Wouter Pronk, biotechnology process engineer, head of the Membrane Technology group in the Urban Water Management Department

Urine Treatment: from Laboratory to Practice

The combination of electrodialysis and ozonation is a possible method for recovering valuable nutrients from urine in a concentrated form. At the same time, hazardous substances can be removed, yielding a perfectly acceptable fertilizer. The processes developed at Eawag are currently being tested at a pilot plant in Canton Basel-Landschaft.

The high nutrient content of urine makes it an obvious candidate for use in fertilizer production. However, it is necessary to ensure that the pharmaceutical residues and hormones which are also excreted in urine are first separated from the nutrient salts. In order to reduce the transport and storage volume of urine and urine-based fertilizer, the salts should also be recovered in a highly concentrated form.

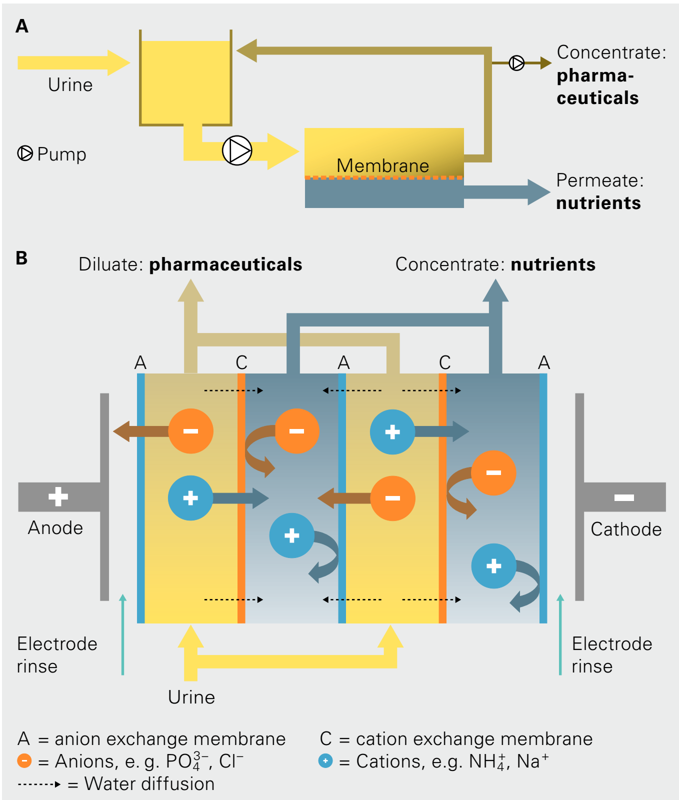
With these goals in mind, researchers at Eawag studied a series of methods in the laboratory, including complexation, precipitation, ozonation and various membrane processes such as nanofiltration and electrodialysis. For the pilot project to produce fertilizer from urine, a two-stage method was ultimately selected, consisting of electrodialysis and ozonation.

Nanofiltration: Separation of Substances on a Molecular Scale. In the process known as nanofiltration, liquids are forced under high pressure (approx. 10–30 bar) through a membrane with a pore diameter on the order of nanometres (Fig. 1A). In principle, the substances dissolved in the liquid can thus be separated on the basis of molecular size, but their electric charge also plays an important role. We wished to establish whether nanofiltration could also be applied to urine, so that the nutrients contained in this solution – nitrogen and phosphorus – could be separated from the undesirable substances.

In laboratory experiments, we tested three different membranes designed to retain substances with a molecular weight greater than about 150–400 daltons (Da) [1]. Urine was spiked with a representative mixture of pharmaceuticals, including the beta-blocker propranolol, the anti-inflammatory agents diclofenac and ibuprofen, and the active ingredient of oral contraceptives ethinyl estradiol. The molecular weights of these compounds are between 180 and 300 Da, while the molecular weights of the nutrients are much lower. In fresh urine, nitrogen occurs predominantly in the form of urea (60 Da), with ammonium (NH_4^+, 18 Da) accounting for only a small fraction (approx. 16%); phosphorus occurs exclusively as phosphate (PO_4^{3-}, 95 Da). In stored urine, however, nitrogen mainly occurs in the form of ammonium. This is produced by bacterial hydrolysis, which converts urea to ammonium and carbon dioxide. As a result, the pH of urine also increases during storage, from 6 to 9. In our nanofiltration experiments, fresh, non-hydrolysed urine was used.

