatment processes to dispose of valuable nutrients. This shows two broken loops of agricultural practices and conventional sanitation systems. These loops can be closed by introducing source separation; using waterless urinals or no-mix toilets to significantly reduce flushing and implement resource recovery. Furthermore, valuable products such as urea, can be recovered from human urine to potentially combat the detrimental impacts of the Haber-Bosch process on the environment. Ultimately, a sustainable future, where human ‘waste’ streams are recognized as valuable resources to address global challenges, such as food insecurity and resource scarcity (Randall & Naidoo, 2018), can be imagined (Figure 1-1).

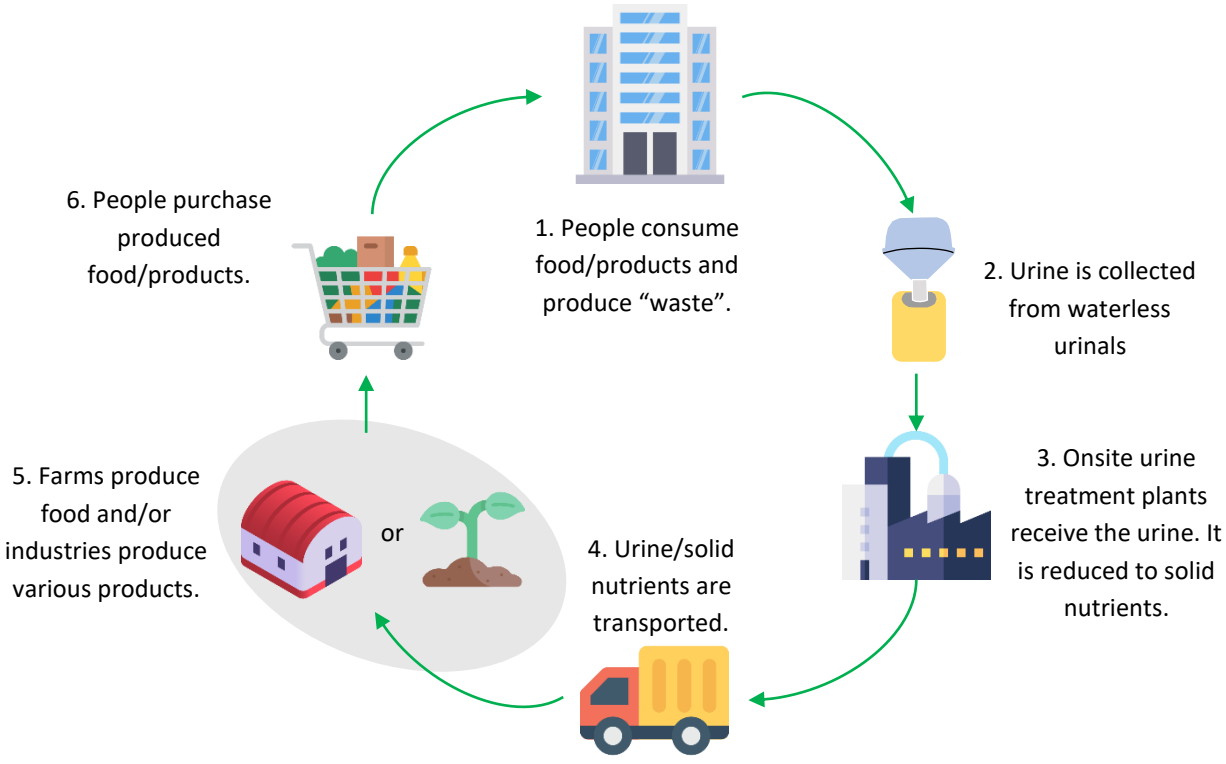


**Figure 1-1:** A conceptual visualization of a closed loop cycle where "wastes" are reimagined as valuable nutrients for ensuring food security and producing value-added products.

## 1.2 Problem statement

The problems in the sanitation, health, water, and agricultural sectors tend to be addressed in isolation. Our current systems have failed to realize the synergistic benefit of integrating the solutions to the challenges facing these sectors. These systems include the Haber-Bosch process which has proved to be unsustainable and a major contributor to climate change. Humans produce valuable nutrients, necessary for sustaining agriculture and food security, and yet these nutrients are discarded daily. Research has been performed on the source separation of human urine and faeces, such as the design of urine separating toilets and urinals. However, few studies have been conducted on the recovery of urea crystals from human urine as an alternative option to the Haber-Bosch process.

## 1.3 Hypothesis, research questions, and objectives

The key objective of this study was to investigate the feasibility of recovering urea crystals from human urine using a novel ethanol evaporation process. Thus, in accordance with this objective, the following hypothesis was developed:

> Urea can be successfully recovered from human urine by evaporating the water from it and dissolving the remaining solids in ethanol to purify the product. The inorganics can be isolated via filtration and the resulting urea-ethanol solution can be evaporated to recover purer urea crystals. This is because most inorganic compounds found in urine are insoluble in ethanol while urea is highly soluble.

To develop the key objectives for this study, the following research questions were posed:

1. At which point during water evaporation does urea crystallize?
2. Is urea recovery achievable at a sufficient purity and yield by simple water evaporation?
3. If intermediate filtration is carried out at 95% and 99% water removed respectively, is the urea purity significantly improved?
4. What is the solubility of urea in ethanol to achieve optimal urea recovery?
5. Can the thermodynamic model be validated through physical experiments?
6. Is the solubility of urea in ethanol impacted by different urine compositions?
7. How does the yield and purity of the three physical experiments compare?
8. Is the urea recovery method introduced in this study scalable and profitable? What is the ideal end-product for this method?

Therefore, based on these research questions and the hypothesis, the key objectives were to:

1. Use a thermodynamic model to investigate when urea and impurities are expected to precipitate during water removal by evaporation;
2. Investigate the yield and purity of urea after 100% water removal and the impact on the purity and yield after an intermediate filtration step at 95% and 99% water removal;
3. Thermodynamically investigate the solubility of urea in ethanol to predict the amount of ethanol required to dissolve urea after water removal by evaporation;
4. Perform physical solubility experiments to validate the thermodynamic model for urea dissolved in ethanol at various temperatures between 20°C and 70°C;

5. Investigate, thermodynamically, how different urine compositions affect the solubility of urea in ethanol and to choose one composition as a standard for the physical experiments to follow;
6. Perform three physical experiments to recover urea from: (i) synthetic urine containing only inorganics (SI), (ii) synthetic urine containing both inorganics and organics (SO), and (iii) real human urine (RU) and compare the yield and purity;
7. Investigate the potential energy requirements and profitability of a urea recovery system, treating 1 $m^3$ of urine per day, through a small-scale conceptual design based on the experimental results of this study.

## 1.4 Scope of research

The scope of this research was limited to determining a procedure for recovering urea from human urine by evaporation. Other urine volume reduction techniques such as freeze crystallization and reverse osmosis were reviewed in Chapter 2, but not explored in this work. The experiments were performed in the Water Quality Lab at the University of Cape Town and the study was not performed beyond lab scale.

The software (OLI Studio 10.0) that was used to thermodynamically model the experiments was not able to model urine with organics present, except for urea. Therefore, simulations were based on urine compositions with urea and inorganics only. The effect of the organics was later investigated experimentally.

The removal of pharmaceuticals from the urine was also not explored. Due to the restrictions imposed on South Africa because of COVID-19, to minimize human interaction, human urine from only three subjects was used in the study. Lastly, the final urea product was not tested for its use as a fertilizer, or in other industries.

## 1.5 Outline of dissertation

From this introductory chapter, the dissertation proceeds to Chapter 2 where literature on human urine, separation technologies, urine treatment and nutrient recovery techniques, the urea market and urea recovery is reviewed. Thereafter, Chapter 3 details the methods used to conduct this study. An outline of the thermodynamic modelling software is provided, as well as an overview of the analytical methods used in this study. Furthermore, a description of the apparatus and experimental procedures, including their aims and conditions is provided.

Chapter 4 presents all the results obtained from this study and the corresponding analyses and discussion of the key findings. An energy estimation is provided through the conceptual design of a small-scale urea recovery unit. This is followed by an evaluation of the cost and profitability of the urea produced in this study by exploring potential markets for it. Chapter 5 provides concluding remarks, summarizes the key findings, and briefly outlines the implications of this study. Recommendations for future studies then follow. Finally, Chapter 6 and 7 list the references used to inform the direction of this research and the raw data and calculations used in this study, respectively.

# 2. Literature review

## 1.1 Urine: the 'liquid gold' of wastewater

Human urine is a liquid by-product of the body and consists mainly of water (~95%), urea, cations ($Na^+$, $K^+$, $NH_4^+$, $Ca^{2+}$) and anions ($Cl^-$, $SO_4^{2-}$, $PO_4^{2-}$ and $HCO_3^-$), creatine and other organic compounds (Kirchmann & Pettersson, 1995). Throughout literature, human urine is increasingly becoming recognized as a valuable resource (Karak & Bhattacharyya, 2011; Lind et al., 2000; Simha et al., 2018b). Although urine accounts for only 1% of the domestic wastewater flow, it is the dominating source of primary agricultural nutrients (Dutta & Vinnerås, 2016). Approximately 80% of the nitrogen (N), 50% of the phosphorous (P) and 60% of the potassium (K) of human 'waste' is present in urine (Dutta & Vinnerås, 2016).

### 2.1.1 Inorganics vs organics in urine

The composition of urine can be divided into its various inorganics and organics. The major component present in urine, other than water, is urea. Figure 2-1 shows a breakdown of the constituents of human urine exceeding 10 mg $L^{-1}$ and distinguishes between inorganic and organic components. The organics make up about 64% of the total urine composition, with urea accounting for 47%. The inorganics make up the remaining 36%, with chloride being the most abundant ion (15% of the total).

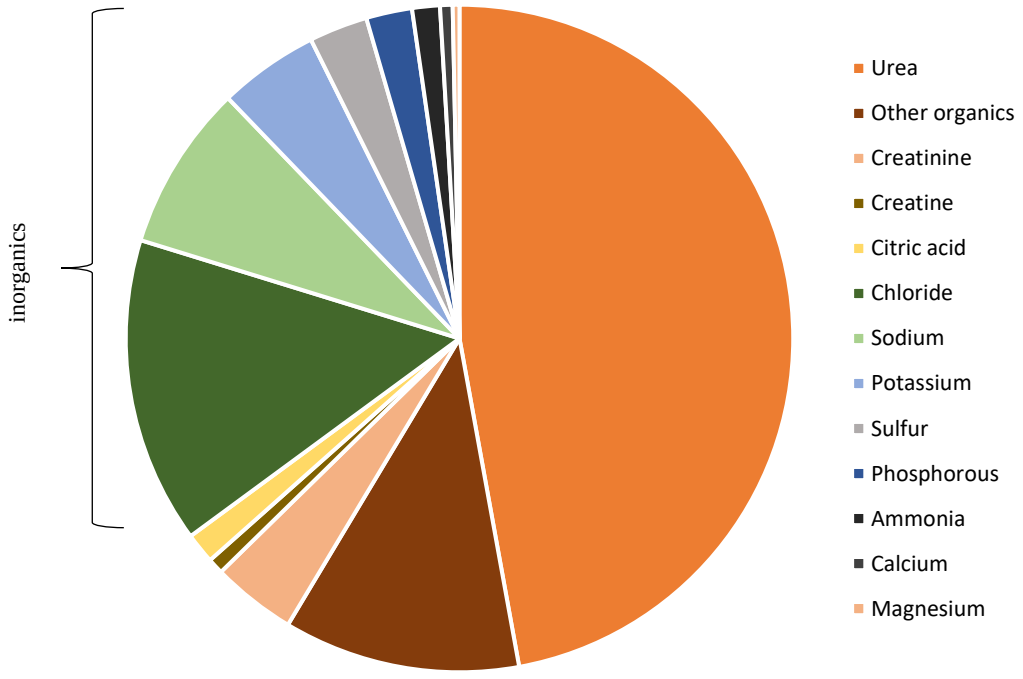


**Figure 2-1:** Typical composition of human urine showing the main constituents (Putnam, 1971). Urea is the most abundant component, accounting for 47% of the total. The split between total organics and inorganics is 64% and 36%, respectively. The "other organics" include hippuric acid, glacuronic acid, uric acid, uropepsin, bicarbonate, sulfur (organic), glycine, phenols, lactic acid, histidine, glutamic acid, androsterone, 1-methylhistidine.

### 2.1.2 The key nutrients

The key nutrients (nitrogen (N), potassium (K) and phosphorous (P)) present in urine are also primary nutrients found in fertilizers. Mihelcic et al. (2011) showed that the phosphorous available from the combination of human urine and faeces could satisfy 22% of the global P demand. Currently, most of the phosphorous used for fertilizer is sourced from phosphate rock, which is a depleting reserve. According to Smil (2000), 90% of the global demand for phosphorus is used to produce food and by 2030, phosphorous is predicted to reach its peak global output. Cordell et al. (2009) anticipates the depletion of the world's phosphate reserves within 60-400 years. Thus, there is an urgent need to develop ways to recover P from human urine as a sustainable alternative to the mining of phosphate rock.

Potassium mainly exists as free ions in human urine (Berger, 1960, *as cited in Dutta & Vinnerås, 2016*). The value of K as a compound in urine is often overlooked (Derese et al., 2015) and there is limited research on its recovery from human urine. Most of the K used in agriculture is derived from mined sources with an estimated mine production of 68.1 million tons globally as of 2018 (National Resources Canada, 2019). The estimated years of reserve are 257, however, the risk of future shortages of potassium needs further investigation (Sutton et al., 2013).

Nitrogen is the most abundant nutrient in human urine. In fresh urine, approximately 77% of nitrogen is fixed as urea, 15% as other organic compounds and the rest (8%) as organic ammonium salts (Putnam, 1971). Ammonia is volatile and substantial losses can occur during transportation, storage and application of source-separated urine (Udert et al., 2006). These losses have detrimental effects on the environment and human health (Galloway & Cowling, 2002). Furthermore, the production technology for most nitrogen-based fertilizers is based on ammonia production via the Haber- Bosch process with a high energy input (Zosfia Ganrot, 2005). Sutton et al. (2013) states that the production of ammonia through this process represents about 2% of the global energy consumption.

There is thus a growing need to source alternative ways to meet and satisfy the global demand for food whilst also addressing the many challenges that arise from an increasing population size. Nutrient recovery from human urine has the potential to secure food security, whilst decreasing the strain on our limited resources and can contribute to a circular economy. One of the ways how this can be achieved is by understanding the benefits and impact of source separation of urine and faeces in dealing with the global 'waste' problem.

## 2.2 Source separation

The common civil engineering approach to the provision of sanitation has been through large, centralized wastewater treatment plants. This has come with high capital and running costs; a dependency on fossil fuels, and has high maintenance costs (Etter et al., 2011). To move away from these unsustainable practices, new technologies, with a focus on the value of wastewater as a resource, have been explored (Guest et al., 2009; Larsen et al., 2013; Tilley et al., 2008a). One of these technologies is source separation, which is the separation and collection of excreta at the source to facilitate the recycling of nutrients (Larsen et al., 2009).

The main advantages of source separation are linked to resource management. Larsen et al. (2013) state that nitrogen and phosphorous are misplaced nutrients which are desperately needed in agriculture, especially in developing countries. However, the authors also note that these resources are polluting water resources globally, and that a significant increase in environmental pollution has been observed due to excess nitrogen. Environmental degradation has also been observed through excess P which is known to cause eutrophication (Schaum, 2018). In addition, it has further been observed that most pathogens are excreted via faeces. These negative environmental impacts are exacerbated by municipal wastewater mismanagement (Randall & Naidoo, 2018) for which source separation is a potential solution. Thus, given the varying impacts of the different constituents of wastewater, it becomes necessary to establish separate treatment solutions to deal with each. This begins with an understanding of the nutrient composition of faeces versus that of human urine.

### 2.2.1 Urine vs faeces in wastewater

Larsen et al. (2009) reported that approximately 1.4 L of urine and 140 g of faeces are produced by each person per day (translating to ~511 L of urine and 51.1 kg faeces per year). Dutta & Vinnerås (2016) estimated similar values of 400 – 500 L of urine excreted per person per year. Of this amount produced per year, they claimed 4 kg is nitrogen, 0.4 kg is phosphorous and 0.9 kg is potassium (Dutta & Vinnerås, 2016). Elsewhere, Wolgast (1993) estimated an annual excretion of 500 kg of urine and 50 kg of faeces (with a dry matter content of 20%) per individual. The nutrient composition for the total excreta was found to be 5.7 kg N, 0.6 kg P and 1.2 kg K (Wolgast, 1993).

A comparable Vietnamese case study estimated a daily urine production of 0.82 – 1.2 kg per person and a daily faeces production of 130 – 140 g per person Polprasert (1981). All these authors note the significantly higher nutrient load carried by urine compared to faeces. Ganrot (2005) compared the amounts of excreted nutrients in human urine to those in faeces using data from (Wolgast, 1993) (Table 2-1). These were then compared to the fertilizer needed to cover the calories and protein intake of the average adult per year (~250 kg grain).

**Table 2-1:** The amount of N, P and K that can be recovered from human excreta, compared to the amount of fertilizer needed for 250 kg of grain. The table shows the significant difference between the nutrient value of human urine compared to faeces. Furthermore, the combined nutrient recovery potential is enough to meet the 250 kg grain demand (Wolgast, 1993).

| Most important nutrients | Urine | Faeces | Total | Fertilizer required for 250 kg of grain |
|---|---|---|---|---|
| | 500 L | 50 L | | |
| N | 5.6 kg | 0.09 kg | 5.7 kg | 5.6 kg |
| P | 0.4 kg | 0.19 kg | 0.6 kg | 0.7 kg |
| K | 1.0 kg | 0.19 kg | 1.2 kg | 1.2 kg |
| N + P + K | 7.0 kg | 0.45 kg | 7.5 kg | 7.5 kg |
| | (94%) | (6%) | (100%) | |

The study by (Wolgast, 1993) illustrates that urine accounts for approximately 94% of the total nutrient load in urine and faeces combined. Furthermore, the recovery of N, P, K from human urine could potentially satisfy the fertilizer need for 250 kg of grain by 100%, 57% and 83%, respectively (Wolgast, 1993).

Finally, the elemental composition of human urine shows that its heavy metal concentration (namely, copper, zinc, chromium, nickel, lead and cadmium) is low compared to faeces (Karak & Bhattacharyya, 2011). Therefore, the separation of faeces (that contain most of the pathogens) from urine reduces the risk of environmental pollution, as well as the risk of transmission of water-borne diseases (Simha & Ganesapillai, 2017).

Recovering nutrients through source separation not only allows for the recycling of nutrients to create value-added products for sustaining humankind, but it also allows for the reduction in nutrient loads at the wastewater treatment plant, rendering the process more energy efficient. This is because, through source separation, the excreta with the highest nutrient load (urine) can be removed from the system through technologies such as urine diversion toilets or urinals.

### 2.2.2 Conventional end-of-pipe systems

The design and operation of conventional wastewater treatment plants (WWTP) is established on the notion that human excreta are ‘wastes’ that require treatment and removal (Simha & Ganesapillai, 2017). The main objectives of these WWTPs are to (i) ensure minimal exposure to these ‘wastes’ by conveying them through a cistern flush toilet and (ii) dispose of these ‘wastes’ by conveying them through an end-of-pipe system (Langergraber & Muellegger, 2005). Some drawbacks of modern WWTPs include: high energy requirements and water intensity; poor financial sustainability; sensitivity to discharge loads and inadequate final treatment, leading to the contamination of water bodies (Winblad et al., 2004). Jenssen et al. (2004) notes the following as the current core problems of conventional sanitation systems:

1. Valuable drinking water is used to carry nutrients and pollutants;
2. Organic and inorganic nutrients are mixed with pollutants and pharmaceuticals;
3. Bacteria are rarely eliminated through conventional sewage treatment;
4. Valuable nutrients cannot be recycled;
5. Water can only be treated to potable standards using highly technical methods.

The removal of N and P from municipal wastewater also requires a substantial amount of energy (Randall & Naidoo, 2018). For example, the required energy for N removal at a treatment plant is estimated to be 45 MJ kg-$N^{-1}$ whilst P removal requires 49 MJ kg-$P^{-1}$ (Maurer et al., 2002). Therefore, reducing these nutrient loads through urine separation could significantly reduce plant operating costs. Furthermore, Wilsenach & Loosdrecht (2006) demonstrated that reducing 50% of the urine volumetric flow to a treatment plant significantly reduces the nitrogen loads for treatment. Thus, at higher urine diversion rates, it could be possible to achieve an energy surplus (Simha & Ganesapillai, 2017).

### 2.2.3 Source separation technologies

Because urine contributes most nutrients and many micropollutants to wastewater, urine separation has many benefits. It can potentially relieve conventional wastewater treatment; enable high nutrient recovery for agricultural purposes and eliminate micropollutants (Larsen et al., 2001). Urine-diversion toilets (UDTs) are a possible route for achieving maximum recovery of nutrients in urine (Lind et al., 2000). These toilets mimic human physiology by separating faeces from urine to facilitate their separate collection. They are available in various forms, including 'no-flush', also referred to as a 'Urine Diversion Dry Toilet' (Simha & Ganesapillai, 2017).

Tilley et al. (2008a) describes a Urine Diverting Flush Toilet (UDFT) as a water-based sewer system that separates and collects urine without water and uses the water to flush (Figure 2-2). The faeces are conveyed through either a low-cost simplified sewer, or a conventional gravity sewer and they undergo conventional wastewater management unit processes (Tilley et al., 2008a). Urine is stored in an underground storage tank and is later emptied and transported to a site for application (Tilley et al., 2008a).

These toilets require less water than cistern flush toilets and are more likely to be generally accepted due to their resemblance to the conventional toilets (Tilley et al., 2008a). However, Tilley et al. (2008a) also highlights that they require a constant source of water and are prone to clogging and misuse.

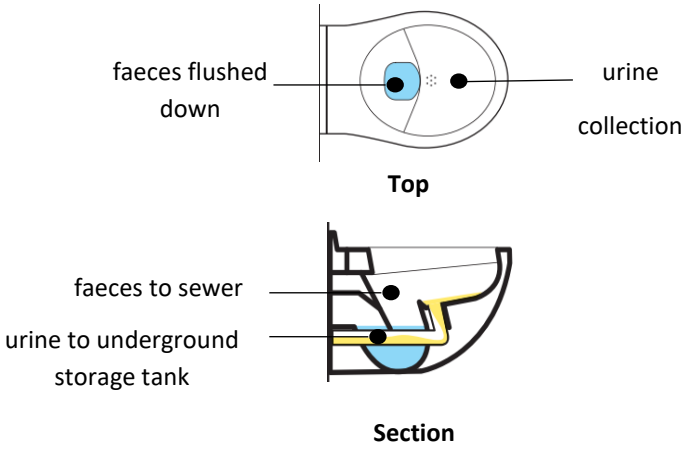


**Figure 2-2:** Urine Diverting Flush Toilet (UDFT). Urine is collected and stored in an underground storage tank, whilst faeces are conveyed to the sewer network. It is a water-based system because water is used to flush the faeces (Tilley et al., 2008a).

There is a way to avoid using water completely by introducing Urine Diverting Dry Toilets (UDDT) (Figure 2-3). A waterless urine diverting system collects and conveys the urine in the same way as the water-based system. The difference is in the collection of the faeces. The faeces are stored in double dehydration vaults, dried and transported for surface disposal to agriculture (Tilley et al., 2008a).

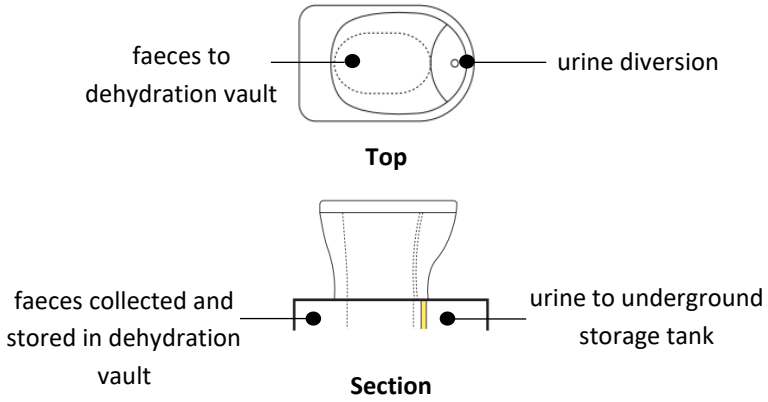


**Figure 2-3**: Urine Diverting Dry Toilet (UDDT). Urine is collected in a storage tank and later transported for application. Faeces are collected and stored in a double dehydration vault and are later used for surface disposal (Tilley et al., 2008a).

This technology does not require a constant water source and resembles the conventional toilet. It will however still require education and acceptance for use, and is prone to clogging with faeces (Tilley et al., 2008a).

The implementation of the abovementioned technologies in an urban context with advanced sewerage systems, an office building for example, presents challenges though. Flanagan & Randall (2018) mention that the existing plumbing system would need to be retrofitted for separate pipes. Additionally, these toilets may cause blockages as solids build up in the piping system (Flanagan & Randall, 2018). A further concern is cross-faecal contamination of the source-separated urine (Simha & Ganesapillai, 2017).

Therefore, the third alternative offers a solution for water conservation and the recovery of nutrients without the challenges of the interference of faecal matter. Flanagan & Randall (2018) produced a waterless, fertilizer-producing urinal with a built-in urea hydrolysis inhibitor to allow for the storage of urine for extended periods of time. Approximately 11.23 g of solid fertilizer per kg of urine was recovered and they concluded that the method is also profitable.

These waterless urinals have been introduced at the University of Cape Town for research purposes and have demonstrated an easy method for collecting urine from bathrooms. The urine stabilization method used in these urinals is based on a study by Randall et al. (2016), discussed in section 2.4.2 of this chapter. The fertilizer-producing urinal is shown in Figure 2-4, including its design characteristics.

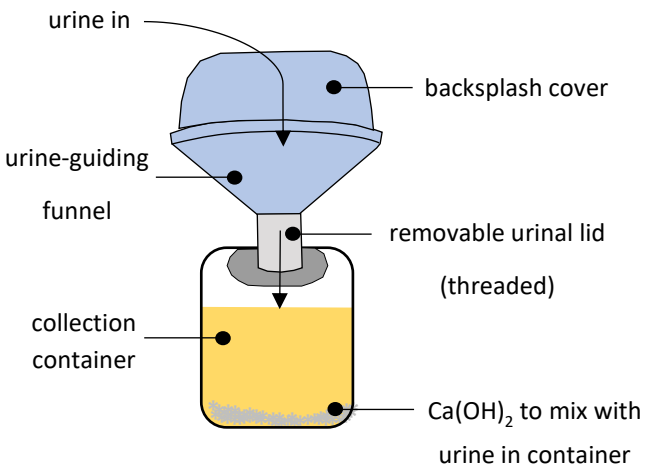


**Figure 2-4:** Diagram showing the design characteristics of a fertilizer-producing urinal. The urinal makes use of passive dosing of 10 g $Ca(OH)_2$ per L of urine as a method for stabilizing the urine to prevent nitrogen losses. The urinals are designed to carry 25 L of treated urine (Flanagan & Randall, 2018).

Urine is guided into the urinal by the funnel into the collection container. The urine then mixes with the $Ca(OH)_2$ at the bottom of the container and is stabilized to prevent nitrogen losses (Flanagan & Randall, 2018). Flanagan & Randall (2018) discovered that this process not only prevents malodour but also causes phosphorous precipitation which could be recovered as fertilizer. Urine from waterless urinals can be collected, undiluted, in a storage tank and transported to a site for agricultural use (Münch & Dahm, 2009).

### 2.2.4 Global examples and public perception of source separation technology

An estimated 26% of the global population does not have access to basic sanitation such as toilets and pit latrines (WHO, 2019). In their annual report on global sanitation, WHO (2019) stated that 31% of the global population use conventional sanitation facilities connected to sewers and a treatment system. They maintain that a large percentage of the population either lacks privacy; is exposed to diseases such as cholera, diarrhoea, and hepatitis A, and fall at risk to crime and sexual assault. This is all due to poor infrastructure.

Globally, measures have been taken to address the sanitation crisis. The feasibility of urine diverting toilets as an alternative to conventional sanitation is a well-established concept across the world (Simha & Ganesapillai, 2017). Examples of such interventions is the sale of over 300 000 UDTs by a company based in Sweden (Münch & Winker, 2011); a rural sanitation programme based in Durban, South Africa encompassing 75 000 UDDTs (Okem et al., 2013) and the installation of 900 UDDTs in Bolivia (Menter, 2016).

In the Durban rural sanitation programme case study on the perceptions and willingness to use urine in agriculture, it was found that less than 5% of participants ended up using urine as fertilizer (Okem et al., 2013). The researchers attributed this to a limited awareness around the nutrient value of urine and its role in sustaining agriculture. Moreover, the public were concerned about their health, as well as the smell. It was therefore recommended that efforts be made in future to create awareness around how human urine can address challenges in sanitation, poverty, and food security.

Elsewhere, a survey on source separation technologies across seven European countries revealed that about two thirds of users were open to the concept and would buy urine-fertilized food (Lienert & Larsen, 2010). In a feasibility study on the implementation of waterless urinals at a public university in Cape Town, South Africa, Chipako & Randall (2019) found that around 87% of respondents would use urine-diverting technology. Furthermore, around 79% stated they would consume urine-fertilized food (Chipako & Randall, 2019).

Waterless urinals are primarily available for males, limiting the potential recovery of nutrients to a smaller target group. While there are urinals on the market for females, they are not as widely accepted. Females have a greater need for privacy because they need to partially undress and sometimes squat uncomfortably (Münch & Dahm, 2009). Examples of squatting-type urinals can be seen in some African and Asian primary schools (Münch & Dahm, 2009), however a significant improvement in the technology is needed to increase acceptance among female users.

Globally, waterless urinals generally have the same level of user acceptance as conventional cistern flush toilets, because for male users, no change in behaviour is required (Münch & Dahm, 2009). Further studies would need to be conducted to investigate alternative solutions for female users to optimize the recovery of urine.

Various authors have demonstrated that urine-separation is practically well-established and is thus a promising solution for shifting away from unsustainable conventional sanitation systems. It not only reduces the environmental externalities of nutrients polluting freshwater reserves, but also encourages the exploration of various nutrient recovery techniques. This demonstrates a gradual embracing of the first step towards achieving a closed loop system.

## 2.3 Urine treatment processes for nutrient recovery

Recent research efforts have been focused on the technological recovery of nutrients from human urine. A paradigm shift is happening where the focus is no longer on ‘source separation, collection and reuse’ but now on ‘source separation, collection, resource recovery and safe reuse’ (Simha & Ganesapillai, 2017). Through exploring the fertilizer production potential of human urine, Winker et al. (2009) concluded that urine is the most promising and well investigated component of the human waste stream. Various authors have developed technologies that facilitate the recovery of nutrients from human urine to produce value-added products. This section describes the well-studied potential processes for urine treatment to achieve nutrient recovery.

