Pilot Experiments with Electrodialysis and Ozonation for the Production of a Fertilizer from Urine

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Abstract
Pilot tests were performed with a process combination of electrodialysis and ozonation for the removal of micropollutants and the concentration of nutrients in urine. In continuous and batch experiments, maximum concentration factors up to 3.5 and 4.1 were obtained respectively. The desalination capacity did not decrease significantly during continuous operation periods of several weeks. Membrane cleaning after 195 days resulted in approximately 50% increase in desalination rate. The Yeast Estrogen Screen (YES), a bioassay that selectively detects estrogenic compounds, confirmed that about 90% of the estrogenic activity was removed by electrodialysis. HPLC analysis showed that ibuprofen was removed to a high extent, while other micropollutants were below the detection limit. In view of the fact that ibuprofen is among the most rapidly transported micropollutants in electrodialysis processes, this result indicates that electrodialysis provides an effective barrier for micropollutants. Standardized plant growth tests were performed in the field with the salt solution resulting from the treatment by electrodialysis and subsequent ozonation. The results show that the plant height is comparable to synthetic fertilizers, but the crop yield is slightly lower. The latter is probably caused by volatilization losses during field application, which can be prevented by improved application technologies.

Keywords
urine treatment, agricultural application, membrane technology, nutrient recovery, micropollutants

INTRODUCTION

The separate collection of urine and its use as a fertilizer in agricultural applications can potentially be a more sustainable alternative to the present way of integrated discharge. However, urine can contain compounds such as viruses, pharmaceuticals and hormones which have an unpredictable effect on the environment. Micropollutants in waste water can include a wide range of compounds from personal care products to pesticides and pharmaceutical compounds (Jannsens *et al*., 1997). The environmental and ecotoxicological effects of these compounds remain largely unknown (Zuccato *et al.*, 2000; Sanderson *et al*., 2003), and it is therefore important to prevent their diffusion into the environment. Most of these compounds are only partly degraded in integrated biological waste water treatment plants (Daughton *et al*., 2001), while other compounds appear to be almost completely persistent (Clara *et al*., 2004). Source control and treatment of separate streams such as urine can provide more sustainable scenarios.

Electrodialysis (ED) processes have been described for a number of processes including the removal of salts from waste waters (Chang *et al*., 2000) and drinking water (Perry *et al*., 1977), as well as numerous other applications. In a laboratory set-up, we used ED for the separation and concentration of salts from urine (Pronk *et al.*, 2006a). The results showed that the major fraction of all ions could be transported into the concentrate compartment. Several micropollutants were spiked in order to monitor the removal of these compounds. Ethinylestradiol was removed completely during the whole operating period. Diclofenac and carbamazepine were initially retained, but

limited permeation (5-10%) occurred after longer operating times. Retentions of propranolol and ibuprofen were also high initially, but substantial breakthroughs occurred during extended operation. Considerable adsorption on the membranes was observed for all compounds (Pronk *et al.,* 2006a). For the removal of the micropollutants remaining in the product stream, ozonation was tested. Laboratory tests with urine confirmed the effective removal of micropollutants which was previously observed with waste water tertiary effluent as a feed (Huber et al., 2005). However, considerably higher ozone doses (1-2 g/L) were required for complete oxidation of spiked micropollutants, due to the high content of organic compounds in the urine matrix (Pronk et al., 2007). Based on the experiences above, it can be concluded that the combination of ozonation and electrodialysis is a suitable process for the removal of micropollutants and the concentration of salts from urine. The pilot experiments presented here were meant to gather information on process parameters and the stability of the pilot-scale treatment of urine with these processes. The experiments were carried out in close collaboration with the Amt für Industrielle Betriebe (AIB), which implemented a urine collection system in the central library of the Canton of Basel-Landschaft in Liestal (CH). It has been shown that untreated urine provides a good substrate for plant growth (Heinona-Tanski *et al*., 2005), but studies on the fertilizer efficiency of electrodialysis products have not been published. In the present study, standardized field tests were carried out with Maize in order to assess the agricultural suitability of the product from the process-combination of ED and ozonation.

