Precipitation to remove calcium ions from stabilized human urine as a pre-treatment for reverse osmosis

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ABSTRACT

Concentration of Ca(OH)₂ stabilized urine by reverse osmosis (RO) has the potential to cause CaCO₃ scaling on the membranes. The aim of this research was to determine whether the addition of carbonate salts could be used to precipitate CaCO₃ prior to RO concentration and how to accurately dose the salts. Dosing of NaHCO₃ or Na₂CO₃ reduced the calcium concentration to 0.18 mmol L⁻¹, whilst maintaining a pH > 11. This is the pH threshold for enzymatic urea hydrolysis in urine, but above the operating pH range of most membranes. However, the pH could be decreased by adding an acid. Measuring conductivity as a proxy for the calcium concentration was found to be an effective method to determine the dose of salt required. Simulations with other carbonate-producing salts (KHCO₃, MgCO₃, and NH₄HCO₃) were also shown to be effective. However, NH₄HCO₃ ($0.53 m⁻³ urine) was the only other salt comparable in cost to NaHCO₃ ($0.49 m⁻³ urine) and resulted in a final pH within the normal operating range of membranes. The addition of NH₄HCO₃ would add extra N to the urine rather than sodium ions when dosing NaHCO₃. The choice of salt will ultimately depend on what liquid fertilizer composition is desired.

Key words: calcium carbonate, calcium hydroxide, fertilizer, membranes, scaling

HIGHLIGHTS

- NaHCO₃ addition can reduce calcium concentrations in stabilized urine to 0.18 mmol L⁻¹.
- NaHCO₃ dosing is preferred to Na₂CO₃ as additional Na⁺ ions and costs are minimized.
- pH is not a good parameter to control NaHCO₃ dosing, but conductivity is.
- Acid addition or dosing NH₄HCO₃ can achieve desired pH values.
- Additional pre-treatment would increase cost of fertilizer product by 0.13%.

GRAPHICAL ABSTRACT

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INTRODUCTION

A common application for reverse osmosis (RO) is brackish water and seawater desalination (Greenlee et al. 2009) and industrial brine treatment (Panagopoulos 2021). However, RO has also been used to concentrate human urine (Ek et al. 2006) and animal effluent (Thörneby et al. 1999) with the aim of producing a concentrated liquid fertilizer while also reducing the cost of storage and transportation. A common barrier to implementing RO technology is brine management and disposal (Bond & Veerapaneni 2007). This would not be the case with urine as the brine would be the product (liquid fertilizer) and the permeate could be used as a recycled water source (Chipako & Randall 2020). Reverse osmosis is also promising compared to other concentrating technologies such as evaporation and freeze concentration due to the low energy consumption (Udert & Wächter 2012).

A common phenomenon affecting the performance of RO systems is membrane fouling and scaling (where scaling refers to the precipitation of sparingly soluble salts) (Greenlee et al. 2010). Scaling results in decreased permeate flux, which can shorten the life span of membranes (Rahardianto et al. 2007). These changes in performance can have significant implications on the overall cost of an RO system (Ansari et al. 2021). Common scaling compounds include: CaCO₃, Mg(OH)₂, CaSO₄, SrSO₄, BaSO₄, CaF₂ and SiO₂ (Sutzkover-Gutman & Hasson 2010) and Ca₃PO₄ (Antony et al. 2011). In terms of scaling components, CaCO₃ is the most common problematic scalant for both seawater and brackish water RO systems (Greenlee et al. 2009) as it is almost insoluble in water (14.25 mg L⁻¹ at 25 °C).

Urine contains many scaling precursor ions (Ca²⁺, SO₄²⁻, Mg²⁺, and PO₄³⁻). In addition, to prevent enzymatic urea hydrolysis, urine can be stabilized with Ca(OH)₂ (Randall et al. 2016), which results in a further increase in the concentration of Ca²⁺ (1,000–1,400 mg L⁻¹) (Courtney et al. 2021). Urine stabilized with Ca(OH)₂ is therefore likely to have a high RO scaling potential. Application of chemicals that result in a pH increase and ultimately precipitate undesirable salts is a widely known pre-treatment technique for RO systems (Sheikholeslami & Bright 2002). Calcium hydroxide can be used to reduce water hardness by increasing the pH, allowing any inorganic carbon and magnesium ions present to be precipitated as CaCO₃ and Mg(OH)₂ via Equations (1) and (2). It is also common to remove the remaining calcium ions with Na₂CO₃ softening (Ayoub et al. 2019), which results in further CaCO₃ precipitation following Equation (3). Stabilization with Ca(OH)₂ is also advantageous as it results in the precipitation of another scaling compound, calcium phosphate (Planagan & Randall 2018), which can be recovered and used as a fertilizer (Meyer et al. 2018).

