Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite

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Abstract

Urine-separation toilets are a possible route for achieving maximum recovery and recycling of urine nutrients not contaminated by hazardous compounds such as heavy metals. However, the direct use of human urine as agricultural fertiliser is problematic and controversial with regard to hygiene, storage, transport and spreading. In this paper, simple methods for capturing the nutrients in urine by transformation into solid mineral form are presented. On the addition of small amounts of MgO to synthetic or natural human urine most of the phosphorous and significant amounts of the potassium and nitrogen were precipitated, with crystalline struvite $[Mg(K, NH_4)(PO_4) \cdot 6H_2O]$ as a major component together with montgomeryite, newberyite, brucite and epsonite. Nitrogen recovery could be improved by adsorption. Clinoptilolite, wollastonite and a natural zeolite all showed excellent adsorbent properties in contact with ammoniacal solutions. In combination with struvite crystallisation 65–80% of the nitrogen was recovered as crystalline or adsorbed ammonium. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Struvite; Clinoptilolite; Wollastonite; Ion exchange; Adsorption; Zeolite; Ammonia; Nutrient recovery

1. Introduction

About 94% of the nitrogen, phosphorus and potassium in toilet wastewater emanates from the urine, together with abundant micronutrients in balanced concentrations (Wolgast, 1993). New ideas for eco-cycling of nutrients from waste water have been proposed based on urine separation, in order to maximise the recovery and recycling of nutrients and to reduce eutrophication in freshwater and coastal ecosystems. Urine separating toilets have been developed and installed in several eco-villages around the world, including different parts of Sweden.

Life cycle comparisons of conventional and urine-separation wastewater systems show that urine-separation systems have many advantages related to emissions and nutrient recovery (Bengtsson et al., 1997). Exergy (energy efficiency) analyses of sewage treatment systems show that phosphorous and nitrogen-recycling efficiency is highest if urine separation is used (Hellström and Kärrman, 1997). However, life cycle assessment-studies of urine-separation systems also show that the storage, transport and spreading of large amounts of urine, presents serious obstacles to system efficiency (Jenssen and Etner, 1996; Larsen and Gujer, 1996; Höglund et al., 1998). Large volumes of urine are needed to fertilise typical farmland, leading to high transport costs. Another problem of urine-separation systems is the loss of nitrogen by ammonia evaporation during storage and spreading (Hanaeus et al., 1996). Furthermore in many countries the spreading of liquid urine fertiliser is restricted to certain periods of the year.

We believe that many of the problems connected with urine separation could be met by transforming the nutrients in the urine into solid minerals. Handling and storage could be substantially improved, the volume would be dramatically reduced compared with liquid urine, loss of nitrogen into the atmosphere would be eliminated, a high level of hygiene could be maintained and spreading on arable land could be much more flexible in terms of time and dosage.

This paper presents the results of a pilot study of nutrient recovery from human urine by struvite crystallisation with further ammonia recovery using zeolites or wollastonite.

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2. Crystallisation and adsorption of nutrients from human urine

Human urine is a complex aqueous solution containing sodium chloride (NaCl) and urea ($CO(NH_2)_2$) as dominant compounds but also potassium (K), calcium (Ca), sulfate (SO_4) and phosphate (PO_4) in low concentrations. One of the most important compounds that can precipitate from human urine is the mineral struvite, $Mg(NH_4)(PO_4) \cdot 6H_2O$, formed by reaction of magnesium with ammonical phosphate solutions and usually found in deposits of guano or animal dung. Human urine contains an excess of ammonium relative to phosphate, but is deficient in magnesium. The normal pH of human urine is between 5.6 and 6.8 and most of the phosphate is present as $H_2PO_4^-$ or HPO_4^{2-}. With the addition of MgO the pH increases, shifting the phosphate equilibrium toward PO_4^{3-} and magnesium is provided for struvite crystallisation. Struvite precipitation may be a method to remove phosphate but if it happens spontaneously it can also cause operational problems in sewage systems. Struvite formation from mixed waste water has been studied by e.g., Liberti et al. (1986), Sen and Randall (1988), Mohajit et al. (1989), Maqeda et al. (1994), Momberg and Oellermann (1992), Pérez Rodríguez et al. (1992), Wrigley et al. (1992a,b) and Battistoni et al. (1997). The potential of struvite crystallisation for direct nutrient recovery from human urine has to our knowledge not been investigated before.

