Development of a Fully Automated Struvite Reactor to Recover Phosphorus from Source Separated Urine Collected at Urine Diversion Toilets in eThekwini

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ABSTRACT

In the present study we attempted to develop a reactor system to recover phosphorous by struvite precipitation which can be installed anywhere in the field without access to a laboratory. A reactor was developed which can run fully automated and recover up to 94 % of total phosphorus (total P). Turbidity and conductivity signals were investigated as automation proxies for magnesium dosage, thus making phosphate measurements to determine exact magnesium dosage unnecessary. We found that turbidity and conductivity signals show the endpoint through signal change while dosing continuously. But conductivity is highly influenced by the dosing parameters (molarity and pump speed), whereas turbidity is affected by particle size distribution issues. We investigated an algorithm based on first data sets using the turbidity signal, but it was not able to detect the precipitation endpoint in real time. A step-wise dosing approach has also been tested and might lead to the goal of full automation.

KEYWORDS

Struvite precipitation, human urine, turbidity, conductivity, automation, magnesium dosage

INTRODUCTION

Worldwide 2.5 billion people lack access to improved sanitation leading to water borne diseases (Unicef and WHO, 2012). In many countries water scarcity makes water born solution nearly impossible. Thus dry sanitation systems have been implemented in many cases to overcome the sanitation backlog such as urine diversion dehydration toilets (UDDT). One example is the eThekwini Municipality where over 75 000 UDDT in the rural and peri-urban areas have been installed (Roma et al., 2011). The advantage of an UDDT is the source separation of the urine from the faeces (Tilley et al., 2008). Source-separated human urine is an ideal source for fertilizer production, as the majority of nutrients found in wastewater streams originate from urine (Larsen et al., 1996). One way to extract nutrients from stored urine is by adding soluble magnesium to urine to recover phosphates by precipitating struvite (magnesium ammonium phosphate hexahydrate; $MgNH_4PO_4 \bullet 6H_2O$) (Tilley et al., 2008). This can be done in industrial processes such as OSTARA or Multiform Harvest. An important factor for struvite recovery in a reactor is the magnesium source itself, as it has an effect on its operating costs (Etter et al., 2011). Low-cost magnesium sources have been studied widely such as bittern or magnesite (Ye et al., 2011; Etter et al., 2011). However, accurate dosage in a struvite reactor is problematic. Chemical analysis has to be undertaken to measure phosphate concentration beforehand and the right over-dosage with magnesium has to be determined experimentally to reach maximum phosphate recovery. To overcome this other methods such as electrical conductivity have been tested to estimate phosphate concentrations by correlation to measurements (Etter et al., 2011) and tried to develop an automated feedback control system (Shepherd et al., 2009). On the other hand turbidity has been successfully used to control crystallisation in pharmaceutical processes (Parsons et al., 2003) and to analyse the struvite crystallization kinetics in urine (Triger et al., 2012). However, no known method exists to the authors' knowledge to dose magnesium accurately in a struvite reactor without prior phosphate measurement of the urine.

In the present study, the focus was to develop a fully automated struvite reactor that incorporates an automated feedback control system to determine the magnesium dosage rate and time given a certain molarity of dosing solution. Electrical conductivity and turbidity were investigated for this purpose.

MATERIALS AND METHOD

Urine source

Urine was collected at UDDTs of around 700 households in the rural and peri-urban areas of eThekwini. Plastic containers (25L) were connected to the urine pipe on the back of the toilet and brought to storage tanks. Collection was done by staff of the eThekwini Municipality Water and Sanitation unit in regular intervals. The collected urine was transported to a central collection point at Newlands Research Site with a total storage capacity of around 15000 L and brought to storage tanks (2200 L) at the university close to the laboratory for reactor trials. Storage time was at least one month.

Urine analysis

Prior to analysis, urine was filtered using a glass fibre filter with an average retention capacity of 0.4 µm (Machery-Nagel, Düren, Germany) and diluted with distilled water. Dissolved phosphate in the stored urine was measured using a Merck NOVA 60 spectrophotometer (Ammonium molybdate spectrometric method, Merck, Darmstadt, Germany). Total phosphate was measured using Merck test kits without filtering.