\[
\text{Ca(OH)}_2 + \text{HCO}_3^- \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O} + \text{OH}^- \quad (1)
\]

\[
\text{Ca(OH)}_2 + \text{Mg}^{2+} \rightarrow \text{Mg(OH)}_2(s) + \text{Ca}^{2+} \quad (2)
\]

\[
\text{Na}_2\text{CO}_3 + \text{Ca}^{2+} \rightarrow \text{CaCO}_3(s) + 2\text{Na}^+ \quad (3)
\]

Research on the concentration of urine using RO is limited to hydrolyzed urine (Ek et al. 2006) and no studies, that we are aware of, have been conducted with Ca(OH)₂ stabilized urine. This may be because of the high membrane scaling potential. A pre-treatment step to reduce the calcium concentration is therefore required. Other pre-treatment methods that have shown to be effective at removing calcium from hard waters are air (85% Ca⁻² removal) (Lisitsin et al. 2008) and CO₂ bubbling (final Ca²⁺ concentration 2–8 mmol L⁻¹) (Bang et al. 2011). Courtney et al. (2021) found that air bubbling is very slow but increasing the CO₂ concentration in the air increased the reaction rate. However, the researchers also observed that the rate at which CO₂ is added needs to be carefully controlled to ensure that the pH does not decrease faster than the rate of CaCO₃ precipitation. In addition, they concluded that the cost of using CO₂ was not economically feasible. An antiscalant could also be used to minimize CaCO₃ scaling potential as it works by inhibiting crystal formation (Antony et al. 2011). However, its effectiveness is limited with increasing CaCO₃ saturation indices and precipitation may still occur (Greenlee et al. 2010).

Whilst the addition of Na₂CO₃ has been widely shown as an effective method to remove excess calcium from hard waters (Mahasti et al. 2017; Ayoub et al. 2019), it was hypothesized that NaHCO₃ could also be used to precipitate excess calcium from human urine stabilized with Ca(OH)₂. This would be advantageous as at $150 ton⁻¹ (compared to $250 ton⁻¹ for Na₂CO₃), NaHCO₃ is significantly cheaper than Na₂CO₃ (Alibaba.com 2021). In addition, dosing NaHCO₃ would only add one sodium ion (Equation (4)), thus minimizing the total dissolved solids (TDS) of the solution. This is important, as
the extent of water removal and flux in an RO system is directly proportional to the TDS (Bergman 2007).

\[ \text{NaHCO}_3 + \text{Ca}^{2+} \rightarrow \text{Na}^+ + \text{H}^+ + \text{CaCO}_3 \]  (4)

The calcium concentration in stabilized urine also varies based on urine composition (Randall et al. 2016). Therefore, the required dose of a carbonate ion-producing salt would vary based on the urine composition. An accurate dosing method that ensures high CaCO₃ precipitation is therefore required. This could be achieved by either a fixed dose that covers a wide range of typical urine compositions, or an exact dose based on the calcium concentration of a given composition of urine. An exact dose is advantageous as it minimizes chemical costs as well as the addition of undesirable sodium ions. Alternatively, it should be investigated if pH or conductivity could potentially be used as a proxy to indicate complete CaCO₃ precipitation and therefore be used to determine the required dosage of the carbonate ion producing salt.

The aim of this research was therefore to determine the feasibility of using bicarbonate and carbonate salts such as NaHCO₃ or Na₂CO₃ as a method to remove excess calcium ions from stabilized human urine, prior to a RO process. The study also investigated how the addition of these salts affected the conductivity and pH of solution and whether one of these parameters could be used as a proxy for the calcium concentration to determine the required salt dosage. Furthermore, considering the complex and unique chemistry of human urine, and how this influences the solubility and buffering capacity of a solution, it was also important to understand how the dosing of different chemicals affects the pH of the solution and the subsequent urea hydrolysis. Finally, we compared the effectiveness of a once-off fixed dose and an exact dose for different urine compositions.

**MATERIALS AND METHODS**

**Urine collection**

Urine used in this research was collected in a fertilizer-producing urinal (Flanagan & Randall 2018), which was pre-dosed with 10 g L⁻¹ of Ca(OH)₂ (98.8%, Kimix, Cape Town, South Africa) and mixed daily to ensure a pH greater than 11 was maintained (Randall et al. 2016). The urine was filtered using a vacuum filtration system and filter paper with a pore size of 1.2 μm (Ahlstrom-Munksjö, Helsinki, Finland). All experiments were conducted on the same day as filtration. A synthetic urine recipe (Table S1) was also used to compare the experimental and simulated results. In this recipe, organics were excluded to ensure that the experimental results (with synthetic urine) could be accurately compared to the simulated results. This is because the simulation software used does not include many of the organics present in urine in its database. The compositions of urine used in this study can be found in Table S2 of the supplementary information.