### 2.3.1 Hygienization

An important step in the process of recovery and re-use of human urine and its nutrients is hygienization. The hygienic hazards of wastewater are mostly brought about by human faecal excreta (Langergraber & Muellegger, 2005). Thus, separation becomes an effective tool for reducing pathogens in human urine by limiting faecal contamination. Various methods for sterilising any solution are available, including UV radiation, heat, and pressure. Furthermore, previous studies have suggested solar radiation as a hygienization method that could potentially degrade pathogens and micropollutants (Antonini et al., 2012). However, these methods have

not been tested for urine. Instead, storage has been explicitly explored as an effective method for hygienization (Maurer et al., 2006).

**Storage**

Urine sourced from many households needs to be stored to ensure hygienization (Richert et al., 2010). The method not only removes pathogens but has also been reported to recover the largest amount of N from wastewater compared to other treatment methods (Wielemaker et al., 2018). During storage, urea hydrolyses, resulting in an increase in pH and ammonium ion concentration (Chipako & Randall, 2020b). Struvite and calcium phosphate precipitation also occurs, and these products can be potentially used as quick release fertilizers (Wielemaker et al., 2018).

Hygienization by storage is dependent on time, temperature and pH (Maurer et al., 2006). Wielemaker et al. (2018) recommended that most UDDT systems store urine for up to six months to achieve proper hygienization. According to the WHO (2016) guidelines, an extreme pH, high ammonia concentration, and elevated temperatures are preferred to kill off pathogens.

Limitations to this treatment method include the possible evaporation of ammonia from storage tanks that are not properly sealed (Udert et al., 2006) which can result in significant loss of nitrogen. It is also not guaranteed that UDDTs for household use will have the capacity to store urine for up to six months at the required temperature and pH. This would likely require larger storage tanks and the installation of technical equipment to control these parameters. Many of the treatment processes discussed in this chapter will influence the hygienic properties of the urine.

### 2.3.2 Volume reduction

Approximately 95% of human urine is water (Kirchmann & Pettersson, 1995), thus the nutrient content of urine accounts for the remaining 5%. To maximize on the nutrient value of urine, it is useful to concentrate these nutrients through various volume reduction techniques. Volume reduction is also beneficial for purposes of storage and transportation. Water removal techniques that have been investigated include (i) evaporation, (ii) freeze-thaw and (iii) reverse osmosis.

**Evaporation**

Evaporation is considered the most straightforward technology for the removal of water from human urine to concentrate its nutrients (Maurer et al., 2006). Water can be evaporated from urine using conventional methods such as heating using coal, or sustainable methods such as solar power (Patel et al., 2020). Evaporation can yield a solid fertilizer rich in nutrients which can be directly applied to agricultural land (Pronk & Koné, 2009).

In a study on the passive evaporation of source-separated urine from dry toilets, Bethune et al. (2014) used gravity-drainage through vertically stacked trays. The configuration consisted of a layer of sand to enhance evaporation, stabilize ammonia, and retrieve a solid product. Through this method, water was evaporated at a flux of 8.5 L $m^{-2}$ $day^{-1}$. A solid product

comprised of Na, Cl, N, P and K was obtained. However, there was a significant loss of nitrogen (~90%) due to ammonia volatilization (Bethune et al., 2014).

Antonini et al. (2012) investigated the solar thermal evaporation of urine to recover nitrogen and phosphorous. After 26 days of exposure to the sun, 360 g of solid fertilizer was obtained from 50 L of urine. The solid product comprised mainly of NaCl and minimal traces of P and N (~2%) (Antonini et al., 2012). Elsewhere, Pahore et al. (2010) investigated using a vertical gauze sheet as an on-site volume reduction system for urine. Water penetrates the sheet, emerges onto the sheet surface and escapes into the atmosphere. An 80% volume reduction of 10 L of urine per day was achieved (Pahore et al., 2010).

A major limitation to this technique is the loss of nitrogen due to ammonia volatilization (Patel et al., 2020). This can be alleviated by various stabilization techniques which will be later expanded in this chapter. Energy consumption is also a concern (Maurer et al., 2006) (with the exception of solar power) in comparison to other techniques.

**Freeze-thaw**

When urine is cooled to a low enough temperature, ice crystals form into a tetrahedral structure (Lind et al., 2001). This formation makes it impossible for other elements, besides water molecules (salts and other impurities), to integrate into the crystalline structure. These impurities, which are mainly ions and compounds, remain in liquid form, leaving the ice free of impurities (Lind et al., 2001). This forms the basis of freeze-thaw technology.

Lind et al. (2001) investigated volume reduction and concentration of nutrients in urine by freezing urine at –14°C. This concentrated approximately 80% of the nutrients in 25% of the original volume. In another study, Gulyas et al. (2004) used a stirred vessel and a falling film freeze concentrator which they claimed separates the solutes and ions more efficiently. A different study by Sinica et al. (2012) achieved an 87% concentration of nutrients from urine using a freezing-melting method.

A thermodynamic study was conducted by (Randall & Nathoo, 2018) to predict the potential financial benefits of a wastewater when operating under eutectic freeze crystallization (EFC) conditions. Eutectic freeze crystallization can be used to recover many resources from wastewater streams by operating at temperatures below zero, where both salts and ice are formed (Randall & Nathoo, 2018). The study showed that the recovery of several different salts from three different streams, namely, reverse osmosis brine, sea water and stored urine was thermodynamically feasible under EFC conditions. To date, EFC has been used to treat various types of wastewaters (Nathoo et al., 2009; Randall et al., 2014), but no experimental study has focused on the treatment of human urine.

Gulyas et al. (2004) claims that added benefits of freezing is the removal of odour and the prevention of ammonia losses. In addition, the heat of freezing is almost 7 times less compared to the heat needed for evaporation, rendering it more energy efficient (Rogers & Mayhew, 1995). However, the option would be more efficient and cost effective in colder climates (Gulyas et al., 2004).

**Reverse osmosis**

Another well-investigated technique for concentrating nutrients in urine, as well as recovering water of high quality from the process, is reverse osmosis (RO). It is a pressure-driven membrane process which allows for 95 – 99% of dissolved solutes to be retained on the membrane, and the permeate (low in salt concentration) to pass through (El-salam, 2003).

Dalhammar (1997) achieved a maximum concentration factor of 5, recovering 70% of ammonium, 73% of phosphate and 71% of potassium through reverse osmosis. Elsewhere, Thörneby et al. (1999) were able to remove 75-80% of the water and retained 93-97% of ammonia. Due to the potential of urine to scale and plug the pores of RO membranes, a pre-treatment is required to increase the life of the membrane (Patel et al., 2020). As a result, Ek et al. (2006) investigated using a pre-filtration with particle separation at 5 µm to avoid membrane clogging. The recovery of N, P and K was 95%, 90% and 99%, respectively (Ek et al., 2006).

The retention of ammonium ions by the RO membrane is better than that of ammonia, thus N recovery is strongly dependent on pH (Maurer et al., 2006). This can be controlled by acidification. Chemical dosage can also be used to limit scaling on the membrane (Patel et al., 2020). Furthermore, reverse osmosis has high energy demands (Patel et al., 2020), but a study by Udert & Wächter (2012) showed that when combined with distillation, the process can be energy efficient. It was estimated that for water removal from nitrified urine (1.5 $L^{-1}$ $day^{-1}$) the energy demand for 80% RO and distillation was 11 W $capita^{-1}$. Reverse osmosis alone would not be suitable for complete water removal as it has been reported to remove only up to 80% of water. In the investigation, the energy demand was reduced by 76% by combining distillation with reverse osmosis (Udert & Wächter, 2012).

### 2.3.3 Stabilization

To achieve optimum recovery of nutrients from human urine and prevent malodour, urine has to be stabilized (Randall et al., 2016). Urine stabilization refers to the prevention of enzymatic urea hydrolysis. Approximately 85% of the N in human urine is present in the form of urea, which quickly hydrolyses to ammonia (Senecal & Vinnerås, 2017). This reaction is catalysed by the enzyme urease (Ganrot, 2005). Carbamite is then produced, which spontaneously hydrolyses into carbonic acid, releasing a second ammonia molecule. Urea hydrolysis results in a significant loss of nitrogen due to the release of free volatile ammonia, and the release of carbon dioxide contributes to environmental pollution (Randall et al., 2016). As a result, various methods for preventing the volatilization of ammonia have been investigated.

**Urine stabilization techniques**

One approach to preventing urea hydrolysis is by pre-treating the urine to limit urease activity whilst concentrating the nutrients in urine through water removal (Senecal & Vinnerås, 2017). Parker et al. (2012) studied the effect of adding inhibitors such as N-(n-butyl) thiophosphoric triamide (NBPT) to limit urease enzymes in agricultural soils. However, Krogmeier et al. (1989) reported observing phytotoxicity in plants, indicating the adverse impacts of NBPT on the environment. Ciurli et al. (1999) also mentions the potential risks of NBPT to human health. Alternatively, urease enzymes can be limited by controlling the pH and the temperature. One

study found the optimum pH value for urea hydrolysis to be 7 at a temperature of 30°C (Hotta & Funamizu, 2008).

Hellström et al. (1999) investigated acidification as a stabilization technique and concluded that dosing 60 meq sulphuric or acetic acid per L of undiluted urine at the beginning of the storage period could inhibit urea hydrolysis. In a different study, Hanaerus et al. (1996) concluded that urea hydrolysis could be inhibited by the addition of 26 mmol of sulphuric acid ($H_2SO_4$) per L of undiluted urine. Elsewhere, nitrification was used to stabilize urine before concentrating the nutrient solution with distillation (Fumasoli et al., 2016). However, acid addition as a stabilization technique is potentially dangerous (depending on the choice of acid) and requires pumping equipment and exact acid dosing (Randall et al., 2016).

**Stabilization by alkalization**

Senecal & Vinnerås (2017) recommend alkalization as an alternative option for urine stabilization. They studied the use of wood ash as an alkaline medium due to its high initial pH, high surface area, and faster dehydration of urine. A 95% reduction during dehydration was observed whilst 90% of the N was preserved (Senecal & Vinnerås, 2017).

In a similar investigation by Randall et al. (2016), calcium hydroxide ($Ca(OH)_2$) was demonstrated to effectively increase the pH of fresh urine above 11 to inhibit urea hydrolysis, and (Simha et al., 2021) showed that magnesium oxide was also effective at stabilizing urine. Randall et al. (2016) were in agreement with Senecal & Vinnerås (2017) that several strong bases such as calcium and magnesium oxides are available as basic salts in contrast to strong acids. They further added that these salts are commonly used to increase the pH of acidic soils. Furthermore, calcium and magnesium form phosphate minerals at these high pH values and allow for the separation of phosphorus from the urine as calcium phosphate (Meyer et al., 2018). In addition, investigations by Eriksen et al. (1996) and Pancorbo et al. (1988) showed a high pH solution could potentially reduce a number of pathogens.

A design chart developed by Randall et al. (2016) shows the conditions where urea degradation is likely to be inhibited (Figure 2-5). This is denoted by the green region. The graph also illustrates the threshold below which enzymatic urea hydrolysis occurs, which is below a pH of 11 for temperatures up to approximately 40°C. After 40°C, Randall et al. (2016) notes the inactivation of urease where urea no longer degrades enzymatically, but rather degrades chemically due to a temperature increase. The solid curve gives an indication of the maximum pH that a solution can hold when $Ca(OH)_2$ has been added. This graph holds true for all urine compositions if the solution is saturated with $Ca(OH)_2$ (Randall et al., 2016).

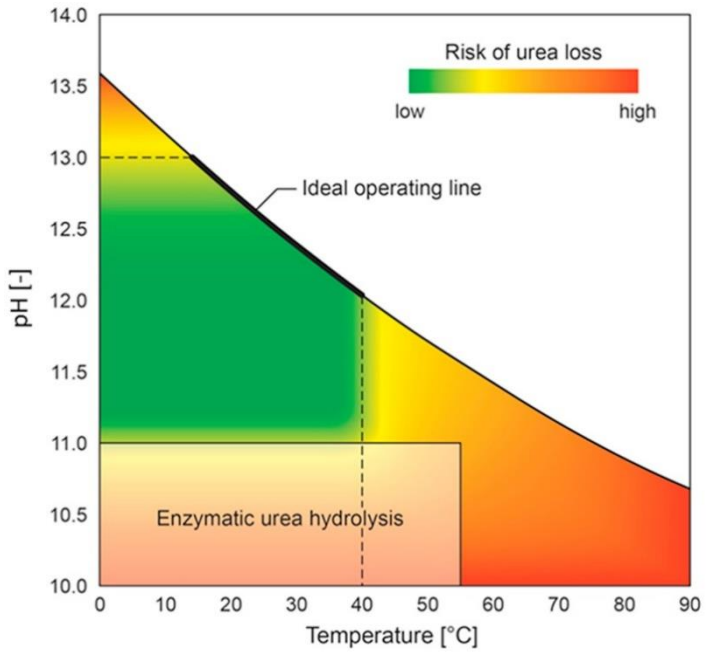


**Figure 2-5:** Design chart showing the conditions where chemical and enzymatic urea hydrolysis is likely to be inhibited. The solid line indicates the maximum pH that a solution can hold when $Ca(OH)_2$ is dosed. Enzymatic urea hydrolysis is likely to occur at a pH below 11, and temperatures up to 40°C. At higher temperatures, chemical urea hydrolysis occurs (Randall et al., 2016).

In summary, alkalization is a favourable method for stabilizing fresh urine because strong bases are more readily available than strong acids, and they present less risks when handling. Calcium hydroxide is also less aggressive and cheaper than MgO, KOH and NaOH (Skousen et al., 2019). Randall et al. (2016) recommend dosing 10 g of $Ca(OH)_2$ per L of urine with no dosing pumps required. This not only inhibits urea hydrolysis but kills bacteria and viruses at high pH values.

### 2.3.4 Phosphorous recovery

The predominant product reviewed in literature for phosphorous recovery is the precipitation of struvite, followed by calcium phosphate (Maurer et al., 2006). Struvite precipitation, which has been favoured by several researchers, recovers a significant amount of P and some N as $NH_4^+$ (Simha & Ganesapillai, 2017). Struvite is formed by the reaction of magnesium with phosphate in the presence of ammonium (Ganrot et al., 2007). Calcium phosphate precipitation has also been reviewed and studied as an alternative form of P-recovery (Etter et al., 2011; Quan et al., 2010; Meyer et al., 2018).

**Struvite precipitation**

Because Mg is a limiting reactant in urine, the total phosphate cannot be precipitated with the Mg already present in the urine (Alemayehu et al., 2020). It requires an external source of magnesium. The precipitating sources of magnesium that have been commonly tested for struvite precipitation include MgO, $MgSO_4$ and $MgCl_2$ (Patel et al., 2020). Sustainable sources of magnesium also investigated for struvite precipitation include sea water and brine (Liu et al., 2013a) and wood ash (Sakthivel et al., 2012).

The recovery efficiency of these magnesium sources is dependent on the solubility (Alemayehu et al., 2020). The more soluble the salt, the more struvite is precipitated, and the solubility decreases in the following order: $MgCl_2$>$MgSO_4$>MgO>$Mg(OH)_2$>$MgCO_3$ (Li et al., 2019).

The pH also influences the precipitation potential of struvite and governs which compounds will precipitate (Alemayehu et al., 2020). Phosphorous availability tends to decrease with an increase in pH as it binds with calcium and precipitates as calcium phosphate. (Cerozi & Fitzsimmons, 2016). In order to recover struvite, Zamora et al. (2017) recommends that the pH remains at 8 to 9. Jordaan et al. (2010) reported a maximum phosphorous recovery at a pH of 9. However, the highest quality struvite precipitate was found at a pH of 7.5 (Jordaan et al., 2010). Hao et al. (2013) confirmed this by reporting a pH range of 7.0 – 7.5.

Various authors have successfully recovered phosphorous via struvite precipitation using different sources of magnesium and Mg:P molar ratios. Liu et al. (2014) were able to recover 99.5% phosphorous via an air-agitated reactor, operating at a pH of 9.3. The magnesium source used to precipitate struvite was sea water and this was achieved at a Mg:P ratio of 1.3:1 (Liu et al., 2014). Elsewhere, Sakthivel et al. (2012) investigated using wood ash as a magnesium source and recovered 99%. The reaction vessel used was a double-walled glass reactor operating at a pH range of 8.8 – 9.3, with a Mg:P ratio of 2.7:1.

Struvite recovered from human urine generally has a good acceptance among farmers because it is odourless (Nagy et al., 2019). Furthermore, it releases nutrients slowly, making it favourable for use in agriculture (Nagy et al., 2019).

**Calcium phosphate precipitation**

Apart from the addition of magnesium to aid the precipitation of phosphate in urine, calcium is also a good alternative. Calcium addition forms amorphous calcium phosphate, which is mineralized into hydroxyapatite ($Ca_5(PO_4)_3(OH)$) (Alemayehu et al., 2020). Although, very limited research has been conducted on the precipitation of calcium phosphate as a P-recovery method.

Flanagan & Randall (2018) showed that phosphorous can be recovered as calcium phosphate by dosing fresh urine with $Ca(OH)_2$. The method can simultaneously preserve urea and produce calcium phosphate as a fertilizer. The study showed that 96% of the phosphorous in urine can be recovered as amorphous calcium phosphate. This translated to 11 g of calcium phosphate precipitated from 1 kg of urine.

In a feasibility study on the logistics of a decentralized urine treatment and resource recovery system, Chipako & Randall (2020a) explored a combination of calcium hydroxide dosing and reverse osmosis. It was shown that if urine was collected from various shopping malls in Cape Town and treated by alkaline stabilization and RO, it could produce ~78 $m^3$ of liquid fertilizer per week with a 3.3-0-0.8 NPK rating (Chipako & Randall, 2020a).

Elsewhere, Quan et al. (2010) presented an efficient integrated process consisting of chemical precipitation and air stripping to simultaneously remove ammonia, phosphorous and COD from wastewater. Calcium hydroxide was used as the precipitant for $NH_4^+$ and $PO_4^{3-}$ and used as an affordable pH adjuster to prevent scaling of the stripping equipment. Quan et al. (2010) noted

that the process could recover $NH_3$ and $MgNH_4PO_3$, which can be used as fertilizers. Furthermore, when the residual $Ca(OH)_2$ is completely consumed, the resulting precipitate is in the form, $CaNH_4PO_4.4H_2O$, which can be used as a slow-release fertilizer (Quan et al., 2010).

Etter et al. (2011) investigated optimizing the process of struvite recovery through the simultaneous collection of the struvite and calcium phosphate precipitated spontaneously due to urea hydrolysis. It was discovered that the overall phosphate recovery could increase by at least 40%.

Calcium phosphate precipitation, in particular, hydroxyapatite is better suited as a resource for the phosphate industry due to its resemblance to phosphate rock (Udert et al., 2006). However, Udert et al. (2003) claims that struvite precipitation is faster and easier.

Sarkar (1991) claims that the precipitation of calcium phosphate as solids is more favourable as they are less sensitive to heat than struvite. Struvite tends to decompose when exposed to temperatures higher than 60°C (Sarkar, 1991). Furthermore, as Randall et al. (2016) was able to show, $Ca(OH)_2$ also performs the function of stabilizing urea to increase the recovery of nitrogen through urea hydrolysis inhibition.

### 2.3.5 Nitrogen recovery

Existing processes for recovering nitrogen from urine are focused on converting urea to ammonia at a high pH (Alemayehu et al., 2020). This is done either through storage, or by dosing with NaOH or $Ca(OH)_2$. Thereafter, the ammonia is stripped and undergoes adsorption by $H_2SO_4$ (Alemayehu et al., 2020). Often, to optimize the recovery of nitrogen, urine is stabilized by adding $Ca(OH)_2$ (Randall et al., 2016). The two most studied and reviewed nitrogen removal processes are namely, ion exchange/adsorption and ammonia stripping.

**Ion exchange**

Tarpeh et al. (2017) showed that ion exchange is a promising technique for recovering nitrogen from source separated urine. During storage, the urea in urine is hydrolysed to ammonium which subsequently is adsorbed onto materials with negatively charged sites (Tarpeh et al., 2017). A commonly used ion exchange adsorbent which is documented for removing ammonium is zeolite (clinoptilolite), because it is extremely abundant and naturally occurring (Beler-Baykal et al., 2011). An added advantage to this adsorbent is that when exhausted, zeolite can be directly used as fertilizer (Patel et al., 2020).

Lind et al. (2000) first proposed the combination of ammonia and phosphate removal by combining ion exchange and struvite precipitation. The adsorbent capacities of clinoptilolite and wollastonite were investigated and a nitrogen recovery of 65 – 80% was achieved (Lind et al., 2000). In a similar study, (Ban & Dave, 2004) observed that the combination of struvite precipitation and adsorption to zeolite resulted in a reduced MgO requirement for P recovery. The process yielded a 99% and 90% recovery of P and N, respectively (Ban & Dave, 2004). Elsewhere, Allar & Baykal (2015) reported a 97% ammonium nitrogen removal using clinoptilolite.

Although zeolite is mostly favoured for this process, its use as a fertilizer comes with some risks. Cincotti et al. (2001) reported that, along with the adsorption of ammonium and potassium, zeolites can also adsorb heavy metals (Cu, Cd, Pb, Zn and Cr). These heavy metals may be transferred to agricultural soils. However, as noted by (Karak & Bhattacharyya, 2011), source-separated urine has a low heavy metal concentration, provided there is no faecal contamination. Another concern is the adsorption of organic micropollutants (Larsen et al., 2013) which could potentially be resolved with an additional urine treatment process targeted at micropollutant removal.

**Ammonia stripping**

Ammonia stripping is a proven technology for nitrogen recovery from source-separated urine. It is a process that requires the addition of a base to convert $NH_4^+$ into volatile ammonia (Tarpeh et al., 2018). This solution is passed through a stripping tower and facilitates the liquid-gas exchange of ammonia. The ammonia-rich air is then transferred to a column and $H_2SO_4$ is used for ammonia adsorption (Larsen et al., 2009). This results in an ammonium sulphate solution. Due to its low cost, ease of installation, and high removal efficiency of ammonia, this method is used for ammonia removal from various wastewaters (Liu et al., 2015).

Much like the ion exchange method, ammonia stripping has widely been investigated in combination with precipitation and absorption processes. Pradhan et al. (2017) used $Ca(OH)_2$ to increase the pH of the urine, which in turn converted the ammonium ions to ammonia, and precipitated P as calcium phosphate. The ammonia gas was stripped to form ammonium sulphate. Through this combined method, 85 – 99% of N and 99% of P could be recovered (Pradhan et al., 2017).

In a different study, Wei et al. (2018) combined struvite precipitation and air stripping and achieved a 93% and 94% N removal and struvite precipitation efficiency, respectively. Ammonium sulphate of 815 kg N and struvite of 46 kg P was recovered from the process. Similarly, Antonini et al. (2011) removed more than 90% of N and 100% of this nitrogen could be recovered as ammonium sulphate. A P recovery of 98% as struvite was also achieved.

Some limitations to stripping, as well as adsorption, are the costs associated with the acid ($H_2SO_4$) requirement and the storage space needed to facilitate urea hydrolysis (Alemayehu et al., 2020). Furthermore, high air flow rates are required in air stripping (Nagy et al., 2019). It is most effective when combined with struvite precipitation as stripping only produces ammonium sulphate, leaving other potential nutrients to be discarded with the supernatant (Alemayehu et al., 2020). Nevertheless, stripping, ion exchange and adsorption are effective and proven techniques for recovering N efficiently.

### 2.3.6 Alternative processes

Some authors have successfully recovered nutrients from human urine by adopting technologies used in water treatment. Dodd et al. (2008) showed that nutrient recovery was achievable through ozonation whilst also attenuating micropollutant loads. However, they found that similar results could be achieved via enhanced wastewater treatment and that a cost

benefit analysis which favourably compared ozonation to conventional treatment would need to be conducted.

Elsewhere, Ganesapillai et al. (2015) used microwave activated coconut shells to recover urea from human urine. An approximate 95% urea recovery could be achieved and the application of the product on agriculture resulted in significant improvement in soil conditions (Ganesapillai et al., 2015). However, the effect of microwave irradiation was only examined with respect to its impact on the urea uptake capacity of the activated carbon. The overall environmental impact was not considered.

Simha et al. (2018) developed an approach to selectively strip urea from urine in a continuously operated column packed with activated carbon from agricultural wastes. It was concluded that this approach could produce approximately 4.5 kg urea per person per year. However, similarly to the Ganesapillai et al. (2015) investigation, activated carbon requires microwave pre-treatment and carbonization at an operating temperature of 500°C. This could result in significant energy costs.

Udert & Wächter (2012) presented a method for recovering all nutrients from source-separated urine by nitrification and distillation. All nutrients were recovered in a dry powder, except for some ammonia which was approximately 3% of the total nitrogen. The energy consumption for the nitrification-distillation process proved to be four to five times higher than removing N and P using a conventional wastewater treatment plant (Udert & Wächter, 2012). Consequently, they proposed that the energy demand could be reduced to close to that of wastewater treatment processes with additional process steps.

A process for nutrient recovery from urine via a forward osmosis dewatering process was investigated by Zhang et al. (2014). Urea recovery in this process was low, whilst a 50–80% recovery of ammonia and phosphate of greater than 90% could be achieved. Zhang et al. (2014) concluded that the process was cost-effective and environmentally friendly.

### 2.3.7 Handling of micropollutants

Micropollutants and pathogens negatively impact on the application of untreated urine, therefore the removal of these impurities via biological and physiochemical processes is recommended (Randall & Naidoo, 2018). Well-researched urine treatment methods for micropollutant removal include: i) electrodialysis, ii) ozonation, iii) nanofiltration and iv) adsorption.

**Electrodialysis**

Electrodialysis involves the permeation of ions through positively and negatively charged membranes which are then concentrated in a separate compartment (Maurer et al., 2006). Through this process, nutrients are selectively extracted and separated from the dilute wherein the micropollutants are retained (Pronk et al., 2006). In a pilot investigation on electrodialysis treatment on urine, the results showed that the nutrients in urine can be concentrated to factors up to 3.5 and 4.1 (Pronk et al., 2007). Furthermore, Pronk et al. (2007) were able to remove about 90% of the estrogenic activity through electrodialysis and most micropollutants were below the detection limit.

If the concentration of micropollutants in the product liquid is acceptable, the product can then be utilized as fertilizer (Pronk & Koné, 2009). Otherwise, a further treatment step should be incorporated to remove the compounds. For this reason, ozonation has been recommended as an effective method for the removal of micropollutants (Dodd et al., 2008). Although the pollutants are effectively removed from the nutrients, some considerable amounts of N, P and other nutrients still form part of the resulting wastewater stream which could be discharged to surface waters. Therefore, ozonation could potentially be a useful step to further remove these compounds from the waste stream.

**Ozonation**

Ozonation is a disinfection method widely employed in water treatment (Sorokhaibam & Ahmaruzzaman, 2014) and is based on the infusion of ozone into water. It involves the production of highly reactive oxygen species which are able to attack a wide range of organics and microorganisms (Mazille & Spuhler, 2011). To produce ozone, oxygen is subjected to a high electrical voltage or UV radiation resulting in an energy intensive and costly process (Mazille & Spuhler, 2011).

A prior study investigating the removal efficiency of ozonation showed that the estrogenic activity of steroid hormones in source-separated urine was completely removed (Escher et al., 2006). This was achieved at an ozone dose of 1.1 g $L^{-1}$. However, the toxicity was only reduced by 50 – 60% (Escher et al., 2006).

In a different study, ozonation was investigated in combination with electrodialysis and more than 90% of the pharmaceuticals and oestrogens were removed (Dodd et al., 2008). From this process, a marketable fertilizer containing up to 12 g N $L^{-1}$, 0.6 g P $L^{-1}$ and 5.6 g K $L^{-1}$.

These studies demonstrated that ozonation is effective at degrading micropollutants but should be coupled with pre-treatment such as electrodialysis and struvite precipitation for optimal nutrient recovery. Although energy demands for ozonation are high (Mazille & Spuhler, 2011), Dodd et al. (2008) demonstrated that by applying ozonation after electrodialysis, energy efficiency can be improved. This is due to an overall decrease in the ozone demand achieved via the method used in that study.

**Nanofiltration**

Nanofiltration is a pressure-driven process that uses membranes with pores as small as dissolved molecules (Escher et al., 2006). The process aims to recover nutrients free of micropollutants by permeating the nutrients and retaining the micropollutants (Pronk et al., 2006) The efficiency of the process is strongly dependent on the pH which influences the electrostatic interactions with the membrane (Maurer et al., 2006).

Pronk et al. (2006) were able to retain more than 92% of all the micropollutants in non-hydrolysed urine. Urea and ammonia were removed, while phosphate and sulphate were retained. Thus, Pronk et al. (2006) concluded that the process is able to produce a permeate that contains most of the nitrogen and significantly reduced amounts of micropollutants. In order to maximize the nutrient recovery, it was recommended to include struvite precipitation to recover the remaining phosphate retained in the permeate (Pronk et al., 2006).

However, as with reverse osmosis, the potential scaling on the membrane caused by precipitation from the urea hydrolysis process is a challenge (Udert et al., 2003a). Pronk et al. (2006) passed urine through a 0.2 µm pore size membrane as a pre-treatment step to remove likely precipitating components and protect the nanofiltration membrane. Furthermore, additional measures are required for the prevention of microbial growth, odour, and urea hydrolysis to optimize nitrogen recovery.

**Adsorption**

Adsorption is a process whereby a surface accumulates and retains molecular or ionic species coming into contact with it (Shintre, 2016). Adsorptive treatment with powered activated carbon (PAC) has proven to be effective for micropollutant removal from an economical and technical perspective (Boehler et al., 2012). Granular activated carbon (GAC) is also considered a viable method for eliminating micropollutants (Benstoem et al., 2017).

Boehler et al. (2012) investigated the addition of PAC to wastewater treatment and achieved a micropollutant elimination of more than 80% from wastewater, comparable to post ozonation. Elsewhere, Sher et al. (2021) obtained a micropollutant removal percentage between 84.4 – 91.3% using only PAC, which increased to 88.9 – 93.6% when a $FeCl_3$ coagulant was added. In a study on the removal of pharmaceuticals from nitrified urine, Köpping et al. (2020) verified that adsorption on GAC in a flow-through filter removes pharmaceuticals from urine without the losing significant amounts of nutrients.

Activated carbon is a commonly used adsorbent due to its extremely porous nature, high surface area per unit weight or volume, and relatively low costs (Shintre, 2016).

### 2.3.8 Summary of urine treatment processes

In this section, a literature survey of the different urine treatment processes for the recovery of nutrients was conducted. These included (i) hygienization, (ii) volume reduction, (iii) stabilization, (iv) struvite precipitation, (v) ion exchange and ammonia stripping, (vi) micropollutant removal techniques and various others. It was demonstrated that many technologies are available with varying strengths and weaknesses, however no single unit process can fulfil the purpose of all. Table 2-2 provides a summary of all the processes and the functions they can fulfil.

