Removal of micropollutants from grey water

Combining biological and physical/chemical processes

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Abstract

Grey water consists of the discharges from kitchen sinks, showers, baths, washing machines and hand basins. The amount of grey water produced per person in The Netherlands is about 90 Ld^{-1}, accounting for up to 75 % of the wastewater volume produced by households, and over 90 % if vacuum toilets are installed. Grey water is relatively low in pollution and therefore, after appropriate treatment, has great potential for reuse in non-potable applications such as infiltration, irrigation, toilet flushing, laundry water, etc. The goal of this thesis was to develop a treatment concept for grey water to exploit its reuse potential. A special focus of this thesis was set on the study of organic micropollutants from personal care and household chemicals.

Grey water (from 32 houses in Sneek, The Netherlands) contains, on average, 724±150 mgL−1 of chemical oxygen demand (COD), 27±12 mgL^{-1} of total nitrogen, 7.2±4.2 mgL^{-1} of phosphorus and 41±12 mgL^{-1} of anionic surfactants. The high biodegradability of grey water (70±5 %) indicated the possibility of recovering COD as methane. Biological treatment of grey water was conducted in three systems, aerobic, anaerobic and combined anaerobic + aerobic, at a total hydraulic retention time (HRT) of 12-13 hours at 32 °C. A erobic treatment in a sequencing batch reactor resulted in COD removal of 90 %, which was significantly higher than 51 % removal by anaerobic treatment in an up-flow anaerobic sludge blanket (UASB) reactor. Grey water treatment in a combined anaerobic + aerobic system resulted in a COD removal efficiency of 89 %. The application of a UASB reactor for the pre-treatment of grey water yielded a small amount of energy. Therefore, the aerobic system was preferred for grey water treatment. Bioflocculation of grey water in a high loaded membrane bioreactor was tested as alternative to aerobic treatment. The concentrated grey water of this process can potentially increase the methane yield by 73 % within 'new sanitation' concepts.

Eighteen compounds of personal care products and household chemicals (UV-filters, fragrances, preservatives, biocides, surfactants) were measured in grey water at low $\mu\mathrm{gL}^{-1}$ levels. During biological treatment most of these compounds were partially removed. In general, the treatment in the aerobic system lead to the highest removal efficiencies of these compounds, where biodegradation and adsorption to sludge were the most likely removal mechanisms. However, the UV-filters PBSA and EHMC and the fragrance tonalide were poorly removed in the tested biological systems. Although reuse standards for these compounds do not exist, the posttreatment of aerobically treated effluent was recommended prior to reuse. Adsorption on activated carbon and ozonation were proven effective as posttreatment options for grey water.

Contents

CHAPTER 1

Grey water: treatment, reuse and concerns about micropollutants

Hernández Leal, L., Temmink, H., Zeeman, G and Buisman, C.J.N.

1.1 Introduction

Human kind has a large foot print on Earth. Overexplotation and misuse of resources has led to problems such as water scarcity and polluted water bodies, with severe consequences for human health and welfare. Almost half of the world's population faces water scarcity of some sort. Furthermore, over half of the world's hospital beds are occupied with people suffering from illnesses linked with contaminated water and 1.8 million children die every year from a water related disease (Corcoran et al., 2010). The World Health Organization reports that 9 % of the global disease burden could be prevented by increasing the access to safe drinking water, improving sanitation and hygiene and improving wastewater management (Prüss-Üstün et al., 2008).

Recovery of resources from waste is a well established practice in the industrial sector. Process water is being recycled, heat exchangers are used to recover energy from process streams and raw materials are recovered from waste streams. Concepts of decentralized sanitation and reuse apply the same logic to household wastewater, no longer seen as a waste stream but as a source of nutrients, energy and water (Otterpohl, 2001). In this way, wastewater management can become more efficient and potentially more successful than conventional wastewater management to increase access to safe drinking water and improve sanitation and hygiene.

Household wastewater can be divided into black water (toilet discharges) and grey water (household wastewater without the input of toilets). Black water can be further separated into urine and feces, depending of the type of toilet used. Each stream has specific characteristics and by keeping them separated treatment and resource recovery can be performed in a more effective way. Black water is a concentrated stream containing most of the nitrogen and phosphorus, a large fraction of the organic matter and most of the pathogens (Otterpohl, 2002). Grey water, due to its substantial amount (up to 75 % of the household wastewater) and the lower concentrations of organic matter and pathogens compared to black water, has been identified as a potential stream for water reuse in applications such as toilet flushing, laundry or irrigation (Eriksson et al., 2002). Because grey water is not mixed with toilet water, the risks for its reuse are lower and the acceptance of treated grey water as reuse water is easier to achieve than in the case of sewage (Po et al., 2003).

Despite of its reuse potential, there are certain concerns regarding the reuse of grey water, in particular with respect to the risks of direct or indirect exposure to pathogens and toxic compounds in the case of insufficient treatment of this stream. Furthermore, there may be consequences for the environment; for instance soil and ground water pollution caused by irrigation with water containing surfactants, boron and high concentrations of sodium (Gross et al., 2005). Emerging contaminants present at concentrations in range of μgL^{-1} (micropollutants) may also represent a risk, an issue that has been investigated only to a limited extent.

1.2 Grey water characteristics

The streams usually considered in the definition of grey water are laundry, hand basins, showers, bath and kitchen, thus household wastewater without the input of toilets. In the Netherlands, water consumption per capita by 2007 was 127.5 Lp^{-1}d^{-1} (Foekema et al., 2008), deducting the water use for drinking (1.8 Lp^{-1}d^{-1}) and toilet flushing (37.1 Lp^{-1}d^{-1}), grey water production amounts to 88.6 Lp^{-1}d^{-1}. About 60 % of it comes from showering and bathing (Table 1.1).

Table 1.1: Production of grey water per inhabitant by source

Source	**Volume (Lp^{-1}d^{-1})**
Shower and bath	52.3
Hand basin	5.3
Laundry	17.2
Kitchen	13.8
Total	88.6

Based on common household activities in the Netherlands, the expected load of chemical oxygen demand (COD) of grey water is 51.2 gp^{-1}d^{-1}, of which 48 % originates from laundry discharges, 33 % from the kitchen, 5.3 % from personal care and 4.5 % from household cleaning (van de Wijst and Groot-Marcus, 1998). In some cases, kitchen and/or laundry discharges are separated from grey water, resulting in the socalled 'light' or 'low strength' grey water (Friedler, 2004). Kitchen and laundry make up to 80 % of the COD in 35 % of the total grey water volume. The resulting water, therefore, would have a COD of less than 100 mgL^{-1}, which may represent and advantage for its treatment and reuse (Friedler, 2004). However, within the total sanitation concept, the focus is not only water reuse but also an overall wastewater management for resource recovery. Black water is collected with vacuum sewers, and treated to recover energy and nutrients. Grey water should be treated combined, because the exclusion of laundry and kitchen water would require an extra treatment system, which is unpractical. In this study, therefore, we focused on the treatment of (mixed) grey water, e.g., including kitchen and laundry discharges.

The characteristics of grey water may vary significantly depending on different factors such as water source, water consumption, climate, cleaning habits, etc. Different studies have been dedicated to characterize grey water for physical, chemical, toxicological and microbiological parameters (Abu Ghunmi, 2009; Eriksson et al., 2002; Li et al., 2009). Briefly, (mixed) grey water contains about 100-681 mgL^{-1} of COD, total nitrogen in concentrations of 3.7-54 mgL^{-1}, total phosphorus in the range of 1-23 mgL^{-1}, and fecal coliforms of 1 x 10^4 to 1.5 x 10^8 counts per 100 mL (Li et al., 2009). As a result of washing activities in the household, grey water contains (anionic) surfactants in the range of 3-76 mgL^{-1} (Al-Jayyousi, 2002; Gross et al., 2005; Shafran et al., 2005; Wiel-Shafran et al., 2006).

1.3 Grey water reuse applications

Treatment of grey water is required before any reuse application, which is usually non potable such as irrigation, toilet flushing, laundry and aesthetic purposes, for example a fountain. Several reuse standards have been developed, based on the type of application. Based on previous experiences in Germany, Japan, China, UK and Australia, Li et al. (2009) proposed a set of standards for non potable grey water reuse (Table 1.2). The reuse applications are divided into recreational impoundments and urban applications, the main difference being a limit set for nitrogen and phosphorus concentrations for recreational impoundments. Standards for unrestricted reuse are meant for close contact with people, for example lakes for swimming (recreational impoundment), toilet flushing, laundry, street washing and surface irrigation of (un)cooked vegetables (urban reuse). Restricted reuse standards are laxer and are meant for applications out of public reach (Li et al., 2009).