In fresh urine ammonium (NH_4^+) is formed from the decomposition of urea (Hanaeus et al., 1996). This offers possibilities for nitrogen recovery by ammonium uptake to specific adsorbents such as zeolite or wollastonite minerals. The ion exchange properties of natural zeolites especially clinoptilolite $[R(Na, K)_6(Al_6Si_{30}O_{72}) \cdot 20H_2O]$ are well documented (c.f. Breck, 1974; Jorgensen et al., 1976; Gottardi and Galli, 1985; Tomazovic et al., 1996). The use of wollastonite for removing heavy metals from aqueous solutions was investigated by e.g. Sharma et al. (1990) and Lifvergren (1997). The use of zeolite or wollastonite as adsorbents for ammonium recovery from human urine has not been investigated before.

3. Methods

Synthetic human urine containing 11 solutes, in concentrations equivalent to the daily average urine of normal healthy men was prepared according to conventional urological methods (Griffith et al., 1976a,b) for use in the experiments. Synthetic urine is free of pyrophosphates, organic macromolecules (matrix) and unspecified substances that could enhance or inhibit the nutrient recovery. In addition struvite precipitation was also tested using fresh human urine from five healthy, young to middle-aged people. For studies of NH_4 ad-sorption a NH_4Cl solution was prepared with concentrations similar to synthetic human urine without and with urea hydrolysis; 0.02 and 1 M, respectively. All solutions were stored at room temperature.

The chemical compositions of the adsorbents are presented in Table 1. The adsorbent minerals were not pretreated or activated in any way, just crushed and sieved to specific grain size fractions. Deionised water was used for all dilution, washing and preparation. Ammonium measurements were made using a Metrohm calibrated ammonia-selective electrode, complemented with Kjeldahl nitrogen analysis.

3.1. Struvite crystallization

Laboratory experiments were based on dephosphatisation procedures, using 98% pure MgO. First, different amounts of MgO were added to 20 ml samples of synthetic urine in 50 ml test tubes. The pH was measured continuously and MgO additions were adjusted to give pH values ranging from approximately 6.5–10. The tests were made at room temperature (20°C). Additional experiments were done using fresh, human urine. The MgO added was more than sufficient to supply the

Table 1
Chemical composition of adsorbent minerals

Component	%
Clinoptilolite, Mad, Hungary	
SiO_2	62.43
Al_2O_3	10.95
MoO_3	0.11
FeO	0.12
MgO	0.79
CaO	3.17
Na_2O	0.13
K_2O	2.74
Total[a]	80.44
Wollastonite, Hulta East, Sweden	
SiO_2	63.16
Al_2O_3	4.20
Fe_2O_3	1.12
MnO	0.26
CaO	3.12
Na_2O	0.12
K_2O	2.62
P_2O_5	0.01
Total[a]	74.61
Zeolite-mix, Mad, Hungary	
SiO_2	68.48
Al_2O_3	12.48
FeO	0.05
CaO	3.46
Na_2O	0.02
K_2O	3.27
MgO	1.12
TiO_2	0.08
Total[a]	88.90

[a] Does not include water.

stoichiometric ratio, Mg:P; 1.71:2.21, for urine containing 0.5 g P/l and to raise the pH to about 10. The precipitates were filtered, dried at 40°C and weighed. Electron microscope, energy dispersive X-ray analysis (EDS) and X-ray diffraction (XRD) analyses were made of the precipitates.

The combination of struvite precipitation with further ammonium uptake by clinoptilolite and wollastonite was also investigated.

3.2. Batch adsorption experiments

At constant room temperature (20°C) 25 ml solution, synthetic human urine or NH_4Cl solution, was used together with 0.5 g of adsorbent mineral for each experiment. Stirring at 200–250 rpm established contact between adsorbent and solution. pH and ammonium were measured during each experiment, after which the liquid was separated from the adsorbent with a vacuum filter. This process was repeated with the following variables:

1. three different mineral adsorbents: clinoptilolite, wollastonite and mixed zeolite,
2. two different concentrations for NH_4Cl and synthetic human urine,
3. four different grain sizes for each mineral,
4. a series of contact times between adsorbents and solutions from 0.5 to 60 min for each adsorbent, grain size and solution type.