While there are numerous processes investigated for the recovery of various nutrients from urine, literature on the recovery of N, particularly urea, is limited. Although the existing synthetic urea recovery processes are successful at producing fertilizers, their operation is energy intensive. If environmentally detrimental processes such as the Haber-Bosch process are to be replaced by more sustainable practices in the future, then the alternative should be energy efficient.

This study involved the recovery of urea by volume reduction (evaporation) at room temperature as a sustainable and alternative method for volume reduction. To further improve the purity after complete water removal, urea purification by recrystallization or solvent extraction with ethanol or methanol (reviewed in the next section) was explored.

**Table 2-2:** Summary of the unit treatment processes and their functions. No single process can fulfil all the functions and therefore, a combination of various processes is recommended to achieve the optimal recovery of nutrients.

| | Hygiene | Volume reduction | Stabilization | P-recovery | N-recovery | Micropollutant removal | Pre/Post Treatment? |
|---|---|---|---|---|---|---|---|
| Hygienization | | | | | | | |
| Storage | ✓ | X | X | X | / | ✓ | - |
| Volume reduction | | | | | | | |
| Evaporation | X | ✓ | X | ✓ | ✓ | X | ✓ |
| Freeze-thaw | ? | ✓ | / | ✓ | ✓ | X | - |
| Reverse osmosis | ? | ✓ | X | ✓ | ✓ | X | ✓ |
| Stabilization | | | | | | | |
| Acidification | ✓ | X | ✓ | ? | / | ? | - |
| Alkalization | ✓ | X | ✓ | / | ✓ | / | - |
| P-recovery | | | | | | | |
| Struvite precipitation | X | ✓ | / | ✓ | / | X | - |
| N-recovery | | | | | | | |
| Ion-exchange | X | ✓ | X | X | ✓ | X | - |
| Ammonia stripping | X | ✓ | X | X | ✓ | X | - |
| Micropollutant removal | | | | | | | |
| Electrodialysis | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | - |
| Ozonation | ✓ | X | ✓ | X | X | ✓ | ✓ |
| Nanofiltration | ✓ | X | ✓ | X | X | ✓ | - |
| Adsorption | ✓ | X | X | X | ✓ | ✓ | - |

✓ = fulfils that function. X = does not fulfil that function. / = fulfils the function, provided there is an additional process. ? = suggested but not yet proven. - = not applicable.

## 2.4 Urea purification methods

The recovery of urea from human urine by evaporation only concentrates the nutrients dissolved in the water, but the recovered urea is not pure. The urea would still need to undergo further treatment processes to be separated from the impurities present after complete water removal. Two recommended purification methods commonly used in organic chemistry are recrystallization and solvent extraction.

### 2.4.1 Recrystallization

A common purification technique for solids is crystallization, which is sometimes referred to as recrystallization when the impure solid is originally formed through partial crystallization (Nichols, 2017). In the case of this investigation, the initial crystallization of urea was in the form of water removal. The recrystallization process involves dissolving an impure solid in a minimal amount of hot, boiling solvent and thereafter, allowing the hot solution to cool (Nichols, 2017). These impurities are usually embedded in the crystalline matrix and can only be isolated by recrystallization (Farina, 2020).

The most important factor in the success of recrystallization is the choice of solvent (Nichols, 2017). Common solvents used include acetone, methanol, ethanol, and water. The solid to be purified must have a very low solubility in the solvent at room temperature and a very high solubility in the solvent at high temperatures (Farina, 2020). The solvent is then heated up near boiling point, minimally added to the impure solid, and mixed until completely dissolved. The impurities that were trapped in the lattice structure are then liberated through the process (Farina, 2020).

After complete dissolution, the cooling process begins causing crystals to form, while the impurities stay in solution. These crystals are a purer form of the impure solid. The crystallized solid is then filtered from the impurities (Nichols, 2017).

Braun (2017) demonstrated this purification technique in a urea recovery experiment from human urine. Urine was boiled to reduce the volume by evaporation to concentrate the nutrients and partially crystallize urea. Thereafter, nitric acid was added to isolate the soluble impurities from the concentrated urea solution to form a simpler compound, urea nitrate. The solution was then crystallized, and the impurities were filtered out. Potassium carbonate was then added to react with the urea nitrate to regenerate urea. This was filtered and recrystallized. Finally, ethanol was added to wash the urea of any other remaining impurities.

There are many limitations to the recrystallization technique though, some of which are evident in the outcome of the Braun (2017) urea recovery experiment. Recrystallization involves the use of a hot solvent and dissolving the solid on a hot plate. This is to ensure the compound dissolves at high temperatures and crystallizes at low temperatures. The method recovered only ~7.8 g of urea from 5 L of urine, which was a low recovery relative to the expected yield of 45 g.

The loss in yield likely occurred during several stages of the process. Firstly, unstabilized urine was boiled to remove the water, potentially causing both enzymatic and chemical urea hydrolysis to occur. The addition of hot solvent to the impure urea and dissolving on a hot plate

likely caused further degradation of the product via chemical urea hydrolysis. Randall et al. (2016) suggested that chemical urea hydrolysis happens at temperatures above 40°C. Furthermore, recrystallization was performed multiple times in the experiment and some product was potentially lost each time. Therefore, it was a trade-off between recovery and purity.

Another limitation to recrystallization is that the technique is more effective if the impurities are present in very small quantities (<5 mol% of the solid) (Nichols, 2017). After water removal, crystallized urea has far more impurities. Furthermore, for the impurities to be easily removed, they must be either much more soluble or much less soluble in the solvent than the compound to be purified. Due to the complex nature of urine, determining a suitable solvent which dissolves urea at high temperatures, and crystallizes it at low temperatures, whilst leaving other impurities dissolved throughout could be a challenge.

### 2.4.2 Solvent extraction

Solvent extraction, which is also referred to as liquid-liquid extraction, is used to isolate a solute from a solution by extraction into another solvent (Towler & Sinnott, 2013). The compound transfers owing to the difference in solubility between the two immiscible solvents (Chen & Wang, 2017). The method can either be used to recover a valuable substance from the original solution or to purify the original solvent by removing impurities (Towler & Sinnott, 2013).

The process depends on the solute having a greater solubility in the solvent used to extract than in the original feed solvent (Towler & Sinnott, 2013). A separatory funnel is used to perform the extraction. The original feed solvent (aqueous layer) containing the solute is poured into the funnel, followed by the extraction solvent, which is usually an organic layer (Farina, 2019). The organic layer will always lie on top as it is less dense. The two layers are then thoroughly mixed, swirled and then left to separate. After separation, the aqueous layer is drained, leaving behind the organic layer. Thereafter, the two solvents are evaporated, resulting in separate substances (Farina, 2019).

The method is relatively simple when two dissolved substances of significantly different solubilities are being separated. If the solubilities are known, one compound can be selectively extracted from the original solvent and transferred to the extraction solvent. However, as the composition of the solute becomes more complex, more iterations of the solvent extraction may be needed to purify the wanted product (Farina, 2019). That is, some impurities that crystallize with urea may have solubilities that are close to urea and end up in the extraction solvent.

Like recrystallization, the success of this method depends on the choice of solvent. The solubility of urea, as well as that of the other impurities present will have to be known. The main limitation of this method is the potential for it to become a tedious and iterative process to achieve a pure product. However, recrystallization presents the same challenge. The main advantage of solvent extraction over recrystallization is that the process happens at room temperature. Therefore, urea losses due to chemical urea hydrolysis can be avoided.

### 2.4.3 Proposed urea purification technique

Drawing from the benefits of the two techniques described in this section, a urea purification technique was developed for this investigation. Using the concept of differences in solubilities it was proposed that to recover pure urea, a solvent that readily dissolves urea and leaves other impurities undissolved would need to be chosen. The urea would then be extracted by retaining it in the solvent, while the impurities are filtered out. The solvent would also need to be volatile so that it can be evaporated off to recrystallize the pure urea.

According to Nichols (2017) the solvent and the compound need to be chosen such that they have similar intermolecular forces. For example, if a compound has moderate polarity, it sometimes can be crystallized from ethanol (Nichols, 2017). Given this, ethanol could be considered as a viable solvent to crystallize urea, because urea is a polar molecule. It is also worth reviewing a variant of ethanol, namely methanol, to compare the solubility of urea and the relative solubilities of the common impurities in each solvent. Table 2-3 compares the solubilities of urea and other common compounds found in urine after complete water removal in water, methanol, and ethanol, respectively.

The solubility of urea in methanol is four times higher than in ethanol. However, the solubilities of impurities in methanol are in the range of 15 – 30 times higher than in ethanol. While the solubility of urea in methanol is favourable, the concern would be the extent at which the impurities are dissolved with urea. Methanol may be able to produce a higher urea yield for a lesser amount of solute. However, this would be at the expense of the product purity. Although urea has a lower solubility in ethanol relative to methanol, most of the impurities are either insoluble or have very low solubilities. Therefore, ethanol as a solvent would potentially result in a purer product.

In industrial and consumer products, ethanol is considered the second most important solvent after water (EasyChem, 2002). Furthermore, it is more suitable for use in industry due to it being the least toxic of the alcohols (EasyChem, 2002). Comparatively, methanol has been described as toxic, unsafe and unsustainable (Shen et al., 2015). In addition, Pohanka (2016) reported that methanol has a high incidence of poisoning world-wide. Although methanol can dissolve more urea, ethanol is the safer option which can potentially produce a purer product.

**Table 2-3:** Solubility of typical inorganic salts and urea in water, methanol, and ethanol. *No values were provided in literature, only solubility states.

| Solvent: water | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | $CO(NH_2)_2$ | NaCl | KCl | $Ca(OH)_2$ | $CaSO_4$ | $CaCO_3$ | Creatinine | Creatine | Citric acid |
| Solubility ($g\ 100g^{-1}\ H_2O$) | 48 | 36 | 35.5 | 0.16 | 0.205 | 0.00066 | 8.03 | 1.23 | 59.2 |
| Temperature (°C) | 25 | 25 | 25 | 25 | 25 | 25 | 16 | 18 | 20 |
| Reference | (Sigma-Aldrich, 2003) | (Lide, 2004) | (Lide, 2004) | (Lide, 2004) | (Lide, 2004) | (Lide, 2004) | (HMDB, 2005b) | (HMDB, 2005a) | (Lopez-Garcia, 2010) |
| Solvent: methanol | | | | | | | | | |
| Compound | $CO(NH_2)_2$ | NaCl | KCl | $Ca(OH)_2$ | $CaSO_4$ | $CaCO_3$ | Creatinine | Creatine | Citric acid |
| Solubility ($g\ 100g^{-1}$ methanol) | 24.11 | 1.86 | 0.539 | insoluble* | no data* | insoluble* | partially soluble* | soluble* | 197 |
| Temperature (°C) | 24.7 | 25 | 25 | 20 | - | - | - | - | 20 |
| Reference | (Lee & Lahti, 1972) | (Feldman, 2011) | (Pinho & Macedo, 2005) | (Chemical Book.com, 2020) | - | (PubChem, 2004a) | (Science Lab.com, 2005) | (BioAustralis, 2020) | (Fisher Scientific, 2020) |
| Solvent: ethanol | | | | | | | | | |
| Compound | $CO(NH_2)_2$ | NaCl | KCl | $Ca(OH)_2$ | $CaSO_4$ | $CaCO_3$ | Creatinine | Creatine | Citric acid |
| Solubility ($g\ 100g^{-1}$ ethanol) | 5.837 | 0.065 | 0.034 | insoluble* | insoluble* | insoluble* | sparingly soluble* | slightly soluble* | 38.3 |
| Temperature (°C) | 25.5 | 25 | 25 | 20 | 25 | - | - | - | - |
| Reference | (Lee & Lahti, 1972) | (Feldman, 2011) | (Pinho & Macedo, 2005) | (PubChem, 2006) | (PubChem, 2005) | (PubChem, 2004a) | (Cayman Chemical, 2014) | (PubChem, 2004b) | (Lopez-Garcia, 2010) |

## 2.5 Urea: the native salt of urine

Urea is one of the important and widely produced chemicals in the world, with more than 90% of its global production used as fertilizer (Edrisi et al., 2016). It is also produced naturally by living organisms, particularly humans, other mammals, and other ureotelic organisms. Although, limited research has been done on its extraction from living organisms. It is currently widely used in its synthetic form.

Among all the common nitrogen-based fertilizers, urea has the highest nitrogen content (Edrisi et al., 2016). Its allure among farmers, especially in developing countries, stems from its stability in terms of transport and storage (Simha et al., 2018a). Furthermore, urea has various uses across multiple industries, though in smaller quantities, accounting for 10% of the global urea production.

### 2.5.1 The Haber-Bosch process and urea synthesis

The commercial production of urea began in the 1920s with the development of the Haber-Bosch process for ammonia synthesis. Contemporary levels of food production have been attributed to the continuous production of fossil fuel-based fertilizers (Vaccari, 2009). In fact, Smil (1999) credits the exponential population growth (from 1.6 billion in the 1900s to the current 7.8 billion) to the Haber-Bosch process.

The process is vital to the production of approximately 100 million tons of fertilizer per year, sustaining about a third of the earth's population (Science Daily, 2010). However, 3 – 5% of the world's natural gas production is consumed in the process, amounting to approximately 2% of the world's energy supply (Science Daily, 2010).

The process works by fixing nitrogen from the air with hydrogen from natural gas to produce ammonia (Briney, 2019). Rae-Dupree (2011) (*as cited in Briney, 2019*) reports that the process operates at temperatures over 426°C and a pressure of around 200 atmospheres. Under these conditions, nitrogen and hydrogen are forced together using a catalyst. Thereafter, the elements are moved out of the catalyst into industrial reactors to be converted into fluid ammonia (Briney, 2019). This fluid is then used to synthesize urea.

To produce urea, an exothermic reaction between liquid ammonia and $CO_2$ takes place at an operating temperature and pressure of 170 – 190°C and 14 MPa (Chemical Engineering World, 2020), respectively. The product, which is ammonium carbamate, is then decomposed to form urea and water. Other impurities in the urea include unreacted ammonia, carbon dioxide and ammonium carbamate which are removed by distillation and evaporation. Thereafter, the molten urea obtained after evaporation is solidified in a prilling tower (Copplestone & Kirk, 2017).

### 2.5.2 Commercial value of urea

Urea is a versatile product, useful in various industries. It is a popular solid nitrogen fertilizer because it has a high nitrogen content (46%) and is widely traded internationally due to its relatively low transportation costs (ICIS, 2011). Urea is also used in the production of many plastics and resins in the form of urea-formaldehyde (UF) (Atkins, 1987). These resins expand

to other industries including adhesives, textile finishes and surface coatings for plastics (Atkins, 1987). Urea resins are manufactured by condensing formaldehyde, a highly reactive gas obtained from methane, and urea in an aqueous solution using ammonia as a catalyst (Rodriguez et al., 2009). The reaction takes place at temperatures between 90 and 95°C (Ormondroyd, 2015) and results in a colourless, viscous solution that can be spray-dried to a powder (Rodriguez et al., 2009).

An important use of urea is in reducing air pollution from diesel engines in vehicles (ICIS, 2011). Because diesel engines run at high temperatures, they allow for the reaction of nitrogen and oxygen from the air to produce high concentrations of nitric oxide (Essential Chemical Industry, 2018). Therefore, a solution of urea (32.5%) in water (67.5%) is injected into the hot gases to thermally decompose it to ammonia and carbon dioxide through a process called selective catalytic reduction (ICIS, 2011).

In a recent feasibility study on a decentralized resource recovery system, Chipako & Randall (2020a) showed that a nitrogen-rich liquid fertilizer could be produced by concentrating urine via an RO system. This niche liquid could be sold as a high-value fertilizer. Furthermore, they showed that calcium phosphate could also be recovered from the process at 11.23 g per L of urine (Flanagan & Randall, 2018). This further maximized the value of urine.

Lambert & Randall (2019) investigated the use of urea to manufacture bio-bricks using a natural process called microbial induced calcium carbonate precipitation (MICP). Bacteria was used to degrade the urea present in the urine to form carbonate ions which combined with calcium ions to produce calcium carbonate. The calcium carbonate was then used as a bio-cement to combine sand particles to form a brick (Lambert & Randall, 2019).

A rocket fuel propellant called hydrazine (Fletcher-Wood, 2016) can also be produced from urea. Hydrazine is produced using the Hoffmann Process which reacts a solution of urea in water with a sodium hypochlorite solution at a ratio of 1:4 with reaction temperatures up to 100°C (Maxwell, 2005). In addition to its use as a rocket propellant, hydrazine is an important reagent in the fine chemical and pharmaceutical industries (Niemeier & Kjell, 2013). Derivatives of hydrazine are used as chemical blowing agents, pesticides, and fungicides.

Due to the hazardous nature of hydrazine such as toxicity, high flammability and combustion in the absence of air, aqueous hydrazine (hydrazine hydrate) has been made commercially available to mitigate these hazards (Niemeier & Kjell, 2013). Hydrazine hydrate is a dilute aqueous form available at concentrations between 15 wt % and 64 wt % (Niemeier & Kjell, 2013).

### 2.5.3 Contribution of fertilizer production to gas emissions

Synthetic fertilizers are mainly derived from fossil fuels. Beckinghausen et al. (2020) reports that approximately 949 $m^3$ of natural gas is required to produce 1 ton of anhydrous $NH_3$ fertilizer. This amount accounts for about 87% of the total energy used in the fertilizer industry. Simultaneously, about 1.6 tons of carbon dioxide are emitted for the production of 1 ton of $NH_3$ (Beckinghausen et al., 2020).

In a study that compares chemical production costs, with ammonia as one of its chemicals, Boulamanti & Moya (2017) found the cost of the fossil fuel feedstock to be the largest factor contributing to the total synthetic urea production cost. This puts a significant strain on a fossil fuel which is finite and geographically limited. This could eventually lead to the depletion of supply, posing serious challenges for future food security. This therefore calls for the production of a urea fertilizer with reduced energy, financial, and environmental costs.

The manufacture of synthetic N fertilizers, including ammonia synthesis and the conversion of ammonia to other N fertilizer products, is a significant source of greenhouse gas emissions (Chai et al., 2019). Thus, there is a growing interest in the application of organic fertilizers to soils as they have the potential to mitigate climate change through the reduction of carbon emissions (Diacono & Montemurro, 2011). Simultaneously, problems associated with waste management can be addressed and the nutrient needs of agricultural soils can be met (Tirado et al., 2010).

In addition to $CO_2$ emissions, synthetic N fertilizer contributes significantly to anthropogenic nitrous oxide ($N_2O$) emissions from agricultural soils (Bouwman, 1996). This is an important greenhouse gas with a long atmospheric lifetime and is roughly 300 times better at trapping heat than carbon dioxide ($CO_2$) (Millar et al., 2014). However, nitrogen fertilizer application to soils, be it organic or synthetic, will inevitably result in $N_2O$ emissions, as it is the by-product of the conversion of N compounds added to the soil (Aguilera et al., 2013).

Most of the N in organic fertilizer has to be converted to inorganic N before it is available for uptake by crops (Millar et al., 2014). When N is not taken up by plants, most of it becomes mobile and can be lost to groundwater or as nitrous oxide ($N_2O$) gas (Millar et al., 2014). These losses become more significant with the excessive application of N to crops, causing N to escape farmlands and become a pollutant. This affects terrestrial and aquatic ecosystems and contributes to global climate change (Zhang et al., 2013).

Agriculture was used as a basis for substantiating the reasons for moving towards the organic production of urea because of its impact on the global population and food security. This move promises to reduce carbon dioxide emissions and decrease the strain on fossil fuel reserves. Global energy consumption can also be reduced with the replacement of the Haber-Bosch process for the synthesis of urea.

## 2.6 Summary of literature review

Urea is the most widely used synthetic fertilizer, responsible for maintaining global food security. It has various uses in multiple industries including agriculture, plastics/resins, diesel engines, bio-bricks, aviation, and aerospace. However, its production in future is threatened by the depletion of fossil fuels. Furthermore, urea synthesis via the Haber-Bosch process contributes significantly to climate change, consuming 1 – 2% of the global energy supply. As a result, it is becoming increasingly important to investigate sustainable alternative methods for producing urea.

Human excreta, particularly human urine, has been widely investigated throughout literature as a major source for key nutrients: N, P and K. Various methods for recovering these nutrients

have been explored and their benefits compared. Source separation has been commonly proposed as an effective way of optimizing the recovery of nutrients from human urine to create value-added products. Three collection methods for source separation explored in this review included: (i) Urine Diverting Flush Toilets, (ii) Urine Diverting Dry Toilet and (iii) waterless urinals.

Various research studies have successfully recovered nutrients from human urine in numerous forms. Processes such as volume reduction by evaporation, freeze-thaw, and reverse osmosis, are proven technologies that can concentrate nutrients and treat human urine. Evaporation at temperatures below 40°C was selected as a favourable volume reduction technique for this investigation.

Storage, electrodialysis, ozonation and nanofiltration have been proposed as effective urine treatment methods for hygienization and micropollutant removal. Successful studies have shown that struvite precipitation, ion exchange and ammonia stripping can recover significant amounts of P and N from human urine. The investigations on the recovery of N, the most dominant compound in urine, are however limited.

Furthermore, the recovery of urea from human urine is still a novel subject in literature. Most of the N present in urine is in the form of urea. Urea recovery is strongly dependent on the inhibition of urea hydrolysis and the eventual release of volatile ammonia. Consequently, alkalization and acidification have been identified as useful techniques for stabilizing human urine. This has resulted in smaller N losses during urine treatment and nutrient recovery processes.

To recover urea of the purest form in this investigation, two crystal purification techniques were reviewed, which were recrystallization and solvent extraction. The benefits and limitations of each technique were compared and the best qualities of each were considered in developing an effective and sustainable purification method. Two potential solvents, methanol and ethanol, were reviewed and compared. Ultimately, ethanol was chosen as the more favourable solvent to extract and crystallize urea and the solubilities of all the urine compounds in ethanol were taken from literature.

This study aims to address the gap in literature on urea recovery methods which could reduce urea produced from unsustainable conventional processes such as the Haber-Bosch process. In this study, urea recovery via water removal by evaporation was investigated and ethanol as a solvent was explored as a potential purifier. This approach offers a potential novel method for recovering and purifying urea from human urine.

# 3. Methodology

This chapter presents the thermodynamic modelling procedure as well as physical experimental procedures for recovering urea. The recovery of urea was based on the concept of volume reduction, evaporating water from urine to concentrate urea. Firstly, a thermodynamic model was used to simulate the point at which urea was expected to crystallize as well as its corresponding purity. The model was also used to determine whether an intermediate filtration step, performed towards the end of the evaporation (95% and 99% water removal), could improve the purity.

The simulation was then used to predict the solubility of urea in ethanol at various temperatures and to investigate the potential purity after ethanol evaporation. This solubility was verified experimentally over a range of temperatures. As a final step for determining the optimal operating conditions for the physical experiments to follow, the model was used to investigate how the solubility of urea changed with urine composition. A composition from literature (Randall et al., 2016) was chosen as the standard and the urea solubility in ethanol was subsequently used as the design specification for all physical experiments that followed.

Three physical experiments were designed and conducted to investigate the feasibility of recovering urea from urine with the following conditions: (i) synthetic urine containing inorganics only (SI), (ii) synthetic urine containing inorganics and organics (SO) and, (iii) real human urine (RU). The results were then analysed and compared to the simulation results.

To conclude the investigation, and to further understand the results obtained from the experiments, two validation experiments were conducted. This was to validate the solubility of urea in ethanol (obtained thermodynamically) for SI. This experiment was repeated for SO to investigate the effect of the organics on the solubility of urea in ethanol.

## 3.1 Thermodynamic modelling

To determine the experimental conditions necessary to produce urea of the highest yield and purity possible, various thermodynamic modelling procedures were conducted. OLI Studio 10.0 was the software used to conduct the thermodynamic modelling using the **Mixed Solvent Electrolyte (MSE)** model to perform all simulations. To simulate the solubility of urea in ethanol, a special database for urea in ethanol called **ETUREA** was purchased and installed. This is because solubility data for urea in ethanol does not exist in the standard MSE database. Fresh urine compositions used in the thermodynamic model were Randall et al. (2016) [U1], Rose et al. (2015) [U2], Udert et al. (2003b) [U3], Udert et al. (2003a) [U4] and Etter et al. (2011) [U5].

**Table 3-1**: Five urine compositions used to thermodynamically model the crystallization of urea during water removal. The fresh urine compositions used in the thermodynamic model were Randall et al. (2016) [U1], Rose et al. (2015) [U2], Udert et al. (2003b) [U3], Udert et al. (2003a) [U4] and Etter et al. (2011) [U5]. [(a)]The potassium value for U1 was modified and taken as an average of the potassium concentrations for Udert et al. (2003a) and (2003b) and Rose et al. (2015) as this reflected a more realistic value. U1 was ultimately chosen as the standard composition for this investigation.

| Component | Units | U1 | U2 | U3 | U4 | U5 |
|---|---|---|---|---|---|---|
| Urea | mg $L^{-1}$ | 11600 | 16300 | 16200 | 18700 | 9540 |
| $NH_4^+$ | mg $L^{-1}$ | 562 | 599 | 613 | 498 | 564 |
| $PO_4^{3-}$ | mg $L^{-1}$ | 260 | 472 | 743 | 559 | 388 |
| $Cl^-$ | mg $L^{-1}$ | 4430 | 5140 | 3900 | 5230 | 6620 |
| $SO_4^{2-}$ | mg $L^{-1}$ | 825 | 2080 | 1540 | 1350 | 878 |
| $Na^+$ | mg $L^{-1}$ | 2510 | 2780 | 2760 | 3730 | 3240 |
| $K^+$ | mg $L^{-1}$ | 2420[(a)] | 1680 | 2190 | 2250 | 1870 |
| $Ca^{2+}$ | mg $L^{-1}$ | 132 | 111 | 185 | 168 | 89.2 |
| $Mg^{2+}$ | mg $L^{-1}$ | 57 | 95 | 94.8 | 121 | 45.4 |
| pH | - | 6.3 | 6.2 | 6.2 | 6 | 5.6 |

### 3.2.1 Crystallization conditions for urea and impurities

Firstly, the simulation was used to predict the expected crystallization conditions for urea and potential solids (impurities) that would form during water removal by evaporation from urine. Fresh urine compositions were used because stabilized urine compositions were not prevalent in literature. Figure 3-1 shows an outline of the thermodynamic modelling procedure used to simulate complete water removal from 0 g to 1000 g of water removal.

The yellow blocks are the names of the steps used in the software. The white blocks on either side, left and right, are the inputs and outputs of each step, respectively. The stream volume, temperature and pressure were 1 L, 22°C, and 1 atm, respectively. The composition breakdown given in Table 3-1 was used to begin the **Water Analysis** which performed a charge balance and a reconciliation of the pH.

Thereafter, to simulate the stabilization, a **Stream Analysis** was conducted by adding 10 g of $Ca(OH)_2$ to the new balanced stream (stream 1) and a **Single Point Isothermal Calculation** was performed. This resulted in a new stabilized saturated urine stream (stream 2). This stream was 'filtered' by using only the liquid components as an input for the next step.

A **Composition Survey** of the filtered, stabilized stream was performed from 0 g to 1000 g of water removal and a plot of the results was generated.

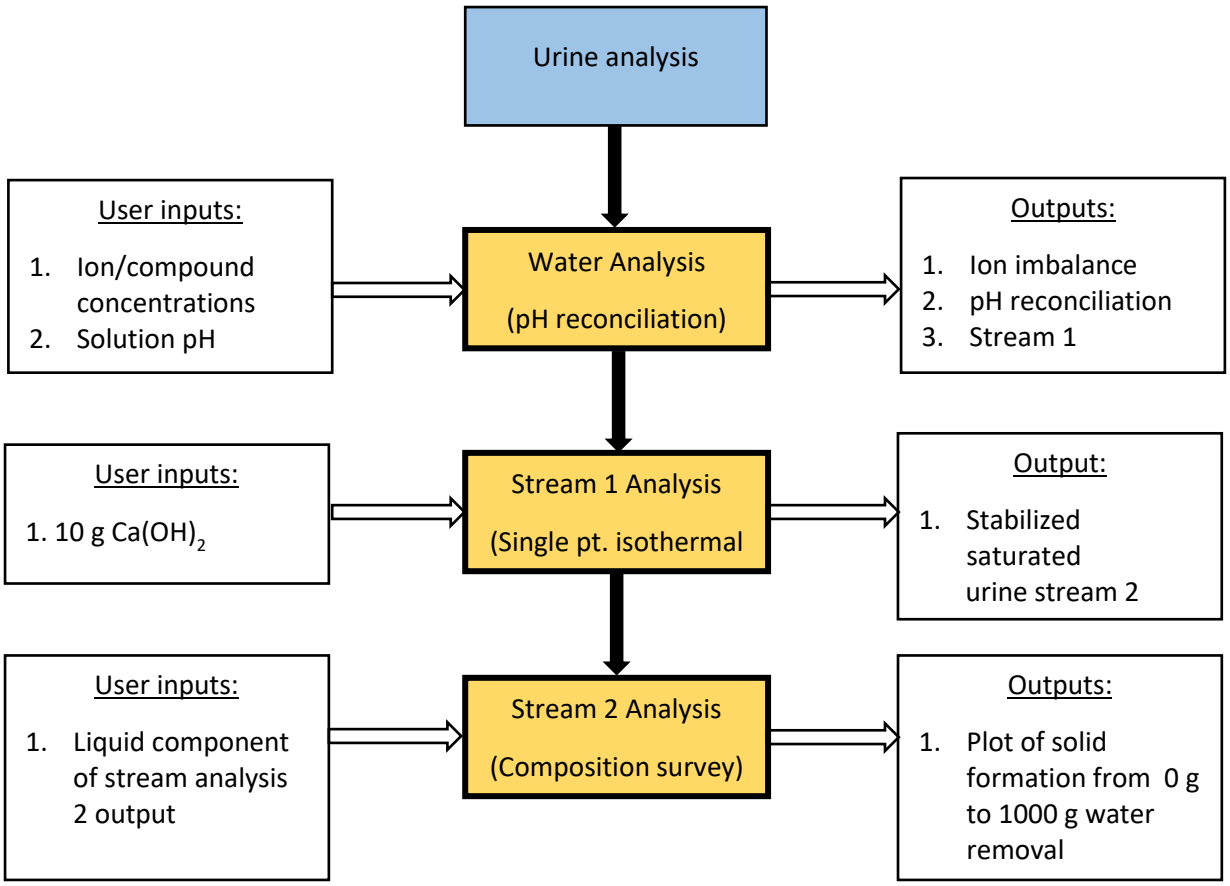


**Figure 3-1:** Thermodynamic modelling procedure for complete water removal by evaporation from urine. All five urine compositions were modelled using this procedure. The yellow blocks are the names of the steps performed in the software and the white blocks on either side represent the inputs and outputs of each step.

From these outputs, the yield and purity of urea at 100% water removal was determined. The purity was computed by taking a ratio of the total urea at 100% water removal to the total solids formed at that point. This procedure was repeated for all five urine compositions.