Table 1.2: Suggested standards for non potable grey water reuse (Li et al., 2009)

	Recreational impoundments		**Urban reuse**	
	Unrestrict.	**Restrict.**	**Unrestrict.**	**Restrict.**
BOD_5 (mgL^{-1})	≤10	≤30	≤10	≤30
TN (mgL^{-1})	≤1.0	≤1.0		
TP (mgL^{-1})	≤0.05	≤0.05		
Anionic surfactants (mgL^{-1})	≤1.0	≤1.0	≤1.0	≤1.0
TSS (mgL^{-1})	–	≤30		
Turbidity (NTU)			≤2	
pH	6-9	6-9	6-9	6-9
Fecal coliforms/100 mL	500	≤10000	3	≤500
Residual chlorine (mgL^{-1})			≤1	≤1

1.4 Grey water treatment

Abu Ghunmi (2009) has reviewed the different grey water treatment systems that have been studied until 2009. There is a wide range of treatment processes including physical, chemical and biological processes. For minimum energy consumption, the review suggested a sequence of anaerobic and aerobic processes for grey water treatment with an additional disinfection step. For anaerobic treatment, upflow anaerobic blanket reactor (UASB) and anaerobic filters are proposed. A subsequent aerobic treatment can be performed in a rotary biological contactor (RBC), sequencing batch reactor (SBR), filter bed or constructed wetland (CW). In spite of the high treatment performance of membrane bioreactors (MBRs), these are not recommended because of their high investment and operational costs.

Li et al. (2009) regarded anaerobic treatment unsuitable for grey water treatment because COD removal in such systems is poor. He suggests the application of aerobic treatment (RBC, SBR, CW), in combination with membrane filtration, or a combined technology such as MBR to achieve an effluent quality for unrestricted non-potable reuse. Besides, in his review he recommends aerobic treatment in combination with sand filtration for restricted non-potable urban reuse. By adding a disinfection step the effluent can also achieve the standards for unrestricted non-potable urban reuse.

1.5 Concerns about micropollutants

Our lifestyle is largely dependent on the chemical products that are mass produced. About 300 million tons of synthetic compounds are annually produced for industrial processes or consumer products (Schwarzenbach et al., 2006). As a result, trace xenobiotic organic compounds (also known as organic micropollutants) are commonly present in the aquatic environment.

A few years ago, the focus of research was on organic micropollutants such as PCBs, DDT, dioxins and pesticides, coming from industry and agriculture. Along with the development of more powerful analytical techniques, such as gas chromatography (GC) or liquid chromatography (LC) coupled with mass spectrometry (MS), which have enabled us to measure concentrations in the range of 1 ngL^{-1}, concerns have been raised about the occurrence of pharmaceuticals, hormones and personal care products in the environment (Daughton and Ternes, 1999; Heberer and Ternes, 2002). Although present in the range of ngL^{-1}-μgL^{-1}, these compounds are biologically active and may influence aquatic organisms (Heberer and Ternes, 2002). Detected contaminants in the environment include antiphlogistics, antibiotics, antidiabetics, antiepileptics, beta blockers, antihistamines, calcium antagonists, psychotropics, muscle relaxants, diuretics, decongestants, antigouts, contrast media and hormones. Examples of the effects of these micropollutants on the environment are populations of fish (wild roach and gudgeon) exposed to high concentrations of sewage effluent (containing complex mixtures of endocrine disrupting chemicals) and showing a high degree of intersexuality (Jobling et al., 2002) and the disruption of several aspects of reproduction of fresh water mussels by exposure to fluoxetine (Prozac) (Robert et al., 2010).

With the aim of protecting surface water from pollution,the European

Water Framework Directive (WFD, 2000/60/EC) has established environmental quality standards (EQS) for 41 dangerous chemical substances, 33 of them classified as priority substances. These EQS must be complied by 2015. This list does not include any pharmaceutical compound or personal care product.

Regarding water reuse, there are recommended non-potable water reuse quality standards, which include pathogens and general organic and inorganic parameters (see section 1.2). For emerging organic micropollutants, such as pharmaceuticals and personal care products, however, threshold concentrations are not yet specified (Ternes and Joss, 2006).

1.5.1 Separation at source and micropollutants

The majority of pharmaceuticals, hormones and personal care compounds used by humans are discharged to the environment via municipal wastewater. Pharmaceuticals and hormones are excreted with urine and feces. The separate collection of toilet water with f.e. vacuum toilets, therefore, allows the concentration of most of the toxic potency of household wastewater in a small stream (de Mes, 2007). Furthermore, a large fraction of pharmaceuticals and hormones are excreted with urine in a volume of only 1.5 $Lp^{-1}d^{-1}$ (Alder et al., 2006). This makes the application of urine separation advantageous in preventing these active compounds from reaching the environment. The specific treatment of either concentrated black water or source separated urine may present a great advantage over the treatment of large volumes of sewage in conventional wastewater treatment plants (Winker et al., 2008).

1.5.2 Grey water as a source of micropollutants

The other group of emerging compounds used in households, which have not received as much attention as pharmaceuticals and hormones, are ingredients of personal care and household products. These usually end up in grey water. Based on an ingredient's inventory of personal care and household products, Eriksson et al. (2002) reported that about 900 micropollutants can potentially be found in grey water. The major groups of substances found are surfactants (especially anionic and nonionic), fragrances and flavors, preservatives and biocides. UV-filters were not considered in this study by Eriksson et al. (2002), but they are an important group of substances which also would end up in grey water (see section 1.5.2).

Surfactants

Surfactants are the active ingredients of detergents and are widely used in many personal care and household products. Surfactants are mainly divided in three types: anionic, nonionic and cationic (Ying, 2006). Linear alkylbenzene sulphonates (LAS) are the most used synthetic anionic surfactants (Temmink and Klapwijk, 2004). Alkylphenol ethoxylates constitute a large portion of the nonionic surfactants that are produced. Concerns about these surfactants arose due to their biodegradation products nonylphenol and octylphenol, of which their toxicity has affected aquatic life (Ying, 2006). Cationic surfactants are based on quaterary ammonium compounds and are commonly used as fabric softeners and antiseptic agents. Examples of these are dihydrogenated tallow dimethyl ammonium chloride and benzalkonium chloride (Ying, 2006). In 2003 there was a total world production of 4.5 million metric tons of anionic surfactants, 1.7 million metric tons of nonionics and 0.5 million tons of cationic surfactants (Brackmann and Hager, 2004).

Fragrances

There are 3000 chemical substances and essential oils used as fragrance materials in perfumes, soaps, detergents, cleaners, shampoos and other consumer products (Villa et al., 2007). Household wastewater is considered the primary environmental pathway of these compounds (Salvito et al., 2004). There are two types of synthetic musks: nitro musks and polycyclic musks. To the first group belong musk ambrette, xylene, ketone, mosquene and tibetene. Nitro musks have been phased out of the market in many places because of toxicity concerns (Daughton and Ternes, 1999). These have been slowly replaced by polycyclic musks, such as 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran (galaxolide) and 6-Acetyl-1,1,2,4,4,7- hexamethyltetralin (tonalide). These two musks are produced with a production volume in the range of 1000-5000 tpa and have been identified as the most important sythetic musk compound residues (Heberer, 2003). Concerns are raised because of their high potential of bioaccumulation (based on a $\log K_{OW}$ of 5.7-5.9) and potential antiestrogenic effects in fish (Schreurs et al., 2005), see section 1.7.

Preservatives and biocides

Preservatives are used to prevent microbiological contamination of consumer products. P-hydroxybenzoic esters (parabens: methylparaben, propylparaben, butylparaben, and ethylparaben), formaldehyde, formaldehyde releasers, and methylchloroisothiazolinone/methylisothiazolinone are some of the most used cosmetic preservatives from the past 20 years. Parabens are the most predominant and are also used as biocides in pharmaceuticals, food and beverages. Concerns about these compounds have been raised because of their (weak) estrogenic effects (Golden et al., 2005).
The EU review programme for biocidal substances comprises 85 substances in the group for human hygiene products, with the most important (in terms of production tonnage) benzoic acid pentapotassium bis(peroxymonosulphate)-bis(sulphate), sodium benzoate and sodium hypochlorite. Another biocide of importance due to environmental concerns is triclosan. In the EU the production of triclosan reached about 450 tons in 2006. About 85 % of the total volume is used in personal care products, 5 % in textiles and 10 % for plastics and food contact materials (European Commission, 2009b). There is evidence that triclosan can cause antimicrobial resistance in bacteria (Yazdankhah et al., 2006).

UV-filters

UV-filters are compounds able to absorb UV-radiation and prevent the effects of direct exposure of the skin to sunlight. UV-filters are used in sunscreening agents, but also in many personal care products of daily use such as cosmetics, skin creams and body lotions (Balmer et al., 2005). Due to a higher incidence of skin cancer in the last decades, the European Union is promoting the use of sunscreen products, as it was estimated that consumers are only using half the necessary amount (Europa press-releases, 2009).
In the Netherlands, the amount of sunscreens sold in 2000 was 950 tons/year (Balk et al., 2001). In 1999, amongst the most used UV-filters in Germany were benzophenone-3 (BP3), 2-phenyl-5-benzimidazolesulfonic acid (PBSA), octocrylene (OC), 2-Ethylhexyl-4-methoxycinnamate (EHMC), 4-methylbenzylidene-camphor (4MBC), 2-ethylhexyl salicylate (2EHS) and 4-tert-Butyl-4'-methoxy-dibenzoylmethane (avobenzone) (Balk et al., 2001).