MATERIALS AND METHODS

Urine

Urine was collected at the cantonal library in Liestal and stored in a tank with a volume of 2.0 m^3. The collected urine was transferred by truck to the pilot facility in Reinach (BL, Switzerland). In average, the urine contained about 2.9 g/L NH_4-N, 0.18 g/L PO_4-P, 1.6 g/L Na^+, 3.0 g/L Cl^-, 1.4 g/L K^+, 0.7 g/L SO_4^{2-}, and 3.6 g/L COD. The pH value was around 8.7 and the alkalinity around 200 mmole/L. The urine was obtained from the storage tank, and therefore completely hydrolyzed (contains no urea).

Analysis

Chloride, sulfate and phosphate, ammonia and urea were analyzed as described before (Pronk *et al.,* 2006a and 2006b). Analysis of micropollutants was carried out after solid-phase extraction. Solid-phase extracts were prepared as described by Escher *et al.* (2005). Pharmaceuticals and the hormones were measured with HPLC using a Chromcart HPLC column with 125/4 Nucleosil 100-5 C18 packing (125 mm x 4mm), and a CC 8/4 Nucleosil 100-5 C18 pre-column with UV and fluorescence detection as described in Pronk *et al.* (2006b).

Electrodialysis equipment

An electrodialysis stack from Mega a.s., Prague, Czech Republic was used with a membrane area of 16x60 cm per membrane sheet, 20 cell pairs, and a total effective membrane area of 3.6 m^2. The thickness of the membranes (dry) is 0.45 and 0.55 mm, their resistance less than 9 and 8 $\Omega.cm^2$, and their ion-exchange capacity is 2.2 and 1.9 mval/g (0.20 resp. 0.16 mval/cm^2) for the cation and anion-exchange membranes respectively.

Recirculation flow rates of diluate, concentrate and electrode rinse were set at 960 L/h. At the start of each electrodialysis test, the circuit of concentrate was filled with water (20 Liter), and the electrode rinse with Na_2SO_4 (0.1 M). In the continuous experiments, stored natural urine was added continuously to the diluate circuit; diluate was removed by an overflow, thus maintaining a constant volume in this circuit. No feed was applied to the concentrate compartment: the concentrate

overflow was generated by water transport through the membranes. All tests were carried with a total voltage of 36 V.

Ozonation equipment
The ozone generator was a G11 type generator obtained from Lenntech Water en Luchtbehandeling B.V., Delft, The Netherlands. It was operated with pressurized air and had a maximum production rate of 3.7 g/h. The ozone concentration was measured with a type Ozomat GM-6000-OEM ozone detector from Anseros GmbH, Tübingen, Germany. The gas flow rate was monitored with a magnetic suspended body gas flow meter (Gawaplast AG, Schaffhausen, CH). The ozonation columns were made of transparent PVC (fill height 1.07 m; inner diameter 10 cm). Ozone was supplied through a sintered stainless steel plate with a pore size of 14 μm. The plate was placed 7 cm above the bottom of the column, and so the effective height of the gas column was 1.0 m.

Microfiltration
Microfiltration was carried out in batch operation with cross flow of approx. 20 m^3/h. The hollow fiber membranes with inner diameter 1.5 mm were hydrophilic polyethersulfon with a cut-off of 0.2 μm. The module (type S-30 FSFC) had a total membrane surface area of 3.6 m^2 and was obtained from X-flow B.V., Enschede, The Netherlands.

Ecotoxicological characterization

Solid-Phase Extraction (SPE)
Solid-phase extracts were prepared from 10 mL of wastewater sample. Polypropylene cartridges (6 mL) with polytetrafluoroethylene frits (Supelco, Bellafonte, U.S.A.) were filled with 100 mg LiChrolut® EN and 250 mg LiChrolut® RP-C18 (Merck, VWR, Dietikon, Switzerland), and extractions were performed as described in (Escher et al., 2005).

Bioassays
The recombinant yeast estrogen screen (YES) was performed as described by Routledge and Sumpter (1996) with minor changes. Non specific toxicity was measured with the 30-min bioluminescence inhibition test using the marine bacterium *Vibrio fischeri.* The test *protocol* was based on the ISO Guideline 11348-3 International Standard Organization (ISO, 1998) but the test was adapted to a 96-well microtiter plate format. Validation studies showed that the results of different reference compounds (3,5-dichlorophenol, zinc sulfate etc.) agree perfectly between the standard guideline and the microtiter plate format (Escher *et al*., 2007). Data evaluation and calculation of removal efficiencies was performed as described in Escher *et al*., 2006.

