ELIMINATION POTENTIAL OF HAZARDOUS SUBSTANCES IN MUNICIPAL WASTEWATER TREATMENT PLANTS

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Abstract. *Having in view the requirements of the EU Water Framework Directive it is necessary to plan future measures for water protection, taking into account the origin and the reduction potential for the hazardous substances of concern. As part of the investigations, elimination tests according to DIN EN ISO 11733 were conducted. A special focus was directed to simulate conditions in the laboratory, reflecting the fate of hazardous substances during the full scale wastewater treatment. The focus of the investigation was put on industrial substances, hormone active substances, pharmaceuticals, volatile halogenated hydrocarbons, cyanides, and organotin substances.*

Key words: *activated sludge process, priority pollutants, elimination*

Introduction

Saxony, one of the new federal states in Germany, has done investigations for the implementation of the EU Water Framework Directive (WFD) on river basin scale. Hazardous substances determining the implementation of the Saxon River Pollution Mitigation Regulation (SächsGewVVO) and the Saxon WFD Regulation (SächsWRRLVO) which were detected in the outflow of Saxon municipal sewage plants, potentially affect the water quality. In order to plan future water protection measures on river basin scale, the knowledge of the origin and the potential for the reduction of the concentrations of the hazardous substances is necessary. Therefore the following focal points were examined:

- Study of the origin and the elimination of those hazardous substances,
- Development of a method for the experimental investigation of the elimination rate for hazardous substances as part of the biological wastewater treatment. The laboratory method was verified using the endocrine disruptor substance nonylphenol,
- Application of the developed method to determine the elimination rate for the following substance groups: industrial substances, hormone active substances, pharmaceuticals, volatile halogenated hydrocarbons, cyanides, and organotins.

The requirement of a good status of surface-, ground-, esturial and coastal waters, aspired by the EU Water Framework Directive (Directive 2000/60/EG)

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combines both good ecological and good chemical status. The first mentioned requirements base upon biological attributes supported by hydromorphological and physico-chemical parameters. The good chemical state is derived from the European Environmental Quality Standards (EQS) for waters. In the EC Directive 2008/105/EG about the environmental quality standard in the field of water politics, such EQS are defined in appendix I for substances with high priority and certain other harmful substances. In the EU Water Framework Directive "hazardous substances" are defined as substances or groups of substances, which have persistent, bioaccumulative and toxic properties and other substances or groups of substances which give rise to an equivalent level of concern. The European Commission defines "priority substances" as substances representing a significant risk for the aquatic environment. In Saxony for many hazardous substances quality standards were defined in the Saxon WFD Regulation.

In several studies for the implementation of the WFD in Saxony, hazardous substances were identified, occurring in the effluents of municipal sewage plants in Saxony. Wastewater emissions can originate from municipal and industrial point sources as well as from not exactly localizable diffuse sources, so called "urban areas". The substances listed in Table 1 were selected for the further investigations due to their occurrence in Saxon rivers.

Table 1: Groups of hazardous substances selected for the experiments.

Groups of hazardous substances	For the experiments selected substitutes
nonylphenols	4-nonylphenol, iso-nonylphenol
nonylphenolethoxylates	nonylphenolmonoethoxylate, nonylphenoldiethoxylate
hormone active substances	bisphenol A, estrone, 17β-estradiol, 17α-ethinylestradiol
phthalates	DEHP (Di-(2-ethylhexyl)-phthalate)
polybrominated diphenyl ethers	2,2′,4,4′,5-pentaBDE (pentabromodiphenyl ether)
phenoxy carboxylic acids	mecoprop, dichlorprop, bentazon, MCPA, diclofenac
volatile halogenated organic compounds	trichloromethane
cyanide	cyanide
organostannic compounds	tributyltin, dibutyltin, dioctyltin, tetrabutyltin, triphenyltin

Almost all sewage plants in Saxony belong to the German sewage plant categories 1 or 2 (Saxon State Ministry for Environment and Agriculture). Either the targeted carbon elimination occurred by a mechanical-biological treatment of the wastewater (category 1: conventional treatment) or the carbon removal is combined with a nitrogen- and/or phosphorus elimination (category 2: advanced wastewater treatment). Up to now, there is a lack of knowledge about many of the hazardous substances elimination, which can serve as a basis for measures to improve the performance of the purification procedure in the plants. Scope of the study was the understanding of the fate and behaviour of the hazardous substances in typical wastewater treatment plants, and if exists elimination potential in the treatment steps for municipal wastewater.