### 3.2.2 Intermediate filtration

From the previous simulation, it was determined when most impurities are formed. Given this, an intermediate filtration step at 95% and 99% water removal (where most impurities have formed and urea is still in liquid phase) was simulated to potentially improve the purity. The procedure is outlined in Figure 3-2.

Using the previous simulation results, the liquid components of the output stream at 50 g of water (95% water removal) was added as a new separate stream. A **Composition Survey** was then performed from 50 g to 0 g of water remaining and a plot of the results was generated. This was repeated for the simulation of intermediate filtration at 99% water removal (10 g of water remaining).

The way this would work physically is to evaporate a sample of urine on a balance. When the balance reaches a mass of solution equivalent to 95% or 99% water removal, the solution would be filtered of any remaining solids. The filtrate would then be placed back into an empty tray and allowed to evaporate to completion.

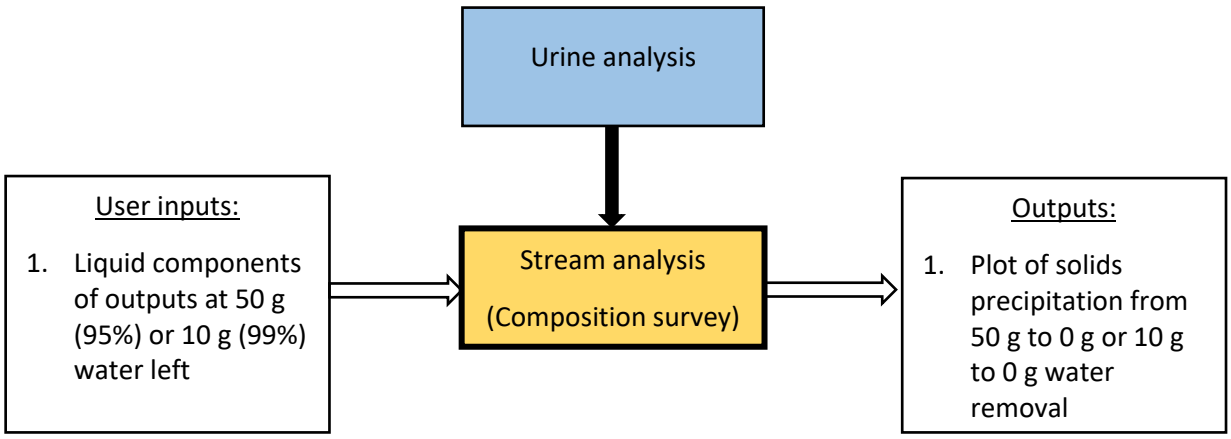


**Figure 3-2:** Thermodynamic modelling procedure for intermediate filtration at 95% and 99% water removal. All five urine compositions were modelled. The yellow blocks are the names of the steps performed in the software and the white blocks on either side represent the inputs and outputs of each step.

From these outputs, the yield and purity of urea after filtering the impurities at 95% and 99% water removal was determined. These were compared to the results for a 100% water removal. This procedure was repeated for all five urine compositions.

### 3.2.3 Solubility of urea in ethanol

In line with the hypothesis of this investigation, that ethanol can potentially isolate most impurities from urea, the solubility of urea in ethanol was simulated. The simulation would give an indication of the exact amount of ethanol needed to recover urea of the highest yield and purity at a given temperature. The simulation was first run using the existing **MSE ($H_3O^+$ ion)** database. To improve the model, a special database for urea in ethanol called **ETUREA** was installed and the model was simulated accordingly. For purposes of comparison, the solubility of urea in water was also simulated.

The procedure used to perform all simulations for the solubility of urea in ethanol is outlined in Figure 3-3. An arbitrary amount of 10 g urea was used to run the model with ethanol as the solvent. A Temperature Survey was conducted on the stream and a plot of urea solubility in ethanol from 20°C to 70°C was generated. The minimum temperature was chosen as 20°C as that was the minimum recorded room temperature in the Water Quality Lab. The maximum temperature was set at 70°C before the boiling point of ethanol (~78.4°C). The same procedure was used to simulate the solubility of urea in water using the **MSE ($H_3O^+$ ion)** database.

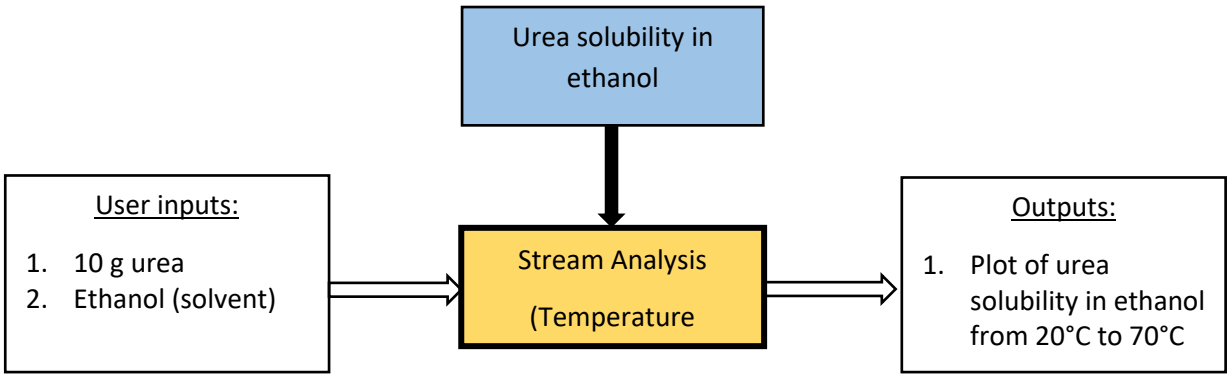


**Figure 3-3:** Thermodynamic modelling procedure for the solubility of urea in ethanol. It was modelled using the MSE ($H_3O^+$ ion) database and ETUREA database, respectively. The yellow blocks are the names of the steps performed in the software and the white blocks on either side represent the inputs and outputs of each step.

### 3.2.4 Model validation

Since the model would ultimately be used to design the physical experiments that followed, an experiment was conducted to validate the solubility of urea in ethanol. Five temperatures along the solubility curve of urea in ethanol were chosen for the experimental validation to obtain a good spread of data points. These were 22°C, 25°C, 40°C, 55°C and 70°C. The data point at 22°C was chosen specifically because it represented the average room temperature in the Water Quality Lab. It would also be the temperature at which water removal by evaporation and urea dissolution in ethanol would take place for all the physical experiments that followed. Therefore, it was crucial to obtain a model validation at that specific temperature.

**Experimental setup**

A 250 mL jacketed reaction vessel was connected to a chiller (MRC Refrigerated Circulator, Essex, England) which was set to one of the temperatures investigated above, starting with 22°C. The connected jacketed reaction vessel (reactor) was placed onto a magnetic stirrer with a stirrer bar inserted inside. Ethanol was measured and weighed in a 250 mL volumetric flask and steadily poured into the reactor to be heated to the desired temperature. Once the ethanol was added, the reactor was sealed with parafilm to prevent any losses in volume due to evaporation. The experimental setup is shown in Figure 3-4.

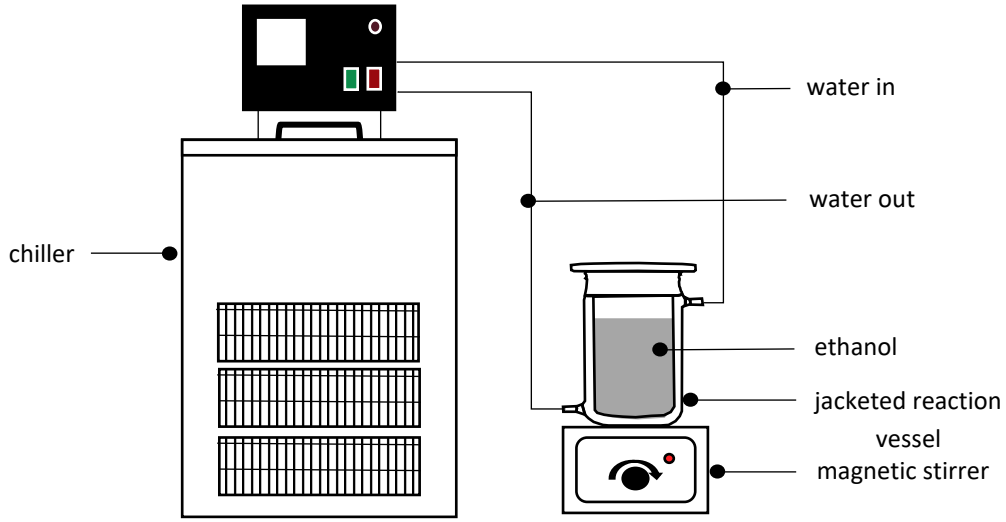


**Figure 3-4:** Experimental setup for the model validation experiment for urea solubility in ethanol. The experiment was conducted in a jacketed reaction vessel connected to a chiller to control the temperature.

This same setup was used to conduct the final validation experiments conducted to validate the solubility of urea in ethanol in U1 (SI), as well as the effect of the organics on the solubility in U1 (SO).

**Experimental procedure**

After approximately 20 minutes, a temperature probe was inserted to measure the temperature of the ethanol. When the desired temperature was reached, enough urea to make a supersaturated solution was poured into the reactor.

To estimate the amount of urea required to make a saturated urea-ethanol solution, the solubility of urea in ethanol obtained from the model was used. It was computed as follows.

$$urea\ required\ for\ saturated\ solution\ (g) = \ urea\ solubilty\ \left(\frac{g}{L}\right) x\ 0.25\ L\ of\ ethanol \quad (1)$$

Slightly more urea was added to this calculated amount to ensure a supersaturated solution. Table 3-2 summarizes the solubility of urea obtained on the model at the investigated temperatures and the amount of urea added for each experiment.

**Table 3-2:** Amount of urea required to make a saturated solution of urea-ethanol. These were calculated at 22°C, 25°C, 40°C, 55°C, 70°C, the temperatures at which the experimental validations would be conducted. Equation 1 was used to compute the amount of urea in g.

| Temperature (°C) | Solubility (g $L^{-1}$) | Ethanol volume (mL) | Urea calculated (x) (g) | Urea added (g) |
|---|---|---|---|---|
| 22 | 40.98 | 250 | 10.24 | 12 |
| 25 | 43.67 | 250 | 10.92 | 13 |
| 40 | 60.81 | 250 | 15.20 | 17 |
| 55 | 86.99 | 250 | 21.75 | 25 |
| 70 | 130.26 | 250 | 32.56 | 35 |

Once added, the mixture was stirred for 20 minutes, and a sample was drawn and filtered for testing. The urea concentration in the sample was tested using a colourimetry method of analysis (Gallery™, ThermoFisher, Massachusetts, USA). This experimental procedure was done in triplicate for each temperature by discarding the solution and preparing a new urea-ethanol solution each time.

This same experimental procedure was used to validate the solubility of urea in ethanol in SI, as well as the effect of the organics on the solubility in SO.

### 3.2.5 Urea solubility in ethanol for different urine compositions

The validation experiments provided the certainty that the model was accurate, and therefore, a final simulation was conducted. This was done to investigate how different urine compositions affect the solubility of urea in ethanol. This would provide a more realistic estimate of the amount of ethanol required to recover urea from a particular urine composition.

To do this, the composition breakdown provided in Table 3-1 was used and the charge balance was simulated. Thereafter, the stream was stabilized as was done for the water removal simulation procedure. From this, a new stabilized, filtered stream was obtained and ethanol was added as a solvent. Using this new stream, a **Temperature Survey** from 20°C to 70°C was conducted and a plot of the solubility of urea in ethanol was generated (Figure 3-5).

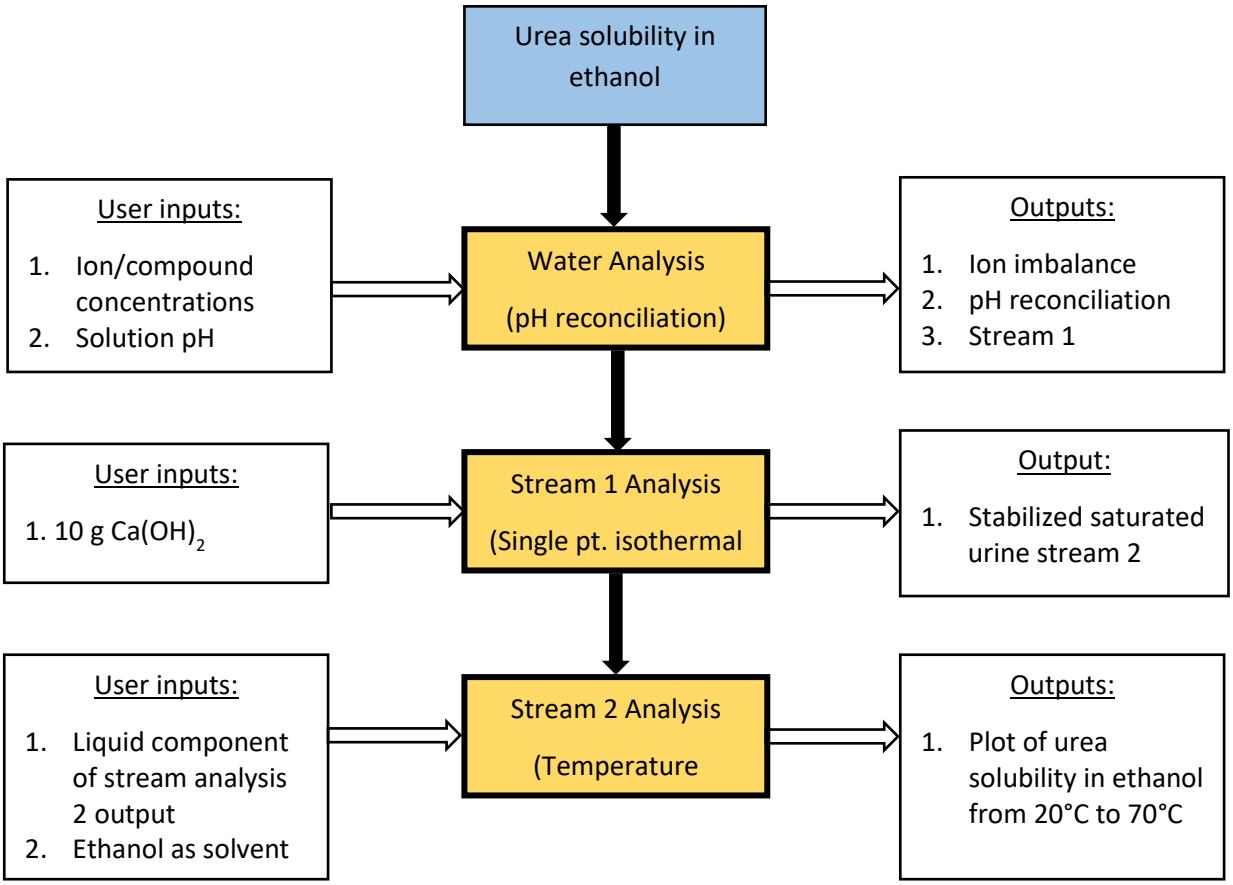


**Figure 3-5:** Thermodynamic modelling procedure for the solubility of urea in ethanol for different urine compositions. It was modelled using the **MSE (H3O+ ion)** database and **ETUREA** database, respectively. The yellow blocks are the names of the steps performed in the software and the white blocks on either side represent the inputs and outputs of each step.

A limitation of the model is that it did not have the necessary database to model organics in urine, other than urea. Therefore, the estimate of the solubility of urea in ethanol was only close enough for urine composition containing inorganics and urea.

This was repeated for all five urine compositions and finally, the composition from Randall et al. (2016) [U1] was chosen as the standard for all physical experiments. The urea solubility in ethanol for this urine composition was taken as the experimental design specification.

## 3.3 Urea recovery experiments

Three physical experiments were designed for the recovery of urea from synthetic and real urine, respectively. The first experiment involved recovering urea from synthetic urine containing only inorganics (SI). In the second experiment, urea was recovered from synthetic urine containing both inorganics and organics (SO), and finally, urea was recovered from real human urine (RU) in a third experiment. The yield and purity of all three experiments were compared, including with the data obtained from the thermodynamic model.

### 3.3.1 Synthetic urine recipe

The fresh urine composition from Randall et al. (2016) [U1] was used to make synthetic urine for the SI and SO experiments for purposes of consistency, and for accurate comparison of the two experiments. Because the urine composition in Randall et al. (2016) was given as ion concentrations, to make up a synthetic solution with salts and compounds the concentrations needed to be converted to masses of common urine compounds.

A standard recipe for fresh urine was developed in the *VUNA Handbook on Urine Treatment* (Udert & Etter, 2016) containing the major compounds commonly found in urine. This recipe was used as a basis to convert the Randall et al. (2016) ion concentrations to masses of compounds and salts, using stoichiometry.

Most urine recipes in literature only provide the urea and common inorganic compounds present in urine. The major organic compounds are usually omitted. For this reason, typical organic compounds prevalent in urine were found in Putnam (1971) and three were selected to make up the SO urine composition. These were namely creatinine (1.41 g), creatine (0.265 g) and citric acid (0.51 g) with given values close to those provided by Putnam (1971).

The magnesium and phosphate content were omitted from the final urine recipe. This is because when fresh urine is stabilized with $Ca(OH)_2$, almost complete precipitation of phosphate and magnesium occurs (Randall et al., 2016) which can be removed by filtration prior to the evaporation step.

Table 3-3 shows the adapted Randall et al. (2016) recipe used for the synthetic urine experiments in this investigation.

**Table 3-3:** Synthetic urine recipe containing inorganics from U1 Randall et al. (2016). U1 was used for all synthetic urine experiments in this investigation. [(a)]Magnesium and phosphate were omitted because they precipitate when fresh urine is stabilized and are removed by filtration.

| | | Randall et al. (2016) |
|---|---|---|
| Component | Units | Quantity |
| Urea [$CO(NH_2)_2$] | g $L^{-1}$ | 11.6 |
| Ammonium chloride ($NH_4Cl$) | g $L^{-1}$ | 1.67 |
| Sodium sulphate ($Na_2SO_4$) | g $L^{-1}$ | 1.22 |
| Sodium phosphate ($NaH_2PO_4$)[(a)] | g $L^{-1}$ | - |
| Potassium chloride (KCl) | g $L^{-1}$ | 4.62 |
| Magnesium chloride ($MgCl_2$)[(a)] | g $L^{-1}$ | - |
| Calcium chloride ($CaCl_2$) | g $L^{-1}$ | 0.484 |
| Sodium chloride (NaCl) | g $L^{-1}$ | 1.47 |
| Sodium hydroxide (NaOH) | g $L^{-1}$ | 2.67 |

### 3.3.2 Synthetic solution make-up and water removal

A fresh synthetic urine solution based on the U1 recipe was made for the first two experiments. For the first experiment, urea and inorganic compounds were measured according to the quantities in Table 3-3 and poured into a 1 L volumetric flask. This was then topped up with de-ionized water up to the 1 L mark and sealed before mixing. The synthetic urine for the second experiment, containing both organics and inorganics, was prepared in the same way with the addition of the three organics. All experiments were run in triplicate.

The solutions were mixed well using a magnetic stirrer until all compounds were dissolved and the solution was clear. Thereafter, 10 g of $Ca(OH)_2$ was measured for each flask, dosed to the fresh synthetic urine, and further mixed. After approximately 30 minutes of mixing, the urine was supersaturated with $Ca(OH)_2$ and sufficiently stabilized. It was then filtered using a vacuum filter and 1.2 µm pore size glass fibre (grade MGC) filter paper (110 mm Ahlstrom Munksjö filter paper, Helsinki, Finland) to remove excess $Ca(OH)_2$.

Three silicon trays of 19.5 x 19.5 x 4.2 cm and 1.6 L volume each were weighed. Silicon was used to make the scraping of solids after water removal easier. After taking note of the volume of the final stabilized synthetic urine, each solution (just under 1 L after filtration) was poured into each tray. The mass of the solution was then recorded, as well as the starting pH (pH electrode ACCSEN, Argentona, Barcelona). Finally, the trays were placed in a fume hood in front of a 170 W desktop fan (Russel Hobbs, Cape Town, South Africa) set at the highest speed. This began the water removal process.

It was decided that the evaporation would be allowed to run to completion (100% water removal) without the intermediate filtration step at 95% or 99%. This was because the thermodynamic model showed an insignificant improvement in the purity after intermediate filtration at 95%. It was therefore not worth adding the step if only a 5% improvement could be achieved.

However, the model did predict a 17% increase in the purity after intermediate filtration at 99%. This was, however, not explored in this investigation because it would require collecting a very large volume of urine to make filtration at this percentage easier. At a lab scale, the working volume was limited to 1 L per trial which translates to 10 mL of water to be filtered out for a 99% intermediate filtration step. This was practically not possible at this scale and therefore, complete water removal was chosen. At a large scale, this could be used as a pre-treatment method to improve the overall purity of the product further.

### 3.3.3 Analytical methods

A sample was drawn from each volumetric flask after the fresh urine stream was made to test for the starting urea concentration and inorganic ions in solution. This was to ensure that they matched the concentrations given by the U1 composition in Randall et.al (2016). These were namely, urea, ammonia, chloride, sulphate, potassium, and calcium. At the time of testing, no testing methods were available for sodium. However, since a known amount was added to make up the solution, it was estimated based on stoichiometry.

After stabilization, another sample was drawn to record the change in the calcium concentration. The urea concentrations and all inorganics in this investigation were tested for using a colourimetry method of analysis (GalleryTM, ThermoFisher, Massachusetts, USA). For the organic synthetic urine, another sample was drawn and sent to an organic chemistry lab where nuclear magnetic resonance (NMR) spectroscopy was performed to test for the concentration of organics.

**Gallery testing**

A gallery analyzer is an automated device which uses discrete cell technology to analyze a sample for several different parameters. In this study the analyzer was used to calculate the concentrations of urea, ammonium, sulphate, chloride, and calcium. Samples are diluted and poured into 2 mL cups which are placed in a rack for analysis. The racks are placed into the analyzer, along with the reagents for the ions or compounds beings tested. The gallery analyzer draws a sample from each cup in the racks and inserts it into a cuvette. Photometry is used to measure the light intensity being emitted by the sample in the cuvette, and this is translated to the concentration of a particular ion or compound present in that sample.

The gallery is only able to measure the common ions present in urine, namely $NH_4^+$, $SO_4^{2-}$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$, $PO_4^{3-}$ and $CO(NH_2)^2$ (a compound). No reagents are available for the testing of the common organics, creatine, creatinine, and citric acid and therefore, NMR technology was used to test for organics instead.

To test for the urea ($CO(NH_2)_2$), ammonium ($NH_4^+$), sulphate ($SO_4^{2-}$), chloride ($Cl^-$) and calcium ($Ca^{2+}$) concentrations, a standard test procedure developed in the Water Quality Lab was used. This involved taking a 1 mL filtered sample of the urine and adding it to a 25 mL volumetric flask. Hydrochloric acid (0.008M) of 50 µL was added to the 1 mL sample to decrease the urine pH to between 7 and 8 to prevent ammonia volatilization which could potentially occur at a pH above 9. After acidification, the flask was then topped up with de-ionized water and mixed with a vortex shaker. The sample was then placed in the Gallery and

all the tests were run in triplicate. This procedure was repeated for stabilized urine as well. The real urine sample (fresh and stabilized) was also tested in the same way.

To test the urea-ethanol filtrate for its ions after ethanol addition and filtration, a 1 mL sample was drawn and the automated dilution in the Gallery was used. Finally, to determine the urea yield and purity, a known mass of the final dry solids was dissolved in de-ionized water and put into the Gallery for testing. The purity was determined by taking a ratio of the concentration of urea in the dry product to the total concentration of all substances found in the dry product. The yield was determined as a ratio of the product of the final dry mass and purity to the initial starting mass of urea.

**Nuclear Magnetic Resonance (NMR)**

Nuclear magnetic resonance (NMR) is a technique used to determine the structure of organic molecules in solution. NMR exploits the magnetic properties of the nucleus to detect the proximity of electronegative atoms, double bonds, and other magnetic nuclei nearby in the molecular structure (Jacobsen, 2007). It was used in this study to detect the presence of creatine, creatinine, and citric acid in the samples.

To prepare the samples for analysis, the liquid samples were lyophilized (freeze dried), redissolved in 700 µL deuterium oxide ($D_2O$) (99.9%, Merck Pty Ltd, Modderfontein, South Africa) and transferred to a 5 mm NMR tube (Aldrich® ColorSpec®, Gillingham, United Kingdom) for data acquisition. Solid samples were first dissolved in 1 mL $D_2O$ before lyophilization. To quantify the compounds, 2.2 mg of dimethyl sulfoxide (DMSO) was added as an internal standard.

All NMR spectra were obtained using an NMR spectrometer (Bruker Advance III 600 MHz, Ettlingen, Germany) equipped with a BBO Prodigy cryoprobe. NMR data was processed using Topsin 3.2 software.

### 3.3.4 Volume of ethanol required

Trusting the prediction of the model that complete water removal would not yield a good enough urea purity, urea extraction from ethanol was investigated. Firstly, the volume of ethanol required to make a saturated urea-ethanol solution was determined by using the urea solubility for U1 predicted by the thermodynamic model. The design solubility was chosen at 22°C, which was the average temperature of the Water Quality Lab at which urea dissolution would take place. The design solubility was determined as 50.05 g $L^{-1}$. The detailed calculation for determining the volume of ethanol required can be found in Appendix B.

The volume occupied by the solids (~16 mL) was determined by taking the product of the mass of each compound that made up the synthetic solution and its density. This resulted in an ethanol volume of 217 mL and a total solution of ~232 mL per tray. Due to working with such small volumes, there was bound to be some losses due to handling when transferring the liquid and solution between containers (~4 mL). Also, some losses due to evaporation during mixing were expected (~3 mL). The mixing took between 30 to 45 minutes. Losses due to sampling also needed to be accounted for (~4 mL). This resulted in a total estimated loss of ~11 mL. It was important that the volume of ethanol be kept constant throughout the experiments.

Therefore, approximately 232 mL was chosen as a conservative value for all experiments considering these potential losses.

### 3.3.5 Ethanol addition and evaporation

When the solids in each tray were completely dry, they were weighed and then removed by scraping. The solids from each tray were then added to their own beaker. The required volume of ethanol (232 mL) ( 99.5% alcohol, Merck Pty Ltd, Modderfontein, South Africa) was added to each beaker and mixed. Thereafter, the mixture in each beaker was filtered using a vacuum filter and 1.2 µm pore size glass fibre (grade MGC) filter paper. The trays were washed, dried, and weighed again before pouring in the filtrate. The pH of the urea-ethanol solution (with some impurities) was measured, and a sample was drawn to test for urea and impurities in the solution.

For the synthetic experiment containing organics, a sample could not be tested on the filtrate as the ethanol would interfere with the analysis method. Therefore, only the final organic content after evaporation could be determined with NMR spectroscopy.

After sampling, the trays were placed in an oven at a slightly elevated temperature of 30°C to speed up the evaporation process. When the solids in each tray were completely dry, the final mass was weighed. This would be used to determine the final urea yield. After that, the solids were removed from the tray by scraping, weighed, and dissolved in de-ionized water. The solution was mixed, filtered, and a sample was drawn for testing in the Gallery to determine the final urea purity and the presence of impurities. For the SO experiment, a small sample of dry solids was taken for NMR testing to determine the concentration of organics in the final dry mass.

To determine the yield, the final dry mass was multiplied by the urea purity determined by the Gallery. The remaining mass would then make up the impurities.

### 3.3.6 Urea recovery from real urine

The experimental procedure for recovering urea from real human urine was the same as for the synthetic urine experiments with a few minor differences. Fresh urine was collected overnight in a 5 L sterilized, glass bottle. The fresh urine was filtered using a vacuum filter and 1.2 µm pore size glass fibre (grade MGC) filter paper to remove any solid particles. The urine composition, determined using the Gallery, is shown in Table 3-4. Because human urine is complex in nature, not all organic compounds present in the urine could be identified using analytical methods. An estimate of the amount of organics present in the beginning had to be made based on a mass balance.

**Table 3-4:** Fresh urine composition of a real urine sample ($U_R$). All inorganics were tested for using the Gallery. No adequate analytical methods were available for organics; therefore, they were estimated based on the dry mass of solids after complete water removal.

| Component | Units | Concentration |
|---|---|---|
| Urea | mg $L^{-1}$ | 11 900 |
| $NH_4^+$ | mg $L^{-1}$ | 664 |
| $PO_4^{3-}$ | mg $L^{-1}$ | 348 |
| $Cl^-$ | mg $L^{-1}$ | 2 560 |
| $SO_4^{2-}$ | mg $L^{-1}$ | 908 |
| $Na^+$ | mg $L^{-1}$ | 1 420 |
| $K^+$ | mg $L^{-1}$ | 1 870 |
| $Ca^{2+}$ | mg $L^{-1}$ | 115 |
| $Mg^{2+}$ | mg $L^{-1}$ | 42.3 |
| Estimated organics | mg $L^{-1}$ | 6 900 |

A volume of 1 L of urine was used for each experiment and samples were drawn to test the fresh urine for its urea and inorganic ion concentrations. The urine was then stabilized by dosing 10 g of $Ca(OH)_2$ for each L of fresh urine. The new stabilized urine was filtered, weighed and the pH was recorded. Water was removed by evaporation at room temperature (22°C) until the solids were completely dry. Thereafter, the ethanol addition and evaporation procedure detailed in 3.3.5 was carried out, using the same volume of ethanol determined in 3.3.4. Finally, the yield and purity were determined and the results compared. The experiments were run in triplicate.

### 3.3.7 Summary of modelling and experimental procedures

This chapter explored the thermodynamic modelling procedures carried out to predict the necessary conditions for recovering urea of the highest yield and purity from urine. It started by investigating whether volume reduction alone would yield a sufficient urea yield and purity. Thereafter, the addition of an intermediate filtration step at 95% and 99% water removal was considered.

As the results will later show, volume reduction alone would not yield a good purity. Intermediate filtration at 95% would only slightly improve it. When intermediate filtration was conducted at 99%, the model showed a significant improvement. However, it would require larger volumes to make filtration at that 99% water removal easier. As a result, 100% complete water removal was recommended for the physical experiments.

Therefore, to improve the purity, the solubility of urea in ethanol was modelled for pure urea and validated with a physical experiment at various temperatures. The impact of different urine compositions on the solubility of urea in ethanol was also explored. From this, a design solubility based on the U1 composition was selected. This assisted with determining the

volume of ethanol required to make a saturated urea-ethanol solution and recover the optimal amount of urea.

Based on the findings of the model, three urea recovery experiments were conducted. Urea was recovered from synthetic urine with inorganics, synthetic urine with organics and inorganics and real human urine. Finally, the yield and purity of all experiments were determined and compared. Table 3-5 summarizes the thermodynamic modelling and physical experiments, each with specific aims and conditions.