Struvite precipitation model

An ionic speciation model was developed to predict conductivity and suspended solids, which are further interpreted as turbidity, during struvite precipitation. The model describes aqueous ionic reactions using an algebraic equilibrium speciation and electrical conductivity model. The speciation model was the same as described by Westergreen et al. (2013). To this was added a kinetic formulation of struvite precipitation driven by supersaturation, based on Ronteltap et al. (2007). Conductivity was calculated from the speciated ionic composition using a model similar to that of McCleskey et al. (2011). This involves a sum of contributions from each charged species calculated at infinite dilution, plus a correction term for ionic strength. An empirical correction term was used, which was calibrated on a series of made-up solutions, based on a recipe for synthetic urine (Wilsenach et al., 2007). The model was used to guide the experiments on the reactor.

Struvite rector

A stirred batch reactor (volume of 50 L) made of PVC was set up as shown in Figure 1. Urine supply and magnesium dosing pumps, an overhead stirrer and the air-actuated ball valve are fully automated using a National Instruments PLC (compact RIO-9075 system; National Instruments, Austin, Texas, USA). Level sensors (Model KQ6001; IFM, Essen, Germany) are attached to the level meter on the reactor wall and the filter housing and are used to indicate the filling level and measure filtration times.

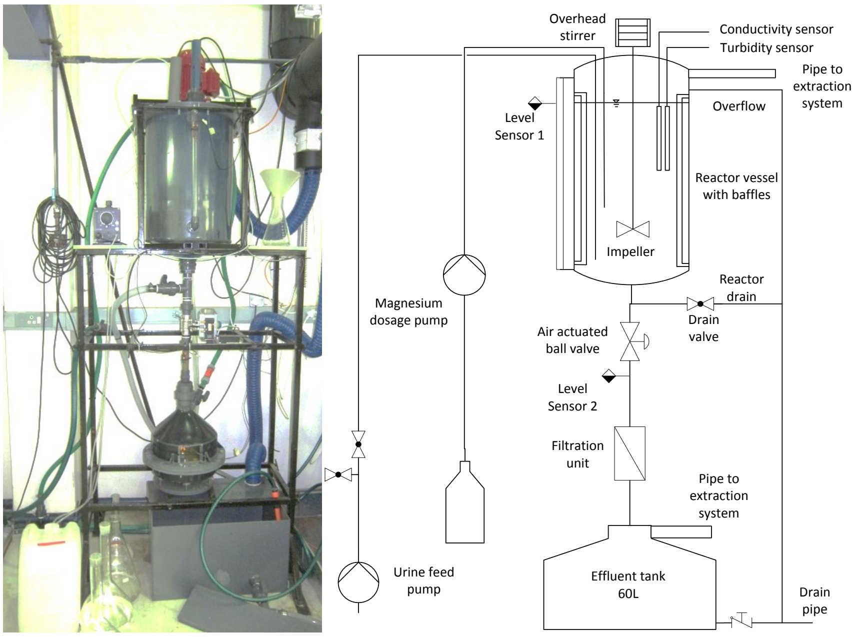

Figure 1: Reactor set up in the laboratory (left), schematic process set up (right).

Reactor sequence control logic was used in these tests to automate fill, mix, dose, react, and drain to filter. The software control panel has been programmed using LabView (National Instruments, Austin, Texas, USA). A view of the software control panel is shown in Figure 2. Industrial conductivity (Model D3727E2T; Hach, Loveland, Colorado, USA) and turbidity (Solitax HS-Line; Hach, Loveland, Colorado, USA) sensors connected to a transmitter (SC200; Hach, Loveland, Colorado, USA) are submersed from the top into the reactor to measure both parameters online. Data were collected from each process sequence for analysis that included reaction time, turbidity, conductivity, dosing pump status, and filter time. Industrial grade $MgCl_2$ and BP grade $MgSO_4$ were used to initiate the precipitation reaction. Struvite crystals were filtered from the liquid using cotton fibre discs placed in between PVC flanges in the filtration unit at the bottom. The reactor vessel and effluent tank were connected to an extraction system to reduce odour. For estimation of the reactor performance magnesium was added in a molar ratio of 1.1:1 (mol Mg : mol P). To calculate the theoretical endpoint for the struvite precipitation, at least two measurements of the feed urine were taken and the needed dose of Mg calculated using a molar ratio of 1:1 (mol Mg : mol P).

