

# Exemplary Treatment Processes For Yellow Water - Nutrients and Pharmaceutical Residues

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**Keywords:** treatment of yellow water, nutrient recovery, elimination of pharmaceutical residues

## Introduction

In the last years more and more problematic substances such as pharmaceutical residues (PhaR) were detected in surface, ground, and drinking waters (Daughton and Ternes (1999)). The main reason is the low ability of today's conventional wastewater treatment to work as a barrier for PhaR (Niederste-Hollenberg (2003)). PhaR mainly are released via the urine fraction, therefore implementation of alternative wastewater treatment like source separation systems are an option to reach systematic cleaning effects (Larsen and Lienert (2004), Niederste-Hollenberg (2003)). Beside PhaR, large amounts of nutrients such as nitrogen, phosphorus, and potassium are in human urine (Otterpohl (2001)). Their recovery to close the nutrient cycle can be realized through usage of urine (also called yellow water) as anthropogenic plant fertilizer. This becomes more and more interesting, since the world demand in fertilizer will increase in the coming years due to economical growth, and even more important due to the population increase and thus a decrease of the available arable land per person. Before the use of these fertiliser products can be recommended in large scale the elimination of PhaR during treatment needs to be investigated (Larsen and Lienert (2004), Niederste-Hollenberg (2003)).

## Material and methods

The most promising processes for resource recovery from separately collected urine are:

- evaporation for volume reduction and content concentration
- following nutrient extraction in form of crystallization, and
- drying of the residues
- stripping of ammonia from yellow water, and
- struvit precipitation.

The effect of these processes on the reduction on PhaR is currently investigated at TUHH. Additional processes, such as UVC-radiation and ozonization will be used for further elimination of micropollutants.

For volume reduction a small evaporation unit (KMU Umweltschutz GMBH) with an evaporation rate of up to 4 l/h at 70 °C and a pressure of 300 mbar is used. This size could be used for processing yellow water of approx. 80 people.

For nitrogen extraction a semi-technical plant is used. To achieve representative values it was designed to process substrate from up to 800 people if operated constantly.

## Operation and evaluation of plants

The evaporation plant is operated in batch processes. To reduce nitrogen losses into the distillate the substrate is acidified prior evaporation respectively pretreated by steam stripping. A silicon based defoamer is used to prevent excessive foaming of the substrate during the evaporation process.

The semi-technical steam-stripping unit is operated to optimize regarding maximum ammonia extraction, thus the unit was partially operated with manual control of the steam volume. Experiments were conducted on untreated yellow water. The residence time inside of the reactor was about 15 min., the temperature slightly above 100°C. To prevent excessive foam production within the steam stripping reactor a defoamer was used. Samples of the substrates, condensed steam, and ammonia depleted substrate of the lab-scale steam stripping unit were prepared for evaluation of PhaR.

## Results and Discussion

Regarding nutrient recovery from yellow water following results were received so far:

With the evaporation a 30x concentration is reached. This was proved by volumetric balance, dry residues, and conductivity. P and K remained in the concentrate but did not precipitate. N-losses into the distillate can be controlled by acidification, or better by N-extraction via steam-stripping prior to evaporation.

In the steam stripping unit with manual steam adjustment NH<sub>3</sub> concentrations in the condensate of more than 100 g/l are obtained, which is equivalent to a NH<sub>3</sub>-solution of more than 12%. Ammonia

concentrations in the depleted substrate were between 1 and 4% of the initial ones. The pH dropped from nearly pH 9 to pH 5.6, which can be used as a simple control for extraction efficiency of ammonia. P and K remained in the depleted substrate. So far no blockings were observed within the unit.

Regarding elimination of PhaR from yellow water the results were as follows:

Of 15 parameters, which are commonly referred to in literature only seven were detected in the initial substrates. This is due to the fact that the users of the public urinal represent only a part of the population.

The process steam stripping with overheated steam showed following results.

$\beta$ -Sitosterol and Pentoxifyllin were eliminated completely. Carbamazepine was obviously not effected; instead, it is possible, that a reforming of Carbamazepine breakdown products occurred. The condensate was nearly free of PhaR, only traces of Ibuprofen were found. Since P-balance did not show substrate overflow into the condensate, and no other PhaR could be detected in the condensate traces of Ibuprofen were obviously stripped out of the substrate.

**Table 1:** Mean values of pharmaceuticals in urine from a public waterless urinal

Substance detected	Amount in [ $\mu\text{g/l}$ ]
Bezafibrate	202
Carbamazepine	22.7
Diclofenac	26.5
Ibuprofen	411
Pentoxifylline	8.3
Phenacetin	23.3
$\beta$ -Sitosterol	30,8

**Table 2:** Detected conc. (DC) regarding initial concentration (IC) of PhaR by steam stripping

DC / IC	$\beta$ -Sitosterol	Bezafibrat	Carbamazepin	Diclofenac	Ibuprofen
Depleted substrate	0%	81%	111%	79%	81%
Condensate	0%	0%	0%	0%	0.4%

Effect of vacuum evaporation (30h:3.5x and 4d 6h:12x) on pharmaceutical residues:

Again  $\beta$ -Sitosterol and in this case Phenacetin were not detected in the concentrates, therefore obviously removed by the thermal treatment. With ongoing evaporation nearly all PhaR were reduced drastically. After 4d 6h all, except Carbamazepine, were reduced by more than 95%. Significant traces of Carbamazepine could be found in the distillate after 30h. Also, more than 50% of the initial concentration of Ibuprofen was found in the distillate after 4d 6h.