The elimination potential of the municipal wastewater treatment plants in terms of hazardous substances was investigated in several studies (Berg et al. 1997; Fahlenkamp et al. 2004; Knepper et al. 2004) having in view that those studies do not follow a standardised approach. For that reason, often the results are not comparable. Ratola et al. (2012) gave a small review on the occurrence of organic microcontaminants in the wastewater treatment process. Martin et al. (2012) focused on the occurrence of pharmaceutical compounds in wastewater and sludge from wastewater treatment plants. Several authors investigated the results of an advanced treatment technology for wastewater, having in the focus a membrane system (Hofmann et al 1993; Quintana et al. 2005; Dolar et al, 2012), a photocatalytic approach (Boreen et al, 2003; Doll & Frimmel, 2004), or the advanced UV irradiation technology (Köhler et al, 2012). Having in view the cost of further wastewater treatment steps, one question of the present investigation was to clarify if the elimination of certain hazardous substances in municipal waste water treatment plants is possible with the typical treatment technology.

Experimental details

As part of the experiments, elimination tests were conducted using an approach similar to activated sludge simulation test in laboratory sewage plant according to DIN EN ISO 11733 with regard to hazardous substances during the wastewater treatment. This standardised method is designed to determine the elimination of a certain substance by absorption, decomposition and evaporation. By comparing the inflow concentration with the outflow concentration of the test substance, the elimination rate of this substance can be determined. A continuously fed in- and outflowing synthetic wastewater serves as a carbon and energy source for the microorganisms. The developed method allows to estimate the percentage of the biological decomposition and to differentiate the elimination characteristics between a one-stage plant with biological basic cleaning and a two-stage plant with advanced treatment steps (coupled carbon and nitrogen removal process).

Methodological concept

The investigation program consisted of several tests with the simultaneous operation of a one-stage lab scale sewage plant for the simulation of the secondary treatment (carbon removal), and a the two-stage system to simulate the targeted nitrogen removal of the wastewater treatment with advanced treatment steps (Figure 1). The parameters of the used systems are enlisted in Table 2.

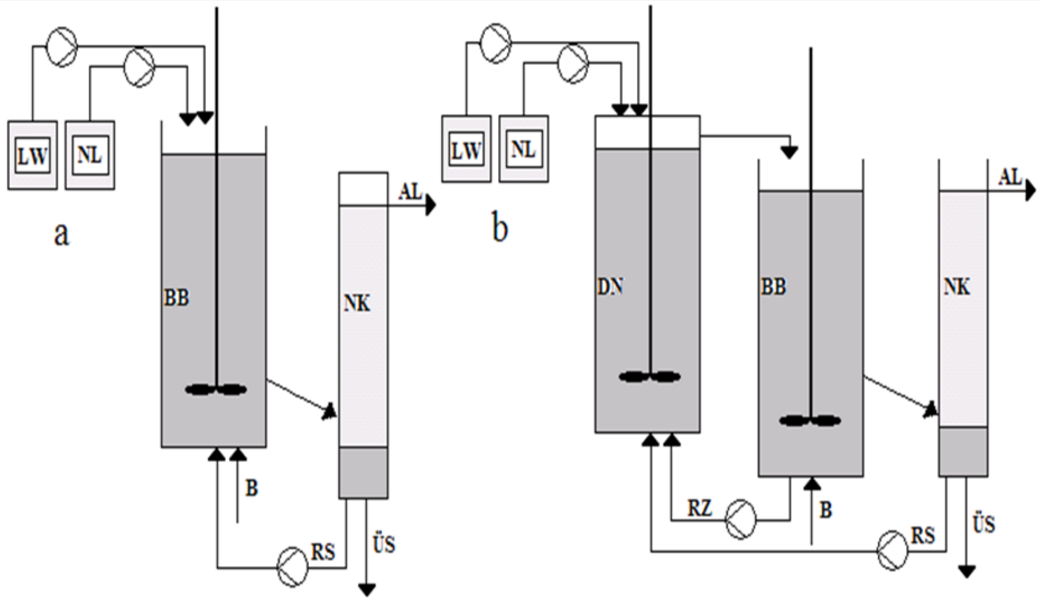
Table 2: Parameters of the lab scale wastewater treatment system.