Agricultural tests
The plant growth field tests were carried out in Kaisten, Switzerland (elevation 410 m). The soil can be characterized as a low-humic silt loem. The test crop was maize (“Amadeo”), which has a relatively high nitrogen demand. Comparative tests of different fertilizers were carried out on basis of the similar dose of available N (110 kg/ha) in four replicants. The fertilizer was applied in two charges of 55 kg/ha at June 16 and Juli 4. In order to prevent gaseous ammonia losses, the urine product was diluted by a factor 5.7 directly before application. The different water content of the fertilizers was compensated by application of appropriate amounts of water after fertilization. Also differences in phosphorus content were compensated by addition of appropriate amounts of mineral PK-Mg fertilizer.

RESULTS AND DISCUSSION

Prefiltration

The urine obtained from the storage tank was not clear, but turbidities were observed in the liquid and during time some precipitate was formed in the storage tank. In order to protect the ED membrane unit from suspended solids, the stored urine was filtrated through a microfiltration membrane (cut off 0.2 μm) before use. After extended storage (longer than 1 week) however again turbidities could be observed. Therefore, the stored urine was microfiltrated directly before treatment. Microscopic observation showed that these turbidities, which are formed after filtration, are mainly of biological origin (bacteria).

Electrodialysis

In view of the limited supply of urine from the cantonal library, the urine was treated batch-wise during the first phase (in the months November – December 2005). The conductivity of the diluate in these batch tests is shown in Fig. 1. At the start of the first batch, the concentrate compartment was filled with water. As shown in Fig. 1, this resulted in a slower rate of desalination, which can be explained by the low conductivity of the concentrate, which is clearly visible, especially at the start of this batch.

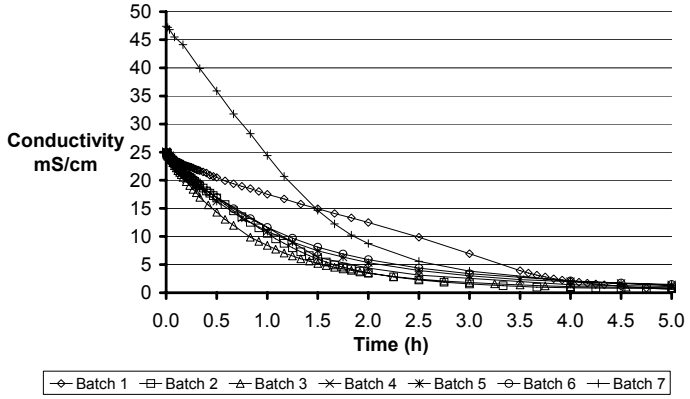

Figure 1: Conductivity of diluate during repetitive batch operation of electrodialysis

In batches 2-7 the desalination rate remains at a constant level which shows that the process is stable in this time frame (total 35 hours). In batch 7, the start concentrated urine was used as a feed, which explains the higher start level of conductivity. The maximum concentration factor (proportion between conductivity in concentrate and feed), reached in batch 7, amounted to 4.1.

Table 1: ED performance parameters during 2 phases of continuous operation.

Feed flow rate	40 L/h (11.1 L/m^2/h)	60 L/h (16.7 L/m^2/h)
concentration factor (-)	2.7	3.5
diluate product loss* (%)	7.0%	13.8%

* Diluate product loss is defined as: $\left(\frac{Q_{dil} \times Cond_{dil}}{Q_{conc} \times Cond_{conc} + Q_{dil} \times Cond_{dil}} \right)$, where Cond = conductivity (mS/cm) and Q = flow rate (L/h) and subscripts conc and dil refer to concentrate and diluate, respectively.