**Table 3:** Detected conc. (DC) regarding initial concentration (IC) of PhaR by evaporation

DC / IC	$\beta$ -Sitosterol	Bezafibrat	Carbamazepin	Diclofenac	Ibuprofen
3.5x Conc. after 30h	0%	61%	119%	28%	19%
Dist. after 30h	0%	0%	12%	0%	40%
12x Conc. after 4d 6h	0%	3%	55%	3%	1%
Dist. after 4d 6h	0%	0%	0%	0%	55%

Although most substances are not easily effected by thermal influences, sufficient time and temperatures at boiling point will remove most PhaR.

Most PhaR could be removed from the matrix of urine by high doses (up to 2.8kWh/l) of UVC-light. Also by the treatment with dosages of 1.6g ozone/l all PhaR could be removed below detection limit.

**Table 4:** Detected conc. (DC) regarding initial concentration (IC) of PhaR by ozonization

DC / IC	$\beta$ -Sitosterol	Bezafibrat	Carbamazepin	Diclofenac	Ibuprofen
After treatment with 1.0 g $\text{O}_3/\text{l}$	99%	32%	0%	0%	37%
After treatment with 1.6 g $\text{O}_3/\text{l}$	0%	10%	0%	0%	13%

UVC-radiation and even more ozonization of N-depleted yellow water showed a higher reduction of PhaR from the matrix of urine. While in not pretreated yellow water  $\beta$ -Sitosterol was reduced by 20% after ozonization with 0.7g $\text{O}_3/\text{l}$  in the N-depleted substrate more than 90% were removed. The reduction of Carbamazepine was increased from 40% to more than 80%. Bezafibrate and Diclofenac

also showed a significant increase in reduction. Only the reduction of Ibuprofen was not higher after steam stripping.

**Table 5:** Detected conc. (DC) regarding initial concentration (IC) of PhaR in yellow water compared to N-depleted yellow water

DC / IC		$\beta$ -Sitosterol	Bezafibrat	Carbamazepin	Diclofenac	Ibuprofen
Yellow water	0.6 g O <sub>3</sub> /l	81%	42%	60%	9%	30%
N-depleted yellow water	0.7 g O <sub>3</sub> /l	8%	25%	18%	4%	29%

The efficiency of ozonization could be increase by acidification of the substrate (for pH-reduction from pH 9 to pH 4: 17ml HPO<sub>3</sub>/l substrate resp. 2.5 ml HPO<sub>3</sub>/l N-depl. substrate). The acidification itself had some impact on some PhaR.  $\beta$ -Sitosterol was effected the most (reduction of more than 40% and in the N-depledet substrate more than 90%).

Ozoneconsumption over time was less in the acidified yellow water, but PhaR reduction was depending more on ozoneconsumption than on time. In both acidified substrates, but even more in the N-depleted acidified substrate the efficiency of PhaR-reduction was slightly increased by combination of acidification and ozonization.

**Table 6:** Detected conc. (DC) regarding initial concentration (IC) of PhaR in yellow water and N-depleted yellow water at pH 8.9 and pH 4

DC / IC			$\beta$ -Sitosterol	Bezafibrat	Carbamazepin	Diclofenac	Ibuprofen
Yellow water	pH 8.9	1.0 g O <sub>3</sub> /l	99%	32%	0%	0%	47%
	pH 4	0.9 g O <sub>3</sub> /l	0%	23%	39%	0%	59%
N-depleted yellow water	pH 6.7	1.4 g O <sub>3</sub> /l	32%	52%	46%	0%	66%
	pH 4	1.3 g O <sub>3</sub> /l	0%	23%	38%	0%	55%

## Conclusion

This research shows that marketable products can be extracted from yellow water, and that pharmaceutical residues can be detached by separation techniques. For an improvement of this investigation also urine of a more heterogeneous population has to be taken into account and treated in the semi-technical plant and with additional processes, such as ozonation.

First steps to achieve the aim to identify techniques for eliminating micropollutants from wastewater are shown and will be followed further. The results herein will have a major influence for reaching the aim "achievement of a safe fertilizer for agriculture" to close the loop for nutrients.

## Acknowledgement

The financial support to the study, a research project of Kompetenzzentrum Wasser Berlin, is provided by Veolia Water and Berliner Wasserbetriebe. Furhermore is it supported by the LIFE financial instrument of the European Commission (Duration: 1 January 2003 – 31 December 2006, LIFE03 ENV/D/000025).

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