Parameter	**One-stage system**	**Two-stage system**
configuration of the lab scale treatment system	Aeration vessel with final clarifier	Aeration vessel with dentrification and final clarifier
working volume denitrification (liter)	-	4,0
working volume stimulation (liter)	3,0	4,0
working volume final clarifier (liter)	1,8	2,3

	
One-stage lab scale sewage plant for the simulation of the secondary treatment (carbon-removal only)	Two-stage system for simulation of advanced wastewater treatment (coupled N- and C-removal)

Fig. 1: Overview on the lab scale sewage plants (lab scale treatment plants KLD 4N/SR, producer Behr Labortechnik).

The principal process of the wastewater treatment follows the scheme illustrated in Figure 2. The tested substance was added into the inflow in defined concentrations. In the one-stage lab scale plant, the influent containing the test compound is fed directly into the stirred and aerated vessel undergoing an aerobic treatment. In the clarifier the sludge and the treated wastewater were separated and the wastewater left the reactor through the outflow. The settled sludge of the final clarifier was recirculated periodically into the aeration stage.



a) one step sewage plant b) two steps sewage plant
LW – potable water NL – nutrition and analyte solution BB - aeration tank (nitrification) DN – denitrification NK – post clarifier (sedimentation) AL – discharge B - ventilation RS – return sludge RZ – recirculation ÜS – excess sludge

Fig. 2: Schematic diagram of the lab scale sewage plants.

In the two-stage denitrification plant the wastewater flows in the denitrification stage. It is mixed with the activated sludge by stirring without additional aeration. The sludge suspension flows by overflow from the denitrification to the aeration stage. Here an aerobic treatment is achieved by intensive stirring and aeration. In the final clarifier the sludge and the treated wastewater were separated. The latter left the sewage plant via the outflow. The settled sludge of the final clarifier as well as the sludge in the aeration vessel are recirculated internally and led back to the denitrification vessel.

Several physical and biological processes are involved in the fate and elimination of hazardous substances (Figure 3). The hazardous substances, supplied to the sewage plant (input) can be eliminated by biological decomposition or biotransformation. A prerequisite for this is that the principal biodegradability of the substance is assured. Besides, the sorption processes can contribute to a segregation and enrichment of the substances on the sludge-matrix.

By the removal of the excess sludge, the adsorbed target substance is eliminated in this way. The percentage of the substance, which is neither decomposed nor adsorbed, leaves the system via the outflow as not eliminated fraction (output).