In the next phase, continuous ED tests were carried according to the process scheme as presented in Pronk *et al.*, 2006a. Different feed flow rates were applied in order to assess the influence on concentration factor and product yield. The first continuous test was carried out at a feed flow rate

of 40 L/d (11.1 L/m^2/h). The conductivity and flow rates of diluate and concentrate effluents are shown in Fig. 2. In order to accelerate the start-up, batch operation was performed during the first day. As shown in Fig. 2, a stable operation could be obtained during extended operation times (12 days). After a short phase of 50 L/d (13.9 L/m^2/h), the feed flow was adjusted at 60 L/d (16.7 L/m^2/h) which was continued during 11 days. In Table 1, the concentration factor and product loss in the diluate are summarized during the 2 periods of extended continuous operations. As discussed before (Pronk *et al*. 2006a), both concentration factor and product loss increase with increasing feed flow rate, due to the influence of flow rate on the transport of salt and water through the membranes. In both phases, stable operation was observed and salt transport rates remained constant during operation. From these results, it can be concluded that membrane fouling was not significant during operation times in the order of 1-2 weeks.

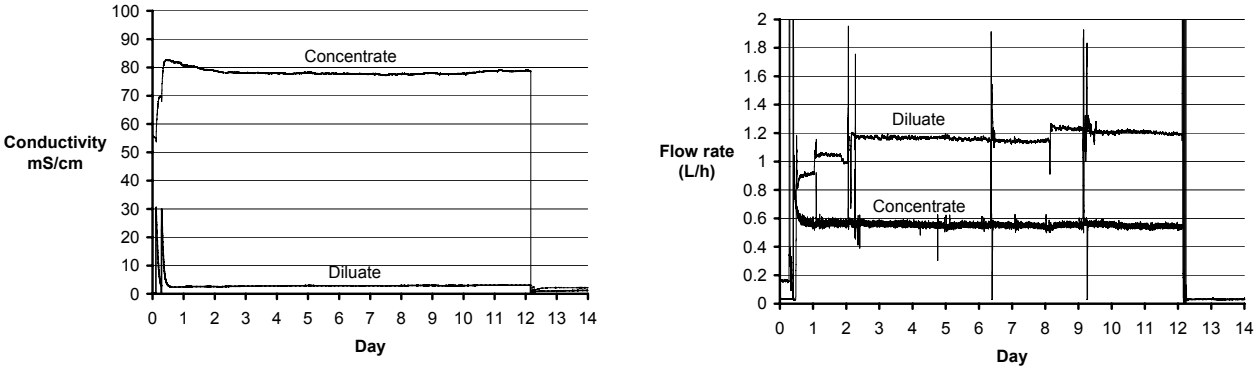

Figure 2: Conductivity (left) and flow rate (right) of concentrate and diluate during continuously operated electrodialysis (flow rate approx. 40 L/h)

In order to assess the membrane fouling after extended operation (stand time 195 days), standardized tests were performed before and after membrane cleaning. Cleaning was carried out after disassembly of the membrane stack. Successively, the membranes were soaked in a basic solution (1 hour in 2% NaOH) and an acidic solution (1 hour in 6% citric acid). The salt transport rate was measured before and after cleaning with 0.2 M NaCl in all compartments as shown in Fig. 3. The results show that the cleaning increased the salt transport rate by approx. 50%. It can therefore be concluded that some membrane fouling had occurred during this extended period of operation. Fouling effects within continuous operation of 1-2 weeks however are comparably small and could therefore not be observed within the time frame of these continuous tests.

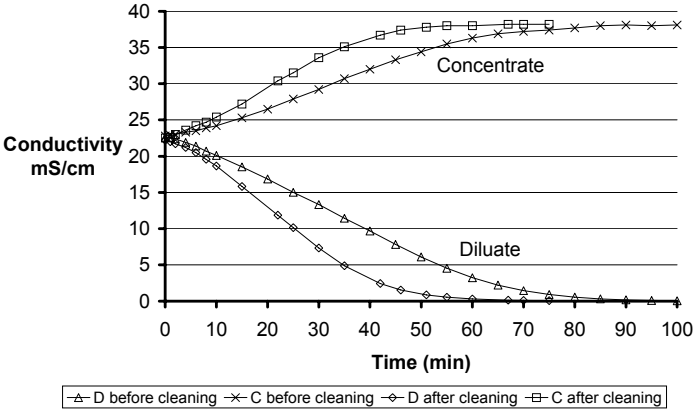

Figure 3: Conductivity *vs.* time during ED batch experiments with salt solution (0.2 M of NaCl) before and after membrane cleaning

Ozonation

The required ozone dose for complete removal of micropollutants was evaluated in previous laboratory experiments as described in Pronk *et al*. (2007). Absorbed ozone doses were adjusted to 2 – 2.5 g/L in the concentrate and 1.4 – 1.6 g/L in the diluate.