Links to the raw data for all thermodynamic modelling and urea recovery experiments can be found in Appendix A.

**Table 3-5:** Summary of experiments and thermodynamic modelling with aims and conditions. T, M and E denotes the thermodynamic modelling, experiments conducted to validate the model and physical experiments conducted, respectively. U1 – U5 are the Randall et al. (2016), Rose et al. (2015), Udert et al. (2003b), Udert et al. (2003a), and Etter et al. (2011) urine compositions. $U_R$ denotes the real urine composition. Each physical experiment was run in triplicate. The ethanol evaporation temperature 30°C.

| Experiment no. | Aims | Urine composition | Volume of urine (L) | Water removal process | Volume of ethanol (mL) | Temperature (°C) |
|---|---|---|---|---|---|---|
| $T_A$ | To thermodynamically predict when urea and impurities are expected to crystallize during water removal by evaporation. | U1 – U5 | 1 | Range up to 100% water removal | N/A | 22 |
| $T_B$ | To investigate the yield and purity of urea after 100% water removal and the impact on the purity and yield after an intermediate filtration step at 95% and 99% water removal. | U1 – U5 | 1 | Intermediate filtration at 95% and 99% | N/A | 22 |
| $T_C$ | To thermodynamically investigate the solubility of urea in ethanol. | Pure urea | N/A | Range up to 100% water removal | - | 20 – 70 |
| $M_A$ | To perform physical experiments to validate the model for urea in ethanol at various temperatures between 20°C and 70°C. | Pure urea | N/A | N/A | 250 | 22, 25, 40, 55, 70 |
| $T_D$ | To investigate, thermodynamically, how different urine compositions affect the solubility of urea in ethanol and to choose one composition as a standard for the physical experiments to follow. | U1 – U5 | 1 | Range up to 100% water removal | - | 22 |
| $E_A$ | To perform a physical experiment to recover urea from synthetic urine containing only inorganics (SI). | U1 (SI) | 1 | Range up to 100% water removal | 232 | 22/30[(a)] |
| $E_B$ | To perform a physical experiment to recover urea from synthetic urine containing both inorganics and organics (SO). | U1 (SO) | 1 | Range up to 100% water removal | 232 | 22/30[(a)] |
| $E_C$ | To perform a physical experiment to recover urea from real human urine (RU). | $U_R$ (RU) | 1 | Range up to 100% water removal | 232 | 22/30[(a)] |
| $M_B$ | To perform physical experiments to validate the model for urea in ethanol for synthetic urine containing inorganics only (SI). | U1 (SI) | N/A | N/A | 250 | 22 |
| $M_C$ | To perform physical experiments to investigate how the presence of organics affects the solubility of urea in ethanol. | U1 (SO) | N/A | N/A | 250 | 22 |

# 4. Results and discussion

The main aim of this work was to purify solid urea recovered from stabilized urine by exploiting the solubility differences of inorganic salts and urea in ethanol and water. This chapter presents the results obtained from all thermodynamic and physical experiments conducted in this study (Table 3-5). The key findings and observations of the experiments are also discussed and comparisons are drawn between the three main physical experiments (SI, SO, RU). The parameters affecting the yield and purity of the final urea product are discussed as well.

A conceptual design of a small-scale urea recovery unit, treating 1 $m^3$ of urine per day, is presented and the potential urea recovery and power requirements are estimated. To make the recovery procedure more sustainable, various techniques for the potential recovery of water and ethanol from the process are compared. Finally, the potential uses for urea, as well as the potential income generation from the urea produced is provided.

## 4.1 Water removal from stabilized urine

### 4.1.1 Crystallization of urea and impurities

When water is removed from urine by evaporation, various solids form as shown in Figure 4-1. The model predicted that the major components to form at 22°C were namely NaCl, KCl, $CaSO_4$, $Ca(OH)_2$ and urea. Due to the high solubility of urea in water (480 g $L^{-1}$ at 22°C (Sigma-Aldrich, 2003)), urea only crystallized when approximately 99% of the water was removed.

The starting point of precipitation of the impurities (denoted by the dark lines in Figure 4-1A) was consistent for all five urine compositions at ~15% water removal. The crystallization of urea (Figure 4-1B) occurred between 99% and 100% water removal for all five compositions. At this point (99%), the other components continued to precipitate gradually until all the water was removed. This demonstrates that the composition generally does not influence the point of precipitation of compounds from human urine during water removal by evaporation. However, the mass of solids will differ based on varying urine compositions as shown in Figure 4-1B. U4 had the highest amount of solids formed at complete water removal, while U1 had the lowest. This is because the U4 composition had the highest starting concentration of ions. Ultimately, this simulation showed that for optimal urea recovery, 100% of the water would need to be removed.

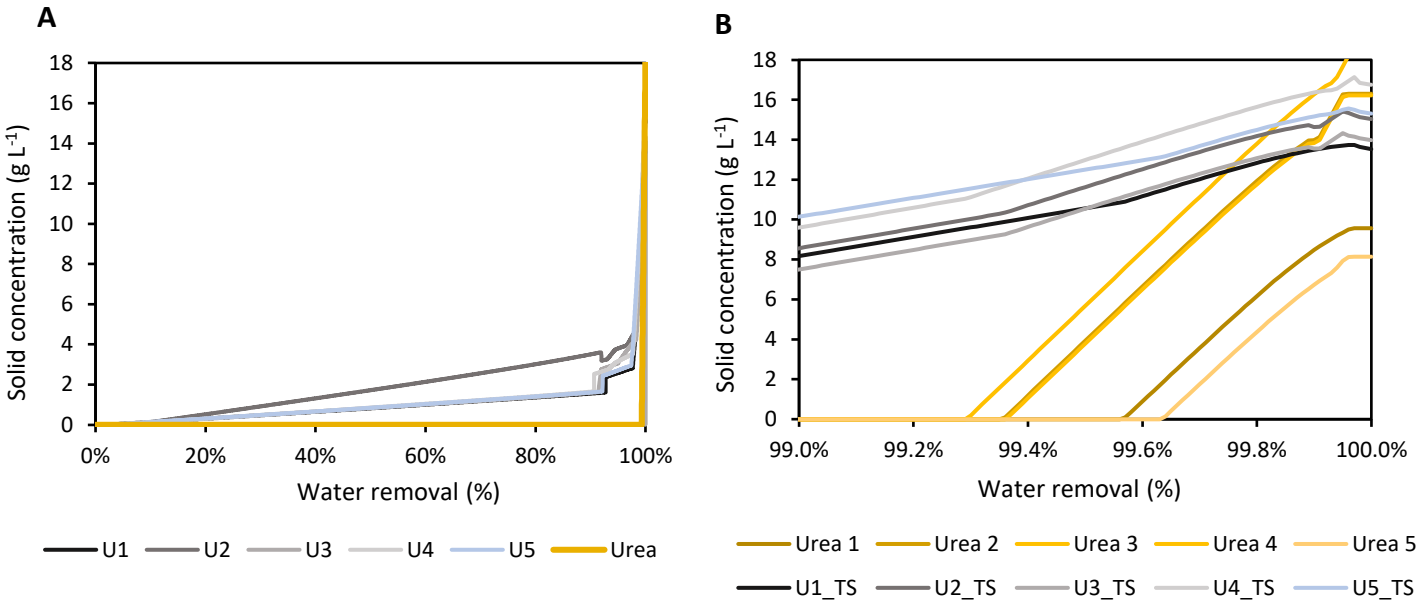


**Figure 4-1:** Expected formation of urea and impurities (inorganic salts) during water removal from 0% to 100% (A). (B) is a zoomed in section of (A) between 99% and 100%, where urea is expected to form. The grey lines show the total impurities precipitated, while the yellow lines show the urea precipitated from different urine compositions. TS stands for total solids (excluding urea). These represent the urine compositions of Randall et al. (2016) [U1], Rose et al. (2015) [U2], Udert et al. (2003b) [U3], Udert et al. (2003a) [U4] and Etter et al. (2011) [U5]. For all urine compositions, impurities (inorganic salts) consistently started precipitating around 15% water removal, whilst urea only precipitated above approximately 99% water removal.

### 4.1.2 Impact of intermediate filtration on urea purity and yield

The simulated results for the impact of intermediate filtration on the yield and purity of urea for all the urine compositions were averaged and summarized in Figure 4-2 after water removal. The results show a slight decline in the yield between complete water removal (100%) and intermediate filtration at 95% and 99%, respectively. While the improvement in the purity from 100% water removal (53% purity) to intermediate filtration at 95% (58% purity) was not as significant (~5% improvement), a notable improvement of 17% was seen for an intermediate filtration at 99% (71% purity).

Intermediate filtration at 95% was not a significant improvement with respect to the potential final purity that could be achieved. However, the potential increase in purity for an intermediate filtration at 99% water removal suggests that this could be used to improve the purity of the product. Figure 4-2 shows that at 95% water removal, the concentration of solids is between 2 g $L^{-1}$ and 4 g $L^{-1}$, while at 99% the concentration rapidly increases to above 6 g $L^{-1}$ at a steep slope. This explains why the improvement in purity at 95% intermediate filtration is not significant, because there are still many impurities present, yet to form just before 98% water removed. At 99% water removal, most impurities have formed and can be removed with only a minimal amount left in solution. Thus, the purity is significantly higher.

Nevertheless, filtering the remaining 1% of water is only feasible when working with large volumes of urine. Due to the scale of this investigation being restricted to the Water Quality Lab, intermediate filtration at 99% was not explored experimentally. Instead, complete water removal was recommended as the viable option for recovering solid urea. The model predicted a yield of 100% with a potential purity of 53% with complete water removal.

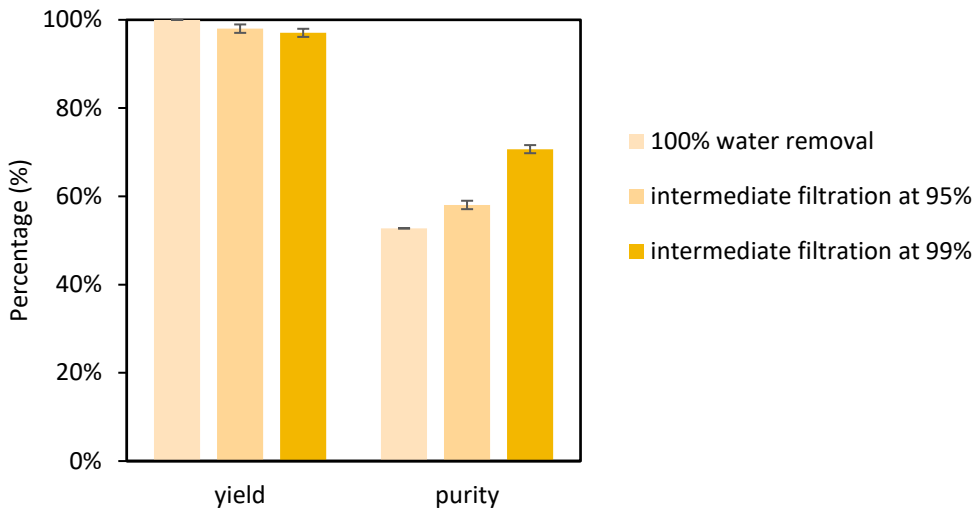


**Figure 4-2:** A comparison of the average yield and purity of five different urine compositions modelled thermodynamically. The model was used to determine the yield and purity after complete water removal. Thereafter, the impact on the yield and purity when filtering the precipitated solids at 95% and 99% water removal was modelled. The graph shows a slight decline in yield, but a significant improvement in purity. The best purity is achieved with 99% intermediate filtration.

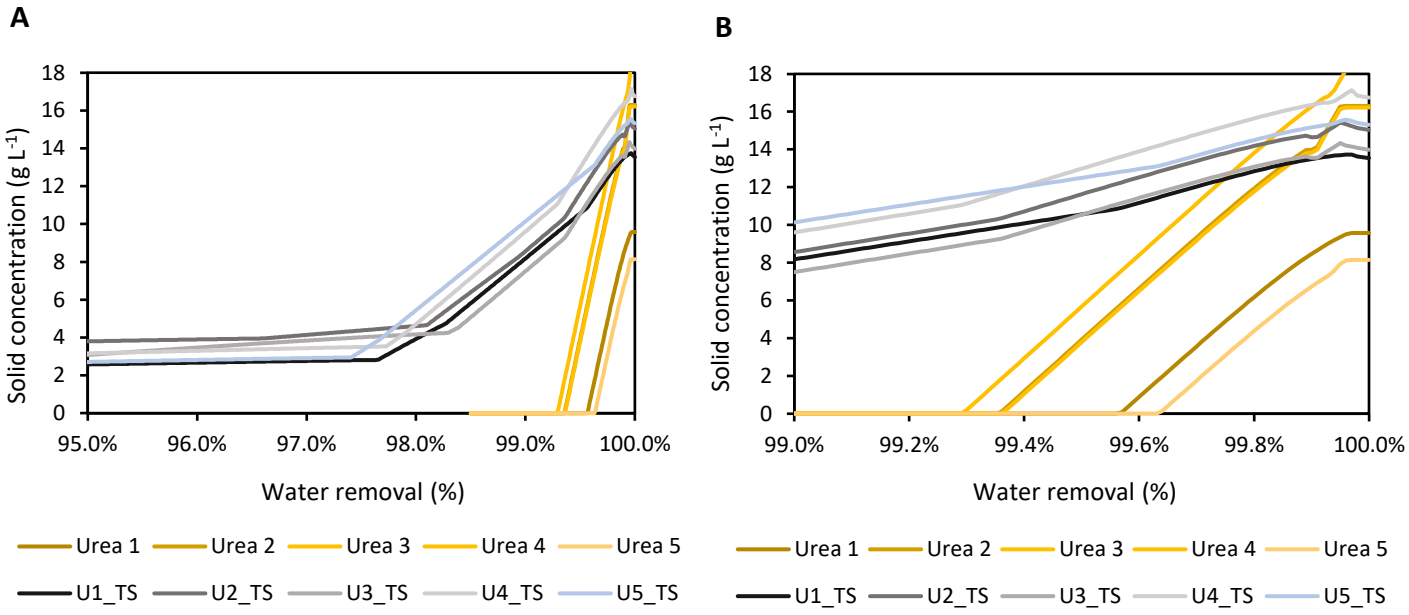


**Figure 4-3:** A comparison of the precipitation of urea and impurities from 95% and 99% water removal, respectively for different urine compositions (U1 to U5).

## 4.2 Thermodynamic investigation of urea recrystallization from ethanol

### 4.2.1 Solubility of urea in water and ethanol

To investigate the conditions for the crystallization of urea from ethanol, the solubility of urea in ethanol was simulated (Figure 4-4). Simulation results initially produced the black dotted line using the existing software database. However, these results were far from the solubility value for urea given in literature (~46.07 g $L^{-1}$ at 25.5°C (Lee & Lahti, 1972)). This is because solubility data for urea in ethanol does not exist in the standard MSE database. This further supports the novelty behind this research. Therefore, a special database for urea in ethanol (ETUREA), which incorporates values from literature, was used to simulate urea in ethanol and the resulting curve was much lower. The resulting solubility at 25°C was 43.67 g $L^{-1}$ which was close to the value given in literature (46.07 g $L^{-1}$).

The solubility of urea in water was up to 14 times higher than urea in ethanol at lower temperatures, and between 10 to 7 times higher than urea in ethanol at higher temperatures. For both curves, the results show an increase in solubility with an increase in temperature. Solubilities generally tend to increase as the temperature increases because entropy favours dissolution (Farina, 2020). While urea is much more soluble in water than in ethanol, the concentration of urea in urine is typically well below the solubility limit of either compound (9.3 – 23.3 g $L^{-1}$) (Randall & Naidoo, 2018). Therefore, the lower urea solubility would not be an issue for the proposed process.

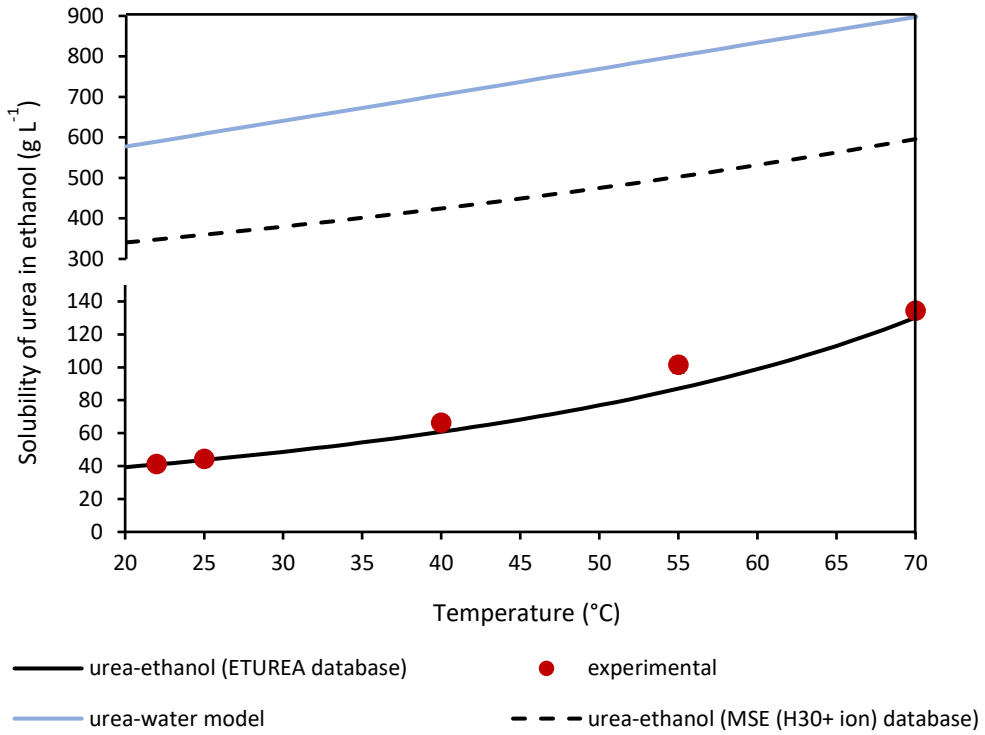


**Figure 4-4:** A solubility curve of urea in ethanol illustrating both experimental and simulated results. The model was first conducted using the MSE database provided by the software, and this is denoted by the black dashed line. To improve the model, a special database for urea in ethanol called ETUREA was used and is shown as the solid black line. Physical experiments were conducted to validate the model and were conducted at 22°C, 25°C, 40°C, 55°C and 70°C. The maximum temperature for determining the solubility of ethanol was chosen to be 70°C, just before the boiling point of ethanol (78°C). The solubility of urea in water was also modelled for purposes of comparison and is denoted by the blue line.

To ensure confidence in the urea-ethanol model, five datapoints along the urea-ethanol solubility curve produced by the ETUREA database were validated experimentally. The experimental results are shown by the red markers along the curve in Figure 4-4. The ETUREA database improves the accuracy of the simulation significantly with a Nash–Sutcliffe model efficiency coefficient (NSE) of 0.96.

### 4.2.2 Impact of urine composition on urea solubility

Knowing that the model is accurate, the effect of each of the five urine compositions on the solubility of urea in ethanol was investigated. Figure 4-5 shows that the solubility values for the different urine compositions are higher than for pure urea in ethanol. These solubilities for different urine compositions were also similar, suggesting that the composition is not a key parameter for determining the urea solubility in ethanol. Given this, one of the compositions (U1) was chosen as the standard for all the urea recovery experiments that followed, with a urea solubility of 50.05 g $L^{-1}$ at 22°C. This translated to requiring an ethanol volume of approximately 232 mL to make a saturated urea-ethanol solution. This would be more accurate than using the solubility of pure urea in ethanol at 22°C (40.98 g $L^{-1}$).

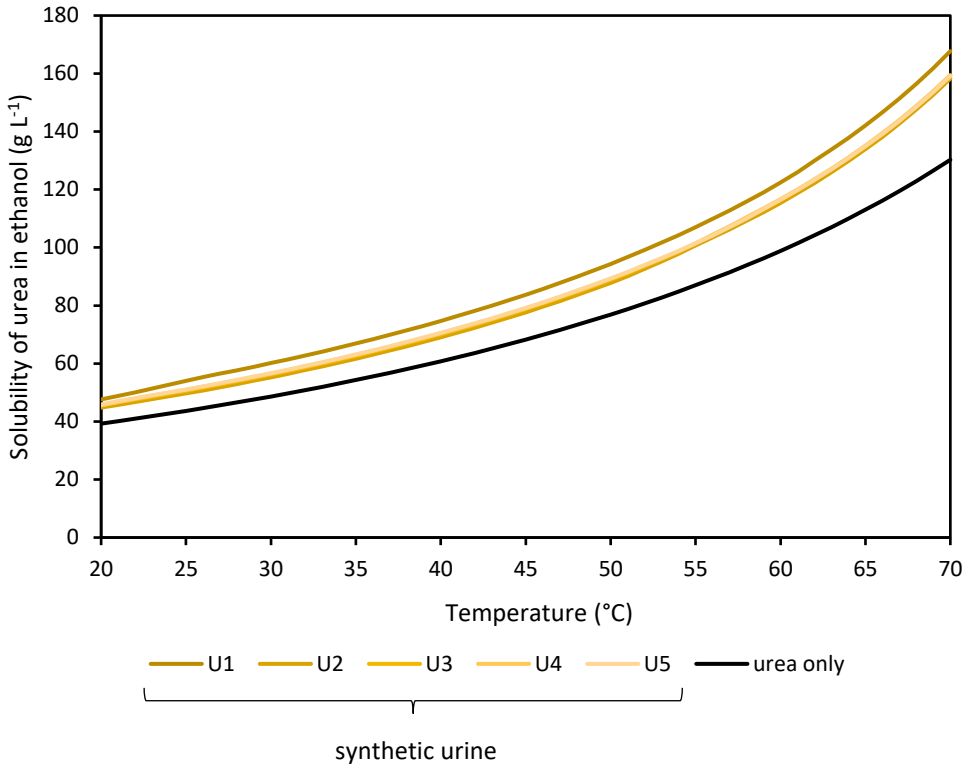


**Figure 4-5:** A comparison of the solubility of urea in ethanol for five different urine compositions and urea and ethanol only. These curves lie slightly above the pure urea in ethanol curve, thus indicating that urea in urine has a slightly higher solubility.

## 4.3 Yield and purity of final urea product

The main objective of this work was to recover pure solid urea crystals from stabilized urine using the optimal experimental conditions predicted by the thermodynamic model. For all the physical experiments, complete water removal was performed to crystallize urea. Thereafter, ~232 mL of ethanol was added each time to re-dissolve the urea while the undissolved impurities were filtered out. The amount of ethanol was based on the solubility of urea in ethanol at 22°C, which was the average room temperature in the lab. The recrystallization of urea was performed in an oven at an elevated temperature of 30°C, below the temperature (40°C) where chemical urea hydrolysis is likely to occur (Randall & Naidoo, 2018), to speed up the evaporation of ethanol. Three different urine compositions were investigated and compared: two synthetic stabilized urine samples (containing inorganics (SI) and both inorganics and organics (SO), respectively) and a real human urine sample.

The first experiment involved recovering urea from synthetic stabilized urine containing only inorganics and urea (Figure 4-6). The urea purity obtained after complete water removal was 42%, which was 11% lower than that predicted by the thermodynamic model. The yield at that point was 93.7%, where some urea was lost due to handling, sample preparation, potential ammonia volatilization and filtration. After ethanol was added and the undissolved species were filtered out, the purity of urea increased to 87% in solution. The final purity after complete ethanol evaporation was 91%. The final yield achieved was approximately 88%.

In the second experiment, urea was recovered from a synthetic urine stream containing both organics and inorganics (Figure 4-7). The urea purity obtained after complete water removal was 40.5% and the yield was ~99%. This value could not be compared to the thermodynamic model because the model is not able to simulate streams containing organics other than urea. Only 1% of urea was lost due to handling because the sample preparation, stabilization and filtration were done whilst being mindful of the potential losses experienced in the first experiment. The purity obtained after water removal was close to that of the SI experiment and only slightly lower. It was expected that the purity of SO should be much lower than that of SI due to the addition of organics contributing to the total impurities. However, the 6% loss of urea in the beginning of the SI experiment may have contributed to the slightly similar purities after water removal.

After ethanol addition and the filtration of undissolved species, the purity of urea increased to 81.8% in solution. The final purity after complete ethanol evaporation was 76.5% and the yield achieved was approximately 76.5%. The final purity of SO was lower than that of SI. This was expected due to the organics potentially dissolving in the ethanol and contaminating the final urea product. Creatinine (~3.6% of the total dissolved solids) was found in the final product and trace amounts of creatine (~0.3%) were also detected thus confirming that these organics did dissolve in the ethanol. Citric acid was not detected in the final product.

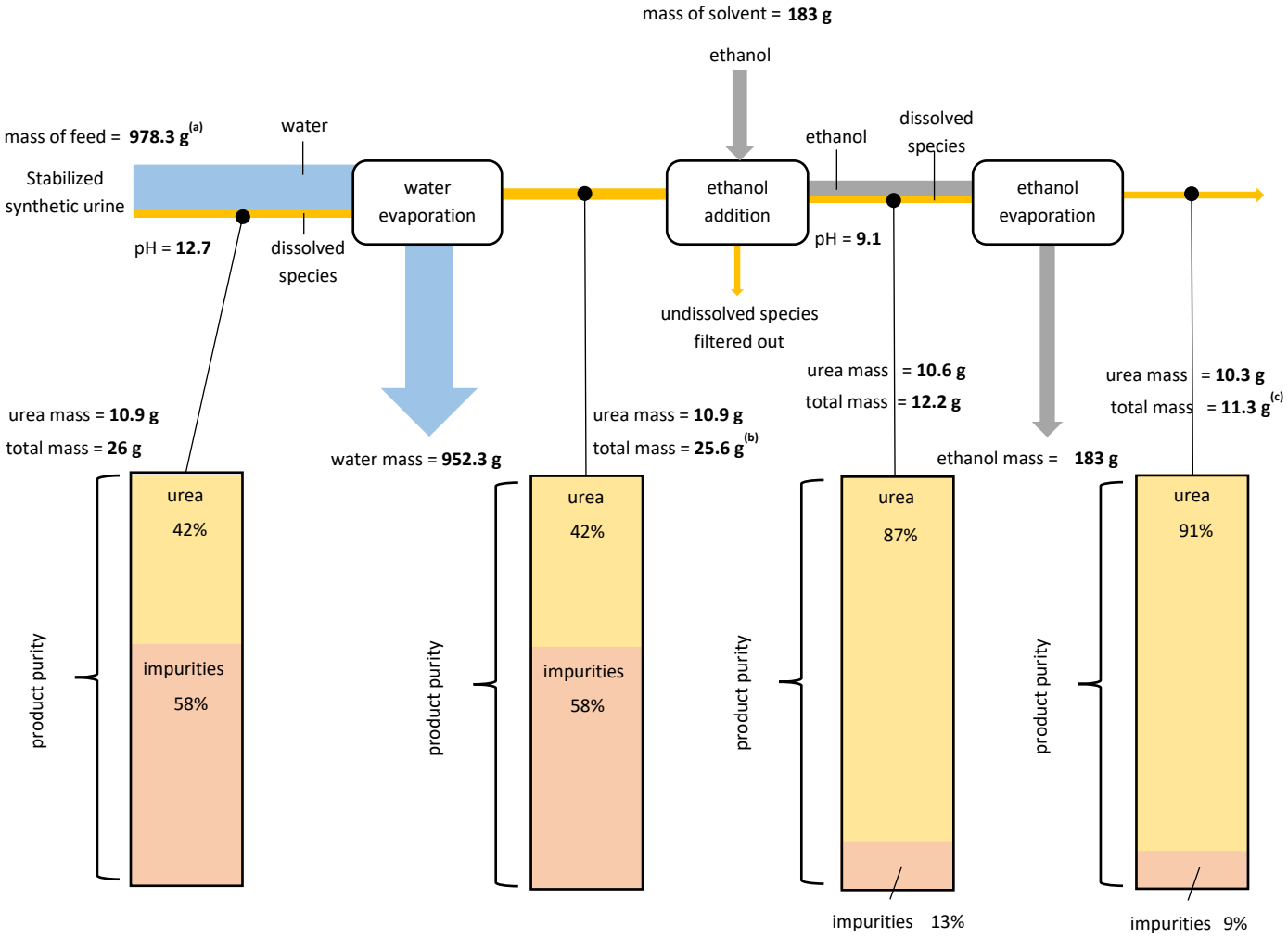


**Figure 4-6:** A process flow diagram of urea recovery from a synthetic urine sample containing only inorganics (SI). The Randall et al. (2016) [U1] composition was used to make up the synthetic solution. A 91% urea purity was obtained with a final yield of 88%. [(a)] Starting mass is less than 1000 g due to sampling, and filtration after stabilization. [(b)] Difference to initial value due to experimental error. [(c)] Some loss of urea yield was experienced during the ethanol evaporation. The total mass is the mass of the final urea product including some impurities.