**Experimental conditions**

A variety of experimental conditions were examined to compare the efficacy of NaHCO₃ and Na₂CO₃ but also to determine the most cost-effective method to control the dosing. This was achieved by assessing how a once-off fixed dose and an exact dose affect the calcium concentration, pH, and conductivity. Each experiment was repeated in triplicate and Table 1 summarizes the experimental conditions. The term carbonate salt is used interchangeably throughout to refer to both bicarbonate and carbonate salts.

**Dosing method**

**Incremental dosing**

Samples of stabilized, filtered (1.2 μm) urine were added to six 100 mL volumetric flasks. An additional 50 mL of the urine sample was further filtered to 0.45 μm (ClearRight, Cape Town, South Africa) and the pH (H15221, Hanna, Johannesburg, South Africa), temperature, conductivity (H15321, Hanna, Johannesburg, South Africa), and calcium concentration was measured. A 1 M solution of either NaHCO₃ or Na₂CO₃ (Sigma-Aldrich) was used for each experiment. A volume of 0.5 mL was added to the first flask, 1 mL to the second, 1.5 mL to the third, and so on. The lid of the volumetric flask was replaced to seal the mixture. It was then mixed with a magnetic stirrer (F-13, Freed Electric, Israel) for 45 minutes. Once the reaction was complete, each sample was filtered to 0.45 μm. The filtered solids were dried in an oven at 100 °C for 24 hours before being weighed. The pH, conductivity, and temperature of the filtered liquid were remeasured at the end of each experiment.
To determine if conductivity could be used as a proxy for the calcium concentration, the 1 M NaHCO₃ solution was dosed in 45s increments (0.4 mL per dose) to 200 mL of synthetic stabilized urine. The solution was continuously mixed, and the conductivity was recorded every 45 seconds.

Once-off and exact dosing

To determine the amount of NaHCO₃ required for the once-off dose, five different urine compositions were collected plus one synthetic urine composition. Each sample was stabilized with Ca(OH)₂ and the calcium concentrations of the solutions were measured. To increase the sample size, the calcium concentrations of three additional stabilized urine compositions from literature (Randall et al. 2016; Flanagan & Randall 2018; Courtney et al. 2021) were also evaluated. The average calcium concentration of these 8 compositions was determined to be 31.9 ± 8.6 mmol L⁻¹. The once-off dose was then calculated as the average plus one standard deviation, which was rounded to 40 mmol of NaHCO₃ L⁻¹. This equates to a 4 mL dose per 100 mL of urine. Overdosing by one standard deviation ensures enough carbonate ions would be added for a wide range of varying urine compositions. For the exact dosing method, the volume for a 1 M NaHCO₃ solution required was calculated based on the measured initial calcium concentration. In addition to the pH, temperature, conductivity, and calcium concentration, the concentration of urea, NH₄⁺, PO₄-P, Mg²⁺, Ca²⁺, SO₄²⁻, Cl⁻, K⁺, Na⁺, and chemical oxygen demand (COD) were measured at the start of each experiment. A 4-point calibration (4.01, 7.01, 10.01, and 12.45) of the pH probe and 3-point calibration of the conductivity meter (84, 1,413, and 12,880 μS m⁻¹) was conducted before each experiment commenced.

Thermodynamic modelling simulations

The results from the experiments conducted with synthetic urine were also compared to thermodynamic modelling simulations using the OLI Stream Analyzer (OLI Systems Inc 2020). The Mixed Solvent Electrolyte (MSE) model was used as this is not limited by the ionic strength of a solution. After determining that OLI could accurately model the experimental results it was used to determine if three other carbonate-forming compounds (KHCO₃, NH₄HCO₃ and MgCO₃) could be used as alternatives for NaHCO₃. Where possible, bicarbonate compounds were chosen over carbonate compounds as they introduced fewer additional cations to the solution. In all simulations, the solutions were modelled based only on the ions measured. OLI Stream Analyzer does not have the database to model the organics present in urine, except for urea, so these could not be included in the simulations.