Review of micropollutants measured in grey water

Only a few studies have been done to determine micropollutant concentrations in grey water (Andersen et al., 2007; Eriksson et al., 2003; Palmquist and Hanaeus, 2005). Eriksson et al. (2003) performed a semi-quantification of organic compounds in grey water. Hundred and ninety one different micropollutants were identified, amongst them several surfactants (mainly long-chain fatty acids but also nonyl- and octylphenol ethoxylates), 8 emulsifiers, 40 fragrances, a UV-filter, 14 preservatives (triclosan included), 9 softeners and plasticizers, 25 solvents and other substances. Palmquist and Hanaeus (2005) studied the occurrence of 81 organic substances in mixed grey water including: nonylphenol and octylphenol ethoxylates, brominated flame retardants, organotin compounds, PAH, PCB, phthalates, monocyclic aromatics and triclosan. 46 of them were actually detected in grey water, e.g., nonylphenol varied in the range of 2.82-5.95 μgL^{-1}, triclosan in the range of 0.56-5.9 μgL^{-1}, and di-(2-ethylhexyl) phthalate in the range of 8.4-160 μgL^{-1}.

If grey water is to be reused, the investigation of occurrence, removal and impact of these compounds is necessary. However, information available regarding the removal of micropollutants from grey water by different treatment systems is very scarce. The removal of the preservatives parabens was studied by Andersen et al. (2007) in a low strength grey water treatment system consisting of a multistage RBC, sand filter and a disinfection step with UV light. They found methyl-, ethyl-, propyl-, butyl- and isobutylparaben in the range of <LOQ to 40 μgL^{-1} and their removal was >97, 99, 99, 96 and 87 %, respectively.

1.6 Selection and occurrence of micropollutants

This thesis focuses on the occurence and removal of micropollutants from grey water. For this purpose, a selection of micropollutant has been made to represent the ingredients of personal care and household products. The list comprises several fragrances, preservatives, biocides, surfactants, UV-filters and one plasticizer. Table 1.3 shows the selected micropollutants along with their properties and Figure 1.1 shows their chemical structures. The selection was based on their persistence to biodegradation, tendency for bioaccumulation (based on $\log K_{OW}$ values) and potential effects in the environment such as endocrine disruption and acute toxicity to aquatic organisms. Data regarding their toxicity are presented later on in this chapter (Section 1.7).

Table 1.3: Selected micropollutants and their properties

Compound	CAS number	Water sol. mg/L	logKow	Aerobic biodegradability
Fragrances				
Tonalide	15323-35-0	1.3	5.7	not[a]
Galaxolide	1222-05-5	1.75	5.9	not[a]
HCA	101-86-0	2.75	4.82	inherent[a]
UV-filters				
BP3	131-57-7	68.6	3.79	
4MBC	38102-62-4		5.1	60–90 %[*,b]
Octocrylene	6197-30-4	0.004	6.9	poor [*,b]
EHMC	5466-77-3	0.155	5.8	ready[c]
Avobenzone	70356-09-1	2.22	4.51	poor[d]
PBSA	27503-81-7			poor[d]
2EHS	118-60-5	0.72	5.77	poor[d]
Plasticizer				
Bisphenol-A	80-05-7	120	3.32	ready[e]
Preservatives				
Methylparaben	99-76-3	1.66	1.66	ready[f]
Ethylparaben	120-47-8	2.19	2.19	ready[f]
Propylparaben	94-13-3	2.71	2.71	ready[f]
Butylparaben	94-26-8	3.24	3.24	
Biocide/surfactants				
Triclosan	3380-34-5	10	4.76	moderate[e]
BaCl	8001-54-5	22.4	2.9	poor[g]
Nonylphenol	104-40-5	4.48	5.43	ready [e]

[a] Simonich et al. (2002)
[b] Kupper et al. (2006)
[c] Straub (2002)
[d] US-EPA (2009)
[e] Stasinakis et al. (2008)
[f] Madsen et al. (2001)
[g] Adams and Kuzhikannil (2000)
[*] biodegradation in wastewater treatment plants

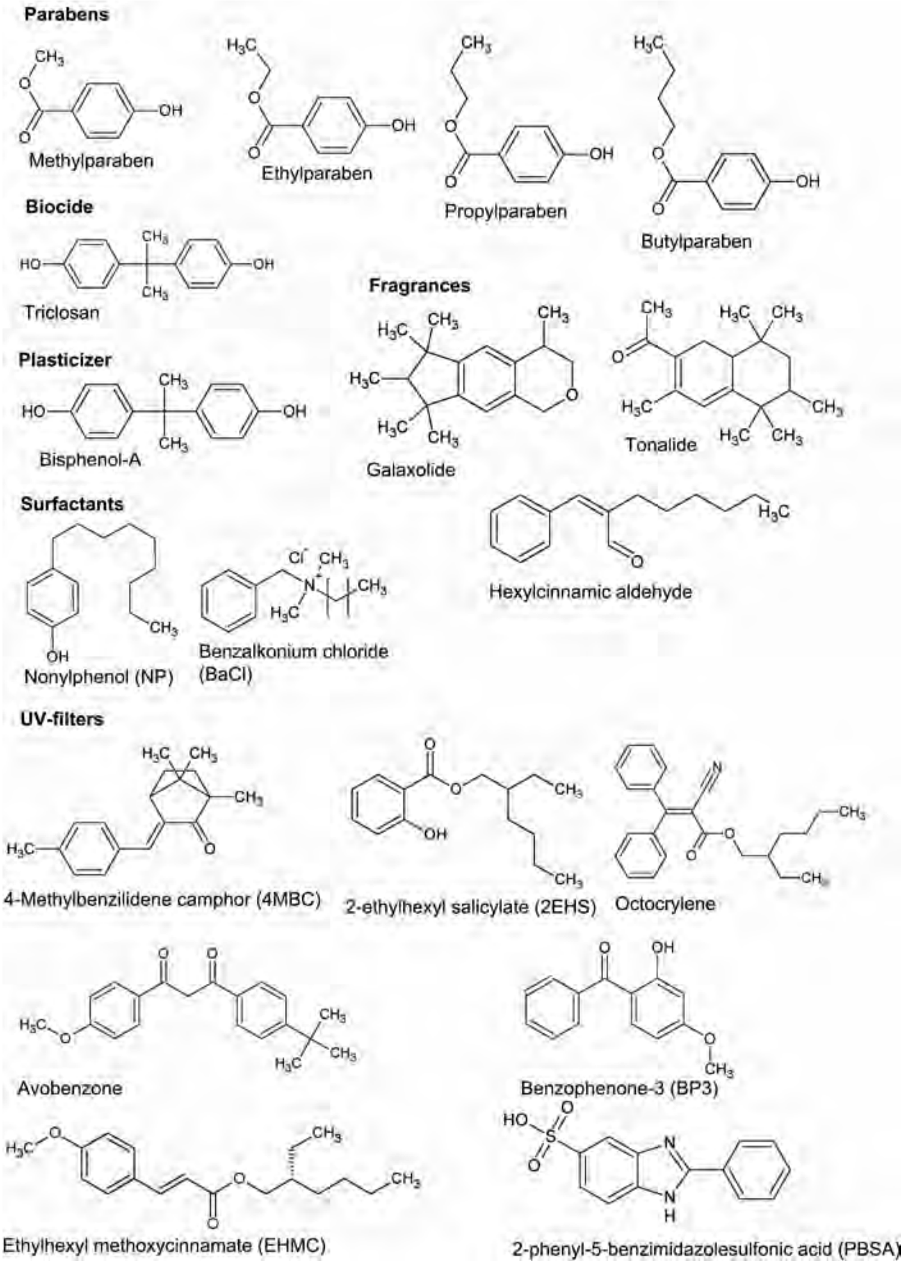

Figure 1.1: Chemical structures of selected micropollutants

As mentioned above, information about the presence of micropollutants in grey water is scarce. Therefore, in this chapter we gathered literature data about sewage concentrations as a reference value for concentrations that can be found in grey water. In general, concentrations of these compounds may be higher in grey water than in sewage. The two other components of sewage, i.e., toilet water and storm water, dilute grey water micropollutant concentrations by a factor 2-4. However, industrial discharge of any of these micropollutants into the sewage may increase the concentration of these micropollutants in sewage.