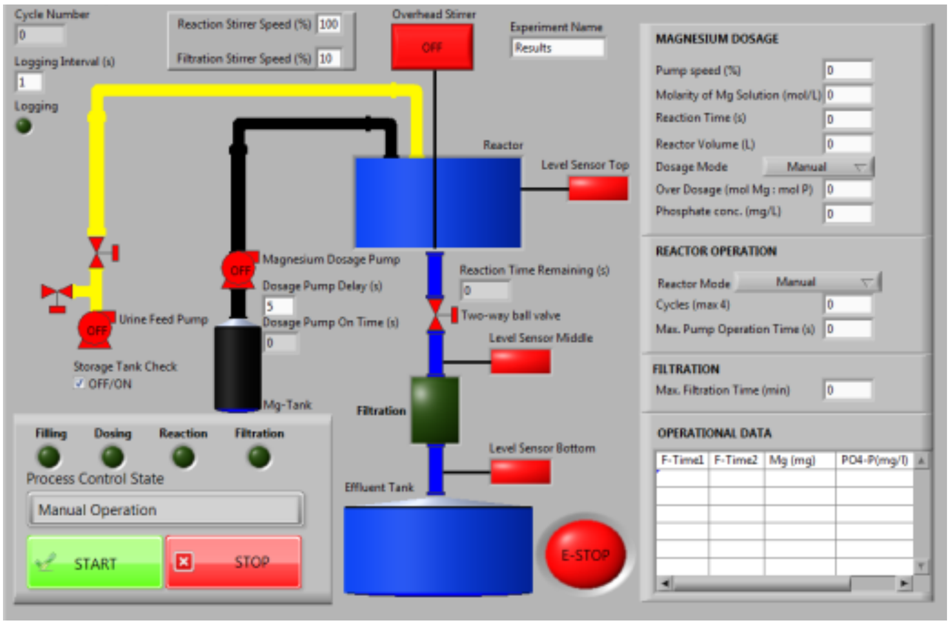

Figure 2: Software panel for reactor control programmed in LabView.

Dosing Experiments and algorithm

To investigate the potential of using turbidity and conductivity for endpoint determination, magnesium was dosed in different ways. In the first experiments the dosing pump was run continuously, adding a constant rate of magnesium into the reactor. In further experiments the dosing pump was switched on and off at intervals. Different molarities and dosing rates were studied in both operation modes of the dosing pump. An algorithm to detect the endpoint was developed. It calculates two 10-point moving averages one time step apart and determines the slope between these values. Two adjustable threshold slope values were implemented. The first detects and neglects the change of signal after dosing start. The second aims to detect the endpoint. The dosing pump switches off when the slope value is less than the second threshold value.

RESULTS AND DISCUSSION

Urine source

The long storage times in the containers guarantees full hydrolysis of the urine converting the urease into ammonia and leading to a high pH. The measured pH was around 8.9, which is in the ideal range for effective struvite precipitation (Munch and Barr, 2001). The average phosphate concentration in the storage tank at the university was 242 ± 14 mg/L.

Reactor operation

The control logic incorporated three different modes where the reactor could be controlled either completely manually, in semi-automatic and or full automatic mode. In semi-automatic mode each operation step, filling, magnesium addition and filtration could be started individually; whereas, in full automation, all steps were started automatically in sequence by the software. The reactor can process several batches of urine automatically in sequence. In some experiments up to seven cycles were processed, treating 350 L urine in total. During such operation the filter was not been changed. Measured phosphate recovery with the used cotton fibre filter was around 94% total P. The build-up filtration cake after several cycles (see Figure 3) even increased recovery slightly through better filtration properties as observed by Etter et al. (2011). But filtration times after several cycles increased drastically up to several hours, making the overall operation time too long.