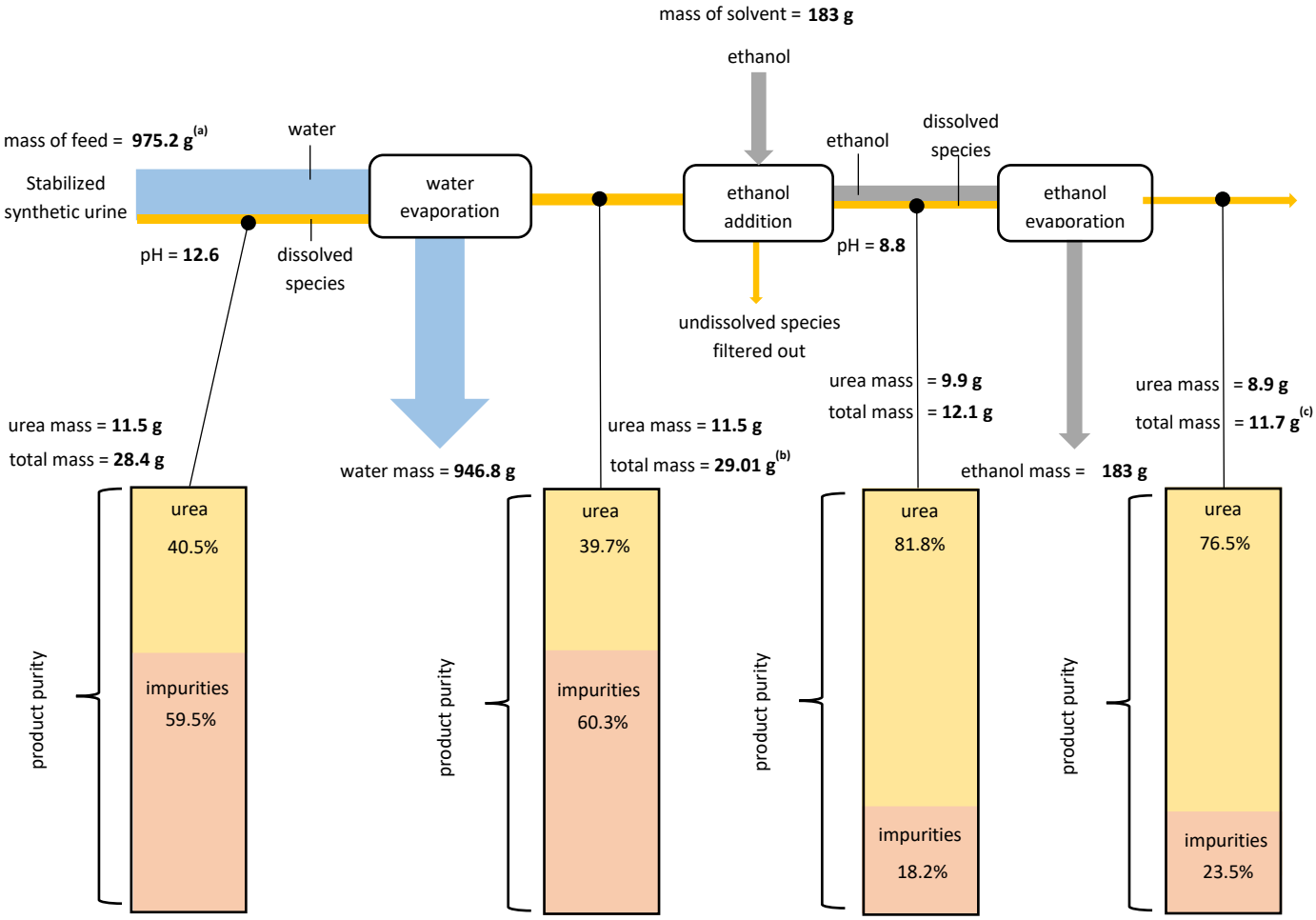


**Figure 4-7:** A process flow diagram of urea recovery from a synthetic urine sample containing both organics and inorganics (SO). The Randall et al. (2016) [U1] composition was used to make up the synthetic solution. A 76.5% urea purity was obtained with a final yield of 76.5%. [(a)] Starting mass is less than 1000 g due to sampling, and filtration after stabilization. [(b)] Difference to initial value due to experimental error. [(c)] Some loss of urea yield was experienced during the ethanol evaporation step. The total mass is the mass of the final urea product including some impurities.

Finally, the results of the urea recovered from real urine (RU) are shown in Figure 4-8. The urea purity obtained after complete water removal was 43.3% and the yield was ~100%. Minimal urea was lost. In this case, a lower purity would be expected due to the complex nature of urine. The composition of urine depends on the diet and habits of the population and nutrient content can vary between men, women and children (Langergraber & Muellegger, 2005). Therefore, the purity of the final urea product will vary because different amounts of other solids will form. However, the analysis of the urine showed that the real urine sample had a lower inorganic content (31.6%) and a slightly higher urea concentration. This resulted in RU having a higher purity than SO.

After ethanol addition and the filtration of undissolved species, the purity of urea increased to 78% in solution. The final purity after complete ethanol evaporation was 75.8% and the yield was approximately 67%. The final purity of RU was close to that of SO which suggests that the organics that were considered in the synthetic organic stream matched the composition well. According to the pie chart developed using the typical concentrations of major urine compounds given by Putnam (1971), the combination of creatinine, creatine and citric acid

accounts for 6% of the total urine composition. In this investigation, that same combination accounted for 7.7% of the SO stream.

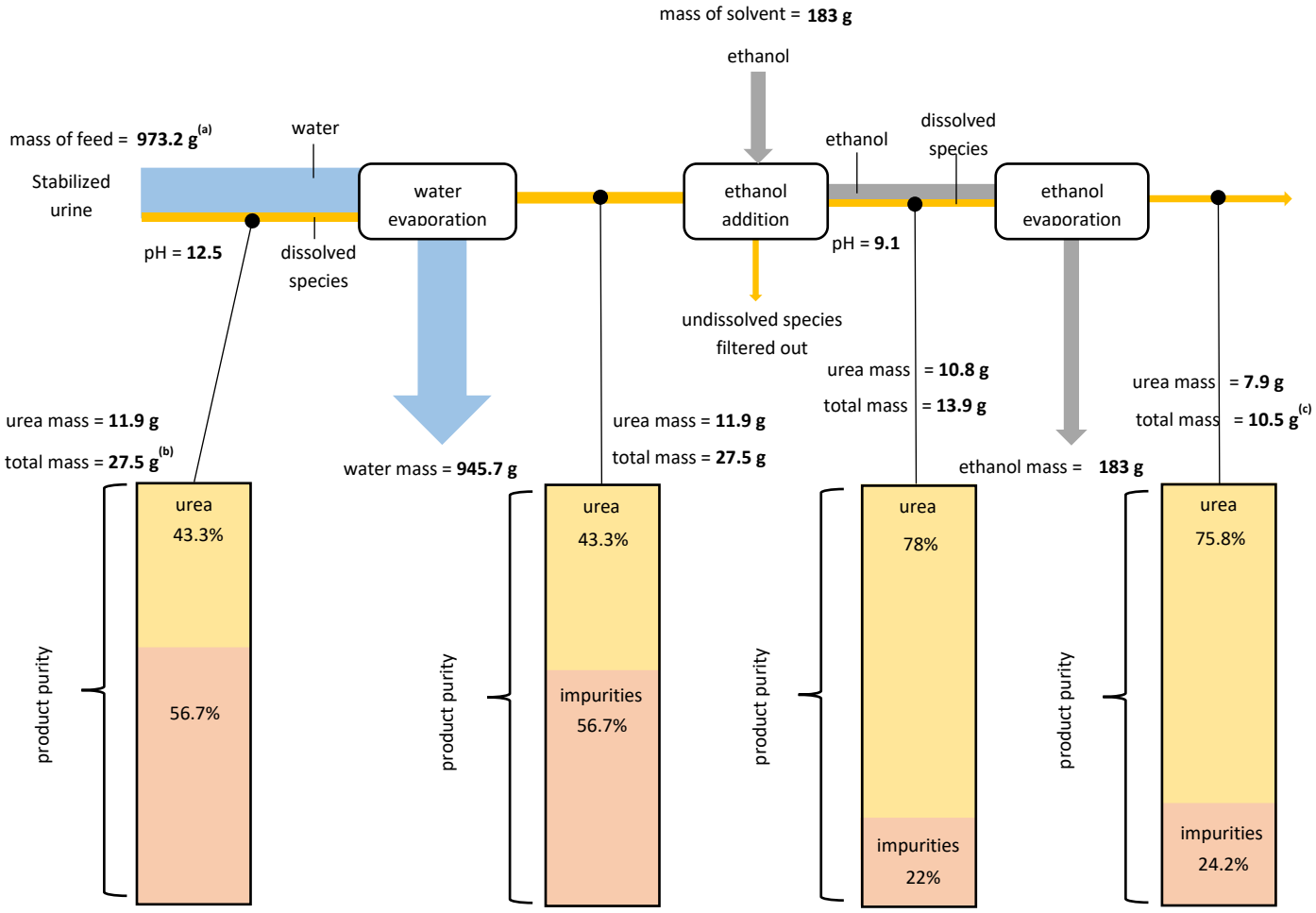


**Figure 4-8:** A process flow diagram of urea recovery from a real urine sample (RU). A 75.8% urea purity was obtained with a final yield of 67%. (a) Starting mass is less than 1000 g due to sampling, and filtration after stabilization. (b) Initial mass of sample was based on the final dry mass after evaporation, because no adequate test methods were available for unknown organic compounds in real urine. (c) Some loss of urea yield was experienced during the ethanol evaporation step. The total mass is the mass of the final urea product including some impurities.

## 4.4 Factors affecting the yield and purity

### 4.4.1 pH and evaporation rate

For all three urine streams, urea purities after complete water removal averaged around 42% whilst the average yield was ~89% (Figure 4-9). The model predicted a 100% yield after complete water removal. The experimental results showed that stabilization by $Ca(OH)_2$ dosing is an effective method for preventing the loss of urea during evaporation at 30°C. For example, between 7% and 16% urea was lost after complete water removal. Bethune et al. (2014) reported that approximately 90% of nitrogen would have been lost during evaporation if urine was not stabilized.

The loss of some urea during the evaporation process was likely due to a gradual decrease in the pH of the solution and subsequent ammonia volatilization. For example, while the initial pH was high (12.5 – 12.7), it decreased during contact with the air since the solution had no residual $Ca(OH)_2$ due to filtration after stabilization. The contact with the air would have resulted in $CO_2$ exchange and a pH decrease (López-Periago et al., 2013) below the enzymatic threshold of 11 (Randall et al., 2016). Any urease-producing bacteria in the urine, evaporation tray or in the air could have aided in the degradation of the urea at the lower pH values during evaporation. It is therefore possible that in real urine, urease-producing bacteria and urease were reactivated once the pH of the solution had decreased below 11 during the drying process. Furthermore, the pH of the solution after dissolution in ethanol was even lower (~9) which may have led to further loss of nitrogen as $NH_3$ gas during the ethanol evaporation process.

The physical experiments showed that the purity of the final product increases after dissolution in ethanol, removal of undissolved solids by filtration and the final evaporation of ethanol. However, the results show a decrease in the yield of urea recovered from SO and RU. Therefore, the presence of organics influences both the yield and purity of the final product. This is because other major organics present in human urine are also soluble in ethanol as shown in Table 2-3. For example, creatinine and creatine are slightly soluble, while citric acid has a solubility of 38.3 g 100 $g^{-1}$ in ethanol. This results in the organics dissolving along with the urea, and this possibly reducing the solubility of urea in ethanol. The detailed solubility aspects of a mixture of organics (with urea) in ethanol should be investigated further.

In addition, the organics make up approximately 17% (excluding urea) of the total mass of solids recovered from human urine (Putnam, 1971). These organics were not accounted for in the simulation of the solubilities which was used for the physical experiments because they do not currently exist in the software's database used for all simulations. Therefore, it is possible that the solubility for the SO and RU streams were underestimated.

The decision to recover urea by water removal only (Figure 4-9A) or by ethanol addition (Figure 4-9B) is a trade-off between maintaining the yield, which is the highest after water removal or improving the purity, which is the highest after ethanol evaporation.

A longer evaporation time at lower pH values could result in more enzymatic urea hydrolysis occurring. It was observed that the first composition, containing only urea and inorganics, had a shorter ethanol evaporation time (approximately 24 hours) compared to the other two streams containing the organics (approximately 48 and 72 hours for SO and RU, respectively). The more complex the stream was, the longer it took to evaporate the ethanol and recover urea.

Mote & Ranade (2017) showed that urea can be converted to organic carbamates and carbonates with a variety of 'green' applications. This results in alkyl carbamate and ammonia through a process called urea alcoholysis (Mote & Ranade, 2017) and could explain the loss of some of the urea. However, no ethyl carbamate was detected in the final dry product after ethanol evaporation. Urine is complex, and therefore there are many components that could potentially react in ethanol.

Assuming that the drop in pH and longer evaporation times are the biggest factors contributing to the loss of urea, the evaporation rate should be improved to limit the loss due to enzymatic

urea hydrolysis. Higher temperatures could be used to speed up the evaporation rate to prevent this degradation from happening, but chemical urea hydrolysis could occur at higher operating temperatures.

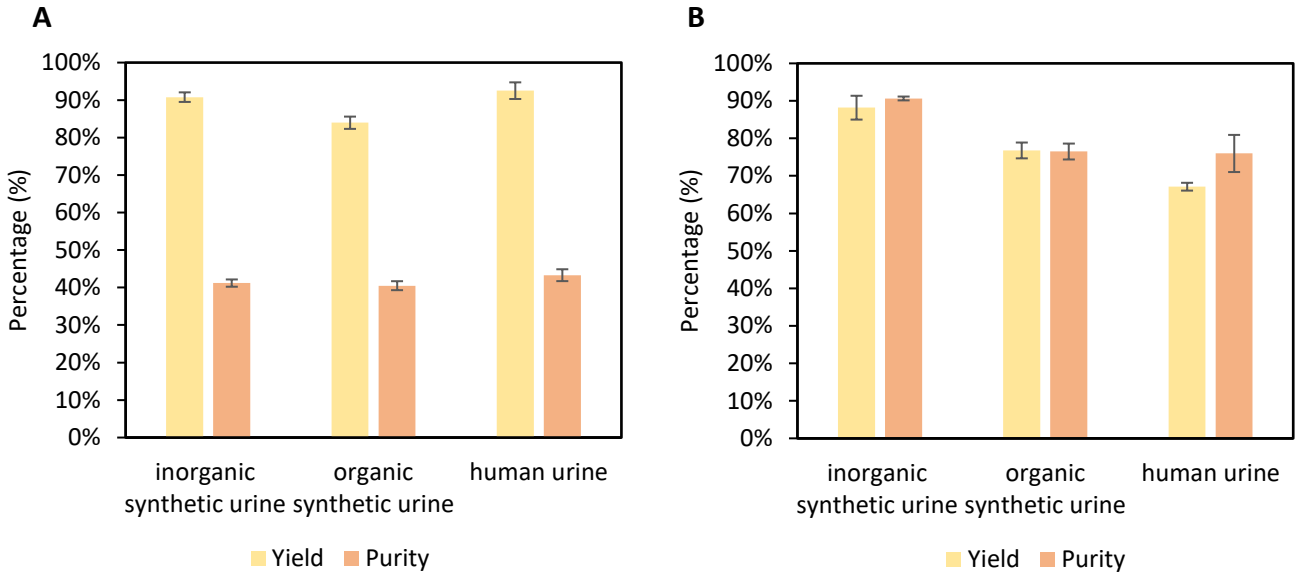


**Figure 4-9:** A summary of the yield and purity for the three experiments conducted to recover urea from urine. **(A)** illustrates the yield and purity after water removal and **(B)** illustrates the yield and purity after ethanol evaporation. Urea was recovered from inorganic synthetic urine (SI), organic synthetic urine (SO) and real human urine (RU) respectively. After complete water removal, yields of 91%, 84% and 93% were achieved. However, the purity was only 41%, 41% and 43%, respectively. Yields of 88%, 77% and 67% were obtained after ethanol evaporation and the purities were improved to 91%, 76% and 76% respectively.

### 4.4.2 Operating temperature

A simulation was run to investigate the effect that temperature would have on the process and is shown in Figure 4-10. The simulation showed that the concentration of urea dissolved in ethanol increases with temperature and that at higher temperatures, the solubility of urea is higher. Given this, it would be expected that the purity would increase with temperature. However, the simulation results show that the purity of the final product remains relatively constant regardless of operating temperature. This is because both the urea and unfiltered impurity solubilities increase with temperature at relatively the same proportion.

Thus, a higher temperature would only improve the evaporation rate of the process, and hence possibly the yield, but not necessarily the purity of the product. It is important to note that these simulated results do not include the organics other than urea, which is a limitation of the model. Experimental results have shown that there is about a 15% decrease in the purity with organics considered, and therefore, the purity would be lower in reality.

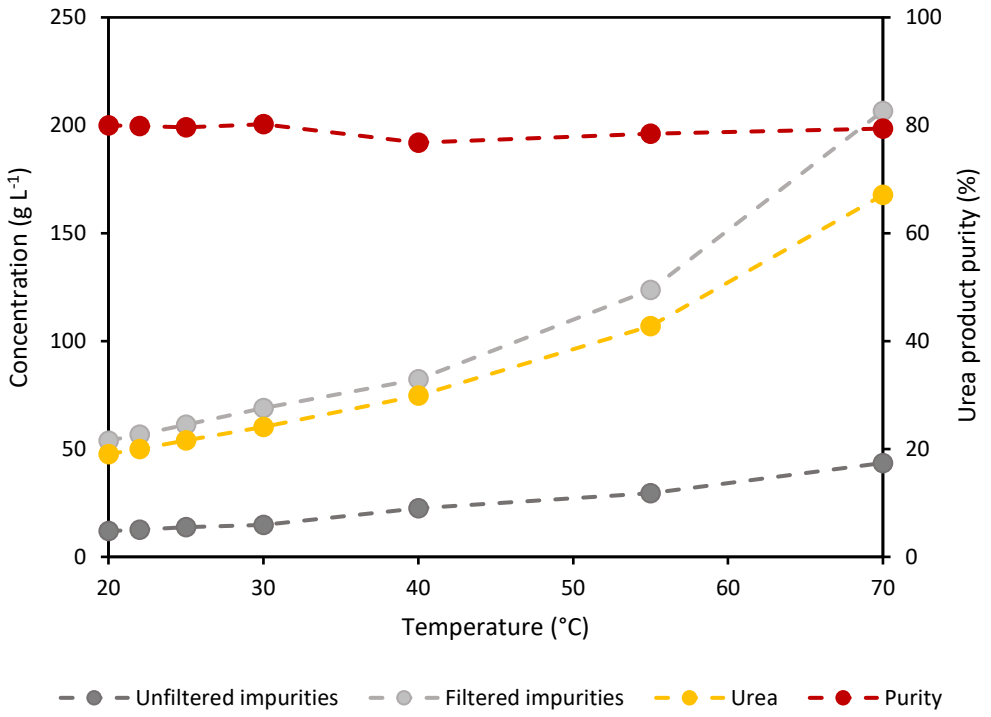


**Figure 4-10:** An illustration of the simulated concentration of impurities that are filtered out, and the impurities that are dissolved (unfiltered) during the ethanol addition process at a range of temperatures. These filtered impurities are mainly NaCl, KCl, $CaSO_4$ and $Ca(OH)_2$. The solubility of urea at various temperatures is also included. The red line illustrates the change in purity with temperature, which remains relatively constant.

### 4.4.3 Dissolved ions

A simulation was run to determine the impurities that are dissolved in ethanol with urea, as well as the impurities that are filtered out (Figure 4-11). The common ions that remain in solution are $Ca^{2+}$, $Cl^-$, $K^+$, $S^{6+}$ and $Na^+$. These ions do not account for the organics that might be present though. These ions remaining in solution could be removed prior to dissolution in ethanol to improve the final purity. For example, ion exchange could be used to remove chloride ions from solution. Hilal et al. (2015) showed that about 70% of the chloride ions in a solution of 5 g $L^{-1}$ NaCl could be removed using ion exchange. In a more recent study, Can et al. (2020) successfully removed 60 – 70% of sulphates from process water with sulphate concentrations of 3000 – 3800 mg $L^{-1}$. This would theoretically increase the purity of the final product from 80% to approximately 85%. Alternatively, the intermediate filtration step at 99%, which was thermodynamically investigated, could be implemented to improve the purity by approximately 17%. However, these additional steps would add to the cost and operation of the process.

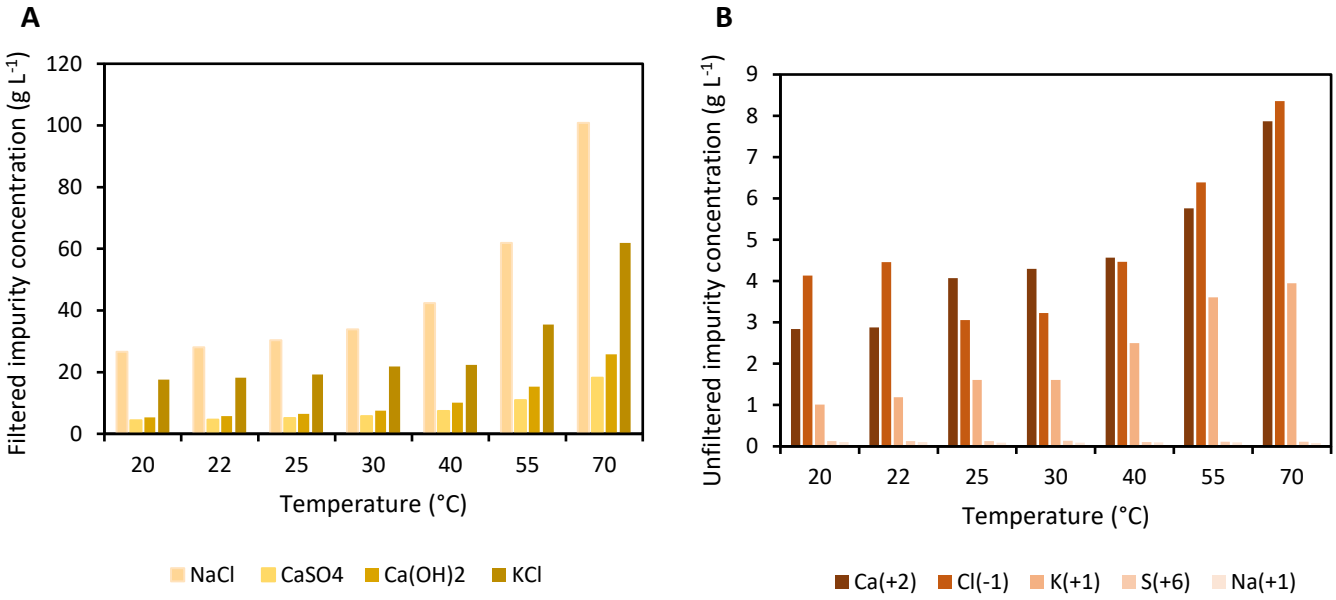


**Figure 4-11:** A comparison of the concentration of impurities filtered out from the urea-ethanol solution, and the impurities dissolved. **(A)** shows the impurities that are filtered out which are namely NaCl, $CaSO_4$, $Ca(OH)_2$ and KCl. **(B)** shows the ions that stay in solution which are usually $Ca^{2+}$, $Cl^{-}$, $K^{+}$, $S^{6+}$ and $Na^{+}$.

## 4.5 Improving the solubility of urea in ethanol

Due to the model not accounting for the organics when estimating the solubility of urea in ethanol, physical experiments were conducted to first verify the solubility of the inorganic urine stream, and to determine the solubility with organics present. These experimental results were compared to the model results of pure urea in ethanol, the experimental validation of pure urea in ethanol, and the model results of U1 containing urea and inorganics (Figure 4-12).

Figure 4-12 shows that the presence of inorganics and organics increase the solubility of urea in ethanol. Inorganics generally result in a higher solubility, approximately 27% more than pure urea in ethanol (based on experimental values). The presence of both inorganics and organics increases the solubility by 38% when compared to pure urea in ethanol. Figure 4-5 shows that varying compositions of urine do not change the solubility of urea in ethanol. Based on this finding, it can be assumed that the solubility of urea in ethanol in a mixture of other components present in human urine is approximately 56.7 g $L^{-1}$. This is higher than the initial solubility used to design the experiments.

This finding could explain the differences in purity between the inorganic synthetic urine stream and the synthetic organic and real urine streams. The SI stream solids after water removal were dissolved in the amount of ethanol required to recover urea, which resulted in a higher purity. Adding the exact amount of ethanol potentially limited the capacity for other impurities to dissolve along with urea. In contrast, the SO and RU streams received more ethanol than required, therefore increasing the capacity for other impurities to dissolve, resulting in a lower purity. Therefore, the revised solubility of 56.7 g $L^{-1}$ should be used instead to improve the purity of the urea recovered from this novel process.

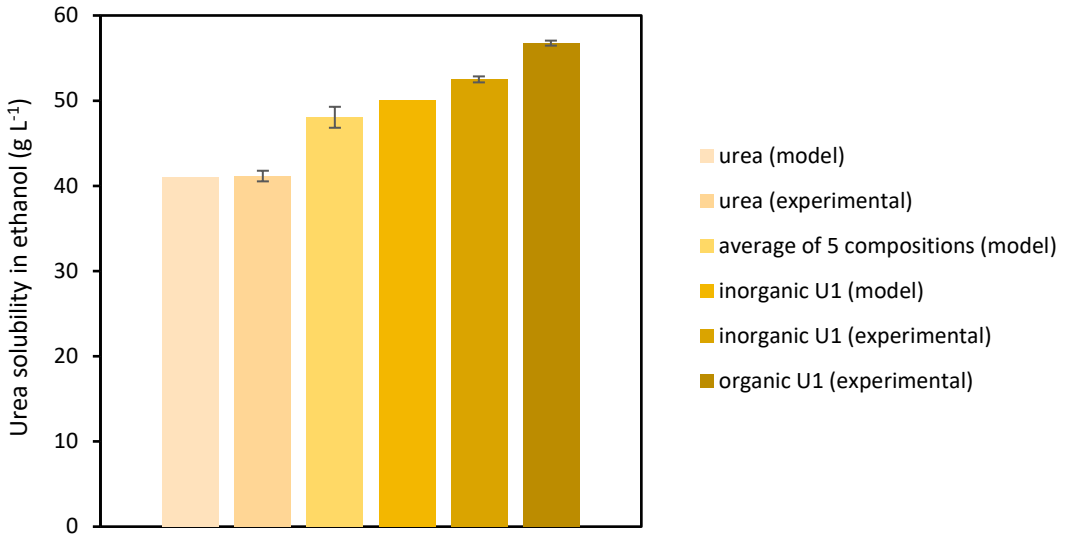


**Figure 4-12:** A comparison of the solubility of urea in ethanol for different conditions, obtained thermodynamically and experimentally at 22°C. The model was used to predict the solubility of urea (only) in ethanol, then the solubility of urea in the U1 composition in ethanol (for inorganics only). These were then validated experimentally at 22°C. Thereafter, the effect of adding organics to the U1 composition was also investigated as this could not be modelled thermodynamically.

In addition, including organics (creatinine, creatine, and citric acid) in the simulations could improve the accuracy of the model. The solubility accuracy of the major inorganic components present in human urine should also be validated to see if this improves the simulated results further. An improved simulation will help with process design and optimization, while also giving a more accurate energy and economic analysis.

## 4.6 Energy considerations

To estimate the energy consumption of the procedure developed in this study and potential selling price of the recovered urea, a conceptual design of a system treating 1 $m^3$ of urine per day was done. It involves two separate systems, one for water removal and the second for ethanol evaporation and urea recovery.

The system design is an adaptation of the study by Bethune et al. (2016) on the passive evaporation of source-separated urine from dry toilets. The urine evaporation system consisted of a box, open at the front, containing 22 vertically stacked cafeteria-type trays with a fan and chimney at the back (Bethune et al., 2016). This configuration achieved an evaporation rate of 2.7 L $m^{-2}$ $day^{-1}$ (5.13 L per day). The operation of the system in this study was designed uniquely to achieve optimal recovery of urea.

### 4.6.1 System description

The basic display of the system is a series of evaporation boxes, approximately 1.2 metres in height, each containing 20 vertically stacked trays. The number of evaporation boxes in a series was determined based on the total volume of urine, or urea-ethanol solution required to be evaporated. A reasonable height was chosen to allow for the average human to place and remove the urine trays with ease. Along the height of each evaporation box, fans are strategically located to allow for efficient water removal or ethanol evaporation from each tray.

The evaporation boxes are kept in a closed system to allow for the potential recovery of water or ethanol.

A tray size with outer dimensions of 53.3 x 38.1 x 2.5 cm and a volume of 4.3 L was chosen as a workable size, big enough to evaporate a large volume of urine but small enough for the average human to carry. A 300 mm diameter axial fan (Flame Proof Axial Fan, Bluetech Fans, Johannesburg, South Africa) was chosen for the design due to its low-pressure and high-volume airflows. The airflow achieved by this 300 mm diameter fan is 2300 $m^3$ $hr^{-1}$ with a pressure of 80 Pa. An equation for evaporation from a water surface was used to determine the evaporation rate that would be achieved for each evaporation box (Engineering ToolBox, 2004). The detailed calculations are provided in Appendix C.

### 4.6.2 Water removal system

The water removal system was designed to treat 1 $m^3$ of urine per day. Given that each evaporation box holds 20 stacked trays each containing 4 L of urine, the total number of evaporation boxes required to treat 1 $m^3$ is 12.5 systems, which can be rounded to 13 systems. A total of 13 systems can hold up to 1040 L of urine, however, for the purposes of these calculations, the volume was kept as 1000 L (1 $m^3$ of urine). This volume translates to a total of 250 trays.

Using the specifications of the 300 mm diameter axial fan, it was calculated that one fan could achieve an evaporation rate of 53 L per day for each evaporation box, when considering the height of the 20 stacked trays. Each evaporation box contains 80 L of urine, of which 27 L would remain after one day. Therefore, increasing the number of fans to two would ensure all 80 L are evaporated within a day.

However, logistically, two fans of 300 mm in diameter over a height of 1.2 m would not be effective over the entire height. To ensure that all the trays receive direct air flow, more fans would be required to cover the entire height of the evaporation box. Therefore, the final configuration of each evaporation box is shown in Figure 4-13.

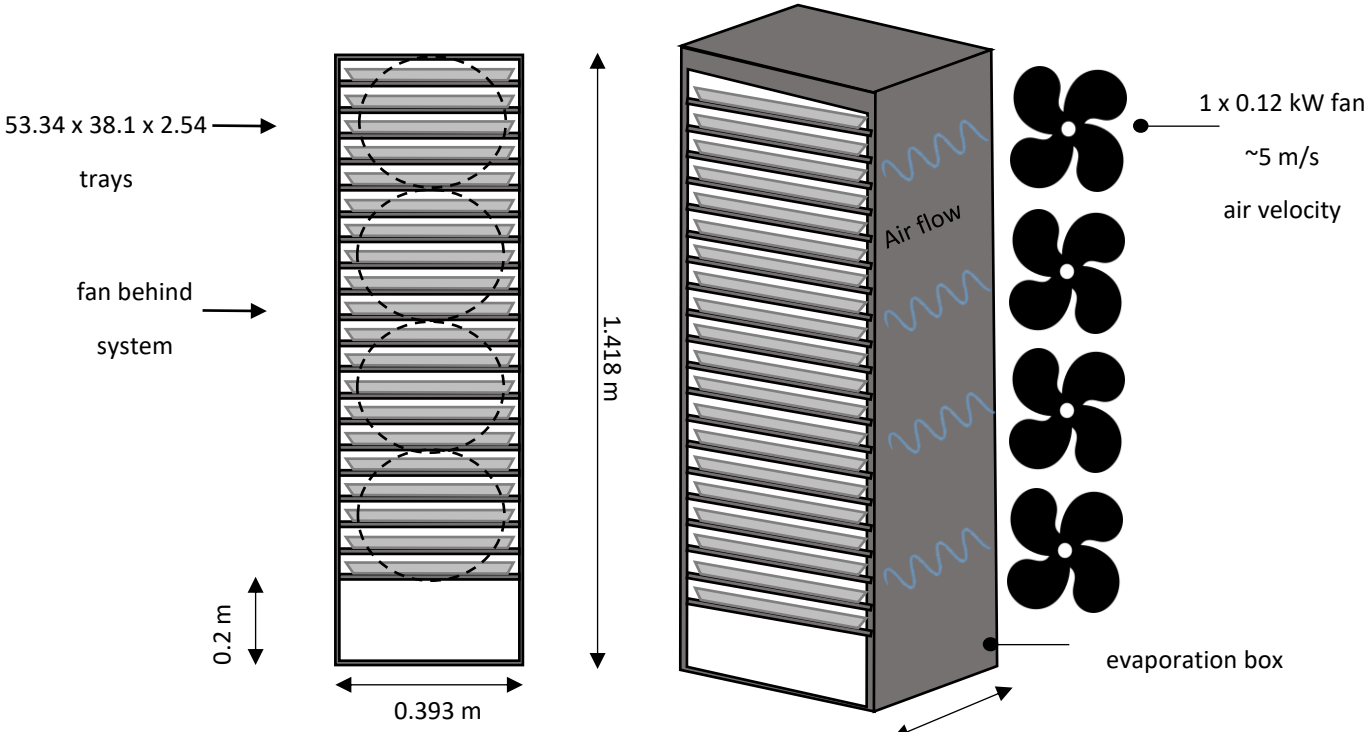


**Figure 4-13:** Diagram of one evaporation box where water removal and ethanol evaporation take place. For water removal, 13 of these systems would be put in place to treat 1 $m^3$ of urine per day. For ethanol evaporation, up to 5 of these systems would be operated based on the urea concentration of the urine being treated and the volume of ethanol used to dissolve the urea.