4. Results and discussion

4.1. Struvite crystallisation

The initial test-tube experiments using synthetic urine resulted in the rapid formation of small crystals which settled on the tube wall. Precipitation of a white sediment occurred immediately and after shaking for 30–50 min, needle-shaped crystals became visible on the tube walls and bottom. After filtration and de-watering of the precipitate a fine crystalline white powder was obtained. Similar results were obtained using human urine.

Electron microscope studies of the precipitate revealed small (up to 1 mm long) crystals of struvite, see Fig. 1. Quantitative EDS analyses of both the crystals and the fine white precipitate gave the results in Table 2. XRD analysis in Table 3 confirmed that struvite was a major constituent in both the crystalline and the fine material. Calculations based on the mass and composition of the precipitates indicated that all phosphorous, 20–60% of potassium and 3–5% of sodium in the original solutions was settled as shown in Table 4.

It can be concluded from the experiments that struvite was formed from both human and synthetic urine by adding MgO to achieve the approximate proportion
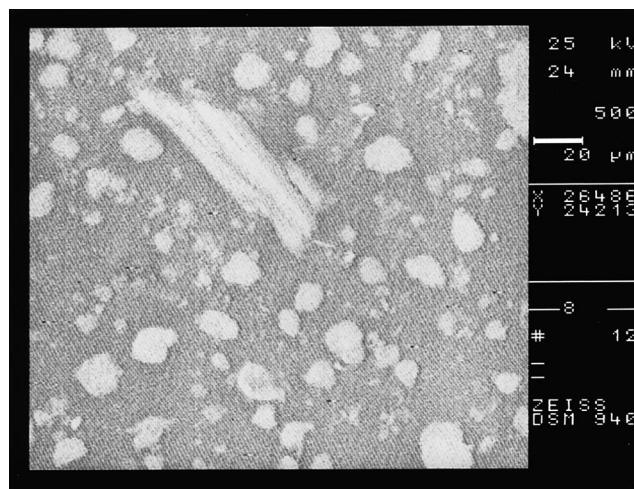

Fig. 1. SEM photo of struvite crystal (×1000).

of 1.71:2.21 magnesium to phosphorous. It is also clear that potassium as well as calcium was included in the precipitate. Natural struvite does not have a pure end-member composition as shown in Table 2. Small amounts of Ca (Mn and Fe) may substitute for Mg and K may substitute for NH_4. A more correct formula for struvite is $[(Ca, Mg)(K, NH_4)(PO_4) \cdot 6H_2O]$. Together with struvite, other minerals, such as montgomeryite $[Ca_4Al_5(PO_4)_6(OH)_5 \cdot 11H_2O]$, $[Ca_4MgAl_4(PO_4)_6(OH)_4 \cdot$

Table 2
EDS quantitative analyses of amorphous precipitate and settled crystal structures

Compound	%
Crystal structure	
Synthetic urine (normal conc.)	
MgO	28.30
P_2O_5	57.79
SO_3	0.63
K_2O	7.63
CaO	0.09
Total[a]	94.48
Human urine (normal conc.)	
MgO	35.34
P_2O_5	47.66
SO_3	0.44
K_2O	10.50
CaO	0.67
Total	94.58
Amorphous structure	
Human urine (normal conc.)	
MgO	38.14
P_2O_5	41.76
SO_3	2.83
K_2O	7.27
CaO	6.50
Total	96.50

[a] Does not include water.

