Science of the Total Environment 586 (2017) 650–657

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Urea stabilisation and concentration for urine-diverting dry toilets: Urine dehydration in ash

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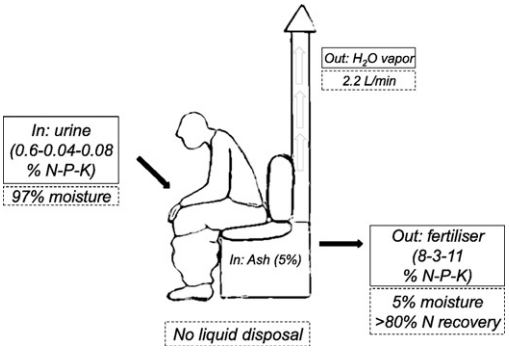
HIGHLIGHTS

- Human urine contains plant nutrients that can be concentrated to produce fertiliser.
- Increasing pH of urine inhibits urease enzymes from hydrolysing urea.
- Urine is reduced by 95%, while preserving up to 90% of the urea.
- No liquid disposal required from the toilet
- End product is a dry fertiliser with 7.8% N, 2.5% P and 10.9% K.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 November 2016
Received in revised form 3 February 2017
Accepted 5 February 2017
Available online 16 February 2017

Editor: Simon Pollard

Keywords:
Alkalisation
Ash
Dehydration
Fertiliser
Human urine
Plant nutrients

ABSTRACT

Human excreta contain the same nitrogen, phosphorus and potassium (N-P-K) as the fertilisers used to produce the food consumed. However, human excreta are considered unwanted waste throughout the world, creating humanitarian and environmental problems. In order to replace the nutrients removed from fields during crop harvesting, more fertilisers are manufactured, in processes contributing to environmental changes at global level. The limitation of human urine as a fertiliser is its low nutrient concentration compared with commercial fertilisers. This study developed a technique to increase the N concentration (from 0.6% to >6%) through urine dehydration to produce a dry fertiliser of monetary value and avoid the need for liquid disposal from the toilet. The technique is intended for a container-based sanitation system that collects, contains, treats and reduces the volume of urine within the container. In tests, fresh human urine was added at various intervals to wood ash at 35 °C and 65 °C, to alkalise and thus inhibit the enzyme urease from catalysing hydrolysis of urea to ammonia. Mass balance calculations demonstrated a 95% reduction during dehydration, while preserving up to 90% of the N. Such a system would greatly simplify the logistics and costs of storage, transportation and application of urine as a fertiliser. The truly innovative feature is the final product: a dry powder with 7.8% N, 2.5% P and 10.9% K by weight, i.e. equivalent to commercial fertiliser.

1. Introduction

The saying 'we are what we eat' is only part of the story. What we eat is what we excrete, and this means plant nutrients. Human excreta contain the same nitrogen, phosphorus and potassium (N-P-K) as the

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http://dx.doi.org/10.1016/j.scitotenv.2017.02.038

fertilisers used to produce the food consumed (Winker et al., 2009). However, human excreta are considered unwanted waste throughout the world, creating humanitarian and environmental problems (Baum et al., 2013). In order to replace the nutrients removed from the fields during harvesting more fertilisers are manufactured in industrial processes that are contributing to environmental changes at global level (Rockström et al., 2009). Recycling human excreta back to agricultural fields would reduce the current dependence on fossil fuel-derived fertilisers (Ramírez & Worrell, 2006). It would also improve crop yields in e.g. sub-Saharan Africa, where fertiliser application is low (FAO, 2015), and protect marine ecosystems in the Baltic Sea by limiting the flow of excess nutrients to surface waters (Rockström et al., 2009).

Urine, rather than faeces, contains the majority of the nutrients excreted annually: 80–90% of the total 4 kg of N excreted, 50–80% of the 0.4 kg of P and 80–90% of the 1 kg of K (Vinnerås et al., 2006). The main limitation with using urine as a fertiliser is that it is mostly water (97%), meaning that the concentration of nutrients is low. For example, the N concentration in urine is 0.6% (Vinnerås et al., 2006), whereas that of the manufactured fertiliser urea is 46%. Lower nutrient concentrations require larger quantities of urine to be applied per hectare as fertiliser, which creates logistics problems in terms of storage (as approx. 550 L of urine are produced per person and year) and increases the costs of transportation and application. Hence urine, as excreted, is not a competitive fertiliser. To better utilise the nutrients, the excess water in urine needs to be removed.

Concentrating the nutrients in urine while retaining N is challenging. Approximately 85% of the N in urine is initially present in non-volatile form, as urea ($CO(NH_2)_2$). Once excreted, the urea is quickly hydrolysed to volatile form, ammonia (NH_3), in a reaction that is catalysed by urease enzymes (urea amidohydrolase, EC 3.5.1.5) (Eq. (1)). The carbamate (H_2N-COOH) produced in this reaction then spontaneously hydrolyses into carbonic acid (H_2CO_3) and releases a second NH_3 molecule (Krajewska, 2009). The volatility of NH_3 means that urine cannot simply be dehydrated, but stopping the urease enzyme is also a challenge.