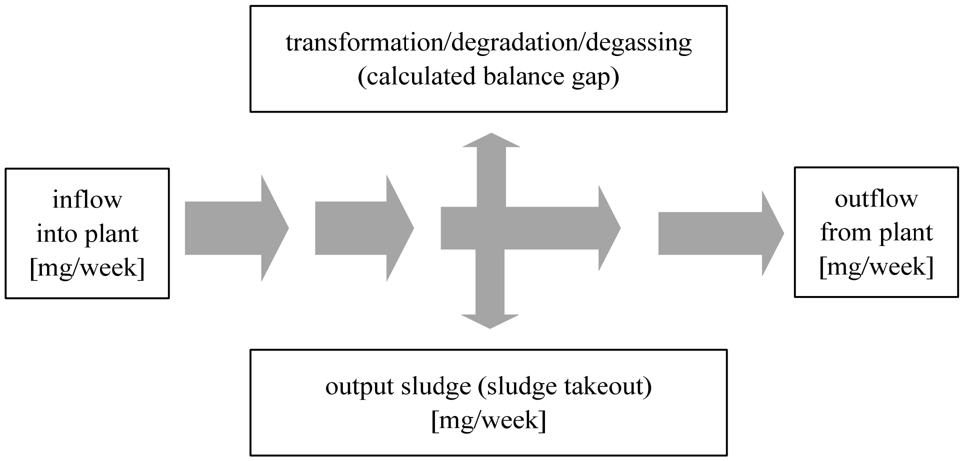


Fig. 3: Simplified illustration of the balance flows of a hazardous substance in the lab scale sewage plant.

The calculation of the load was carried out on a weekly basis and comprised the mean weekly volume flow rate, the weekly sludge output and the concentration of the target substance in the in- and outflow. The gap in the balance was interpreted as elimination. The elimination includes the biological decomposition as well as physical elimination processes (evaporation). The duration of the assessment period must be sufficiently long to ensure that the wastewater purification process is not significantly influenced by the hazardous substances and to gain a sufficient number of weekly composite samples.

Process parameters

As fundamental process factors, the hydraulic residence time and the sludge retention time of the construction were regulated (Kreuzinger et al. 2003). Both parameters are significantly different between sewage plants with mechanical-biological and plants with advanced treatment steps (Table 3). The sludge retention time was adjusted to values < 8 days. Under these conditions carbon removal is achievable, but not a targeted nitrogen elimination. In the two-stage plant a nitrogen elimination is achieved by nitrification/ denitrification. Therefore the hydraulic residence times of the wastewater were prolonged to 14 h and the total sludge retention time was set to 20 days. These conditions enable slow growing nitrifiers to sustain in steady state equilibrium and to form a stable population. Return sludge of the municipal sewage plant Jena-Zwätzen was used as seed sludge for both plants. Aliquots of methanolic stock solutions, containing a defined mixture of the hazardous substances, were added to the synthetic wastewater.

Table 3: Process parameters of the experimental plants.

Parameter	Unit	One-stage plant	Two-stage plant
Mean hydraulic residence time	hours	6	14
Sludge retention time (total)	days	8	20
Ratio inflow : recirculation (final clarifier vessel)	%	225	240
Ratio inflow : recirculation (from aeration vessel to denitrification)	%	-	240
Activated sludge concentration	g dry weight/l	3-5	3-5
O_2-concentration in the stimulation vessel	mg/l	2-4	2-4
O_2-concentration in the denitrification vessel	mg/l	-	< 0,3
pH		7,5 ± 0,5	7,5 ± 0,5
Temperature	°C	20-25	20-25

The synthetic wastewaters consisted of defined substrates. The COD-nominal value of the synthetic wastewater was about 300 mg O_2/l. This corresponds to a DOC of about 130 mg C/l. Via two parallel operating peristaltic pumps, the nutrient solution concentrate and supply water were fed separately in defined flow rates to the reactors yielding after mixing the synthetic wastewater (Table 4).

Table 4: Composition of the synthetic wastewater (according to DIN 38412 L26).

Parameter	Concentration [mg/l]
Pepton	160
Meat extract	110
Urea	30
Dipotassium hydrogen phosphate	28
Sodium chloride	7
Calcium chloride-dihydrate	4
Magnesium sulfate-heptahydrate	2
Sodium hydrogen carbonate	196

The sampling procedure was designed to cover working day, three-day and weekly sampling. Concentrations of the hazardous substances in the inflow and outflow of the reactors were determined with a weekly frequency. The determined parameters and the applied methods are summarised in Table 5. To gain the solid samples, the sludge suspensions were taken from the aeration vessel every working day and unified to weekly composite samples. In the two-stage plant samples were taken from the stimulation vessel and the denitrification vessel.