Figure 3: Struvite retained on cloth filter from 100 L urine processed and dried struvite.

Continuous dosing experiments

For first trials with $MgCl_2$, the model was used to predict the conductivity response for different molarities added at the same pump rate of 2 mL/s. In Figure 4, a study with only minor changes of molarity from 0.2 to 0.26 mol/L is shown. It can be seen that conductivity is already affected by little changes in molarity. Lower concentrations of around 0.21 mol/L lead to more addition of water thus diluting the solution and decreasing the conductivity and leading to a continuous drop. The endpoint can only be seen by slight change of slope. On the other hand with higher molarities around 0.25 mol/L, the conductivity starts to rise after the endpoint making it easier to detect. The curves showed a trade-off between the magnitude of response and the change in slope at the endpoint. The clearest indication of the endpoint appears to be between 0.23 and 0.25 mol/L. Experimental results as seen in Figure 4 confirmed the model results. The overall change of conductivity from start to endpoint is very little with around 0.5 mS/cm in most experiments. The precision of the sensor is given by the supplier with 0.5% of reading, which means 0.145 – 0.165 mS/cm in the measured range and could lead to difficulties in detecting endpoints.

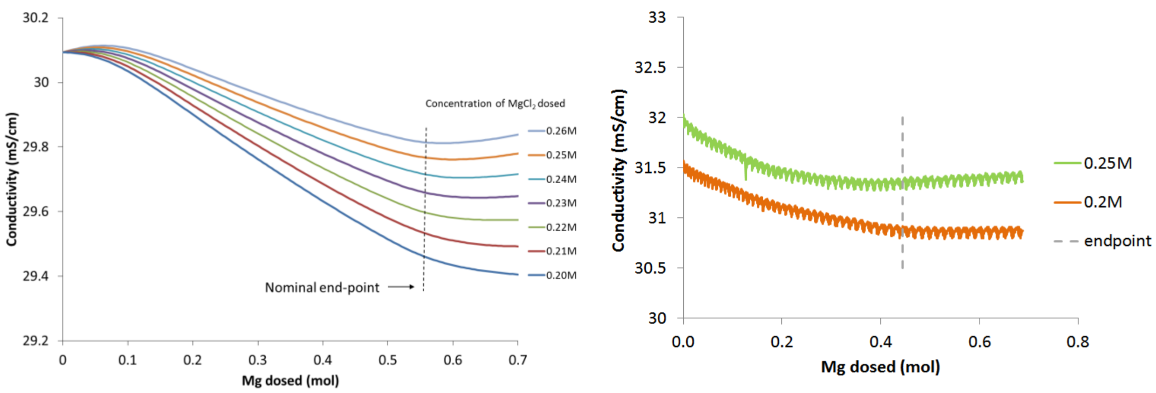

Figure 4: Modelled conductivity for different MgCl2 solutions (left) and experiments on the reactor with selected molarities (right).

Experiments with $MgSO_4$ showed similar tendencies, except that, because the $MgSO_4$ has a lower contribution to conductivity than $MgCl_2$, a higher molarity of $MgSO_4$ is required to generate similar curves. With 0.5 mol/L $MgSO_4$ solution dosed at the same rate, the conductivity starts to rise after the endpoint (Figure 5). At the same time it can clearly be seen that the turbidity signal gives a stronger response to the crystallisation process. The model curve for turbidity was obtained from the modelled concentration of precipitated struvite scaled linearly according to the initial and final turbidity readings.