Analytical methods

Colorimetric methods were used to determine the concentration of urea, total ammoniacal nitrogen (TAN), PO₄-P, Mg²⁺, Ca²⁺, SO₄²⁻, Cl⁻ and K⁺, where required. This process was automated with a Gallery™ Discrete Analyzer (ThermoFisher Scientific, Massachusetts) using standard methods of the equipment. The concentration of sodium was determined using

### Table 1 | Experimental conditions for different experiments

| Exp. # | Urine comp. | Dose (mmol L⁻¹) | Reactant | Aim |
|--------|-------------|----------------|----------|-----|
| A1     | U1          | 5, 10, 15, 20, 25, 30 | NaHCO₃   | To compare NaHCO₃ and Na₂CO₃ in terms of calcium removed, solids formed, pH, and conductivity. |
| A2     | U1          | 30             | Na₂CO₃   |      |
| A3     | Synth       |                | NaHCO₃   |      |
| B1     | U1-U5 Synth | 40             | NaHCO₃   | Determine the effect of a once-off dose on varying urine compositions. |
| C1     | U2          | 32.4           | NaHCO₃   | Determine the effect of an exact dose based on the initial measured calcium concentration. |
| U3     | 31.7        |                |          |      |
| U4     | 57.9        |                |          |      |
| U5     | 38.6        |                |          |      |
| Synth  | 32.9        |                |          |      |
| D1     | Synth       | 2.0 (Every 45 s)| NaHCO₃   | Determine if conductivity could be used as a proxy for the calcium concentration. |

*During experiment C1, the U1 container accidentally broke and the remaining urine sample was lost.*
inductively coupled plasma-optical emission spectrometry (5900 SVDV, Agilent, USA). The chemical oxygen demand (COD) was measured with medium-range reagent vial (H194754B-25, Hanna, Johannesburg) and a multiparameter photometer (H183599, Hanna, Johannesburg). The samples were diluted, and the pH adjusted to between 7 and 8 with HCl (30–33%, Kimix, South Africa) to prevent ammonia volatilization where necessary. All liquid samples were analyzed within 30 minutes of sampling.

To confirm the formation of CaCO₃, the solids formed were analyzed via powder X-ray diffraction (XRD). A D8 Advance diffractometer (Bruker, Germany) outfitted with a position-sensitive detector (LYNXEYE) in Bragg Brentano geometry was used for the analysis. Power to the Co anode was set at 35 kV and 40 mA. A range of 20° to 120° (d¹ =0.19 to 0.97 Å⁻¹) with a 0.017° step size (0.84 seconds per step) was used to acquire the diffraction patterns. The ICDD database (PDF-4+, released in 2020) was used to compare the diffraction patterns to reference data files.

RESULTS AND DISCUSSION

**NaHCO₃ and Na₂CO₃ incremental addition**

The addition of either NaHCO₃ or Na₂CO₃ had the same resulting effect on the remaining calcium concentration and the mass of solids formed, as shown in Figure 1(a) and 1(b). The calcium removed was > 99.6% for both NaHCO₃ and Na₂CO₃. This is greater than the 92% calcium removal achieved by Mahasti et al. (2017) using Na₂CO₃ in a fluidized-bed homogeneous crystallization process and the same as achieved by Ayoub et al. (2019), who used a combination of NaOH and Na₂CO₃ addition. In addition, the number of moles of calcium removed was proportionate to the number of moles of NaHCO₃ or Na₂CO₃ added. Therefore, the salt can be dosed according to stoichiometry, unlike with struvite precipitation where the reagent needs to be dosed in excess (Altinbaş et al. 2002). The mass of solids formed deviated slightly from the theoretical value from 15 mmol L⁻¹ onwards. The XRD analysis confirmed the formation of a pure CaCO₃ solid. Deviations in the mass of solids formed could not be explained using XRD. However, it was hypothesized that it may be due to the formation of small amounts of amorphous compounds such as monohydrate calcite (CaCO₃·H₂O) and ikaite (CaCO₃·6H₂O).

For Na₂CO₃, the conductivity remains relatively stable until 20 mmol L⁻¹ and then increases, whilst for NaHCO₃ a continuous decrease in conductivity is observed (Figure 1(c)). This was expected as every mole of Na₂CO₃ adds two moles of Na⁺ ions compared to one mole if NaHCO₃ is dosed. For Na₂CO₃ this results in no net increase in cations until all the Ca²⁺ is precipitated, after which there is an increase in conductivity. Whereas with NaHCO₃ addition, there is a net decrease in cations (−1) until all the Ca²⁺ is precipitated. Therefore, the conductivity decreases until all the CaCO₃ is precipitated and, if sufficient NaHCO₃ is added, the conductivity should begin to increase again.