1.6.1 Fragrances

Galaxolide and tonalide are non-biodegradable compounds with highly bioaccumulating potential (logK_{OW}s of 5.9 and 5.7, for galaxolide and tonalide, respectively). They have a proven endocrine disrupting potential (see Table 1.9) (Schreurs et al., 2005). Galaxolide, tonalide and HCA were considered in this study based on a prioritization of chemical compounds performed by Eriksson et al. (2002). Of 211 compounds which were evaluated based on biodegradability, bioaccumulation potential and toxicity, 66 were considered priority compounds with HCA ranked 1 (not biodegradable, bioaccumulation factor > 100, log$K_{OW} > 3$ and EC/LC$_{50}$[a] < 1 mgL^{-1}) and galaxolide and tonalide ranked 2 (biodegradable, bioaccumulation factor > 100, log$K_{OW} > 3$ and EC/LC$_{50}$ < 1 mgL^{-1}). Table 1.4 shows sewage concentrations of galaxolide, tonalide and HCA collected from a number of studies. Concentrations of the synthetic musk galaxolide are usually higher than those of tonalide, but still with a wide range of 0.030–12.5 μgL^{-1}. HCA has been found at levels of 0.2-0.35 μgL^{-1}. Despite HCA being classified as a priority substance (Eriksson et al., 2002), not many studies are available on its occurrence in environmental samples.

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[a] EC/LC$_{50}$ = effect or lethal concentration 50 %, represents the concentration at which 50 % of the population of a tested organism dies or shows decreased growth, reproduction, mobility, etc.

Table 1.4: Sewage concentrations of fragrance materials (μgL^{-1})

Tonalide	**Galaxolide**	**HCA**
0.11[a]	1.65[a]	0.196±0.056[g]
0.26[a]	1.25[a]	0.342±0.020[g]
0.29[a]	3.00[a]	
12.5±12.1 [b]	1.85[f]	
5.97±3.88 [b]	0.020-12.5[c]	
0.030-6.8 [c]	9.71±5.09[b]	
0.95±0.09 [d]	1.99±0.14[d]	
0.58±0.10 [e]		

[a] Zhou et al. (2009)
[b] Simonich et al. (2002)
[c] Heberer (2003)
[d] Kreuzinger et al. (2004)
[e] Bester (2004)
[f] Oppenheimer et al. (2007)
[g] Rodil et al. (2009)

1.6.2 UV-filters

Most of the UV-filters considered in this study are persistent to biodegradation and possess a high potential for bioaccumulation, except for PBSA which is hydrophilic, with logK_{OW} values in the range of 3.79–6.9. Furthermore, there is evidence that BP3, 4MBC, EHMC and octocrylene can cause endocrine disruption. Sewage concentrations of the most studied UV-filters are shown in Table 1.5.

Table 1.5: Sewage concentrations of UV-filters (μgL^{-1})

4MBC	**EHMC**	**Octocrylene**	**BP3**	**PBSA**
0.070±0.007[a]	0.146±0.023[a]	0.072±0.006[a]	0.62[e]	0.196±0.056[a]
0.041±0.019[a]	<0.003[a]	<0.03[a]	2.95[f]	0.342±0.020[a]
2.2-6.5[b]	0.4[d]	2.9[c]		
7.1[c]	3.3[c]			

[a] Rodil et al. (2009)
[b] Buser et al. (2005)
[c] Balmer et al. (2005)
[d] Loraine and Pettigrove (2006)
[e] Lee et al. (2005)
[f] Oppenheimer et al. (2007)

No information was available on sewage concentrations of 2EHS and avobenzone. The concentrations at which UV-filters have been measured in sewage vary within 2 orders of magnitude, from below quantification limits (in the level of few ng^{-1}) to a few μgL^{-1}. This large variation may be due to the fact that UV-filters are used more extensively during the summer months (Loraine and Pettigrove, 2006).

1.6.3 Preservatives

Parabens are compounds which are not as hydrophobic ($\log K_{OW}$ values in the range of 1.66-3.24) as the polycyclic musks or UV-filters and they are readily biodegradable. These compounds were selected in this study because they are used in the majority of personal care products (Darbre and Harvey, 2008) and because of their activity as endocrine disruptors (Golden et al., 2005).

Table 1.6: Sewage concentrations of parabens (μgL^{-1})

Methylparaben	**Ethylparaben**	**Propylparaben**	**Butylparaben**
0.62[a]	0.1[a]	0.73[a]	0.11[a]
2.95[b]	4.5-5.5[c]	1.1-1.3[c]	0.15-0.18[c]
1.9-5.1[c]	0.129[d]	0.43[d]	0.211[d]
0.724[d]	0.06[f]	5.27[e]	0.026[f]
0.81[e]		0.27[f]	
0.86[f]			

[a] Lee et al. (2005)
[b] Oppenheimer et al. (2007)
[c] Gonzalez-Marino et al. (2009)
[d] Jonkers et al. (2009)
[e] Canosa et al. (2006a)
[f] Canosa et al. (2006b)

Methyl- and propylparaben are the most frequently used parabens (Eriksson et al., 2008a), and also are found in higher concentrations compared to ethyl- and butylparaben (see Table 1.6). Methyl- and propylparaben are present in sewage in concentrations in the range of 0.27-5.27 μgL^{-1}. Ethyl- and butylparaben, with the exception of the study of Gonzalez-Marino et al. (2009), have been measured in concentrations below 0.25 μgL^{-1}.

1.6.4 Biocides, surfactants and bisphenol-A

Triclosan is a biocide with a moderate potential for bioaccumulation (logK_{OW} = 4.76), a moderate aerobic biodegradability and an acute toxicity to aquatic organisms (Orvos et al., 2002). Its presence in sewage ranges between <0.05 and 5.2 μgL^{-1} (Table 1.7).

Benzalkonium chloride (BaCl) is a cationic surfactant often used as a biocide/ disinfectant in hospitals, which explains why generally high concentrations are measured in hospital wastewaters. BaCl is poorly biodegradable and acutely toxic to aquatic organisms with an EC_{50} on *Daphnia magna* as low as 20 μgL^{-1}.

Table 1.7: Sewage concentrations of triclosan, benzalkonium chloride (BaCl), nonylphenol and bisphenol-A (μgL^{-1})

Triclosan	**BaCl**	**Nonylphenol**	**Bisphenol-A**
1.35[a]	1900[*,f]	0.24-19[g]	0.25-5.62[g]
5.2[b]		0.2[h]	14.6[a]
<0.05-0.936[c]		15.3±12.1[i]	0.473[j]
0.45[d]		12.8±7.27[i]	
2.8[e]			

[a] Lee et al. (2005)
[b] Oppenheimer et al. (2007)
[c] Gonzalez-Marino et al. (2009)
[d] Loraine and Pettigrove (2006)
[e] Balmer et al. (2005)
[f] Kummerer et al. (1997)
[g] Vethaak et al. (2005)
[h] Espejo et al. (2002)
[i] Simonich et al. (2002)
[j] Jonkers et al. (2009)
[*] measured in hospital wastewater

Of all selected micropollutants only nonylphenol is classified as a priority substance in the European Water Framework Directive (European Comission, 2009a). Nonylphenol is a nonionic surfactant with estrogenic potency (Routledge et al., 1998). It is prohibited from commercial use in Europe, but is still found in sewage effluents at concentrations around 15 μgL^{-1}.

Bisphenol-A is a monomer used in the production of epoxy resins and polycarbonate plastics. It is readily biodegradable, moderately hydrophobic (logK_{OW} of 3.32) and produced in large quantities (over a million tons per year worldwide) (Sharma et al., 2009). The estrogenic activity of bisphenol-A has been proven in several studies and even carcinogenesis may result from the exposure to bisphenol-A (Sharma et al., 2009). Sewage concentrations are in the range of 0.25 to 14.6 μgL^{-1}.

1.7 Ecotoxicity

Ecotoxicology is concerned with finding the relationship between the quantity of a chemical to which an organism is exposed and the nature and degree of consequent harmful effects (Walker et al., 2006). Endpoints are measures of toxicity, the most common endpoint is death, but there are also other indices such as biochemical, physiological, reproductive and behavioral effects. Toxicity tests usually provide an estimate dose or concentration that will cause toxic response to 50 % of the population (Walker et al., 2006), e.g., EC_{50} is the median effect concentration that will cause a toxic effect on 50 % of a population. In toxicity testing it is also possible to determine concentrations that cause no toxicity, e.g., a no observed effect concentration (NOEC).

All of the selected micropollutants have been assessed for risks to humans and a large amount of data is available related to allergies and dermatological reactions. Less information is avalable regarding their environmental risks. Table 1.8 gathers information about ecotoxicity endpoints on water flea (*Daphnia magna*).

Because BaCl is acutely toxic at 20 μgL^{-1}, its discharge of hospital wastewater with concentrations as high as 1900 μgL^{-1}, definitely represents a risk to the aquatic environment. The concentrations of nonylphenol in sewage are close to the determined NOEC for *Daphnia magna*. The other compounds in Table 1.8 have effective toxic concentrations much higher than the actual concentrations in which they can be found in sewage and eventually receiving water bodies. The risks associated to the discharge of these micropollutants, therefore, may seem low. However, besides the conventional aquatic toxicity endpoints for assessment of environmental risks, some of the selected compounds can cause endocrine disruption (e.g., estrogenic and androgenic effects).