Recovery of Urea from Urine by Nanofiltration. In a comparison of various types of membrane, the NF270 membrane (manufactured by Dow Inc.) showed the best performance. But even

Fig. 1: Schematic view of nanofiltration (A) and electrodialysis with two cell pairs (B). In practice, membrane stacks comprising up to 100 cell pairs are used in electrodialysis.



Pilot plant for the production of a liquid fertilizer from urine. The urine used comes from the Basel-Landschaft Cantonal Library in Liestal, a new building fitted exclusively with NoMix toilets.

with this membrane not all pollutants were retained (Fig. 2A). In addition, the membrane was not permeable to phosphate, and barely half of the ammonium was able to pass through (Fig. 2B). Satisfactory results were only obtained in the case of urea. Phosphate, for example, is retained as a result of electrostatic repulsion between the membrane and solute. In contrast, the uncharged urea molecules can permeate the membrane. In view of this complex situation, nanofiltration is of limited suitability if nutrients are to be fully recovered.

Electrodialysis: Movement of Substances in an Electric Field. A more suitable process is electrodialysis (Fig. 1B): arranged alternately between a pair of electrodes (an anode and a cathode) are positively and negatively charged membranes, which in principle permit the passage of charged molecules with a weight of up to around 200 Da. Positively charged molecules, known as cations, are attracted towards the cathode, while negatively charged molecules, the anions, migrate towards the anode. However, as the cations are unable to pass through the positively charged (anion-exchange) membranes, their concentration increases in the adjacent compartment. The same applies – in the opposite direction – for the anions. Substances are thus removed in the diluate compartments and enriched in the concentrate compartments. Urine is fed into the diluate compartments. Water diffuses from the urine through the membranes into the concentrate compartments, determining the concentrate flow rate.

Almost Complete Separation of Nutrients and Micropollutants by Electrodialysis. With electrodialysis, the aim is that the low-molecular-weight nutrients should migrate into the

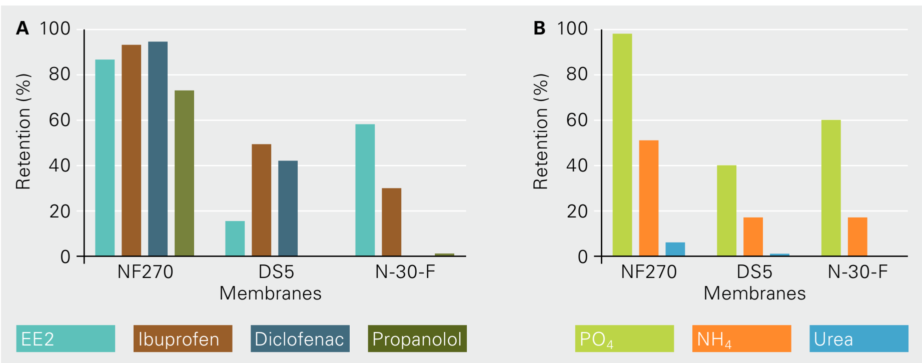


Fig. 2: Retention of pharmaceuticals (A) and nutrients (B) with nanofiltration, using three different types of membrane (EE2 = ethinyl estradiol).