Table 5: Sampling frequency of the chemical-analytical parameters

Parameter	Unit	Frequency	Methode
Inflow rate	ml/min	daily	determination of the flow rate per minute
Outflow rate	l/d	daily	determination of the outflow volume per day
Temperature	°C	daily	DIN 38 404 (C4)
pH		daily	DIN 38 404 (C5) 1984-01
Dissolved oxygen	mg/l	daily	DIN EN 25814 (G22) 1992-11
Dry matter	g/l	2 x per week	DIN 38409 (H2) 1987-03
Sludge volume index	ml/g	3 x per week	DEV S 10
COD	mg O_2/l	wcw	DIN 38 409 (H41) 1980-12
DOC	mg/l	wcw	DIN EN 1484 (H3) 1997-08
Ammonium nitrogen (NH_4-N)	mg/l	wcw	DIN EN ISO 11 732 (E23) 1997-09
Nitrate nitrogen (NO_3-N)	mg/l	wcw	DIN EN ISO 10 304-1 (D19) 1995-03
Nitrite nitrogen (NO_2-N)	mg/l	wcw	DIN EN 26 777 (D10) 1993-04
Kjeldahl-nitrogen (TKN)	mg/l	as required	DIN EN 25 663 (H11)

wcs - weekly composite sample

The tested hazardous substances are in very low concentrations in the wastewater (µg/l to ng/l-range). Therefore, the elimination of these substances must be quantified in the water and the sludge by a very sensitive substance-specific analysis, and specific requirements on the performance of the analysis are necessary (table 6).

Table 6: Analytical methods and detection limits for the hazardous substances in water and sludge samples and nominal concentrations of the substances in the inflow of the lab scale sewage plants.

Substance	Analytical method	detection limit water (µg/l)	detection limit sludge (mg/kg)	Nominal Inflow-concentration (µg/l)
4-Nonylphenol, iso-Nonylphenol	according to ISO/CD 18857	1	1	100
Nonylphenolethoxylate (Mono-, Di-)	according to ISO/CD 18857	50	10	1.000
Diethylhexylphthalate (DEHP)	after extraction analysis of the DEHP by GC/MS	1	5	500
Bisphenol A	Enriched with LiChrolut EN by solid phase extraction and eluted with methanol/ethyl acetate; after derivatisation GC/MS quantified	0,1	0,1	50
Estrone, 17β-Estradiol, 17α-Ethinylestradiol	solid phase extraction enriched with LiChrolut EN and eluted with methanol/ethyl acetate; after derivatisation determination of the substances by LC/MS	0,1	1	10
Pentabromodiphenyl ether	DEV S 20 or DIN 38414-20	0,1	0,1	50
Mecoprop, Dichlorprop, Bentazon, MCPA	DEV F 20 or DIN EN ISO 15913	0,1	0,01	20
Diclofenac	DEV F 20 bzw. DIN EN ISO 15913	0,1	0,01	10
Trichloromethane	DIN EN ISO 10 301 (F4)	1	0,1	500
Cyanide	DIN EN ISO 14403 (liquid phase); DIN ISO 11262 (solid phase)	2	0,1	100
Tributyltin, Dibutyltin, Dioctyltin, Tetrabutyltin, Triphenyltin	after extraction analysed by GC-MS. The procedure was carried out according to DIN ISO 23161	0,01	0,01	10

Results

Based on the developed methodology, the elimination characteristics for municipal sewage plants have been determined experimentally for several hazardous substances under defined conditions. Table 7 presents the laboratory determined elimination rates of the hazardous substances from the wastewater of the one-stage and two-stage lab scale wastewater treatment plants.

Table 7: Elimination rates of the hazardous substances from the wastewater of the one-level and the two-level laboratory activated sludge plant.