Table 1.8: Toxicity endpoints for *Daphnia magna* compared to sewage concentrations

Compound	**Test system (endpoint)**	**Effective concentration (mgL^{-1})**	**Range of concentration in sewage (μgL^{-1})**
Tonalide	Reproduction	NOEC/21d = 0.196[a]	0.03-12.5
Galaxolide	Reproduction	NOEC/21d = 0.111[b]	0.02-12.5
BP3	Acute toxicity	EC_{50}/48h = 1.9[c]	0.62-2.95
4MBC	Acute toxicity	EC_{50}/48h = 0.56[c]	0.04-7.1
Bisphenol-A	Acute immobilization	EC_{50}/48h = 10[d]	0.25-14.6
Methylparaben	Acute immobilization	EC_{50}/48h = 62[e]	0.62-5.1
Ethylparaben	Acute immobilization	EC_{50}/48h = 32[e]	0.06-5.5
Propylparaben	Acute immobilization	EC_{50}/48h = 23[e]	0.27-5.27
Butylparaben	Acute immobilization	EC_{50}/48h = 9.2[e]	0.026-0.21
Triclosan	Survival and reproduction	NOEC/21d = 0.40[f]	0.05-5.2
BaCl	Acute toxicity	EC_{50}/48 h = 0.02[g]	1900
Nonylphenol	Survival and reproduction	NOEC/21d = 0.025[h]	0.02-19

[a] SEA (2002a)
[b] SEA (2002b)
[c] Fent et al. (2009)
[d] Ike et al. (2002)
[e] Terasaki et al. (2009)
[f] Orvos et al. (2002)
[g] FeF (2009)
[h] Comber et al. (1993)

An estrogenic chemical is one that can imitate an estrogen by binding to the estrogen receptor (ER), either stimulating activity (agonistic effect) and causing feminization of an organism (estrogenic effect) or by (partially) blocking it (antagonistic effect) resulting in masculinization of an organism (antiestrogenic effect) (Walker et al., 2006). In Table 1.9 data from a number of selected studies on endocrine disruption are summarized. The synthethic musks tonalide and galaxolide presented antagonistic effects toward androgen and progesterone receptors, this latter at an IC_{50} as low as 0.02 μM (about 5 μgL^{-1}). UV-filters BP3 and 4MBC showed weak estrogenic effects but potent PR antagonism, with IC_{50}'s [b] of 0.9 and 0.5 μM, respectively. Parabens are compounds with weak estrogenic potency, with butylparaben being the most potent of them.

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[b] IC_{50} = inhibitory concentration 50 %

These endpoints indicate the potency of each compound individually. However, these compounds are usually present simultaneously in environmental samples, and synergistic effects may result in a higher impact in the environment (Kunz and Fent, 2006).

Table 1.9: Selected end points for endocrine disruption in vitro

Compound	**Test system (endpoint)**	**IC_{50} (μM)**
Tonalide	Androgen Receptor (AR CALUX), antagonistic effects[a]	3.6
	Progesterone Receptor (PR CALUX), antagonistic effects[a]	0.02
Galaxolide	Androgen Receptor (AR CALUX), antagonistic effects[a]	2.9
	PR CALUX, antagonistic effects[a]	0.2
BP3	Estrogen Receptor (ER), activation transcription hERα[a]	2.9
	AR CALUX, antagonistic effects[a]	2.0
	PR CALUX, antagonistic effects[a]	5.2
4MBC	ER, activation of transcriptionfor hERα[a]	6.2
	AR CALUX, antagonistic effects[a]	7.1
	PR CALUX, antagonistic effects[a]	0.9
EHMC	PR CALUX, antagonistic effects[a]	0.5
OC	Anti-estrogenic in yeast hERalpha transactivation assay[b]	2570
	Androgenic in the yeast hAR transactivation assay[b]	627
Methyl- and ethylparaben	Detection of competitive ligand binding to ER [c]	1/1000000*
	Regulation of CAT gener expression [c]	1/10000*
	Proliferation of MCF-7 cells [c]	1/1000000*
Propylparaben	Detection of competitive ligand binding to ER[c]	1/100000*
	Regulation of CAT gener expression [c]	1/10000*
	Proliferation of MCF-7 cells[c]	1/100000*
Butylparaben	Detection of competitive ligand binding to ER [c]	1/100000*
	Regulation of CAT gener expression [c]	1/1000*
	Proliferation of MCF-7 cells[c]	1/100000*
Bisphenol-A	Estrogenic effects with in vitro yeast bioassay [d]	1/10000*
Nonylphenol	Estrogenic effects with in vitro yeast bioassay [e]	1/30000*

[a] Schreurs et al. (2005)
[b] Kunz and Fent (2006)
[c] in MCF-7 cells Golden et al. (2005)
[d] Miller et al. (2001)
[e] Routledge et al. (1998)
* Relative effect to estrogen (molar ratio)

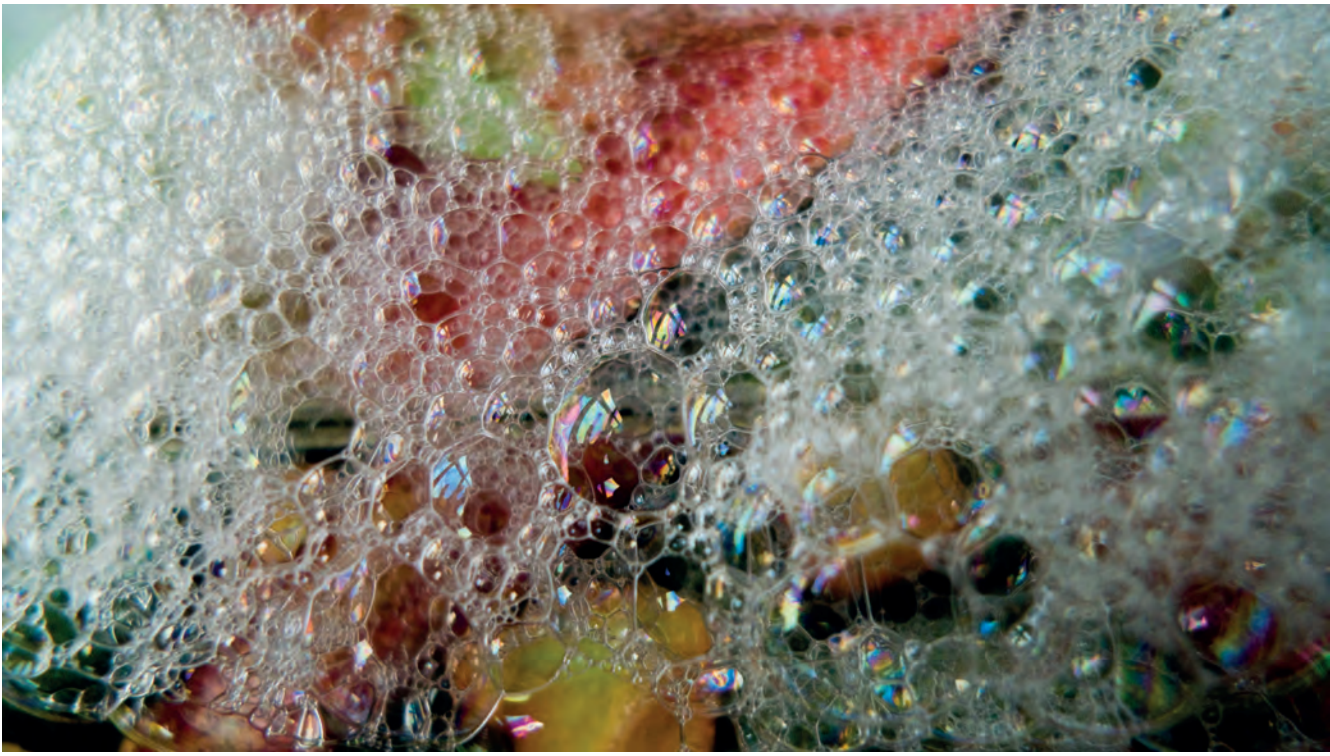
Ecotoxicity data of chemicals help us to prioritize the substances that should be monitored in wastewater before discharging it to the environment, for it is impossible to individually measure all of the 100,000 substances of the technosphere (Palmquist and Hanæus, 2004). Monitoring of a few indicator substances helps to assess the pollution situation in wastewaters, sludge or receiving water bodies. Limitations to this approach are, however, the overlooking of important substances that may cause harmful effects to aquatic organisms and the possible effects caused by mixtures of substances. In these cases, whole effluent toxicity (WET) testing is a very useful tool to assess the combined effect of an environmental sample (Maltby et al., 2000). WET testing is used to complement wastewater evaluation procedures based on chemical data. Monitoring of a list of priority substances in combination with WET testing provides a more complete picture of the quality of an effluent and provides more information for the assessment of risks.

1.8 Scope of this thesis

Grey water, after proper treatment, has a great reuse potential for non potable applications. The aim of this project was to develop a concept for the treatment of grey water that can enable its safe reuse. Special focus was set on the removal of organic micropollutants. A proper characterization of grey water is key for the definition of a treatment scheme. Chapter 2 presents a thorough characterization of grey water regarding general organic and inorganic parameters, as well as anaerobic biodegradability. Biological processes are the core of the treatment of grey water. Chapter 3 and 6 explore different biological grey water treatment systems, focusing on COD removal, sludge production and energy consumption/production. Micropollutants are a growing concern and in Chapter 4 we describe the occurrence in grey water of eighteen micropollutants, already introduced in this chapter, and their removal in three grey water treatment systems. The removal of micropollutants in biological treatment systems is seldom complete. Therefore, Chapter 5 compares the application of ozone and activated carbon to further remove micropollutants from grey water. In Chapter 7, we propose a treatment system based on the information gathered in this thesis and we discuss the reuse of treated grey water.