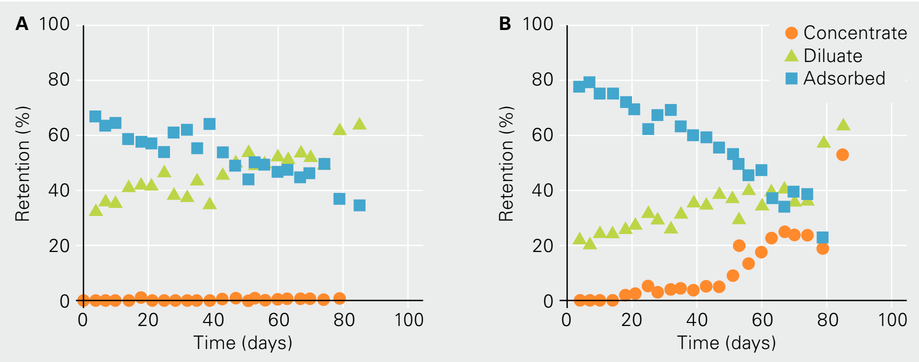


Fig. 3: Mass balances of ethinyl estradiol (A) and propranolol (B) in electrodialysis.

concentrate, while the higher-molecular-weight pharmaceuticals and hormones remain in the diluate. Some of the micropollutants, such as ethinyl estradiol (Fig. 3A) and diclofenac, are effectively retained over an extended period. For propranolol, however, the membrane only represents a barrier at the beginning of electrodialysis, and diffusion occurs with prolonged operating times (Fig. 3B). Among the nutrients, ammonium and phosphate, as expected, are fully transported into the concentrate [2], where they are enriched by a factor of 3–4. With this method, urea cannot be completely recovered: as the molecule does not carry a charge, only a relatively small fraction diffuses into the concentrate. In general, however, the urine to be treated has been stored for some time and no longer contains urea.

Elimination of Remaining Micropollutants by Ozonation. Since it was not possible to separate all of the unwanted substances from the nutrients by electrodialysis, we tested an additional treatment step. From earlier Eawag experiments involving purified wastewater, it was known that pharmaceuticals can be largely destroyed by oxidation with ozone. Our supplementary laboratory tests indicated that this is also possible in the case of urine or the products of electrodialysis. The dose required – 1–2 g of ozone per litre of urine – is, however, higher than for other applications [3].

Pilot Experiments in Canton Basel-Landschaft. In a project initiated by the utilities agency of Canton Basel-Landschaft (AIB), NoMix toilets and a urine collection system were installed at the newly built Basel-Landschaft Cantonal Library in Liestal. Together with the AIB, Eawag decided that the urine collected here should be treated in a pilot plant, combining the processes of electrodialysis and ozonation. Initially, we tested two different combinations of these methods: ozonation of untreated urine prior to electrodialysis, and ozonation of the concentrate and diluate following electrodialysis. It was shown that, overall, ozone and energy requirements were lower with subsequent treatment than with prior treatment. Since surface-active substances released when untreated urine is stored may lead to foaming during ozonation, an additional step is required: the untreated urine is prefiltered using a microfiltration membrane. Treatment at the pilot plant thus now comprises microfiltration, electrodialysis and subsequent ozonation of the two product streams. This combination of urine treatment processes has proved effective: the plant has experienced more than a year of stable operation.

The liquid fertilizer yielded by processing at the pilot plant has been named “Urevit”. Details of the composition of this product, its effectiveness as a fertilizer and the fertilizer approval procedure are to be found in the article by Markus Boller on p. 17.

A Milestone for NoMix Technology. The development of a feasible method for the production of a urine-based fertilizer is a milestone in the implementation of the NoMix concept. Among the public, the motivation to install and continue using urine-diverting toilets has been shown to be increased if realistic options for recycling urine can be demonstrated. Although definitive regulatory approval for the liquid fertilizer produced using our method is still outstanding, we are highly confident that it will be granted.

The pilot project at the Cantonal Library in Liestal, including the urine treatment plant, is supported by the ETH Domain Novatlantis sustainability programme. ○○○

[1] Pronk W., Palmquist H., Biebow M., Boller M. (2006): Nanofiltration for the separation of pharmaceuticals from nutrients in source-separated urine. Water Research *40*, 1405–1412.

[2] Pronk W., Biebow M., Boller M. (2006): Electrodialysisfor recovering salts from a urine solution containing micropollutants. Environmental Science & Technology, *40*, 2414–2420.

[3] Pronk W., Dodd M.C., Zuleeg S., Escher B.I., von Gunten U. (in preparation): Ozonation of micropollutants in source-separated urine: Feasibility and process modeling.