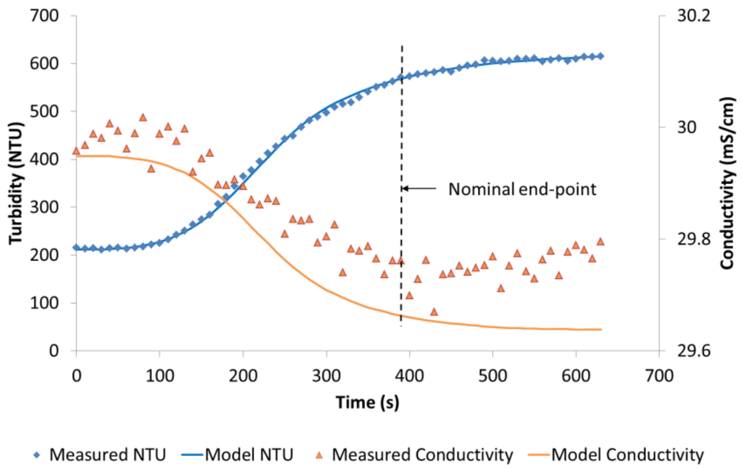

Figure 5: Measured and modelled conductivity and turbidity readings for a 0.5 mol/L $MgSO_4$ solution added at 2 mL/s.

Further experiments indicated that the turbidity is less sensitive to changes in the dosing parameters than the conductivity. In Figure 6, it can be seen that a switch of parameters while keeping the actual added mol Magnesium per seconds constant, hardly affects the change of turbidity whereas the conductivity signal behaves differently. Turbidity reaches its maximum shortly after the theoretical endpoint.

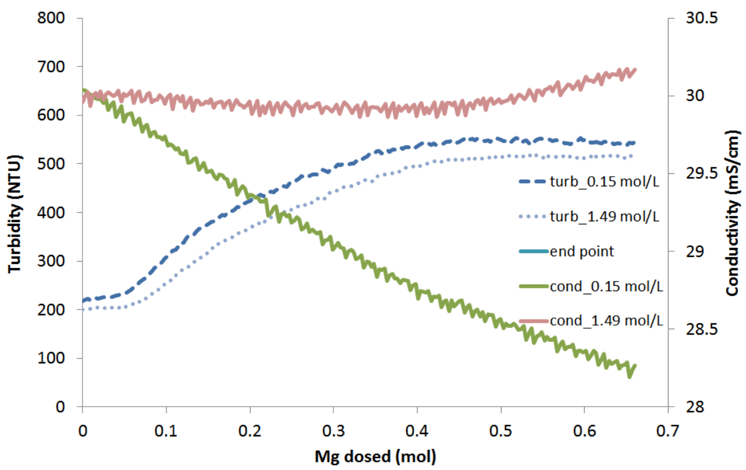

Figure 6: Conductivity and turbidity readings when switching the dosing parameters using $MgSO_4$, 0.15 mol/L and 2 mL/s compared to 1.49 mol/L and 0.2 mL/s while keeping the added magnesium per second (0.3 mmol/s) constant.

As the turbidity showed less sensitive behaviour for endpoint detection when changing parameters, the first tests with the algorithm was used for this data set. With threshold settings of 5 for the first threshold and 0.1 for the second one, the dosing pump stopped about 3% later then the theoretically calculated time. However when the method was applied to new data sets with new batches of urine the algorithm stopped the dosing far too early as the measured turbidity fluctuated strongly (Figure 7). The algorithm for endpoint detection stopped the pump when reaching a first small plateau. Increasing the smoothing did not lead to better results. When running the reactor under fully automatic control, the detection always stopped the Mg dosing too early because of fluctuations in the signal.