For experiments with Na₂CO₃, the pH remained relatively constant whilst for NaHCO₃ addition a decrease in pH was observed. The equilibrium constant for the HCO₃⁻/CO₃²⁻ carbonate system is 10.33 (Lide 2004). Therefore, at a pH above 10.33 the formation of CO₃²⁻ is favored. When NaHCO₃ is added, the salt dissociates to form Na⁺ and HCO₃⁻ ions. Because the pH of stabilized urine is approximately 12.45, the speciation of HCO₃⁻ and CO₃²⁻ ions are released. When Na₂CO₃ is added it dissociates to 2Na⁺ and CO₃²⁻ and no shift in the carbonate ion speciation is observed. The H⁺ ions from NaHCO₃ addition result in a decrease in pH which does not occur with Na₂CO₃ addition. In both cases, after 30 mmol L⁻¹ (and once the calcium concentration was at a minimum) addition of either Na₂CO₃ or NaHCO₃, the pH remained above 11. This is the pH threshold for enzymatic urea hydrolysis (Randall et al. 2016) and it indicates that the urine would still be stabilized.

**Simulation vs. experimental results**

As the OLI Stream Analyzer does not have a database for organic compounds, the simulation was compared to experimental results conducted with synthetic urine of the same composition and with no organics present, other than urea. With regards to the calcium concentration (Figure 2(a)), a comparison of the experimental and simulated results shows an identical trend. However, the absolute value for calcium differs. This may be due to the simulation overestimating the initial calcium concentration. The experimentally measured mass of solids (up to 25 mmol L⁻¹ of NaHCO₃ added) is slightly higher than the value predicted by the simulation (Figure 2(b)). It is hypothesized that this is due to the formation of amorphous CaCO₃ compounds at those conditions. The conductivity and pH predicted by the simulation (Figure 2(c) and 2(d)) are a good fit and have a Nash-Sutcliff model efficiency (NSE) coefficient of 0.93 and 0.99, respectively. This indicates that the model simulates the experimental data accurately and can be used with confidence to predict the results for different urine compositions. For Na₂CO₃ addition, the simulated results show a similar trend for pH. With regards to conductivity for both NaHCO₃ and
Na$_2$CO$_3$, there are two observable gradients with the change in gradient occurring approximately at the minimum calcium concentration. This suggests that conductivity could potentially be used as a proxy to determine the required NaHCO$_3$ or Na$_2$CO$_3$ dose. As NaHCO$_3$ addition was shown to be as effective as Na$_2$CO$_3$ all further experiments were conducted with NaHCO$_3$ only. This is because NaHCO$_3$ was the preferred salt as it is cheaper and adds less unwanted sodium ions.

**Figure 1** | Comparison of the incremental addition of either NaHCO$_3$ or Na$_2$CO$_3$ and its effect on the calcium concentration (a), the mass of solids formed (b), the conductivity (c), and the solution pH (d) for synthetic urine. Where the theoretical solid mass represents the mass of solids formed based on CaCO$_3$ formation.

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**Once-off dosing for varying urine compositions**

**Figure 3(a)** compares the initial and final calcium concentration for six different urine compositions each dosed with a fixed concentration of 40 mmol L$^{-1}$ NaHCO$_3$. For five out of six of the urine compositions, a dose of 40 mmol L$^{-1}$ was sufficient to remove more than 99.5% of the calcium with a final calcium concentration of less than 0.072 mmol L$^{-1}$. However, urine composition four had an abnormally high initial calcium concentration (53 mmol L$^{-1}$) and therefore the fixed dose was not sufficient and only 83% of the calcium was removed. The mass of solids formed (**Figure 3(b)**) was comparable to the theoretical value.

**Figure 3(c)** shows the change in conductivity compared to the initial calcium concentration. As the dose of NaHCO$_3$ was added to each urine composition a fixed change in conductivity was expected. However, in some cases (composition 4) not all the calcium was precipitated and indicates a potential for a further drop in conductivity. However, in other cases (composition 1), significantly more NaHCO$_3$ was added than required. The additional Na$^+$ ions would therefore have contributed to the conductivity increasing above the minimum. Whilst all urine samples received a fixed dose of NaHCO$_3$, the final
pH differed significantly between compositions. This may be due to the varying concentration of organics present in the urine that affect the buffering capacity of each composition. This indicates that pH would not be a good proxy for determining the correct dosage for calcium removal.

**Exact dosing for varying urine compositions**

In all cases, the calcium removed using an exact dose (see Table 1 for values) was greater than 95% (Figure 4(a)). The final calcium concentration varied from 0.8 to 1.6 mmol L\(^{-1}\). Although the percentage removal was still high, the final calcium concentration for the exact dose was higher than the fixed dose (maximum final calcium concentration of 0.072 mmol L\(^{-1}\)). This may be due to slightly underdosing because of measurement error in the initial calcium concentration. However, it is also possible that without the additional CO\(_3^{2-}\) ions added with a fixed dose that the reaction driving force, according to Le Chatelier’s principle, is limited. To overcome both potential measurement error and the reaction driving force, the exact dose was increased by 5% to ensure maximum calcium removal as deviations in the calcium measurement varied as much as 4.2%.