CHAPTER 2

Characterization and anaerobic biodegradability of grey water



Abstract

Grey water consists of the discharges from kitchen sinks, showers, baths, washing machines and hand basins. Thorough characterization of 192 time proportional samples of grey water from 32 houses was conducted over a period of 14 months. COD concentrations were 724±150$\mathrm{mgL^{-1}}$, of which 34 % was present as suspended COD, 25 % as colloidal COD and 38 % as soluble COD. The maximum anaerobic biodegradability of grey water of 70 ± 5 % indicates the possibility of recovering the COD as methane. Surfactants accounted for 15 % of the total COD. The concentrations of anionic, cationic and noninonic surfactants were 41.1±12.1 $\mathrm{mgL^{-1}}$, 1.7±0.8 $\mathrm{mgL^{-1}}$ and 11.3±3.9 $\mathrm{mgL^{-1}}$, respectively. Of the trace elements which were measured were present below limits suggested for irrigation. Only boron (0.53±0.19) in a few measurements exceeded the 0.75 $\mathrm{mgL^{-1}}$ limit established for long term irrigation.

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This chapter has been submitted to Desalination.

2.1 Introduction

The separation of household wastewater streams provides advantages for wastewater management allowing for resource recovery (Otterpohl, 2002). Household wastewater is mainly divided in: black water and grey water. Black water consists of the discharges from toilets. Especially when collected with vacuum toilets, black water contains nitrogen and phosphorous in high concentrations and most of the pathogens, hormones and phamaceutical residues (Zeeman et al., 2008). Grey water consists of the discharges from kitchen sinks, showers, baths, washing machines and hand basins. It accounts for up to 75 % of the wastewater volume produced by households, and over 90 % if vacuum toilets are installed. Grey water is relatively low in pollution and therefore, after appropriate treatment, has great potential for reuse in non-potable water applications such as infiltration, irrigation, toilet flushing, washing water, etc.

The characteristics of grey water vary greatly upon factors such as the quality of the source water and activities of the household (Eriksson et al., 2002). Table 2.1 shows the characteristics of grey water from a number of selected studies. This table excludes those studies on low-strength grey waters, which exclude laundry and kitchen sink discharges. Reported values for COD range from 171-4770 mgL^{-1}. Very diluted grey water is usually obtained from hotels (e.g., 171 mgL^{-1} of COD from a hotel in Spain), probably due to the higher water consumption in hotels (in Europe it is estimated between 170 and 360 L per guest-night) (Bohdanowicz, 2005). High COD values of 1352 and 4770 mgL^{-1} can be related to a low water consumption (due to scarcity) such as in the rural areas of Jordan and South Africa. In terms of climate and customs, grey water from Germany, Sweden and the Netherlands are more comparable. Yet, there are some differences in composition. For example, from the same site in Germany COD values in 2003 were 258-354 mgL^{-1} (Li et al., 2003) and much higher, 640±130 mgL^{-1}, in 2007 (Elmitwalli and Otterpohl, 2007).

An average BOD_5/COD ratio of 0.45±0.13 gives an indication of the good aerobic biological treatability of grey water. A COD:N:P ratio of 100:20:1 is required for aerobic treatment (Metcalf and Eddy, 2003) and a ratio of 350:5:1 is required for anaerobic treatment.

Table 2.1: Characteristics of grey water in different locations, all values are presented in mgL^{-1}, AS= anionic surfactants, D=Germany, S=Sweden, NL=The Netherlands, SA= South Africa, E=Spain, J=Jordan, IS=Israel, CR= Costa Rica

Grey water source	**Sampling**	**COD**	**BOD_5**	**total N**	**$NH_4{}^+$-N**	**orthoP**	**total P**	**AS**
111 houses, D[a]	4 months	258-354		9.7-16.6			5.2-9.6	
111 houses, D[b]	9 months, n = 6	640		27.2	4.2	8	9.8	
37 houses, S[c]	2 months, n = 8	361		18.1			3.9	
47 houses, S[d]	n = 4	588		9.7			7.5	
150 houses, NL[e]	2 weeks, n = 104	425	215	17.2	7.2	2.3	5,7	
32 houses, NL[e]	4 months, n = 10	1583		47.8	16.4	2.3	9.9	
81-room-hotel, E[f]	1 year, n = 24	171		11.4				
6 person-farm, IS[g]	9 months, n = 72	686	270	14			18	40
House 1, IS[h]	1 year, n = 96	474	195					17
House 2, IS[h]	1 year, n = 96	200	62					3
6 houses, IS[i]	5 weeks, n = 5		133	19			31	34
13 families, J[j]	n = 6	1351	873	17				76
Villages, SA[k]	n = 100	4770		72				
University, SA[l]	not indicated			206	157	40	69	
4 houses, CR[m]	1 year, n = 11		167			6.28		
One family, USA[n]	n = 10			0.6-5.2	0.12-2.49	1.9-16.9		

[a] Li et al. (2003)

[b] Elmitwalli and Otterpohl (2007)

[c] Fittschen and Niemczynowicz (1997)

[d] Palmquist and Hanaeus (2005)

[e] Hernandez Leal et al. (2007)

[f] March et al. (2004)

[g] Gross et al. (2005)

[h] Shafran et al. (2005)

[i] Wiel-Shafran et al. (2006)

[j] Al-Jayyousi (2002)

[k] Carden et al. (2007)

[l] Jackson et al. (2006)

[m] Dallas et al. (2004)

In grey water, this ratio is 100:3.5±1.3:1.6±0.7, which indicates a nitrogen deficiency for aerobic treatment, but not for anaerobic treatment. Only about 3 % of the nitrogen from household wastewater is discharged with grey water, as about 87 % is in urine and 10 % in feces (Otterpohl, 2002). Furthermore, a large fraction of the total nitrogen in grey water was organically bound, the fraction of ammonium-nitrogen was on average 0.34±0.13, which is significantly less than in sewage where most nitrogen is present as ammonium. It is uncertain whether organically bound nitrogen in grey water would be available for biological processes, increasing perhaps the nitrogen deficit.

Preferably grey water should be treated anaerobically because of lower treatment costs and the possibility of recovering energy (Lettinga, 1995). Common pre-treatment of grey water consists of a septic tank (Jefferson et al., 2001). Upflow anaerobic sludge blanket (UASB) reactors have been suggested as an alternative pre-treatment (Abu Ghunmi, 2009; Elmitwalli and Otterpohl, 2007). Information regarding anaerobic biodegradability and hydrolysis rate of grey water, therefore, is valuable for the design of an anaerobic treatment step. Elmitwalli and Otterpohl (2007) reported a total anaerobic biodegradability of 74 % for grey water from Germany. This value was similar to the 70 % biodegradability reported for low-strength dormitory grey water from Jordan (Abu Ghunmi, 2009).

Proper characterization of wastewater is essential to defining the treatment to be applied. Furthermore, knowing the characteristics of grey water can give an indication of the contents (such as heavy metals, boron, etc.) of treated water and its reuse prospects. Therefore, in this study we show a thorough characterization of grey water from a residential area in Sneek, the Netherlands.

2.2 Materials and Methods

2.2.1 Grey water source

Grey water was collected from a 32 house residential area in Sneek, the Netherlands. These 32 houses are equipped with vacuum toilets and grey water is collected separately. An autosampler with built-in cooling system

(ASP-Station 2000, Endress + Hauser) was installed on-site for the collection of time proportional samples at 4 °C. A total of 192 samples were taken over a period of 14 months, the time intervals during sample collection varied over the whole sampling period, ranging from 2 hours to 2 days. Samples were transported to the lab facilities, stored at 4 °C and analyzed within 48 hours.

2.2.2 Chemical analyses

Chemical Oxygen Demand (COD) was measured according to Standard Methods (APHA et al., 1998) using Dr. Lange test kits. Suspended COD was defined by a particle size of $>$12–25 μm (Schleicher & Schuell 589/1 black ribbon filters). Soluble COD was defined by a particle size of $<$0.45 μm. Colloidal COD was calculated from the difference of the COD of black ribbon filtered samples and dissolved COD. Total Organic Carbon (TOC) was measured with a TOC analyzer (TOC-V CPH, Shimadzu).

Metals (Al, B, Cd, Cu, Cr, Fe, Mn, Ni, Pb, Se, Sn, Zn) and earth elements (Ca, K, Mg, S, Na, P) were measured according to Standard Methods (APHA et al., 1998) with an Inductively Coupled Plasma (ICP) instrument (Perkin Elmer Optima 3000 XL). Analysis of anions (nitrate, nitrite, sulphate, chloride and phosphate) was done according to Standard Methods (APHA et al., 1998) using Ion Chromatography (761 Compact IC Metrohm). Prior to analysis samples were filtered through a $<$0.45 μm membrane filter.