During operation of the ozonation columns some problems occurred with foam formation which led to overflowing of the columns at several points of time. A correlation existed between foaming potential and turbidity of the feed and furthermore, the foam formation and foam stability increased with time after the turbidity had formed. In view of the fact that the turbidity is mainly caused by bacteria (see 3.1), and the fact that bacterial EPS formation increases with time, it is assumed that the excessive foam formation is caused by EPS (extracellular polymeric substances). In a completely continuously operated process chain of MF, ED and ozonation, the residence times between the different stages are small enough to prevent growth and thus, the foam problems can be minimized.

Analyses

Estrogenicity (YES)

At different points of time during the operation of the pilot plant, samples taken from feed, diluate and concentrate were analyzed by the Yeast Estrogenic Screening method. The results show that the influent contains significant estrogenic activity (Table 2). The absolute level varies during the test period, which can be explained by the fact that the feed occurred from different periods of urine collection. Furthermore, it can be observed that a high removal of estrogenicity is obtained during the whole operation period. Compared to the results of ibuprofen, no substantial increase in permeation is observed during the operation period.

Table 2. Estrogenicity and standard error in feed, diluate and concentrate of the ED at different points of time. Removal efficiency is defined as: 1-($EEQ_{conc.}$/EEQ_{feed})

	Date	2005.11.22 (batch)	2006.04.04 (continuous)	2006.05.13 (continuous)
Feed	EEQ (ng/L)	879	588	595
	Std. error	255	60	90
Diluate	EEQ (ng/L)	899	584	436
	Std. error	180	170	191
Concentrate	EEQ (ng/L)	125	38	59
	Std. error	37	9	22
Removal efficiency (%)		86%	94%	90%

Non-specific toxicity (Bioluminescence inhibition test)

Table 3: Non-specific toxicity in feed, diluate and concentrate of the ED at different points of time. EC_{50} is dimensionless.

	Date	2005.11.22 (batch)	2006.04.04 (continuous)	2006.05.13 (continuous)
Feed	EC_{50}	0.30	0.24	0.15
Diluate	EC_{50}	0.31	0.23	0.09
Concentrate	EC_{50}	0.33	0.25	0.15

As shown in Table 3, the non-specific toxicity as measured by bioluminescence was approximately the same in feed, concentrate and diluate. An EC_{50} of 0.3 means that the sample needs to be diluted

by a factor 3.33 to exhibit 50% of effect in the bioassay. As shown before (Escher et al., 2005), the non-specific toxicity was rather determined by urine matrix components than by micropollutants. From our results it can be concluded that the matrix components responsible for this type of toxicity are equally distributed among the concentrate and diluate stream. Presumably, this is caused by a rapid diffusion through the membrane, which would imply that the respective compounds are non-charged and have a relatively small molecular weight.

Single compound analytics (HPLC)
Samples were taken from feed, concentrate and diluate (at 2006.05.13) and concentrated by SPE and HPLC analysis was carried out as described in § 2.2. All compounds except ibuprofen were below the detection limit. The concentrations of ibuprofen were: 105 µg/L in the feed, below detection limit (< 5 µg/L) in the concentrate and 50 µg/L in the diluate. From the laboratory experiments performed before, it was concluded that among the range of compounds spiked, ibuprofen has the highest saturation and permeation rate (Pronk *et al.,* 2006a). The laboratory experiments were carried out with spiked compounds at relatively high concentration (2063 µg/L). The results presented here indicate that at "naturally" occurring levels of micropollutants the permeation rate after extended operation is much lower. This can be explained by the fact that the permeation of ibuprofen occurs by a mechanism mainly based on adsorption: After saturation of the membrane, significant permeation occurs. If it is assumed that permeation is only dependent on the total exposure to a compound, the point of breakthrough can be calculated by comparison with experiments in which micropollutants were spiked. In the laboratory experiments described before (Pronk *et al.*, 2006a), the permeation amounted to 60% after exposure to 300 µmole of ibuprofen. In the pilot plant, the membrane area was 40 times higher, and therefore this amount of breakthrough is expected after exposure to 12000 µmole, which corresponds to 400 days of continuous operation with the concentration levels measured here. The micropollutants diclofenac, carbamazepin, propranolol were below the detection limit in the HPLC even after SPE. In view of these low concentration levels and the fact that ibuprofen is among the best permeating compounds, it can be assumed that the retention of ED for other micropollutants remains at a high level during periods much longer than 400 days.