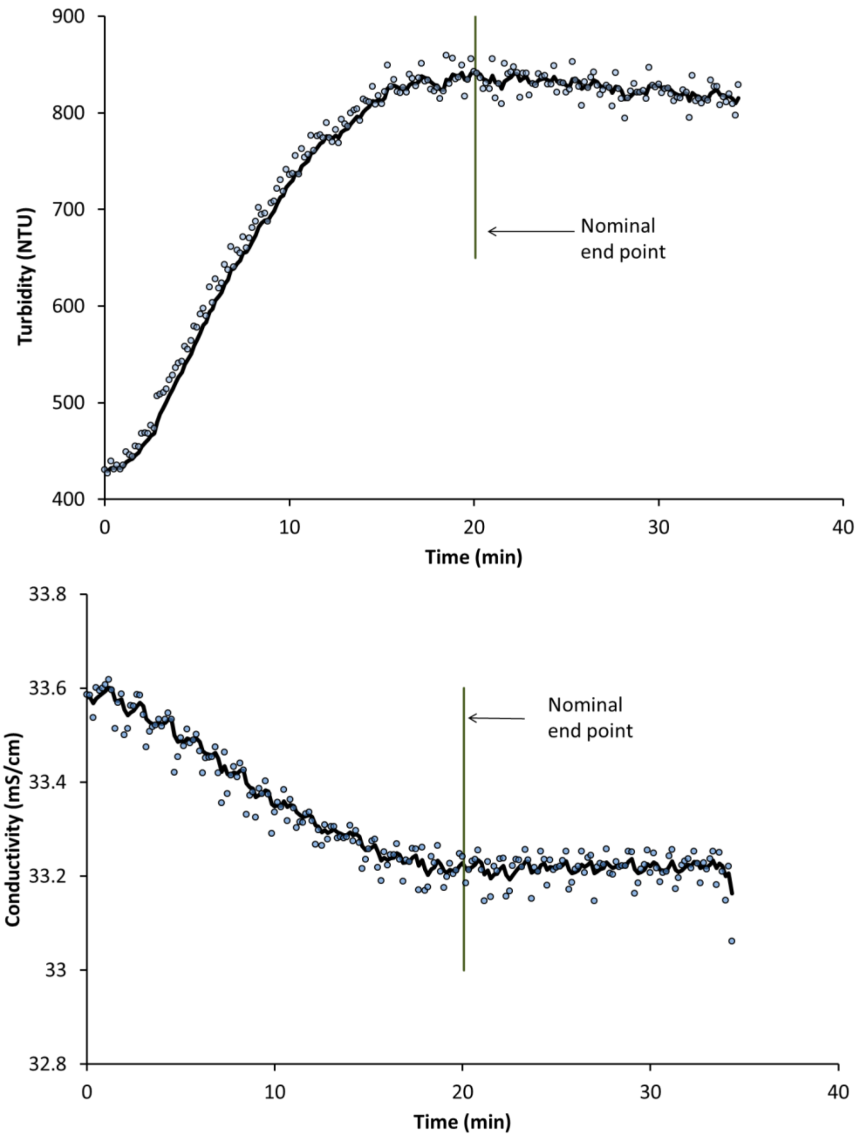

Figure 7: Conductivity and turbidity for continuous dosing of 0.5 mol/L $MgSO_4$ at 0.73 mL/s. The dark line represents a smoothed signal, which still exhibits significant fluctuations.

Step-wise dosing experiments

A further problem was revealed during attempts to model the process, namely that the precipitation is not yet complete when the magnesium dose reaches the endpoint. Thus it is necessary to anticipate the endpoint from the indicator curves. To investigate this, tests were conducted with intermittent dosing, which allowed the precipitation process to continue.

In Figure 8, the conductivity trace appears to be more informative than the turbidity. The continued precipitation during the periods when the dosing is off is evident from the slow decline in conductivity, which cannot be detected from the turbidity. Furthermore as the endpoint is approached, there is a clear change in behaviour in the conductivity curve, with a slight increase before a slight decrease, whereas the turbidity shows no apparent response. A further advantage of the conductivity signal is that smoothing is very effective, the smoothed signal should be effective for control purposes. However, the behaviour at the endpoint, while forming an easily recognisable visual pattern, will be complex to formulate as a control algorithm.