Total phosphorus, total nitrogen and total ammonium nitrogen (NH_3-N plus ${NH_4}^+$-N) concentrations were measured with Dr. Lange test kits based on Standard Methods (APHA et al., 1998); samples were diluted 10 times to avoid interferences by other ions.

The analysis of anionic surfactants as methylene blue active substances (MBAS) was done with cuvette tests based on Standard Methods APHA et al. (1998); the reference compound for this method is sodium dodecylbenzene sulphonate. Cationic surfactants were measured as complexes of bromophenol blue photometrically using cuvette tests (LCK 331, Dr. Lange), the referece compound for this method is cetyltrimethylammonium bromide. Non-ionic surfactants were measured by a reaction with the indicator tetrabromophenolphthalein ethyl ester (TBPE) to form complexes, which are extracted in dichloromethane and photometrically evaluated (LCK 333, Dr. Lange).

Measurements higher or lower than two times the standard deviation were considered outliers and are excluded from the tables shown in this paper. The average COD values in the different seasons were compared statistically with hypothesis testing, at a confidence interval of 95 % using the software Statdisk 9.1. Populations were normally distributed (statistical values of kurtosis and skewness z between ±1.96).

2.2.3 Anaerobic biodegradability

Maximum anaerobic biodegradability was determined with a multibottle non-inoculated test. Twenty 100 mL serum bottles were filled with 50 mL of grey water (without addition of inoculum). The headspace was flushed with nitrogen gas to eliminate the presence of oxygen. The serum bottles were then incubated at 35 °C. Two bottles were sacrificed every week for the first 5 weeks and the frequency of sampling was decreased as the differences in COD values decreased. Bottles were analyzed for COD and surfactants. Total biodegradability was calculated with the initial and the final measurements of COD and surfactants. Final measurements were considered when the change in COD between samples was less than 5 %, approximately after 60 days of incubation.

Two anaerobic batch tests were conducted to determine the hydrolysis constant of grey water. This was done in 0.5 L Schott bottles with an active volume of 0.2 L fitted with pressure heads (Oxitop). Each 30-day test was performed in triplicate, including three controls with only inoculum sludge to be able to sustract the COD contribution and eventual methane production due to the addition of inoculum. The inoculum was flocculant sludge from the anaerobic digester of Leeuwarden wastewater treatment plant. The pH of all bottles was set to neutral at the beginning of the test. The headspace of each bottle was flushed with nitrogen gas to eliminate the presence of oxygen. Methane production was calculated from the pressure increase according to the ideal gas law and the methane fraction in the headspace. Calculations of the first order hydrolysis constant were done according to Angelidaki and Sanders (2004).

2.3 Results and Discussion

2.3.1 Organics

Concentrations of COD in grey water were 724 ± 150 $\mathrm{mgL^{-1}}$ (Table 2.2); which rectifies the COD values previously reported for this site, which were about 1500 $\mathrm{mgL^{-1}}$, because of the limitations of the sampling point (Hernandez Leal et al., 2007). COD concentrations in grey water were higher than grey water from places with similar weather and customs, such as Germany (Elmitwalli and Otterpohl, 2007), Sweden (Palmquist and Hanaeus, 2005) and another location in the Netherlands (Hernandez Leal et al., 2007)(see table 2.1). High COD measurements in our study are due to the lower grey water production in these 32 houses, i.e. 60–70 $\mathrm{Lp^{-1}d^{-1}}$ (Hernandez Leal et al., 2007) as opposed to the average Dutch water consumption (excluding water use for toilet flushing) of 88.6 $\mathrm{Lp^{-1}d^{-1}}$ (Foekema et al., 2008). Based on the consumption of personal care and household products and other organic pollutants (dirt) in the Netherlands, the calculated amount of COD discharged into grey water is 18.7 $\mathrm{kgp^{-1}y^{-1}}$ (van de Wijst and Groot-Marcus, 1998). The COD loads from grey water in the Netherlands in Groningen was 14.2 $\mathrm{kgp^{-1}y^{-1}}$ (Hernandez Leal et al., 2007) and 15.9–18.5 $\mathrm{kgp^{-1}y^{-1}}$ in Sneek (this study). These are similar to the calculated value.

Table 2.2: Concentrations of organic compounds and surfactants in grey water.

	Average	**Stdev**	**Min**	**Max**	**n**
COD_{total}	724	150	414	1082	182
$\mathrm{COD}_{suspended}$	249	129	10	596	168
$\mathrm{COD}_{colloidal}$	180	43	76	291	171
$\mathrm{COD}_{soluble}$	279	98	91.1	479	180
TOC	157	46	71	249	87
Surfactants					
Anionic	41.1	12.1	10.7	70.5	46
Cationic	1.7	0.8	0.668	3.57	17
Non-ionic	11.3	3.9	5.875	16.88	17

Suspended COD accounted for 34 % of the total COD, colloidal COD was 25 % and soluble COD was 38 % of the total COD. Elmitwalli and

Otterpohl (2007) reported a larger suspended fraction of 50 % and a lower soluble fraction (20 % of the total COD). The fractions of COD are relevant for treatment including anaerobic processes, e.g., in a up-flow anaerobic sludge blanket or a septic tank. A too large fraction of colloidal COD and a slow hydrolysis may limit the application of anaerobic treatment (Elmitwalli, 2000). Direct treatment of grey water with high amount of suspended solids in constructed wetlands or sand filters would cause clogging very soon after the start of the operation.

COD concentrations varied between seasons, especially during summer and autumn (Figure 2.1). During the summer, total COD was 643±136 mgL^{-1}, significantly lower than COD concentrations of spring and autumn. This was possibly related to an increased water consumption due to warmer weather in summer time. In autumn, total COD concentrations increased to 840 ±154 mgL^{-1}, due to an increased concentration of suspended COD during this season (414±132 mgL^{-1}). In winter the amount of suspended COD dropped to less than half of the suspended COD in autumn. The variations in suspended COD will have an effect on the accumulation of solids in storage or septic tanks or in the treatment system.

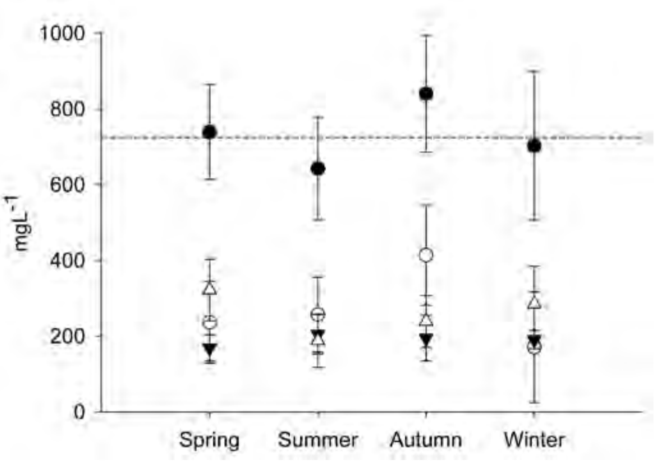

Figure 2.1: Concentrations of COD_{total} (●), $\mathrm{COD}_{suspended}$ (○), $\mathrm{COD}_{colloidal}$ (▼) and $\mathrm{COD}_{soluble}$ (△)in different year seasons. De dotted line represents the average COD_{total} of the total amount of samples.

2.3.2 Surfactants

Anionic surfactants are widely used in many personal care and household products. In 2003 there was a total world production of 4.5 million metric tons of anionic surfactants, 1.7 million metric tons of nonionics and 0.5 million tons of cationic surfactants (Brackmann and Hager, 2004). Based on average composition of personal care and household products, in the Netherlands, a person discharges 6.2 $kgCODy^{-1}$(van de Wijst and Groot-Marcus, 1998) of surfactants, about 30 % of the estimated COD discharges mentioned above. Anionic surfactants, such as linear alkyl sulphonates (LAS), were present in grey water in the range of 41±12 mgL^{-1} (Table 2.2). Nonionic surfactants were present at concentrations of 11.3±3.9 mgL^{-1} and cationics at 1.7 ±0.8 mgL^{-1}.

The contribution of surfactants to the total COD of grey water can be estimated from the measured concentrations and the theoretical COD value of the reference compounds used for chemical analysis. Dodecylbenzene sulphonate has a specific COD value of 2.4 $gCODg^{-1}$, cetyltrimethylammonium bromide of 5.3 $gCODg^{-1}$ and triton x 100 of 2.6 $gCODg^{-1}$. It was calculated that surfactants in the researched grey water accounted for 15 % of the total COD, half the amount estimated by van de Wijst and Groot-Marcus (1998). The difference can be due to a decrease in surfactant use in the drainage area or to a possible decrease in consumption of surfactants in the Netherlands since 1998.