The total height of the system is 1.42 m and the first tray is placed 0.2 m above the ground. Each tray has a height of 2.54 cm and they are spaced 2.5 cm apart vertically to allow for easy removal and air to flow freely. Four fans are placed along the height of each evaporation box to ensure all trays receive sufficient air flow. Each fan, servicing 5 trays, can evaporate ~32.7 L per day which is 13 L more than is required.

The total system of 13 evaporation boxes containing 1000 L of urine has a footprint of 6.87 m, considering the 10 cm spacing between the evaporation boxes. The fans would be fixed to the wall, about 5 – 10 cm from each evaporation box. Finally, the fan power requirements for the water removal system are approximately 6.0 kW $m^{-3}$ urine.

### 4.6.3 Ethanol evaporation system

The ethanol evaporation system has the exact same configuration as the water removal system (Figure 4-13). However, it is designed to evaporate a smaller volume of ethanol and therefore has a smaller footprint. The number of fans as well as the positions are kept fixed to ensure sufficient airflow over all the trays. Based on the best urea solubility in ethanol that was achieved in this study (56.76 g $L^{-1}$) and the highest recorded amount of urea per L of urine (23.3 g $L^{-1}$, Putnam (1971)), the volume of ethanol required to make a saturated urea-ethanol solution was estimated to be 385.7 mL $L^{-1}$ of urine.

Therefore, assuming all the water from 1000 L of urine is evaporated, and each litre yields 23.3 g of urea, a total volume of 385.7 L of ethanol would be required to dissolve all the urea. This

would require five evaporation boxes to evaporate all 385.7 L of ethanol. Therefore, the entire system could potentially hold 400 L of urea-ethanol solution, which translates to 100 trays.

Because of the lower density of ethanol (789 kg $m^{-3}$) as compared to urine (assumed to be 1024 kg $m^{-3}$), the evaporation rate is faster. Therefore, each fan servicing 5 trays can evaporate approximately 42.4 L per day, which is 22 L more than is required. The ethanol evaporation system is therefore more efficient and would be complete within half of the time compared to the water removal system.

The total system of five evaporation boxes containing 385.7 L of urea-ethanol solution has a footprint of 2.7 m, considering the 10 cm spacing between the evaporation boxes. Finally, the fan power requirements for the water removal system are approximately 2.4 kW $m^{-3}$ urine.

### 4.6.4 Water and ethanol recovery

The water removal and ethanol recovery systems could be designed as closed systems to aid the recovery of both water and ethanol. For the water removal system, the technology used in solar distillation which condenses water vapor above a seawater basin (Fujiwara et al., 2021) could be used to recover water. To prevent urea hydrolysis from happening, the water vapor would be produced from the fan evaporation rather than from solar energy.

The ethanol that is transferred to the gas phase during evaporation could be recovered by distillation (Vane, 2008), depending on the operating temperature, but this is an energy intensive process. Vacuum distillation could also be used to recover the ethanol at lower operating temperatures. However, these operating conditions might still lead to chemical urea hydrolysis and loss of valuable urea. Therefore, the kinetics of the process also needs to be considered since a faster evaporation process might result in a reduced loss of urea even though the operating conditions are favourable for chemical urea hydrolysis.

Alternatively, membrane processes such as vapour permeation, pervaporation (Conde-Mejía & Jiménez-Gutiérrez, 2020), membrane distillation (MD) (Rácz et al., 2014) or vacuum membrane distillation (Karanasiou et al., 2018) could be used at reduced energy costs. For example, MD has a low operating temperature of between 30°C and 70°C (Rácz et al., 2014). These same technologies could also be adopted for water recovery. An overall cost-benefit analysis would have to be considered between water and ethanol recovery and reuse versus capital and operating costs of the chosen recovery process.

If successful, the recovery of ethanol from the process could reduce the cost requirement of ethanol, as recycled ethanol could be used for the next batch of urea. Furthermore, recovered water could be conveyed to a nearby building for reuse.

### 4.6.5 System operation, limitations, and advantages

Both systems would be closed to aid in the recovery of water and ethanol. The temperature in the evaporation room would be set to the desired temperature to speed up the evaporation process, as long as it is kept below the threshold of 40°C where chemical urea hydrolysis is likely to occur (Randall et al., 2016).

Urine would be collected in waterless fertilizer-producing urinals (Flanagan & Randall, 2018) dosed with 10 g $L^{-1}$ of $Ca(OH)_2$ (Randall et al., 2016). To reduce transportation costs (Flanagan & Randall, 2018), urine should be treated on-site where large volumes of urine are generated, such as office blocks. Alternatively, the stabilized urine could be transported from various commercial buildings to a decentralized resource recovery plant.

The urine would then be transferred to a filtration unit to remove excess $Ca(OH)_2$ and other undissolved impurities. Thereafter, the filtered, stabilized urine would be poured into each tray, up to 4 L per tray, and the water removal process would commence after the desired temperature is set and the fans are switched on. Approximately 24 hours later, the dry solids would be removed by scraping and gathered in a reactor. The volume of ethanol required to dissolve the concentration of urea found in the urine would be added to the reactor and thoroughly mixed.

Thereafter, the urea-ethanol solution with some dissolved impurities would be filtered and placed in the ethanol evaporation system. The temperature would be set and the fans switched on. Within 10 hours, a dry urea product would have formed in each tray which could then be removed by scraping and collected.

The water removal and ethanol evaporation rate (32.7 and 42.4 L per day) per five trays serviced by one fan are just over 6 and 15 times faster than the rate recorded by Bethune et al. (2016) (5.13 L per day) for various reasons. In the Bethune et al. (2014) urine evaporation system, only one fan was used, and its location was set closest to the vertical centre of the stack of 22 trays. Therefore, the airflow distribution was not sufficient for the trays situated above and below not receiving direct airflow. Furthermore, only an average airflow velocity of 0.5 m $s^{-1}$ was achieved by the single fan (Bethune et al., 2014) compared to the average air flow of 5 m $s^{-1}$ achieved by each fan in this system. Therefore, theoretically, the system is a significant improvement to the system used by Bethune et al. (2016) system.

However, it is important to note that this design does not consider the effect of humidity on the evaporation rates, as well as the potential for evaporation rates to reduce over time as the solution becomes more concentrated. In addition, the design does not consider the formation of the thin layer of scale that forms during water removal which also reduces the evaporation rate. The design is based on one operating temperature (30°C) and the footprint could be further reduced by operating at higher temperatures.

This is a simplified estimate of what a small-scale urea recovery system could look like. A more detailed thermodynamic model with evaporation rates for urine should be investigated. Furthermore, an actual system should be constructed and tested.

### 4.6.6 Potential urea recovery and energy consumption

The potential urea recovery from this design, assuming a urea concentration of 23.3 g $L^{-1}$, could be 15.61 kg per day, considering the yield achieved by the real urine composition in this study (67%). As previously discussed, measures such as increasing the rate of evaporation and reducing losses due to handling could improve this yield closer to ~20.5, kg assuming an 88% yield. The potential purity would be 76%, the highest achieved for real urine in this study. However, this could be improved to ~91% by using a more accurate solubility of urea in

ethanol, adding an intermediate filtration step, or implementing ion exchange to selectively remove dissolved ion impurities.

The total power required for this system to operate is 8.4 kW $m^{-3}$ urine. This estimate excludes the energy required to run the filtration unit, as well as the reactor used to dissolve the solids in ethanol. Furthermore, the energy required to heat air to temperatures higher than 30°C and the potential power requirement for the heating equipment is also not accounted for.

Ek et al. (2006) used evaporation as a volume reduction technique and reported an energy requirement of 30 kWh $m^{-3}$ urine evaporated. In a different study, Wang et al. (2020) developed a novel reverse osmosis process that employs low-salt-rejection (LSRRO) membranes to desalinate or concentrate highly saline streams. The energy consumption of the LSRRO process ranged from 2.4 to 8.0 kWh $m^{-3}$. Elsewhere, Eltawil et al. (2009) summarized the energy requirements of various desalination systems and reported values ranging from 9 – 17 kWh $m^{-3}$. Therefore, in comparison to these existing evaporation techniques, the system proposed in this study is only slightly higher than an RO system at this scale.

### 4.6.7 Cost and profitability estimations

The calculations for a basic estimation of the small-scale urea recovery unit designed to treat 1 $m^3$ of urine in this study is provided in Appendix D. It was estimated that the cost per day to recover 20.5 kg of urea would be R964 $m^{-3}$ urine. This estimate includes costs for electricity, calcium hydroxide and ethanol. This was based on an 88% urea yield with a purity of 91%, the highest achieved in this study. The calculation also assumed an ethanol recovery of ~90%, which would be reused for the next batch of urea, thereby reducing the cost of ethanol by 90%.

The potential profit that could be made from the urea produced in this study was determined (see Appendix D). Flanagan & Randall (2018) showed that calcium phosphate could also be recovered as solid fertilizer at a yield of 11.23 g per L of urine. This would be recovered during the solid filtration of the collected urine, where excess $Ca(OH)_2$ used for stabilization is filtered out (Chipako & Randall, 2020a). The potential revenue from the sale of Ca-P fertilizer and solid urea fertilizer produced in this study was determined to be R166 per day. The cost of production, however, was R964. Therefore, the solid bulk urea fertilizer market was deemed not profitable for the urea recovered in this study and would incur a loss of R798 per day.

Thus, it was necessary to explore other markets with more valuable products to maximize the profitability of the urea recovery procedure developed in this study. The profitability of producing diesel engine fluid, urea-formaldehyde, hydrazine hydrate, and a niche urea-rich liquid fertilizer was therefore investigated. In this study, the liquid fertilizer would be produced by combining ~12 parts water with 1 part urea crystals, resulting in a high-value urea-rich liquid fertilizer.

Table 4-1 compares the potential production of each product per day, the selling price of each end-product and the basic cost of production. The added cost of converting urea into these products through various processes was also considered in the profitability estimation. The detailed calculations can be found in Appendix D.

**Table 4-1:** Estimation of the cost of production and profitability of different urea markets. These estimations are based on urea recovered from 1m$^3$ of urine. All amounts are based on an 88% urea yield (20.5 kg per day) and a 91% urea purity. The bracketed values indicate a loss.

| | Bulk solid urea fertilizer | Niche liquid urea fertilizer | Diesel engine fluid | Urea-formaldehyde | Hydrazine hydrate |
|---|---|---|---|---|---|
| Selling price | R4.88 per kg | R153 per L | R31.7 per L | R17 per kg | R33.9 per kg |
| Reference | (IndexMundi, 2021) | (Chipako & Randall, 2020a) | (Sherman, 2017) | (indiamart, 2020) | (CEIC Data, 2021) |
| Production per day | 20.5 kg | 200 L | 49.4 L | 111 kg | 42.4 kg |
| Potential sales | R166 | R30 600 | R1570 | R1880 | R1440 |
| Cost of production | R964 | R1060 | R1360 | R1340 | R2390 |
| **Profit/(Loss)** | **(R798)** | **R29 500** | **R206** | **R542** | **(R950)** |

It was determined that from 20.5 kg of solid urea, 200 L of niche liquid urea fertilizer, 49.4 L of diesel engine fluid, 111 kg of urea-formaldehyde, and 42.4 kg of hydrazine hydrate could potentially be produced per day. Potential sales of R166, R30 600, R1570, R1880 and R1440 for solid urea, liquid fertilizer, diesel engine fluid, urea-formaldehyde, and hydrazine hydrate, respectively, could be achieved per day. The potential conversion of urea to 80% hydrazine hydrate was found to incur the most losses per day based on the procedure developed in this study (~R950 per day). Diesel engine fluid and urea-formaldehyde were found to be profitable using this recovery process with potential profits of R206 and R542 incurred per day, respectively.

The niche urea-rich liquid fertilizer was found to be the most profitable end-product by a high margin (R29 500 per day). This niche fertilizer is ~30 times more valuable than bulk fertilizer, which is why this high profit is possible. In order to assess whether the sale of 200 L per day of niche fertilizer is practical, the market for niche fertilizer in the Cape Town region was investigated, as an example but the market could be expanded further if it is feasible. Chipako & Randall (2020a) found that various nurseries around Cape Town each sell roughly two litres of liquid fertilizer every week. It was also estimated that there are about ~70 nurseries that sell fertilizers in the Cape Town region. This translates to a total of 140 L sold per week. Therefore, there would be a limited market for large volumes of a niche fertilizer.

From this study, it was estimated that 1400 L of liquid fertilizer could be made per week (see Appendix D for detailed calculations). This is substantially more than the market demand which is only 10% (140 L per week in the Cape Town region (Chipako & Randall, 2020a)) of the potential supply. Therefore, a maximum of 20 L of niche liquid fertilizer could be sold per day, and the remaining urea could be sold as bulk fertilizer, urea-formaldehyde, and diesel engine fluid.

Diesel engine fluid and liquid fertilizer are the most simplistic products to produce from urea as they only require the mixing of solid urea with water. The water used to produce these products could be recovered from the evaporation of urine by condensation. Conversely, urea-formaldehyde is a complex process which requires an additional chemical (methanol) to react with urea at high temperatures (between 90 and 95°C (Ormondroyd, 2015)). The production of urea-formaldehyde could therefore be disregarded for this investigation, and the daily production of diesel engine fluid and liquid fertilizer from recycled water could be estimated (Appendix D). The remaining urea, after liquid fertilizer production, could all be converted to diesel engine fluid because it is more profitable than bulk fertilizer.

The total amount of water that could potentially be recovered from the evaporation of 1 $m^3$ of urine is ~880 L per day. This is assuming that only 90% is recovered after potential losses are accounted for. The total production of a niche liquid fertilizer per day was determined to be 20 L, considering that the market for it is only 10% in the Cape Town region. This amount would only require 18.5 L of water per day for production. The remaining water (~862 L) would therefore be available for diesel engine fluid production.

It was found that 44.6 L of diesel engine fluid can be produced per day from the remaining urea crystals (18.5 kg of urea) that were not used for liquid fertilizer production. The water demand for diesel engine fluid was therefore determined to be 30.1 L per day, leaving an excess of 831 L of water to either be sold or recycled for other purposes. A mass balance for the daily production of diesel engine fluid, liquid fertilizer and calcium phosphate is provided in Figure 4-14.

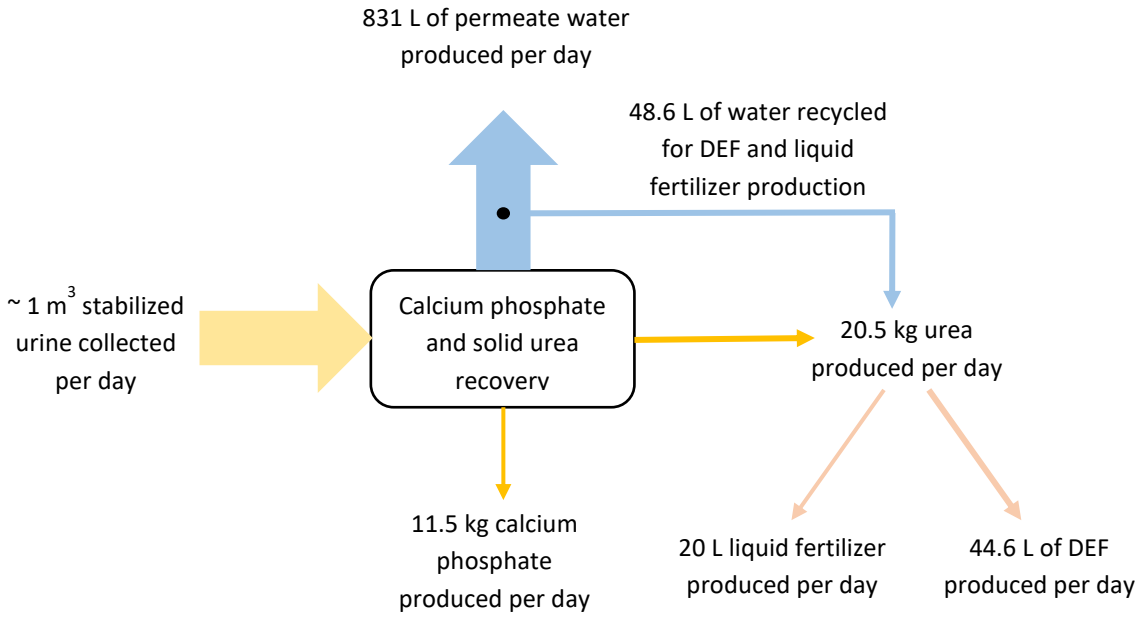


**Figure 4-14:** Mass balance for the inputs and outputs for urea-recovery and the subsequent production of calcium phosphate, diesel engine fluid and niche liquid fertilizer per day.

Niche liquid fertilizer is a high-value product and therefore contributes to the majority of the daily estimated profits (~68%). The potential income generated from the production of diesel engine fluid, calcium phosphate fertilizer, and liquid fertilizer is R4540 per day. Assuming a daily cost of production per day of R1430, the estimated daily profits would be R3110 per day.

This is significantly higher than the profits generated from solely producing either diesel engine fluid or urea-formaldehyde.

It is important to note that the exact purity of urea for these products (which is expected to be high) was not considered, and hence the cost for further purifying the urea product was not included in the calculations but should be investigated further in future work.

It is assumed that the required purity can be achieved with the process developed in this study through the implementation of various interventions to improve the purity of the final product. The process for producing diesel engine fluid assumes that the urea is synthetic, with a purity of ~98% (Bhaskar & Das, 2007) and does not provide recommendations for acceptable purities lower than 98%. This is likely due to the possibility that the production of diesel engine fluid from urine-derived urea has not been explored in literature.

The are many indirect benefits of recycling human urine that should be considered. Sanitation could be improved in low-income regions in Africa by introducing various urine diverting technologies, particularly waterless, fertilizer-producing urinals. On-site recovery systems could be introduced in these communities and fertilizer could be locally produced, improving food security in the region. Furthermore, this would create employment opportunities and improve the economy and quality of life in low-income communities.

In the urban context, cities could potentially benefit from the reduction of carbon taxes if they adopt and implement processes that are greener and require less energy. The collected urine could be conveyed to nearby resource recovery sites for the production of goods (e.g., fertilizer and diesel engine fluid). Moreover, the increased use of waterless urinals could significantly reduce the nutrient loads entering wastewater treatment plants. Since urine contains most of the nutrients found in wastewater, the overburdening of wastewater treatment plants could be remedied and the risk of untreated wastewater contaminating freshwater bodies would be minimized. This would ultimately improve the water quality. Cities could also implement a municipal sewage rebate to incentivise nutrient recycling initiatives such as source separation and treatment of urine.

The reduction of greenhouse gas emissions is also an important indirect benefit. Diesel engine fluid can potentially meet the near-zero nitric oxide emission requirements imposed in the US and Europe, according to US-based consultants, SRI Consulting (ICIS, 2011) and achieve 3 – 5% greater fuel efficiency. If the purity of urine-derived urea can be produced to be comparable to established, commercially available urea, it could potentially supplement the urea produced from the energy intensive Haber-Bosch process. This would significantly reduce greenhouse gas emissions.

# 5. Conclusions and recommendations

This chapter covers the conclusions to the work presented in this study. The research overview is outlined and it is shown how the literature review, approach, and results and discussion helped accomplish the hypothesis of this investigation. Following that, the key findings from both the thermodynamic and experimental aspects of the study are outlined. Thereafter, the implications of this work are outlined and finally, recommendations for future studies are made.

## 5.1 Research overview and accomplishment of objectives

This study aimed to develop a sustainable and novel method for recovering urea from human urine by evaporation, followed by a dual method of solvent extraction and recrystallization of purer urea from ethanol. A thorough review of existing urine treatment technologies as well as urine stabilization techniques was conducted and the appropriate methods for recovering urea were chosen. The appropriate purification method and a solvent for extraction and recrystallization was recommended after a critical review.

Three approaches were adopted to address the key objectives and hypothesis of this investigation. The first approach was a thermodynamic investigation to predict the experimental conditions for the urea recovery procedure. The model predicted the point of crystallization of urea during water removal, assisted in determining whether intermediate filtration would improve the purity, and the solubility of urea in ethanol. An experiment was also conducted to validate the model. The second approach involved the recovery of urea from two synthetic urine streams (urea with inorganics (SI) and urea with both inorganics and organics (SO)) and a real urine stream (RU) through physical experiments. The yields and purities of the different streams were compared, and a final physical experiment was conducted to establish the actual solubility of urea in a stream containing organics. This was done because the model could not simulate urine streams containing organics, other than urea.

The final approach was the conceptual design of a small-scale urea recovery unit treating 1 $m^3$ of urine per day. The design was used as a basis for estimating the potential power requirements of the process and potential profits generated from the production of different urea products.

For this investigation, it was hypothesized that urea can be successfully recovered from human urine by removing all the water from it and dissolving the remaining solids in ethanol to purify the product. After dissolution, most impurities can be filtered out and the resulting urea-ethanol solution can be evaporated to isolate purer urea crystals. This is because most inorganic compounds found in urine are insoluble in ethanol while urea is highly soluble. This work developed a novel urea recovery and purification method from stabilized human urine using an ethanol crystallization and evaporation process. Therefore, the hypothesis was confirmed and all seven key objectives detailed in Chapter 1.3 were successfully addressed.

## 5.2 Key findings

The key findings presented in this section were drawn in fulfilment of the research objectives proposed for this study. The section is divided into the three approaches used in this investigation which are namely, thermodynamic modelling, urea recovery experiments, and energy and economic considerations.

### 5.2.1 Thermodynamic modelling

The main findings of the thermodynamic modelling investigations were that:

1. During water removal, most impurities started to form after ~15% water removal, while the urea only crystallized between 99% and 100% water removal. This demonstrated that complete water removal was necessary to ensure the optimal recovery of urea.
2. The points of solids formation for the five different urine compositions were relatively the same, demonstrating that the composition did not have an influence on the results.
3. The addition of an intermediate filtration step would not be feasible for this investigation. This is because the purity after intermediate filtration at 95% only improved by 5% which was not significant with respect to the final purity that could be achieved. In addition, the simulation results showed that intermediate filtration at 99% yielded a 17% increase in purity. This is because at that point, most solid impurities had formed, leaving only a few impurities in solution. However, the volumes used in this investigation (1 L) would make filtration at this point very difficult. A volume of at least 5 L would be required to perform intermediate filtration at 99% (~50 mL of water).
4. Complete water removal without intermediate filtration was recommended as the preferred evaporation method for this investigation and a yield and purity of 100% and 53% was predicted by the model.
5. The solubility of pure urea in ethanol was determined to be 43.67 g $L^{-1}$ at 25°C, which compared well with the value given in literature for the same temperature (46.07 g $L^{-1}$).
6. The model was successfully validated for five data points along the urea solubility curve developed using the thermodynamic model. The results fitted well with an NSE coefficient of 0.96.
7. A temperature of 22°C was established as the appropriate operating temperature to conduct the water removal experiment as it was the average temperature in the laboratory. The physical experiments were to be conducted at room temperature to reduce energy requirements. The solubility was 40.98 g $L^{-1}$ at this temperature.
8. Thermodynamic modelling revealed that a typical urine composition resulted in a higher urea solubility in ethanol of 50.05 g $L^{-1}$ at 22°C.

### 5.2.2 Urea recovery experiments

The main findings of the urea recovery experiments were that:

1. After complete water removal, yields of 91%, 84% and 93% were achieved for SO, SI and RU, respectively. After ethanol evaporation, those yields decreased to 88%, 77% and 67%.
2. The purities after complete water removal were 41%, 41% and 43% for SO, SI and RU, respectively. As a result of recrystallization from ethanol, these purities increased to 91%, 76% and 76% respectively.
3. The yields after ethanol evaporation were lower for the urine streams containing organics because it was shown in the literature review that some major organics are soluble in ethanol. Real urine had the lowest yield, suggesting that there were more organics that were unaccounted for.
4. Stabilization by alkalization ($Ca(OH)_2$ addition) was a successful method for preventing urea hydrolysis during water evaporation as it was observed that <10% urea was lost.
5. The average yield for all three experiments after water removal (89%) did not match the 100% yield predicted by the model. This was likely due to a gradual decrease in the solution pH caused by a potential $CO_2$ exchange with residual $Ca(OH)_2$ upon contact with the air. Furthermore, urease-producing could have also contributed to the degradation of urea at these lower pH values which was not accounted for in the model.
6. For SO and RU, significant losses in yield were observed during ethanol evaporation. Longer ethanol evaporation rates were observed for SO and RU which likely contributed to the loss in yield as more time was allowed for the possible enzymatic hydrolysis of urea. Furthermore, a drop in pH after ethanol addition (~9) was likely also a contributor to the loss in yield during ethanol evaporation due to possible enzymatic urea hydrolysis. Therefore, it was proposed that operating at temperatures up to 40°C could speed up the ethanol evaporation and improve the yield.
7. Common ions that were found to remain in solution after ethanol addition and filtration were $Ca^{2+}$, $Cl^{-}$, $K^{+}$, $S^{6+}$ and $Na^{+}$ and these negatively impacted the final purity. Added to that, some organics were also dissolved in the SO and RU experiments, resulting in a much lower purity. Therefore, it was suggested that the selective removal of these ions by ion exchange could potentially improve the purity by 5%.
8. A final experiment revealed that the actual solubility of a urine stream containing organics is 56.7 g $L^{-1}$ demonstrating that the solubility increases with the presence of organics. Therefore, for more complicated urine streams a lower volume of ethanol would be sufficient (~190 mL).

### 5.2.3 Energy and economic considerations

The main findings of the energy and economic considerations were that:

1. A total system power of 8.4 kW $m^{-3}$ urine was determined based on the design with a potential urea recovery of 15.61 kg per day (67% yield) at a purity of 76%.
2. The yield and purity could potentially be improved up to 20.5 kg at 88% yield and 91% purity.

3. The system proposed in this study is only slightly higher than an RO system at this scale. However, the energy requirements for operating at higher temperatures as well as for the other apparatus used for small-scale urea recovery were not accounted for. Therefore, total power required could be higher.
4. The potential recovery of water and ethanol from the process was also explored to potentially reduce the cost of ethanol, as recycled ethanol could then be used to produce the next batch of urea. Furthermore, recycled water could be used to make other products from urea, such as diesel engine fluid and liquid fertilizer.
5. The cost of producing urea per day through this small-scale urea recovery unit was determined to be R964.
6. The profitability of this procedure was determined by comparing the use of urea in four different markets (fertilizer (solid and liquid), diesel engine fluid, urea-formaldehyde, and hydrazine hydrate). It was determined that from 20.5 kg urea, 49.4 L of diesel engine fluid, 111 kg of urea-formaldehyde and 42.4 kg of hydrazine hydrate could be produced per day.
7. The use of urea as solid bulk fertilizer was not profitable, with an incurred loss of R798 per day. Diesel engine fluid and urea-formaldehyde were found to be profitable, incurring profits of R206 and R542 daily, respectively.
8. A niche urea-rich liquid fertilizer was determined to be the most profitable, high-value end-product for this process with a potential profit of R29 500 per day for 200 L. However, the market for liquid fertilizer is only 10% in the Cape Town region. Therefore, a maximum daily production of 20 L was recommended, and the excess urea would be used to produce 44.6 L of diesel engine fluid.
9. Recycled water condensed from the evaporation of urine would be more than enough to produce diesel engine fluid and niche liquid fertilizer, with an excess of 831 L, which could be used for other purposes.
10. The daily production of diesel engine fluid, liquid fertilizer and calcium phosphate could potentially incur daily profits of R3110.

## 5.3 Implications of study

Urea is a versatile product with uses that span across a range of different industries. These industries include agriculture, plastics, diesel engines, bio-bricks, aviation, and aerospace. This research did not only propose a method for recovering urea from human urine to potentially replace the energy intensive Haber-Bosch process, but it also introduced the possibility of producing high-value products from urine using a novel process. This offers a multitude of indirect benefits such as the reduction of greenhouse gas emission, improve sanitation and water quality in low-income areas, reduction of nutrient loads entering wastewater treatment plants and the potential reduction of carbon taxes.

## 5.4 Recommendations

Further research should be conducted to improve the method of urea recovery developed in this study. This would bring the research closer towards creating the paradigm shift of reimagining ‘wastes’ as valuable resources. The following recommendations for future studies are to:

1. Improve the thermodynamic model to include a database to model organics in urine. This would improve the predictions of the final purity as well as the volume of ethanol required for the recrystallization and extraction of urea.
2. Improve the system design to include intermediate filtration at 99% water removal as this could potentially improve the final purity by 17%.
3. Investigate if the loss in yield was possibly due to a gradual decrease in the pH and longer evaporation rates, as a result of enzymatic urea hydrolysis. This could be done by monitoring the pH throughout the water removal process and investigating how the yield changes with different rates of evaporation.
4. Investigate whether urea recovery at higher temperatures can significantly improve the rate of evaporation and ultimately, the purity.
5. Measure a full range of organic compounds throughout the urea recovery process.
6. Determine the solubility of a mixture of organics and urea in ethanol to gain a better understanding of the effects of the organics on urea recovery process.
7. Investigate the selective removal of dissolved ions (impurities) from the urea-ethanol solution by ion exchange to further purify the final product. The additional costs of adding this purification method should also be considered.
8. Investigate the feasibility of recovering and reusing ethanol and water.
9. Investigate the effect of humidity on the evaporation rate for different designs and concentrations.
10. Build, commission and test the conceptual small-scale design of the urea recovery process developed in this study.
11. Improve energy estimations to incorporate all unit processes involved in the urea recovery process. A thorough cost-benefit analysis which compares to similar nutrient recovery processes should also be conducted.
12. Investigate the feasibility of converting urea into diesel engine fluid and niche liquid fertilizer as part of an integrated process that incorporates the novel urea recovery method developed in this study.
13. Investigate the range of acceptable urea purities to successfully convert urea to diesel engine fluid.
14. Perform a full life-cycle assessment of the proposed system and compare it to the Haber-Bosch process.