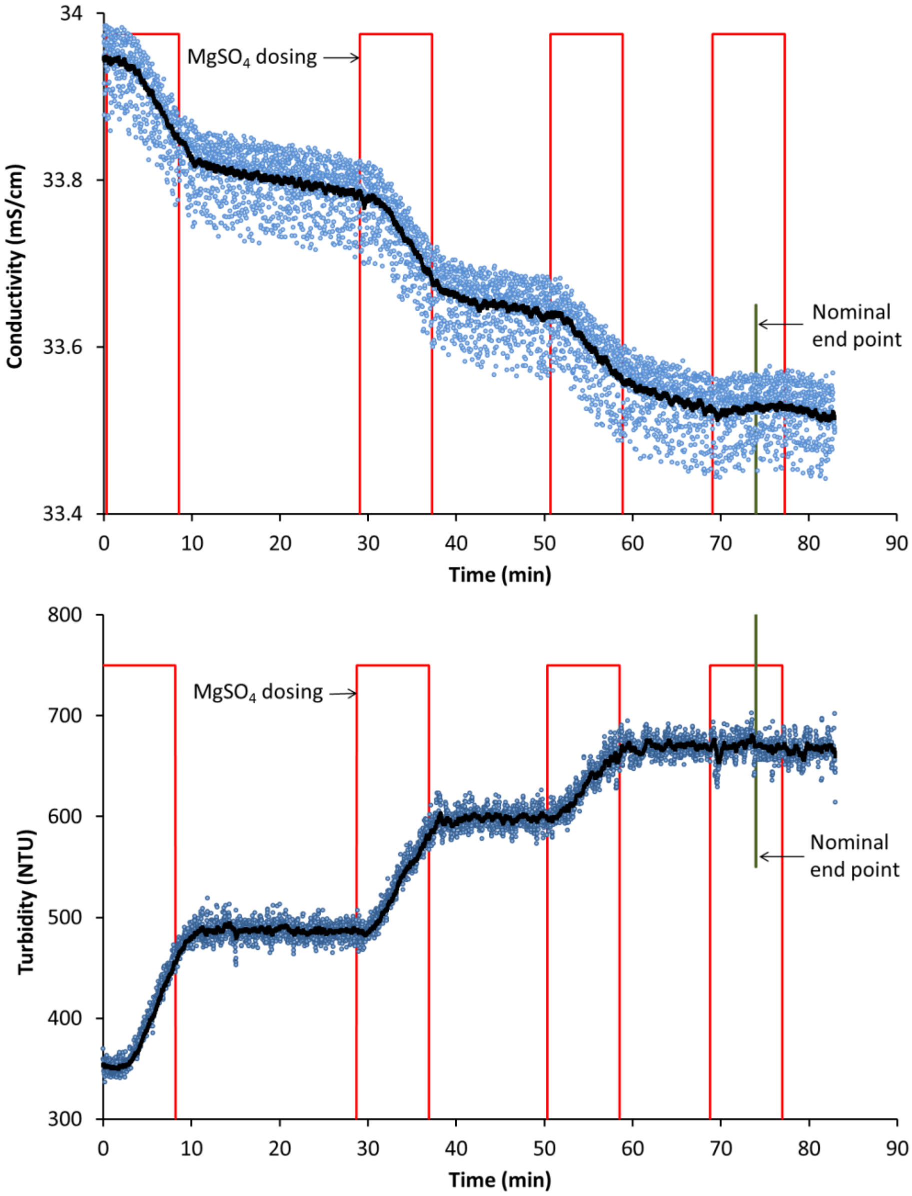

Figure 8: Conductivity and turbidity for intermittent dosing of 0.5 mol/L $MgSO_4$ at 0.73 mL/s. The dark line represents a smoothed signal. The red line indicated when the dosing pump was switched on or off.

CONCLUSIONS

An automated reactor was successfully operated with real human urine collected at urine diversion dehydrating toilets in the rural area of eThekwini. The reactor could operate on its own, processes several batches of urine, and achieve recovery rates of 94% total P. Filtration is still the critical part of the operation as the struvite crystals lead to clogging of the filter after several cycles. Conductivity and turbidity were studied as automation proxies for controlling the dosing. Molarities around 0.25 mol/L for $MgCl_2$ and 0.5 mol/L $MgSO_4$ at 2 mL/s showed good results to detect the endpoint. Continuous and intermittent dosing strategies were investigated.