A direct correlation between the change in conductivity and the initial calcium concentration was expected with an exact dose. However, the change in conductivity is relatively constant at \(\Delta 5.55 \pm 0.6\) mS cm\(^{-1}\). With regards to pH, the final pH (Figure 4(d)) differs significantly based on urine composition, thus again confirming that the buffer capacity of the solution varies based on urine composition. Therefore, pH is not a good parameter to use to control the chemical dosing. It should be
noted that for the five urine compositions tested, after an exact dose of NaHCO₃, the final pH was always greater than 11 (Figure 4(d)). Typical pH operating conditions for RO and NF membranes are between 2 and 11 (Greenlee et al. 2009). The final pH after NaHCO₃ treatment falls outside this advised membrane operating range. The long-term effects on the membrane’s lifespan and efficiency should therefore be considered and confirmed experimentally.

Conductivity as a proxy for calcium concentration

Conductivity was measured while NaHCO₃ was dosed in 45 second increments and compared to a simulation of the same process for synthetic urine (Figure 5(a)). Figure 5(b) shows the change in conductivity per mmol L⁻¹ of NaHCO₃ added. The initial conductivity measured experimentally was lower than the simulated value. This may be because the simulation predicted an initial calcium concentration of 38.5 mmol L⁻¹ whilst experimentally only 33.5 mmol L⁻¹ was measured. Based on the initial calcium concentration an exact dose of NaHCO₃ would be 38.5 mmol L⁻¹ for the simulation and 33.5 mmol L⁻¹ for the experiment (indicated by the vertical dashed lines in Figure 5). There is a change in the slope of the conductivity (Figure 5(a)), which aligns with the exact dose of NaHCO₃ required to precipitate all the calcium. It was therefore hypothesized that this change in slope could be used as a proxy for the calcium concentration.

Figure 3 | Comparison of how the composition of the urine affects the start and end calcium concentration (a), the measured and theoretical mass of solids formed (b), the change in conductivity compared to the initial calcium concentration (c), and the start and end pH (d), for a fixed dose of 40 mmol L⁻¹ of NaHCO₃.
The criteria for dosing would be such that the first measured change in conductivity would be used as a reference. Once the change in conductivity reached 50% of the reference value, dosing would stop. This dose (actual dose) was then compared to the exact dose based on the initial Ca\(^{2+}\) concentration. Based on the simulation, 3.5% more NaHCO\(_3\) would have been dosed than required and experimentally 5.9% more NaHCO\(_3\) would be dosed than required. However, it was determined that even for a known calcium concentration the exact dose should be increased slightly (in this case a 5% increase was chosen) to account for various forms of error. The end calcium concentration measured experimentally using this method was 0.03 mmol L\(^{-1}\) which is equivalent to a 99.9% calcium removal. These results show that using conductivity as a proxy for calcium concentration would provide an accurate dose that is comparable to using an exact dosing method based on measuring the initial calcium concentration.

**Comparison of dosing methods**

As the composition of urine varies so will the dose of NaHCO\(_3\) required to remove the maximum amount of Ca\(^{2+}\) ions, whilst also minimizing additional Na\(^+\) ions in the product stream. Three possible dosing methods were investigated: a once-off fixed dose based on the average calcium concentration of seven different urine compositions plus one standard deviation, an exact dose calculated by measuring the calcium concentration in a specific urine composition, and finally, dosing in fixed increments and using a change in conductivity as a proxy to determine when to stop dosing.

**Figure 4** | Comparison of how the composition of the urine affects the percentage of calcium removed (a), the final calcium concentration (b), the change in conductivity compared to the initial calcium concentration (c), and the start and end pH (d), where the NaHCO\(_3\) dosed is calculated based on the start calcium concentration.
A once-off fixed dose is the simplest method; however, it can result in up to 25% more NaHCO₃ being added to the solution than required. This would increase operating costs and may have downstream limitations on the water recovery possible with RO due to the additional Na⁺ ions. It is also important to consider that any outlying urine compositions would not be adequately treated and could result in potential RO membrane scaling. Furthermore, the unnecessary Na⁺ ions could be problematic if the product stream is to be used as a liquid fertilizer as many plants do not tolerate high concentrations of Na⁺ ions (Zhu 2001).