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# Appendix A: Thermodynamic and Experimental results

The link to a Google Drive folder containing all the thermodynamic model simulations and spreadsheets, as well as the physical experimental results is provided below:

https://drive.google.com/drive/folders/1M2g3LCV-sANz1XWS7x3KkUaKIldf7Yy9?usp=sharing

Individual links containing thermodynamic and experimental raw data:

1. Summary of water removal and intermediate filtration simulations: https://drive.google.com/file/d/1K8pCRuxomUr_0885kJr_bL-RrDDwNCaP/view?usp=sharing
2. All water removal simulations: https://drive.google.com/drive/folders/1ibH8nbrDtUdMn_71_0mXOvsg7BQv6fxp?usp=sharing
3. Urea solubility in ethanol and model validation: https://drive.google.com/file/d/19x7pCdSXBLawva4V7YAELzJc46ARBmJm/view?usp=sharing
4. Urea solubility in ethanol simulation files: https://drive.google.com/drive/folders/1SKXK0NEDJQJJRZiqOWjolKK9uli_WdLS?usp=sharing
5. Urine recipe: https://drive.google.com/file/d/1TKbuCjwLD1vbzBPwGV-JXW9ez1jkoT5e/view?usp=sharing
6. Urea recovery experiments: https://drive.google.com/file/d/1Lk03QPMmBFBNMZt09qMQnH3YnmdY6Cb3/view?usp=sharing
7. Improving urea solubility in ethanol: https://drive.google.com/file/d/12cIlGN-3NhFrSzj6kRGIr07TbsT0wKFH/view?usp=sharing

# Appendix B: Estimating the volume of ethanol required

To estimate the volume of ethanol required to dissolve and recrystallize urea, the first step was to compute the volume that would be occupied by the solids (Table A-1). To do this, the masses of each compound were divided by the density to get their individual volumes. The organic components were not considered because the model could only predict a solubility of urea in ethanol for an inorganic urine composition. The masses were taken from the U1 (Randall et al., 2016) recipe. All values are shown to 3 significant figures.

**Table A-1:** Estimation of the volume occupied by solids in a mixture of urea, inorganic compounds, and ethanol.

| Name | Compound | Mass (g) | Density (g $mL^{-1}$) | Reference | Volume (mL $L^{-1}$) |
|---|---|---|---|---|---|
| Urea | $CO(NH_2)_2$ | 11.6 | 1.34 | (PubChem, 2004c) | 8.71 |
| Sodium sulphate | $Na_2SO4$ | 1.22 | 2.66 | (BYJU's, 2020) | 0.46 |
| Ammonium chloride | $NH_4Cl$ | 1.67 | 1.53 | (Softschools.com, 2020) | 1.09 |
| Potassium chloride | KCl | 4.62 | 1.98 | (Inchem.org, 2017) | 2.33 |
| Calcium chloride | $CaCl_2$ | 0.484 | 2.15 | (American Elements, 2020) | 0.225 |
| Sodium chloride | NaCl | 1.47 | 2.16 | (Shapley, 2011) | 0.681 |
| Sodium hydroxide | NaOH | 2.67 | 2.10 | (Inchem.org, 2010) | 1.27 |
| Calcium hydroxide | $Ca(OH)_2$ | 2.83 | 2.24 | (Microkat, 2020) | 1.26 |
| **Total** | | **26.6** | | | **16.0** |

The design solubility predicted by OLI was 50.05 g $L^{-1}$ for U1. Therefore, using equation (A-1), the volume of ethanol was estimated.

$$\text{volume of ethanol required (L)} = \frac{\text{mass of urea (mg)}}{\text{design solubility (mg L}^{-1})} - \text{volume occupied by solids (L)} \quad \text{(A-1)}$$

$$\text{volume of ethanol required (L)} = \frac{11\,600\ \text{(mg)}}{50\,050\ \text{(mg L}^{-1})} - 0.0160\ \text{(L)} = 0.216\ \text{L} = 216\ \text{mL}$$

It was established that an estimated loss of 11 mL of ethanol would be lost from the transferring of liquid between containers (~4 mL), evaporation during mixing (~3 mL), and due to sampling (~4 mL). Therefore, to account for these losses, the volume of ethanal required was conservatively taken as ~232 mL.

# Appendix C: Detailed calculations for conceptual design

To estimate the potential power requirements for treating 1 $m^3$ of urine per day, a small-scale urea recovery system had to be designed. The system was based on the Bethune et al. (2014) urine evaporation system which consisted of an evaporation box containing a vertical stack of 22 cafeteria-sized trays and a fan to remove the water.

To design the system, firstly a tray size with inner dimensions of 49.53 x 34.9 x 2.54 cm with a volume of ~4.3 L was chosen. The amount of urine poured into each tray would be restricted to 4 L to avoid any spills. Using the dimensions of the tray as a guide, and the average height of a human (1.7 m) as a restriction, each evaporation box was specified at a height of 1.4 m and consisted of 20 trays. The first tray was positioned at ~0.2 m above the ground and vertical spacing between the trays was ~2.5 cm.

**Water evaporation**

For the water evaporation system, to treat 1 $m^3$ of water per day, the number of 20-tray systems required would be:

$$\text{No. of systems} = \frac{1000\ \text{L day}^{-1}}{(20\ \text{trays x 4 L each})} = 12.5\ \text{systems (A-2)}$$

This translated to a total volume of:

$$\text{total volume of urine treated per day (L)} = 12.5\ \text{systems x 20 trays each x 4 L per tray} = 1000\ \text{L}$$

To hold all 1000 L, a round number of 13 systems would need to be built which can hold a total of 1040 L. However, the total evaporated volume will be kept as 1000 L (1 $m^3$) for the purposes of these calculations. Therefore 250 trays would be required to hold 1000 L of urine. The footprint covered by 13 systems, each with a width of ~42.1 cm and allowable space of 10 cm between each evaporation is ~6.87 m.

A 0.12 kW axial fan with a diameter of 30 cm (Flame Proof Axial Fan, Bluetech Fans, Johannesburg, South Africa) was chosen for the design. The system was positioned such that the width of 34.9 cm would be parallel to the wall where the fans are placed, and the length of 49.53 cm would be perpendicular to the wall. This configuration was chosen such that the 30 cm diameter would cover most of the width of the trays (34.9 cm) with only 2.45 cm left on either side. It was assumed that the coverage would be sufficient to allow for the urine in the trays to receive direct airflow from the fans.

The fan was specified to have a power of 0.12 kW, an airflow of 2300 $m^3\ hr^{-1}$ and a pressure of 80 Pa. Using a generic equation (A-3) for the evaporation of water from an open surface (Engineering ToolBox, 2004), the potential evaporation rate that could be achieved by one fan for each system was calculated.

$$g_h = \theta \text{ x } A \text{ x } (x_s - x) \text{ (A-3)}$$

Where:

$g_h$ = amount of evaporated water per hour (kg $hr^{-1}$)

$\theta = (25 + 19\ v)$ = evaporation coefficient (kg $m^{-2}$ $hr^{-1}$)

v = velocity of airflow (m $s^{-1}$)

A = water surface area ($m^2$)

$x_s$ – maximum humidity ratio of saturated air (kg $H_2O$ in kg dry air)

x = humidity ratio of air (kg $H_2O$ in kg dry air)

The variable $x_s$ was found using Figure A-1 and was determined to be 0.271 kg $H_2O$ in kg dry air at a temperature of 30°C. The variable x was determined to be 0.0135 kg $H_2O$ in kg dry air using the Mollier diagram representing the relationship between air temperature, moisture content and enthalpy (Figure A-2).

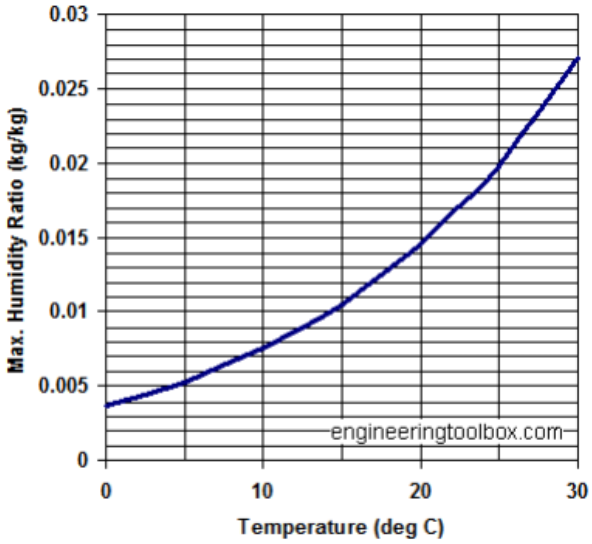


**Figure A-1:** The maximum saturation humidity ratio of air at a temperature range between 0°C and 30°C (EngineeringToolBox, 2004a).

The airflow velocity in the equation is expressed in m $s^{-1}$, and the velocity specified by the fan is given as $m^3$ $hr^{-1}$. Therefore, the fan airflow velocity was converted as follows:

$$\text{airflow velocity (m s}^{-1}) = \frac{\text{fan airflow (m}^3\text{ hr}^{-1})}{\text{system surface area} \perp \text{to direction of airflow (m}^2)} \text{ x } \frac{1}{3600} \text{ (A-4)}$$

Where, the system surface area was taken as the system width for one evaporation box (42.1 cm) and the height occupied by the trays (120.8 cm).

$$\text{airflow velocity (v) (m s}^{-1}) = \frac{2300 \text{ (m}^3\text{ hr}^{-1})}{(1.208 \text{ x } 0.421) \text{ (m}^2)} \text{ x } \frac{1}{3600} = 1.26 \text{ (m s}^{-1})$$

Theta (θ) was then computed:

$$\theta \text{ (kg m}^{-2}\text{hr}^{-1}) = 25 + (19 \text{ x } 1.256 \text{ m s}^{-1}) = 48.9 \text{ (kg m}^{-2}\text{hr}^{-1})$$

It is important to note that the units for θ do not match, i.e., inside the equation the only units used are m $s^{-1}$, whereas the resulting units are kg $m^{-2}$ $hr^{-1}$. This is because it is an empirical equation, a result of experience and experiments (Engineering ToolBox, 2004).

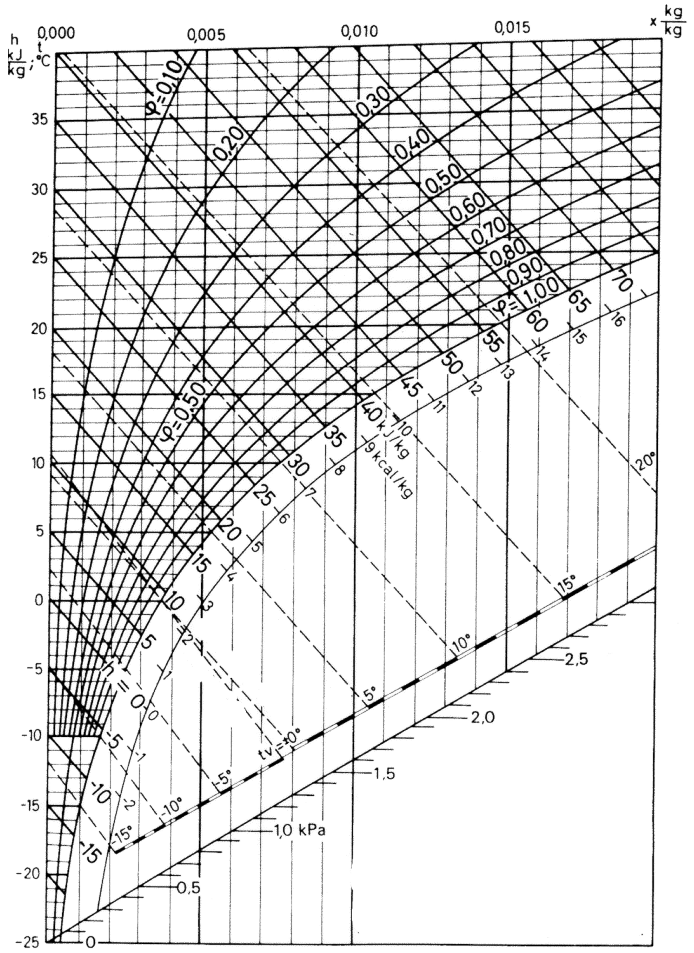


**Figure A-2:** Mollier diagram representing the relationship between air temperature, moisture content and enthalpy (EngineeringToolBox, 2004b).

Now that all the variables have been computed, the evaporation rate that can be achieved by one fan over the height of ~1.2 m can be determined as follows:

$$g_h\ (\text{kg hr}^{-1}) = 48.87\ (\text{kg m}^{-2}\text{hr}^{-1})\ \text{x}\ (0.4953\ \text{x}\ 0.3429\ \text{x}\ 20\ \text{trays})\text{m}^2\ \text{x}\ (0.027125 - 0.0135)\ \text{kg}$$
$$= 2.26\ (\text{kg hr}^{-1})$$

To express the result in L per day:

$$\text{evaporation rate (L per day)} = \frac{(g_h\ \text{x}\ 24\ \text{hrs})}{\text{density of urine (kg L}^{-1})} \quad \text{(A-5)}$$

The density of urine was assumed to be that of saltwater (1024 kg $m^{-3}$) because urine is saline.

$$\text{evaporation rate (L per day)} = \frac{2.26\ (\text{kg hr}^{-1})\ \text{x}\ 24\ \text{hrs}}{\frac{1023.6}{1000}\ \text{kg L}^{-1}} = 53\ \text{L per day}$$

Therefore, according to this calculation, one fan over a height of ~1.2 m can evaporate 53 L per day. The amount of urine in one system containing 20 trays is 80 L (20 trays x 4 L each). Therefore, to evaporate all 80 L, two fans would be required over the entire length.

However, this equation does not consider the fact that some trays are not receiving direct airflow, because the fans do not cover the entire length. Therefore, to account for this, the system was divided vertically into four sections, each with one fan servicing five trays. Therefore, the evaporation rate achieved by one fan servicing five trays was then computed. The surface area used to convert the airflow velocity from $m^3\ hr^{-1}$ to $m\ s^{-1}$ was divided by four:

$$\text{airflow velocity (v) (m s}^{-1}) = \frac{2300\ (\text{m}^3\ \text{hr}^{-1})}{\frac{(1.208\ \text{x}\ 0.421)}{4}\ (\text{m}^2)} \text{x}\ \frac{1}{3600} = 5.03\ (\text{m s}^{-1})$$

This changed the value of θ to:

$$\theta\ (\text{kg m}^{-2}\text{hr}^{-1}) = 25 + (19\ \text{x}\ 5.025\ \text{m s}^{-1}) = 120\ (\text{kg m}^{-2}\text{hr}^{-1})$$

The evaporation rate in $kg\ hr^{-1}$ was therefore:

$$g_h\ (\text{kg hr}^{-1}) = 120.48\ (\text{kg m}^{-2}\text{hr}^{-1})\ \text{x}\ (0.4953\ \text{x}\ 0.3429\ \text{x}\ 5\ \text{trays})\text{m}^2\ \text{x}\ (0.027125 - 0.0135)\ \text{kg}$$
$$= 1.39\ (\text{kg hr}^{-1})$$

Finally, the evaporation rate in L per day was computed as:

$$\text{evaporation rate (L per day)} = \frac{1.39\ (\text{kg hr}^{-1})\ \text{x}\ 24\ \text{hrs}}{\frac{1023.6}{1000}\ \text{kg L}^{-1}} = 32.7\ \text{L per day}$$

Therefore, one fan servicing five trays can achieve an evaporation rate of 32.7 L per day, which is 12.7 L more than is required. Therefore, the system design is adequate.

The fan power requirements were computed using the fan power specification of 0.12 kW. Therefore, 12.5 systems, each with four fans operating with a power of 0.12 kW (12.5 systems x 4 L x 0.12 kW) is 6.0 kW $m^{-3}$ urine.

**Ethanol evaporation**

To size the ethanol evaporation system, the volume of ethanol required to recover the potential urea obtained from the water evaporation system was calculated. The procedure outlined in Appendix B was conducted to do this. A maximum urea yield of 23.3 g $L^{-1}$ was assumed based on the highest urea concentration recorded by (Putnam, 1971). This was chosen to account for the highest possible urea output to ensure that the system can accommodate it.

The volume of ethanol was based on the best urea solubility in ethanol that was achieved in this study (56.76 g $L^{-1}$). Therefore, using equation (A-1) from Appendix B, the volume of ethanol was estimated.

$$\text{volume of ethanol required (L)} = \frac{23300\ (\text{mg})}{56760\ (\text{mg L}^{-1})} - 0.02478\ (\text{L}) = 0.3857\ \text{L} = 386\ \text{mL}$$

Therefore, assuming all the water from 1000 L of urine is evaporated, each litre yields 23.3 g of urea, and therefore a total volume of (1000 L x 386 mL) 386 L of ethanol is required.

Using the same 20-tray system configuration as for the water removal, the number of systems required would be:

$$\text{No. of systems} = \frac{386 \text{ L day}^{-1}}{(20 \text{ trays x } 4 \text{ L each})} = 4.8 \text{ systems}$$

This can be rounded to five evaporation boxes which would hold (20 trays x 4 L each x 5 systems) 400 L (100 trays).

The footprint covered by 5 systems, each with a width of ~42.1 cm and allowable space of 10 cm between each evaporation box is ~2.7 m. This is just over 1/3$^{rd}$ of the footprint covered by the water removal system.

The same fan configuration for the water removal system was used with four fans located over the length of each evaporation box. Therefore, the evaporation rate achieved by one fan servicing five trays was computed. The variables $x_s$ and x remained constant for the system. The airflow velocity conversion as well as the values for theta also remained unchanged as the system configuration was maintained. However, the resulting evaporation rate for the ethanol evaporation system was faster and this was due to the density of ethanol (789 kg m$^{-3}$).

Finally, the evaporation rate in L per day was computed as:

$$\text{evaporation rate (L per day)} = \frac{1.39 \text{ (kg hr}^{-1}) \text{ x } 24 \text{ hrs}}{\frac{789}{1000} \text{ kg L}^{-1}} = 42.4 \text{ L per day}$$

Therefore, one fan servicing five trays can achieve an evaporation rate of 42.4 L per day, which is 22 L more than is required. Therefore, the system is twice as efficient as the water removal system.

The fan power requirements were computed using the fan power specification of 0.12 kW. Therefore, five systems, each with four fans operating with a power of 0.12 kW (5 systems x 4 L x 0.12 kW) is 2.4 kW m$^{-3}$ urine.

**Power requirements**

The total fan power requirements for both systems were therefore 8.4 kW m$^{-3}$ urine.

The potential yield per 1 m$^3$ of urine was (23.3 g urea L$^{-1}$ x 1000 L x 67% yield / 1000) 15.61 kg per day based on the yield achieved by the real urine composition in this study. Assuming that the yield and purity can be maximized to 88% and 91%, respectively (the highest achieved in this study), the potential yield per day could increase to (23.3 g urea L$^{-1}$ x 1000 L x 88% yield / 1000) 20.5 kg.

# Appendix D: Cost and profitability estimations

A basic cost estimate of the urea recovery procedure developed in this study for a 1 $m^3$ small-scale unit is provided in Table A-2.

**Table A-2:** Estimation of the potential profit generated from the production and sale of 20.5 kg of urea per day, using the urea recovery system developed in this study for 1 $m^3$ of urine. This is based on an 88% recovery and it was assumed that at least 90% of the ethanol would be recovered and reused [(a)]. Costs due to labour and rental of the warehouse were not considered.

| Item | Unit | Value (R) | Quantity (per day) | Total cost (R per day) | Reference |
|---|---|---|---|---|---|
| Electricity | R $kWh^{-1}$ | 2.18 | 8.4 kWh over 24 hrs | (440) | (Eskom Ltd., 2016) |
| Calcium hydroxide | R $kg^{-1}$ | 23.2 | 10.4 kg | (241) | (Masiye Labs, 2020) |
| Ethanol | R $L^{-1}$ | 7.35 | 38.6 L[(a)] | (284) | (U.S. Grains Council, 2020) |
| Potential income from sale of Ca-P and $CaCO_3$ | R $kg^{-1}$ | 5.75 | 11.5 kg | 66.1 | (Flanagan & Randall, 2018) |
| Potential income from sale of urea | R $kg^{-1}$ | 4.88 | 20.5 | 100 | (IndexMundi, 2021) |
| **Total cost of production** | **R** | | | **(964)** | |
| **Total sales** | **R** | | | **(166)** | |
| **Profit/Loss** | **R** | | | **(798)** | |

To calculate the potential income from the sale of calcium phosphate (Ca-P) recovered after water removal, a Ca-P yield of 11.23 g per kg of urine was assumed (Flanagan & Randall, 2018). Therefore, assuming a density of 1024 kg $m^{-3}$ for urine, 1000 L of urine weighs 1023.6 kg. Thus, a total of (1024 kg x 11.23 g of urea per kg) 11.5 kg of Ca-P could be produced from 1 $m^3$ of urine.

In a theoretical economic assessment, Flanagan & Randall (2018) estimated a production of 281 kg per day of Ca-P and $CaCO_3$ with an income of $111 per day. These values were then used to obtain a cost of Ca-P based fertilizer per kg per day, which is ($111 ÷ 281 kg per day) $0.395 per kg. This translates to R5.75 (at an exchange rate of R14.56 per US Dollar) per kg of Ca-P based fertilizer. This was the value used to estimate the income generated from the sale of Ca-P and $CaCO_3$ in Table A-2.

To produce ~20.5 kg of urea per day, it will cost R964 which will result in a loss of R798 per day if it is only used as solid urea fertilizer. Therefore, this particular market is not profitable for the urea recovered in this study.

As a result, four other potential markets for urea were chosen to determine the most valuable product to maximize on the profitability of the urea produced in this study. These markets were namely diesel engines (diesel engine fluid (DEF)), plastics/resins (urea-formaldehyde),

aerospace (hydrazine), and agriculture (a niche urea-rich liquid fertilizer). Solid urea fertilizer was also included for purposes of comparison with these products. The detailed calculations below are for the values found in Table 4-1 in section 4.6.7, which compares the potential production of each product per day, the selling price (per L or kg) of each end-product and, the cost of production (per L or kg). To obtain the total cost of production of each end-product, the cost of further unit processes would need to be considered and added to the initial cost of producing the urea.

**Urea-rich liquid fertilizer**

Based on the total volume of urine evaporated per day (1 $m^3$) and assuming the urine is concentrated by 80%, the total volume of liquid fertilizer produced per day is determined as follows:

$$\text{volume of liquid fertilizer} = 1000 \text{ L (urine)} - (80\% \text{ x } 1000) = 200 \text{ L per day}$$

Assuming a urea density of 1340 kg $m^{-3}$, the volume occupied by 20.5 kg of urea in the liquid fertilizer is:

$$\text{volume occupied by urea (L)} = \frac{20.5 \text{ kg}}{1340 \text{ kg m}^{-3}} \text{ x } 10^3 = 15.3 \text{ L}$$

Therefore, the remainder (200 L – 15.3 L) is the volume of water required to make liquid fertilizer which is 185 L.

Since the process for producing this liquid fertilizer is simplistic, mixing ~12 parts water with 1 part urea, it can be assumed that its contribution to the total urea production cost is minimal. Therefore, the cost of production of liquid fertilizer could be taken as the cost of urea production, multiplied by a safety factor of 1.1 to account for any additional costs incurred.

$$\text{cost of production (R)} = \text{R964 (urea production) x 1.1 (safety factor)} = \text{R1060 per day}$$

The potential selling price of liquid fertilizer is \$10.5 $L^{-1}$ (Chipako & Randall, 2020a) (~R153 $L^{-1}$ at an exchange rate of R14.56 per US Dollar). Therefore, the potential income generated from selling 200 L of liquid fertilizer per day is:

$$\text{income generated from liquid fertilizer sales (R)} = 200 \text{ L x R153 } L^{-1} = \text{R30 600 per day}$$

However, Chipako & Randall (2020a) showed that 70 nurseries selling liquid fertilizer currently exist in the Cape Town region and each only sell 2 L per week. This translates to a total demand of 140 L per week. In this study, potentially 200 L of liquid fertilizer could be produced per day (1400 L per week) which is substantially more than the demand. Therefore, there is a market for just 10% of liquid fertilizer:

$$\text{Liquid fertilizer market (\%)} = \frac{140 \text{ L (demand)}}{1400 \text{ L (supply)}} \text{ x } 100 = 10\%$$

Thus, the daily production of liquid fertilizer would need to be reduced to 10%.

$$\text{Revised liquid fertilizer production} = 200 \text{ L per day x } 10\% = 20 \text{ L per day}$$

The remaining urea could be sold as bulk fertilizer or converted to other products such as urea-formaldehyde or diesel engine fluid.

$$\text{Remaining urea available for other products} = 20.5 \text{ kg (urea) x } 90\% = 18.5 \text{ kg per day}$$

**Diesel engine fluid**

Diesel engine fluid is a mixture of 32.5% urea and 67.5% deionized water (Capital Reman, 2020). To calculate the amount of urea required to make 1 L of diesel engine fluid, the following calculations were done:

$$\text{If, 1 L DEF} = \ 1.09 \text{ kg}$$

$$\text{And, 1 L deionized water} = 1.0 \text{ kg}$$

$$\text{Then, 67.5\% x 1.0 kg (deionized water)} = 0.675 \text{ kg water}$$

$$\text{Therefore, the remainder, } 1.09 \text{ kg} - 0.675 \text{ kg} = 0.415 \text{ kg urea per L}$$

Reference: (Rentech, 2013)

Thus, 0.415 kg of urea is required per L of DEF. If 20.5 kg of urea is produced per day, then 49.4 L (20.5 kg ÷ 0.415 kg $L^{-1}$) of DEF can be produced per day.

The cost of production of DEF per day was determined as follows:

$$\text{Cost of production (R)} = \$0.55 \text{ L}^{-1} \text{ x } 49.4 \text{ L x R14.56 (exchange rate)} = \text{R396}$$

Reference: (Ou et al., 2019)

Therefore, the total production, including the preparation of urea is R1360 (R396 + R964 (urea production)).

**Urea-formaldehyde**

To calculate the potential production of urea-formaldehyde per day, a formaldehyde to urea ratio of 4.4:1 was assumed (Ali et al., 2019).

$$\begin{aligned}&\text{Urea} - \text{formaldehyde production (kg)}\\ &= (4.4 \text{ kg formaldehyde x } 20.5 \text{ kg urea}) \ + \ 20.5 \text{ kg urea}\\ &= \ 111 \text{ kg urea} - \text{formaldehyde}\end{aligned}$$

Cost of production for urea-formaldehyde was taken as a sum of the cost of raw materials and cost of utilities per day (R376 per day) from (Ali et al., 2019). Therefore, the total costs of production per day is:

$$\text{Cost of production (R)} = \text{R376 (urea} - \text{formaldehyde)} + \ \text{R964 (urea production)} = \text{R1340 per day}$$

**Hydrazine hydrate**

Using the estimates from a techno-economic analysis of hydrazine hydrate technologies (Nikhitha & Saibabu, 2010), the potential production per day was computed. For every ton of hydrazine hydrate, 483 kg of urea is required. Therefore, the amount of hydrazine hydrate that can be produced per day is (20.5 kg urea ÷ 0.483 kg) 42.4 kg.

To estimate the cost of production, the techno-economic analysis by Nikhitha & Saibabu (2010) for the production of 7056 tons of hydrazine hydrate per annum was used. Therefore, to obtain an estimate of the production costs for 42.4 kg of hydrazine hydrate per day, the following calculations were done:

$$\frac{7056 \ \cancel{\text{tons}}}{\cancel{\text{annum}}} \text{ x } \frac{1000 \text{ kg}}{1 \ \cancel{\text{ton}}} \text{ x } \frac{1 \ \cancel{\text{annum}}}{365 \text{ days}} = 19\,300 \text{ kg } \textit{per day}$$

The analysis determined an estimated cost of production of $16 200 000 per annum (sum of raw materials, utilities, and operating supplies), which translates to:

$$\text{cost of production (R)} = \frac{\$16\,200\,000 \text{ x } 14.6 \text{ (exchange rate)}}{365 \text{ days}} = \text{R}648\,000 \text{ per day}$$

Therefore, for each kilogram of hydrazine hydrate, the production cost would be:

$$\text{cost of production (R)} = \frac{\text{R}648\,000}{19300 \text{ kg}} = \text{R}33.6 \text{ kg}^{-1} \text{ per day}$$

Therefore, the cost of production for the hydrazine hydrate process is R1420 (42.4 kg hydrazine hydrate x R33.6 $kg^{-1}$ per day). The total, including the preparation of urea is therefore R2390.

**Daily production of liquid fertilizer and diesel engine fluid**

Assuming that the volume occupied by solids in 1 $m^3$ of urine is ~20 L (this can vary depending on the urine composition), water accounts for the remainder (~980 L). This is therefore the maximum amount of water than could be recovered after water evaporation. Considering that there could be potential losses during water recovery, a recovery of 90% can be assumed. Therefore, the water available for diesel engine fluid and liquid fertilizer production is:

$$\text{water available for DEF and liquid fertilizer (L)} = 980 \text{ L x } 90\% = 880 \text{ L per day}$$

The amount of water required to make 200 L of liquid fertilizer was estimated to be 185 L. Reducing this by 10% for a production of 20 L of liquid fertilizer per day translates to a daily water demand of 18.5 L per day.

The remainder volume of water, which is 862 L, is therefore available for diesel engine fluid production. The daily production of diesel engine fluid and the water demand can therefore be estimated. It was already established that 0.415 kg of urea is required per L of DEF. If 18.5 kg of urea remains after liquid fertilizer production, then 44.6 L (18.5 kg ÷ 0.415 kg $L^{-1}$) of DEF can be produced per day.

Therefore, the amount of water required to produce 44.6 L of DEF is 30.1 L per day (0.675 kg $L^{-1}$ x 44.6 L).

Therefore, to produce 44.6 L of DEF and 20 L of liquid fertilizer, ~ 48.6 L of water is required per day. This leaves an excess of 831 L of water which can be recycled and used for other purposes.

**Economics for liquid fertilizer and diesel engine fluid production**

The potential income generation from the sale of both products is therefore:

$$\begin{aligned}\text{Income (R)} = {} & (20 \text{ L x R}153) \text{ liquid fertilizer} + (44.6 \text{ L x R}31.7) \text{ diesel engine fluid} \\ & + (\text{R}66) \text{ calcium phosphate} \\ & = \text{R}4540 \text{ per day}\end{aligned}$$

The cost of production per day can be estimated as follows:

$$\begin{aligned}\text{cost (R)} = {} & [\text{R}1060 \text{ (200 L liquid fertilizer) x } 10\% \text{ (reduced to 20 L)}] \\ & + [\$0.55 \text{ L}^{-1} \text{ x } 44.6 \text{ L (DEF) x R}14.56 \text{ (exchange rate)}] + \text{R}964 \text{ (urea prod.)} \\ & = \text{R}1430 \text{ per day}\end{aligned}$$

The potential profit per day is therefore:

$$\text{Profit (R)} = \text{R4540} - \text{R1430} = \text{R3110 per day}$$

# Appendix E: Ethics clearance

Appendix Removed

Due to having unremovable

Signatures