Groups of hazardous substances	Tested substances	Elimination rate (%) one-stage plant (aearation)	Elimination rate (%) two-stage plant (denitrification and stimulation)
Nonylphenols	4-Nonylphenol	**81**	**91**
	p-iso-Nonylphenol	**83**	**88**
Nonylphenolethoxylates	Nonylphenolmono- und diethoxylat	**96**	**99**
Hormone active substances	Estron	**94**	**91**
	17β-Estradiol	**62**	**78**
	17α-Ethinylestradiol	**68**	**71**
	Bisphenol A	**85**	**93**
Phthalates	DEHP	**90**	**97**
Brominated diphenylethers	2,2´,4,4´,5-PentaBDE	**n.m.**	**n.m.**
Phenoxy carboxylic acids	MCPA	**60**	**40**
	Bentazone	**19**	**35**
	Dichlorprop	**28**	**27**
	Mecoprop	**58**	**83**
	Diclofenac	**58**	**48**
Volatile halogenated organic compounds	Trichloromethane (Chloroform)	**95**	**97**
Cyanide	Cyanide	**63**	**100**
Organotins	Tetrabutyltin	**89**	**94**
	Dioctyltin	**84**	**96**
	Dibutyltin	**50**	**47**
	Tributyltin	**70**	**79**
	Triphenyltin	**62**	**69**

n.m. – not measurable

For all substances, except pentabromodiphenyl ether, the tests were successfully executed. For 2,2´,4,4´,5- pentabromodiphenyl ether no reliable elimination values could be determined during the test runs. The low water solubility and the high log Kow-value of this substance caused experimental difficulties. There were indications that the substance was not distributed homogenous in the inflow and probably heavily adsorbed on the surface of the equipment. A mass balance of the elimination of pentabromodiphenyl ether was not possible.

Conclusions

As result of the laboratory experiment can be concluded, that the elimination rates of hazardous substances in wastewater plants are very different. While selected pesticides are eliminated only in a small extent, high elimination rates up to 99 % were determined for nonylphenolethoxylate, phthalate and trichloromethane. It was ascertained that these substances are eliminated with a high efficiency in the one-stage plant as well as in the two-stage plant, whereas for other hazardous substances significant differences were determined. This concerns for example the pesticide mecoprop (the difference of the elimination rate between the one-stage and the two-stage treatment accounts for 25 percentage points), bentazone (16 percentage points) and cyanide, which could be eliminated only by the further treatment (the difference compared to the one-stage treatment accounts for 37 percentage points). For the following substances were determined elimination rates below the average: bentazone (<40 %), dichlorprop (< 30 %) and dibutyltin (<50 %). By classifying the hazardous substances relating to their potential for elimination, the majority of the substances are attached in the group with the highest elimination rate (>80 %): 4-nonylphenol, p-iso-nonylphenol, nonylphenol ethoxylate, DEHP, estrone, bisphenol A, trichloromethane, tetrabutyltin and dioctyltin. By classifying the hazardous substances relating to their potential for elimination, the majority of the substances are grouped together in the category with the highest elimination rate (>80 %): 4-nonylphenol, p-iso-nonylphenol, nonylphenol ethoxylate, DEHP, estrone, bisphenol A, trichloromethane, tetrabutyltin and dioctyltin.

The group of hazardous substances with a mean removal rate (60 % to 80 %) includes: 17β-estradiol, 17α-ethinylestradiol, MCPA, mecoprop, diclofenac, tributyltin and triphenyltin. The following hazardous substances had low elimination rates (<50 %): bentazone, dichlorprop and dibutyltin. The experiments show, that there is no provable significant difference between an one-stage biological treatment and a treatment with further treatment steps in terms of the elimination of the most hazardous substances. Excepted of this are selected pesticides such as mecoprop, bentazone and cyanide. Furthermore it should be noted that in general no complete elimination occurred. Despite the wastewater purification in sewage plants hazardous substances can enter the receiving water courses in concentrations above the EQS.

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