To provide an exact dose, the calcium concentration of each batch of urine would have to be measured. This can be achieved in multiple ways including colorimetric methods (complexometric Ethylenediaminetetraacetate (EDTA) titration (Baird 2017)), ion chromatography, or using a calcium ion selective electrode (ISE). Whilst ISEs are simple to operate they are prone to interference from other ions such as Na⁺, K⁺, and Mg²⁺, which are present in urine (Mettler-Toledo AG 2010). Further research to confirm the accuracy of ISEs when testing urine is therefore required. Many colorimetric methods and ion chromatography require expensive laboratory equipment and would not always be economical. However, complexometric titration is simple and could be done on site as it requires only basic laboratory equipment and skill. It is therefore the preferred calcium measurement option.

Using conductivity measurements as a proxy for the calcium concentration provides an accurate dosing method. However, the NaHCO₃ would need to be dissolved in water such that it could be dosed with a pump. Whereas with the other two methods, the salt could simply be weighed and mixed into the batch of collected and filtered urine. Table 2 summarizes the advantages and disadvantages of each method. Both the exact dosing method and using conductivity as a proxy are preferred to a fixed dose as they minimize chemical use and overall operating costs. Both methods are comparably accurate and therefore the design choice may be based on a preference for complete automation or manual operation.

The final pH of urine after an exact dose of NaHCO₃ is likely to be above 11 and therefore outside the design range for most commercial RO membranes. To reduce the pH to within the RO membrane operating pH range, either additional NaHCO₃ could be dosed to a lower pH, or an acid could be added. Modeling of synthetic urine showed that an additional 11.4 mmol L⁻¹ NaHCO₃ or 4.7 mmol L⁻¹ H₂SO₄ would be required to reduce the pH to 10.5. Whilst simply dosing NaHCO₃ to a fixed pH is the simplest option, it is advised that H₂SO₄ should rather be added to adjust the pH as this minimizes the additional ions added. This also reduces the impact on the solutions osmotic pressure and downstream concentration using RO.

**Alternative carbonate salts and cost considerations**

To remove the excess calcium in stabilized urine requires the addition of carbonate ions. These can be added in forms other than NaHCO₃, such as KHCO₃, NH₄HCO₃, and MgCO₃. These four options were compared, using a simulation, in terms of
calcium removal, pH, conductivity, and cost as shown in Figure 6. All four options provided equal removal of calcium ions. With regards to pH, KHCO₃ resulted in an identical pH change as NaHCO₃. The addition of NH₄HCO₃ resulted in the largest pH decrease due to the addition of ammonium ions. The pKa for the NH₃/NH₄⁺ system is 9.25 (Lide 2004) and therefore pH values above 9.25 will favor the formation of NH₃, which does not contribute to conductivity. However, as the pH drops below 9.25, NH₃ will be converted to NH₄⁺, which will contribute to conductivity.

### Table 2 | Comparison of the advantages and disadvantages of three different dosing techniques

| Method           | Advantages                                      | Disadvantages                                          |
|------------------|-------------------------------------------------|--------------------------------------------------------|
| Fixed dose       | Simple and does not require any additional      | More NaHCO₃ is used than required thus increasing      |
|                  | equipment or operator skill.                    | operating costs.                                       |
|                  |                                                  | Urine compositions with abnormally high calcium       |
|                  |                                                  | concentrations would not have complete calcium        |
|                  |                                                  | removal.                                               |
| Calcium testing  | Reagent costs are minimized.                    | Requires an operator on-site for regular calcium       |
| Conductivity as  | Reagent costs are minimized.                    | measurements.                                          |
| a proxy          | Automated system                                | System would require NaHCO₃ to be dissolved in water   |
|                  |                                                  | and dosed via a dosing pump.                          |

**Figure 6** | The simulated effect of the addition of NaHCO₃, KHCO₃, NH₄HCO₃, and MgCO₃ to Ca(OH)₂ stabilized urine on the calcium concentration (a), pH (b), conductivity (c), and cost (d). The cost includes the chemical cost, dose required, and overall cost to treat 1 m³ of urine. All compounds overlap in (a) and NaHCO₃ and KHCO₃ overlap in (b).
below 9.25, equilibrium favors NH$_4^+$ ion formation, thus resulting in an increase in conductivity. The addition of MgCO$_3$ results in both the precipitation of CaCO$_3$ and brucite (Mg(OH)$_2$) and therefore explains both the decrease in pH (due to the precipitation of OH$^{-}$ ions) and the steeper decrease in conductivity.

The total dosing chemical cost to treat 1 m$^3$ of stabilized urine is a function of the chemical cost and the chemical dose required (Figure 6(d)). The most expensive option is KHCO$_3$ ($3.4$ m$^{-3}$ urine) followed by MgCO$_3$ ($1.6$ m$^{-3}$ urine), NH$_4$HCO$_3$ ($0.53$ m$^{-3}$ urine) and NaHCO$_3$ ($0.49$ m$^{-3}$ urine), the cheapest option (Figure 6(d)). Whilst all the carbonate ion producing salts provided equal calcium removal, both MgCO$_3$ and KHCO$_3$ are significantly more expensive and therefore would not be favorable. When dosing with NaHCO$_3$ if the high pH is shown to affect the operation of the RO/NF membranes, the additional H$_2$SO$_4$ required to decrease the pH to 10.5 would increase the operating cost to $0.56$ m$^{-3}$ urine.