Table 3
XRD analysis results for 'struvite' composition. Crystallization made in synthetic human urine. Struvite, montgomeryite and brucite as main components

Detected compound	Standard d (Å)	Standard (I)	Detected d (Å)	Detected (I)	Counts
Struvite	4.2570	100	4.2540	100	746
	5.6010	60	5.6.30	24	178
$NH_4MgPO_4 \cdot 6H_2O$	2.9190	55	2.9199	11	79
	2.6900	50	2.6896	10	77
Lattice: Orthorhombic	2.6600	45	2.6602	11	79
Mol. Weight: 245.41	5.9050	40	5.9020	41	307
Volume (CD):477.58	2.8020	35	2.8020	9	66
Montgomeryite	12.0000	100	Outside	–	–
	5.1100	65	5.1121	100	181
$Ca_4MgAl_4(PO_4)_6(OH)_4 \cdot 12H_2O$	2.8950	45	2.8948	47	46
	2.5800	30	2.5793	6	102
Lattice: Monoclinic	2.8740	25	2.8744	13	23
Mol.Weight: 1146.59	2.6150	25	2.6154	56	102
Volume (CD):1502.79	3.1330	20	3.1340	61	111
Brucite	2.3650	100	2.3649	100	316
	4.7700	90	4.7680	91	285
$Mg(OH)_2$	1.7940	55	1.7940	95	300
	1.5730	35	Outside	–	–
Lattice: Hexagonal	1.4940	18	Outside	–	–
Mol. Weight: 58.32	1.3730	16	Outside	–	–
Volume (CD): 40-50	1.3100	12	Outside	–	–

Table 4
Results of MgO addition to synthetic human urine. Grams MgO added to 25 ml urine. Percentage uptake from solution

MgO (g)	pH	Precipitate (g)	Uptake from solution		
			P (%)	K (%)	Ca (%)
0.04	8.55	0.1186	100	22	2
0.06	9.1	0.1476	100	28	2.5
0.12	9.55	0.1820	100	35	3
0.16	10.2	0.2208	100	42	4
0.24	10.4	0.3325	100	64	5.6

$12H_2O$], brucite [$Mg(OH)_2$] or epsomite [$MgSO_4 \cdot 7H_2O$] may form depending on the amounts of Ca and metals available. The crystallisation process thus gives a much more complete precipitation of nutrients than suggested by the formation of struvite alone.

4.2. Ammonium uptake

The results from ammonium uptake by clinoptilolite, wollastonite and mixed zeolite are presented in Figs. 2–4.

Ammonium uptake was related to grain size, ion concentration and contact time. Higher adsorption at smaller grain sizes was shown at both low and high ammonium contents. This illustrates the obvious relationship between the amounts of adsorbent and the ammonium content.

The ammonium adsorption was stabilised after a few minutes and showed good results with 70–80% uptake from low-concentration solutions for the clinoptilolite,

about 50% for the wollastonite and 50–60% for the mixed zeolite.

4.3. Combined crystallisation and adsorption

A series of experiments with a combination of struvite crystallisation and ammonia adsorption was made using cliniptilolite and wollastonite as adsorbents. 0.06g MgO and 0.5g of each adsorbent separately (grain size 0.125–0.250 mm) was added to 25 ml of synthetic urine. Results for contact times of 5 and 10 min are shown in Table 5. In experiments 1 and 2 the adsorbent was added to the separated supernatant after struvite precipitation whereas in experiments 3 and 4 the adsorbent was mixed simultaneously with the MgO. The results show that 67–80% of the nitrogen was taken up by struvite and clinoptilolite and 64–75% by struvite and wollastonite. The addition of MgO increased the pH to 9.0–9.5, which leads to the decomposition of urea and formation of ammonium ions. At pH 9.0–9.1 between 65 and 95% of the urea decomposes, depending mainly on storage time
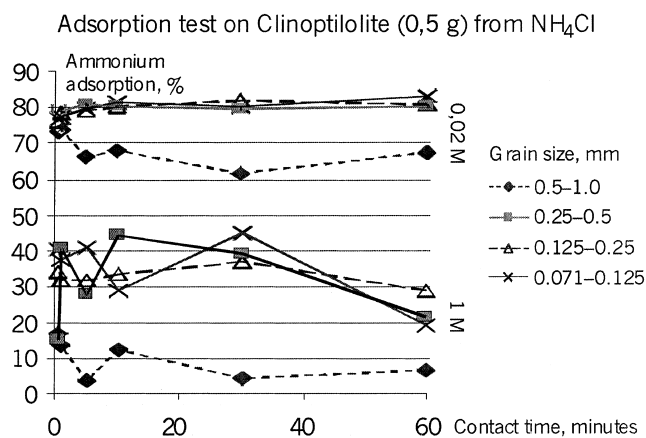
Adsorption test on Clinoptilolite (0,5 g) from NH$_4$Cl