Field crop growth tests
Field tests with maize under standardized conditions were carried out using the product of ED and subsequent ozonation (which was called "Urevit") produced in the months of March and April 2006. The measurements of plant height were carried out in the middle of the growth period (Juli, 19th). As shown in Fig. 4 (a), the crop height of the "Urevit" product is similar to that of the ammonium nitrate fertilizer and higher than other organic fertilizers tested.

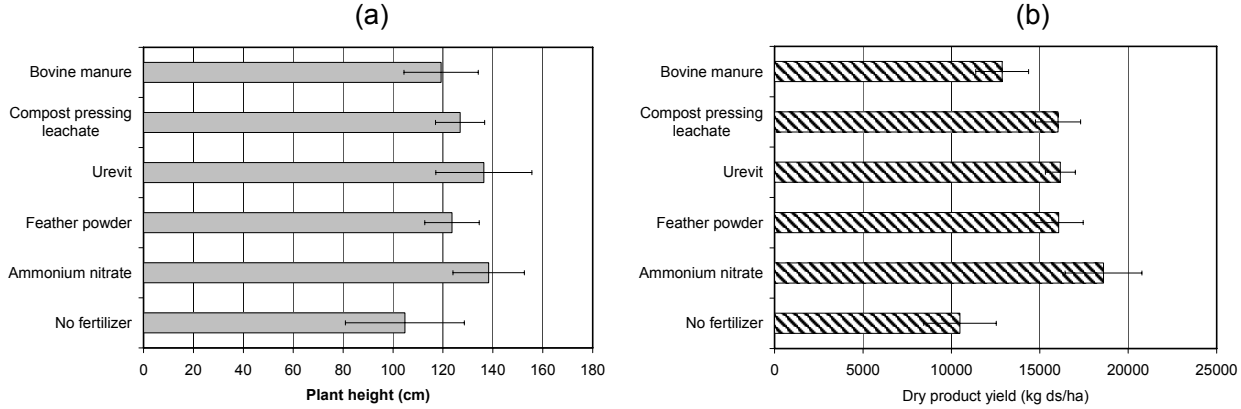

Figure 4: (a): Maize plant height as measured at Juli, 19th (left); (b): total plant yield at the moment of harvesting (Sept. 12th). ANOVA $p < 0.001$

The total plant yield as shown in Fig. 4(b) was measured at the moment of harvesting. “Urevit” showed a slightly decreased yield in comparison with ammonium nitrate (13% lower). The decreased yield can probably be explained by ammonia losses during the application of urine product on the field. This can be prevented by using specific distribution equipment such as for example slurry injection systems. It can be concluded that the urine product is suitable for application in agriculture. If the appropriate application technology is used, similar fertilizing efficiencies as ammonium nitrate can be expected.

CONCLUSIONS

A combination of electrodialysis and ozonation was operated with high performance stability during a test period of about one year. YES analysis showed that the estrogenic activity was removed to a high extent in the electrodialysis process. The non-specific toxicity as measured by bioluminescence inhibition was distributed evenly among diluate and concentrate. The removal of ibuprofen in the ED remained at a high level during the period of experimentation. On basis on laboratory results and the concentration levels measured here, it was calculated that significant permeation (60%) of ibuprofen would occur after a continuous operation time of 400 days. Other micropollutants (diclofenac, carbamazepin, propranolol) in the product were below the detection limit, and based on similar calculations no significant breakthrough is expected for these compounds. Standardized plant growth tests in the field showed that the product derived from the process presented here is an effective fertilizer.

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