At $0.03$ m$^{-3}$ urine, using less NH$_4$HCO$_3$ could provide an alternative to the slightly more expensive NaHCO$_3$ and H$_2$SO$_4$ combination. This method resulted in an approximate final pH (with an exact dose) of 9.5. Whilst this is well within the operating pH range of many RO and NF membranes, it is below the limit for enzymatic urea hydrolysis. However, Courtney et al. (2021) showed that urine can remain stabilized up to 24 hours after a pH decrease below 11. They hypothesized that this was due to a delay in the reactivation of bacterial activity. Importantly, if NH$_4$HCO$_3$ was used for pre-treatment, conductivity measurements would not be a viable proxy for the calcium concentration and an exact dose would need to be determined via measurement of the calcium concentration. This is because the dose of NH$_4$HCO$_3$ that results in a minimum in conductivity does not align with complete calcium removal. Both NaHCO$_3$ and NH$_4$HCO$_3$ should be tested as pre-treatment step for an RO system to determine the most suitable dosing chemical.

A desktop feasibility study for the concentration of source separated urine using RO (assuming 80% water removal) determined that the concentrated liquid fertilizer would need to be sold at $1.57$ L$^{-1}$ in order for the business model to break even after 5-years (Chipako & Randall 2020). At the time of this study, the scaling potential of Ca(OH)$_2$ stabilized urine had not yet been considered. Adding a carbonate compound as a pre-treatment step would therefore require the fertilizer sales price to be increased by only 0.15% to maintain a 5-year break even period.

**CONCLUSIONS**

Addition of carbonate salts to urine stabilized with Ca(OH)$_2$ has been shown to be a simple and effective method to reduce the concentration of calcium ions and the theoretical scaling potential of RO membranes. Both NaHCO$_3$ and Na$_2$CO$_3$ addition were shown experimentally to reduce the calcium concentration in Ca(OH)$_2$ stabilized urine to at least 0.18 mmol L$^{-1}$ ($7$ mg L$^{-1}$). Sodium bicarbonate is preferred over Na$_2$CO$_3$ as it is cheaper, adds half the amount of Na$^+$ ions, and results in a change in the measured conductivity which can then possibly be used as a proxy for the calcium concentration. Dosing of either of these salts would also effectively prevent enzymatic urea hydrolysis from occurring because a high operating pH ($>11$) would be maintained. It was found that the pH buffering capacity of urine varies with composition and therefore pH could not be used as a proxy for the calcium concentration. However, when dosing NaHCO$_3$ there was a correlation between calcium concentration and conductivity. It was shown experimentally that conductivity could be used as a proxy for the calcium concentration and would only require 3.2–5.9% additional NaHCO$_3$.

It is advised that either complexometric titration, to determine the initial calcium concentration, or using conductivity as a proxy for calcium concentration should be used to determine the exact dose of NaHCO$_3$ required. This will ultimately minimize chemical costs and the addition of undesirable Na$^+$ ions. Should the operation of the membrane process require a pH lower than 11, then H$_2$SO$_4$ should be dosed to correct the pH. Whilst simply dosing additional NaHCO$_3$ to a fixed pH is simpler, the addition of H$_2$SO$_4$ would minimize the number of additional ions added.

Modelling of the experiments was shown to be accurate and used to simulate the addition of other carbonate producing salts. Excess calcium can also be removed by dosing other carbonate producing salts such as KHCO$_3$, NH$_4$HCO$_3$, and MgCO$_3$. Whilst K$^+$ ions from KHCO$_3$ are more desirable than Na$^+$ ions and MgCO$_3$ results in the lowest TDS, these two options were significantly more expensive and therefore not favored. Ammonium bicarbonate ($0.53$ m$^{-3}$ urine) was comparable in cost to NaHCO$_3$ ($0.49$ m$^{-3}$ urine) and would result in a solution pH within the operating range of most RO membranes and extra N would be added to the stream instead of Na$^+$ ions. It is advised that both NaHCO$_3$ and NH$_4$HCO$_3$ be tested as a pre-treatment method for an RO system to determine the preferred dosing chemical. The work presented in this study could also be used as a pre-treatment step for different wastewater streams where the objective is to remove a major cation to reduce subsequent membrane scaling.
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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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