$$H_2N\text{–}CO\text{–}NH_2 + H_2O \xrightarrow{\text{Urease}} H_2N\text{–}COOH + NH_3 \xrightarrow{H_2O} H_2CO_3 + 2NH_3 \quad (1)$$

$$H_2N\text{–}CO\text{–}NH_2 \xrightarrow{\text{Uncatalysed}} HN{=}C{=}O + NH_3 \xrightarrow{2H_2O} H_2CO_3 + 2NH_3 \quad (2)$$

Urease is a group of highly proficient natural enzymes used in plants, algae, fungi and several microorganisms to catalyse the hydrolysis of urea (Ciurli et al., 1999). The structure varies between different urease-forming bacteria (enzyme molar mass range 190–300 kDa; Krajewska, 2009), but all have a common feature of two nickel ions at the active site. Urease is an extracellular enzyme that can be immobilised on particles and there continue its degradation of urea (Ciurli et al., 1996). Urease enzymes are most commonly known for their role in soil fertilised with urea but, unknown to most toilet users, human faeces contain large amounts of urease-forming bacteria (Wozny et al., 1977). Even in urine-diverting dry toilets, these urease enzymes accumulate in urine piping systems due to cross-contamination from faeces and biofilm formation on the pipe surface and cause rapid hydrolysis of urea to NH_3 (Vinnerås, 2002).

The potential source of nutrients in human urine has led to various trials to concentrate urine that has already been hydrolysed. Examples include NH_3 stripping (Antonini et al., 2012), nitrification (Udert et al., 2015), electrolysis (Udert et al., 2015), struvite formation by the addition of magnesium (Etter et al., 2011), and reverse osmosis, many of which are reviewed in Maurer et al. (2006). However, the implementation of such treatments is limited due to the sensitivity, high requirements for chemical inputs or the complexity of the system. In addition, most of the concentrating techniques collect only some of the elements in the concentrated fraction, e.g. N in NH_3 stripping and P in struvite.

Another approach is to first pre-treat the urine to limit the urease activity to enable dehydration of the excess water in urine. To limit the urease enzymes in agricultural soils, inhibitors such as N-(n-butyl) thiophosphoric triamide are being developed (Parker et al., 2012). However, due to the potential risks to human and environmental health (Ciurli et al., 1999), they cannot be considered a viable option for use in household toilets. The urease enzymes can also be limited by pH and temperature (Hotta & Funamizu, 2008; Huang & Chen, 1991; Sizer, 1940). Examples of stabilisation techniques include acidification (Hellstrom et al., 1999), alkalisation (Randall et al., 2016), freeze-thaw (Lind et al., 2001) and salinisation (Pahore et al., 2011), so that the N is preserved as urea and the excess water in the urine can be removed by dehydration. When the urease enzyme is limited by elevated pH and/or elevated temperature, then uncatalysed urea hydrolysis occurs (Eq. (2)) (Jespersen, 1975). However, this uncatalysed hydrolysis is 10^{10} times slower than enzyme-catalysed hydrolysis (Table 1).

Stabilising urine by alkalisation is an attractive option, as there are several sources of strong bases available and as alkalisation of soils in the humid northern temperate and humid tropic zones is a common existing practice for treating acidic soils (FAO, 1986). Calcium hydroxide ($Ca(OH)_2$) has been demonstrated to effectively increase the pH above 12 and inhibit the urease activity in a chemical reactor prior to drying in a separate system (Randall et al., 2016). The objective of the present study was to test the alkalinisation approach using another alkaline medium, wood ash, and performing the drying continuously in the same alkalising bed. Wood ash was selected not just for its high initial pH (>12.5), but also for its high surface area, to enable faster dehydration of the urine. The aim was to retain the majority of N (>90%) in a continuous drying process with daily addition of fresh source-separated urine. The urine was dehydrated under constant ventilation at two elevated temperatures, 35 and 65 °C. The approach is intended for container-based sanitation systems where the urine is diverted during excretion and collected, contained, treated and reduced within the same container. The installation of such a technique, along with full servicing from a central provider, would offer the experience of a flush toilet ('flush and forget') at an affordable cost. A container-based-sanitation system requires no pit, plumbing or sewer connection, greatly reducing the cost and complexity of the system. The potential for container-based sanitation technologies is immense, with 4.1 billion people currently lacking access to improved sanitation systems (Baum et al., 2013).

2. Methodology

2.1. Human urine

Human urine from one woman and one man in their mid-20s was collected in new containers 4 days a week, in the morning. The initial density and pH of the urine were measured and a cumulative samples was stored frozen until the end of the experiment. The N concentration was analysed at the end of the experiment by Koroleff's method, using an N (total)-Spectroquant Cell test kit (1.14763.0001, Merck-Chemicals).

Table 1
Examples of the half-life of urea varying on temperature, pH and catalyst.

	t½
Unanalysed (neutral pH, 25 °C)[a]	40 yrs
20 °C (pH > 10)[b]	Neg. at 32 days
38 °C (pH < 12)[c]	3.6 yrs
65 °C (pH < 12)[d]	15.3 days
65 °C (pH > 12.5)[d]	14.1 days
Enzymatic (Jack-bean, neutral pH, 25 °C)a	0.02 s

[a] (Callahan et al., 2005).
[b] (Kabdaşlı et al., 2006).
[c] (Zerner, 1991).
[d] Derived from Warner (1942).