The following points will be relevant in the formulation of the eventual dosing control system:

- Conductivity sensors are less expensive than turbidity sensors, and require less maintenance.
- Turbidity gives a much stronger response to precipitation than conductivity; however, the conductivity signal is more predictable and informative.
- Both signals are subject to noisy fluctuations; however, the conductivity signal can be smoothed more successfully.
- The relationship between turbidity and mass concentration of crystals appears to be complex, probably due the variations in the crystal size distribution that occur during precipitation.
- Intermittent dosing provides information about the precipitation kinetics that is masked during continuous dosing. A dosing control strategy might be able to take advantage of this to improve the accuracy of endpoint detection. However, the algorithm to implement this will be relatively complex, and requires further investigation.

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REFERENCES

Etter, B.; Tilley, E.; Khadka, R.; Udert, K.M. (2011) *Low-cost struvite production using source-separated urine in Nepal*; Water Research, 45:2, 852 – 862.

Larsen, T.A.; Gujer, W. (1996) *Separate management of anthropogenic nutrient solutions (human urine)*; Water Science and Technology, 34:3-4, 87 – 94.

McCleskey, R.B.; Nordstrom, D.K.; Ryan, J.N.; Ball, J.W. (2012)

A new method of calculating electrical conductivity with applications to natural waters; Geochimica et Cosmochimica Acta, 77, 369–382.

Munch, E. V.; Barr, K. (2001) *Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams*; Water Research, 35, 151–159.

Parsons, A.R.; Black, S.N.; Colling, R. (2003) *Automated measurement of metastable zones for pharmaceutical compounds*; Trans IChemE, 81, Part A.

Roma, E.; Holzwarth, S.; Buckley, C.A. (2011) *Large-scale peri-urban and rural sanitation with UDDTs, eThekwini (Durban), South Africa*; Sustainable Sanitation Alliance 2011 accessible at www.susana.org.

Ronteltap, M.; Maurer, M.; Gujer, W. (2007) *Struvite precipitation thermodynamics in source-separated urine;* Water Research, 41, 977–984.

Shepherd, T.A.; Burns, R.T.; Moody, L.B.; Raman, D.R.; Stalder, K.J. (2009) *Investigating conductivity to predict magnesium addition requirements for struvite precipitation in swine manure slurries*; American Society of Agricultural and Biological Engineers, 25:1, 103 – 108.

Tilley, E.; J. Atwater, J.; Mavinic, D. (2008) *Recovery of struvite from stored human urine*; Environmental Technology, 29:7, 797 — 806.

Tilley, E. et al (2008) *Compendium of Sanitation Systems and Technologies;* Swiss Federal Institute of Aquatic Science and Technolog, Eawag, Dübendorf, Switzerland.

Triger, A.; Pic, J.S.; Cabassud, C. (2012) *Determination of struvite crystallization mechanisms in urine using turbidity measurement*; Water Research, 46, 6084 – 6094.

Unicef and WHO (2012) *Progress on Drinking Water and Sanitation: 2012 Update*; I. WHO/UNICEF Joint Monitoring Programme for Water Supply and Sanitation, UNICEF and World Health Organization 2012, New York, USA.

Westergreen, S.; C. J. Brouckaert, C.J. ; Foxon, K.M. (2012) *Modelling of ionic interactions with wastewater treatment biomass*; Water Science and Technology, 65:6, 1014-1020.

Wilsenach, J.A.; Schuurbiers, C.A.H.; van Loosdrecht, M.C.M. (2007) *Phosphate and potassium recovery from source separated urine through struvite precipitation*; Water Research, 41, 458–466.

Ye, Z.L.; Chen, S.H.; Lu, M.; Shi, J.W.; Lin, L.F.; Wang, S.M. (2011) *Recovering phosphorus as struvite from the digested swine wastewater with bittern as a magnesium source*; Water Science & Technology, 64:2, 334 – 339.