Fig. 2. Ammonium adsorption (concentration change in %) on clinoptilolite, from 0.02 and 1 M NH$_4$Cl.
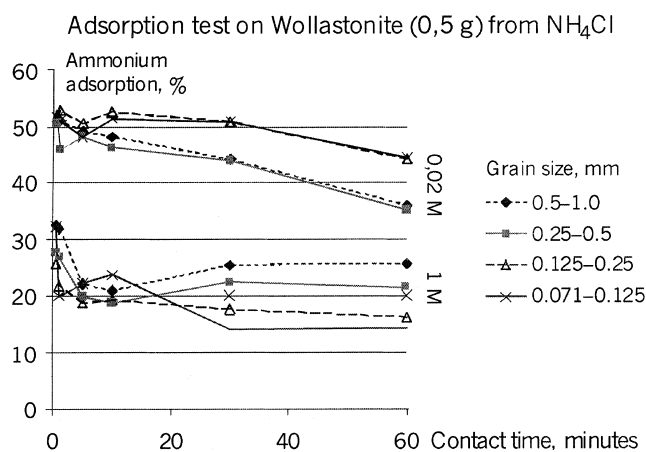
Adsorption test on Wollastonite (0,5 g) from NH$_4$Cl

Fig. 3. Ammonium adsorption (concentration change in %) on Wollastonite, from 0.02 and 1 M NH$_4$Cl.

Adsorption test on mixed Zeolite (0,5 g) from NH$_4$Cl
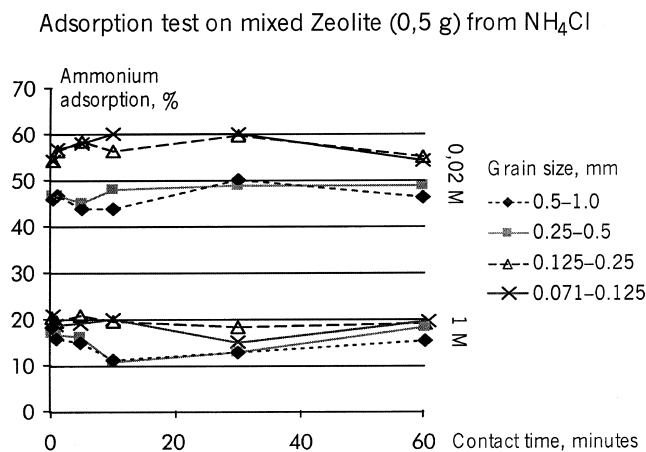
Fig. 4. Ammonium adsorption (concentration change in %) on mixed zeolite, from 0.02 and 1 M NH$_4$Cl.

Table 5
Results for nitrogen fixation as ammonia in combined struvite precipitation and adsorption experiments (% nitrogen fixed)

Exp. no	Contact time	Struvite +Clinoptilolite % uptake	Struvite +Wollastonite % uptake
1	5 min	67	64
2	10 min	75	64
3	5 min	79	74
4	10 min	80	75

(Hellström, 1998). Thus the MgO-addition and struvite precipitation would facilitate the nitrogen (ammonium) uptake by the adsorbent.

5. Conclusions

It proved possible to capture the majority of nutrients contained in urine in the form of solid minerals. By adding small amounts of MgO, struvite was obtained and identified as a main component together with montgomeryite, newberyite, brucite and epsonite in the precipitated crystalline mixture.

Natural zeolites, especially clinoptilolite, as well as natural wollastonite showed excellent ammonium adsorbent qualities in contact with human urine. In combination with struvite crystallisation, most of the phosphorous and potassium and 65–80% of the nitrogen could be recovered. The mixture of struvite and natural mineral adsorbent has good nutrient qualities and can be used as soil conditioner. Ammonia-clinoptilolite mixed with apatite is a well-known slow release fertiliser. Struvite and ammonia-clinoptilolite may have the same qualities.

Simple, effective, easy manageable and economically viable eco-technology is much in demand all over the world. We believe that the recovery of nutrients from separated urine reported here could play a role in the urban sanitary system of the future, which will almost certainly be much more diverse than it is today, with many different technologies at different places.

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