Surfactants may have negative effects if present in irrigation water, for instance anionic surfactants at concentrations in the range of 30 mgL^{-1} may cause chlorosis in plants and water repellence in soils (Wiel-Shafran et al., 2006). For reuse as irrigation water, it is recommended that the concentrations of anionic surfactants do not exceed 1 mgL^{-1} (Li et al., 2009). Therefore, grey water treatment is required to remove these surfactants.

2.3.3 Anaerobic biodegradability

Data shown in Table 2.3 indicate that 70±5 % of the COD of grey water can be biodegraded under anaerobic conditions. A similar biodegradability was measured for the different COD fractions. Anaerobic biodegradability values are consistent with grey water from a student flat in Jordan, with a value of 70±6 % (Abu Ghunmi, 2009) and grey water in Northern Germany, with a value of 74±4 % (Elmitwalli and Otterpohl, 2007).

Anionic surfactants showed a poor anaerobic degradability of 35±13 %. Anionic surfactants, besides their poor removal during anaerobic digestion, may inhibit the process of hydrolysis. Garcia-Morales et al. (2001) reported that LAS can inhibit acidogenesis in anaerobic sludge, and measured an EC_{50} of 10 mgL^{-1}. Anaerobic biodegradability of cationic surfactants was 71±13 %. Literature data on anaerobic degradation of cationic surfactants vary greatly, poor biodegradability was shown for cationic surfactants called alkylquats (19–38 %) (Garcia et al., 1999), but high biodegradability (78-100 %) for cationic surfactants called esterquats (Garcia et al., 2000). Based on the biodegradability results obtained in this study, the cationic surfactants seemed to belong to the esterquat group. Nonionic surfactants are considered relatively resistant to anaerobic degradation (Scott and Jones, 2000). However, we found a biodegradability of 80±4 %, which is consistent with the high anaerobic biodegradation of linear alcohol ethoxylates (nonionics) demonstrated by Mezzanotte et al. (2002).

Table 2.3: Maximum anaerobic biodegradability of COD and surfactants removal (in %) and first order hydrolysis constant of grey water (d^{-1})

	Average	Stdev
COD_{total}	70	5
$COD_{suspended}$	67	15
$COD_{colloidal}$	77	6
$COD_{soluble}$	64	12
Anionic surfactants	35	13
Cationic surfactants	71	13
Nonionic surfactants	80	4
Hydrolysis constant	0.02	0.01

The hydrolysis constant for grey water was low, with an average of 0.02±0.01 d^{-1}. This indicates that even though the biodegradability is high, the process of biodegradation will be slow due to the low hydrolysis rate. Poor anaerobic grey water treatment efficiencies have been shown in the past, with COD removal efficiencies ranging from 40 to 65 % (Abu Ghunmi et al., 2010; Elmitwalli and Otterpohl, 2007; Hernandez Leal et al., 2007; Hernández Leal et al., 2010). Although the colloidal fraction presented a high biodegradability, poor removal in a UASB reactor may occur because this fraction cannot be retained in the sludge blanket (Elmitwalli, 2000). Furthermore, the slow hydrolysis of grey water components may cause the accumulation of solids in septic tanks and other anaerobic treatment systems and therefore the size of the system may have to be larger.

2.3.4 Nutrients

Total nitrogen concentrations were 26.3±12 mgL^{-1}, of which only 16 % was inorganic, with 10 % ammonium (Table 2.4) and 3 % nitrate and nitrite, respectively. That means that the major part of the nitrogen was organically bound, which is contrary to the case of sewage, in which a large fraction (50–93 %) of the nitrogen is present as ammonium (Elmitwalli et al., 2000). This is probably due to the absence of urea from urine, which transforms very quickly into ammonium and accounts for up to 90 % of the nitrogen in sewage.

Concentrations of phosphorus were 7.2 ±4.2 mgL^{-1}, of which 35 % was in the form of phosphate and 65 % was particulate phosphorus. Total phosphorus was similar as in other studies, were total P ranged from 3.9–9.9 mgL^{-1} (Table 2.1). Since the mid eighties no phosphate is allowed in laundry detergents (Kroes, 1980), therefore, the sources of phosphate in grey water may come from food processing and dishwashing liquids.

The ratio COD:N:P for grey water was 100(20.7):3.6(1.7):1(0.6), a similar ratio as in other grey water studies, indicating possible nitrogen deficiency for aerobic treatment.

2.3.5 Cations and anions

Concentrations of trace elements are shown in Table 2.5. Cadmium, chromium, lead, nickel, tin and selenium were below the quantification limit of 0.05 mgL^{-1} in all analyzed samples. For all trace elements, the concentrations in grey water were well below the recommended limits for long and short term irrigation (Feigin et al., 1991), except for boron which concentrations in some measurements exceeded the limit recommended for long term irri-

Table 2.4: Concentrations of nutrients in grey water

	average	stdev	min	max	n
Total N	26.3	12.0	3.66	87.5	156
NH_4-N	2.7	2.0	0.25	7.32	158
NO_2	0.84	1.30	0.01	1.98	134
NO_3	0.77	1.07	0.01	7.95	153
Total P	7.2	4.2	2.3	34.5	119
PO_4-P	2.36	2.48	0.03	6.89	150

gation of 0.75 mgL^{-1}. Concentrations of metals like copper and manganese can be reduced significantly (by >70 %) by biological treatment, caused by adsorption to sludge (Karvelas et al., 2003). Also some removal (up to 50 %) can be expected for metals like cadmium, chromium, lead, iron, nickel and zinc due to adsorption to sludge (Karvelas et al., 2003).

Boron in household wastewater comes primarily from cleaning products (Dyer and Caprara, 1997). Its removal in biogical systems is limited and similar concentrations can be found in the effluent as in the influent of the treatment system (Fujita et al., 2005). Therefore, boron might represent a problem if treated grey water is used for long term irrigation. Typical toxic effect of boron can be seen in leaf burn, fruit disorders and bark necrosis. Safe concentrations of boron in irrigation range from 0.3 mgL^{-1} for sensitive plants (e.g., apple) to 2-4 mgL^{-1} for tolerant plants (e.g., carrot) (Nable et al., 1997).

Concentrations of sodium in grey water were 144 ± 26 mgL^{-1}, twice as high as tap water in Sneek. Concentrations of calcium and magnesium were 30 ± 11 mgL^{-1} and 10 ± 1.4 mgL^{-1}, practically unchanged from tap water in Sneek. It becomes clear that sodium, calcium and magnesium concentrations in tap water have a great influence on their final concentrations in grey water. The removal of calcium and sodium in primary, secondary and tertiary treatment is minimal (Asano et al., 2007). For reuse of treated grey water for irrigation, the sodium adsorption ratio (SAR, $([Na^+]/([Mg^{++}]+[Ca^{++}])/2)^{1/2}$) should not exceed 3 for unrestricted irrigation. For grey water the average SAR was 3.3. The possible removal of magnesium during water treatment, may lead to an increased SAR with a

Table 2.5: Concentrations of cations and anions in grey water

	average	stdev	min	max	n	Recommended limits for irrigation (Feigin et al., 1991) long term	short term
Al	1.22	3.66	0.23	3.65	91	5	-
B	0.53	0.19	0.20	0.91	109	0.75	2
Cu	0.07	0.05	0.04	0.12	96	0.2	5
Fe	0.74	0.49	0.05	1.69	109	5	-
Mn	0.06	0.05	0.02	0.10	98	0.20	-
Zn	0.05	0.02	0.02	0.08	55	2	10
Na	144	26	50	216	103		
Ca	30	11.4	17	49	110		
Mg	10	1.4	7.4	17	109		
K	12	2.0	8.8	15	109		
S	20	9.5	6.0	35	108		
Cl	65.4	16.8	36.0	96.7	106		
SO_4	7.23	7.59	0.10	21.10	150		

value of 4. Therefore, the application of treated grey water for irrigation would require either the selection of a more sodium tolerant crop, such as tomato, barley and red beet (Asano et al., 2007), or a sodium removal step of the incoming tap water or the grey water itself.

2.4 Final discussion

Grey water was thoroughly characterized. Unlike previous grey water studies, this paper presents data from an extensive sampling campaign over a period of 14 months. Due to the high concentrations of COD and surfactants, treatment is required prior to any reuse applications. The high COD concentrations of 724±150 mgL^{-1} contradict the general belief that grey water is very diluted compared to sewage. In fact, it contains approximately 50 % of the COD discharged by households (Otterpohl, 2002). The high anaerobic biodegradabilty of 70±5 %, indicates the possibility of recovering COD as methane, however the low hydrolysis constant of 0.02±0.01 d^{-1}, may limit the application of anaerobic grey water treatment. Surfactants were found at high concentrations, especially anionics (41.1 ±12.1 mgL^{-1}). At this concentration, anionics have the potential to inhibit anaerobic processes. Aerobic treatment, therefore, may be more suitable for grey water treatment because anionics do not present toxicity for aerobic processes and are even biodegraded to a large extent. From the trace elements measured in grey water, in a few measurements boron exceeded the concentrations for reuse in long term irrigation. The relatively high concentration of sodium in grey water (144±26 mgL^{-1}) may restrict its reuse as irrigation water to sodium tolerant crops.

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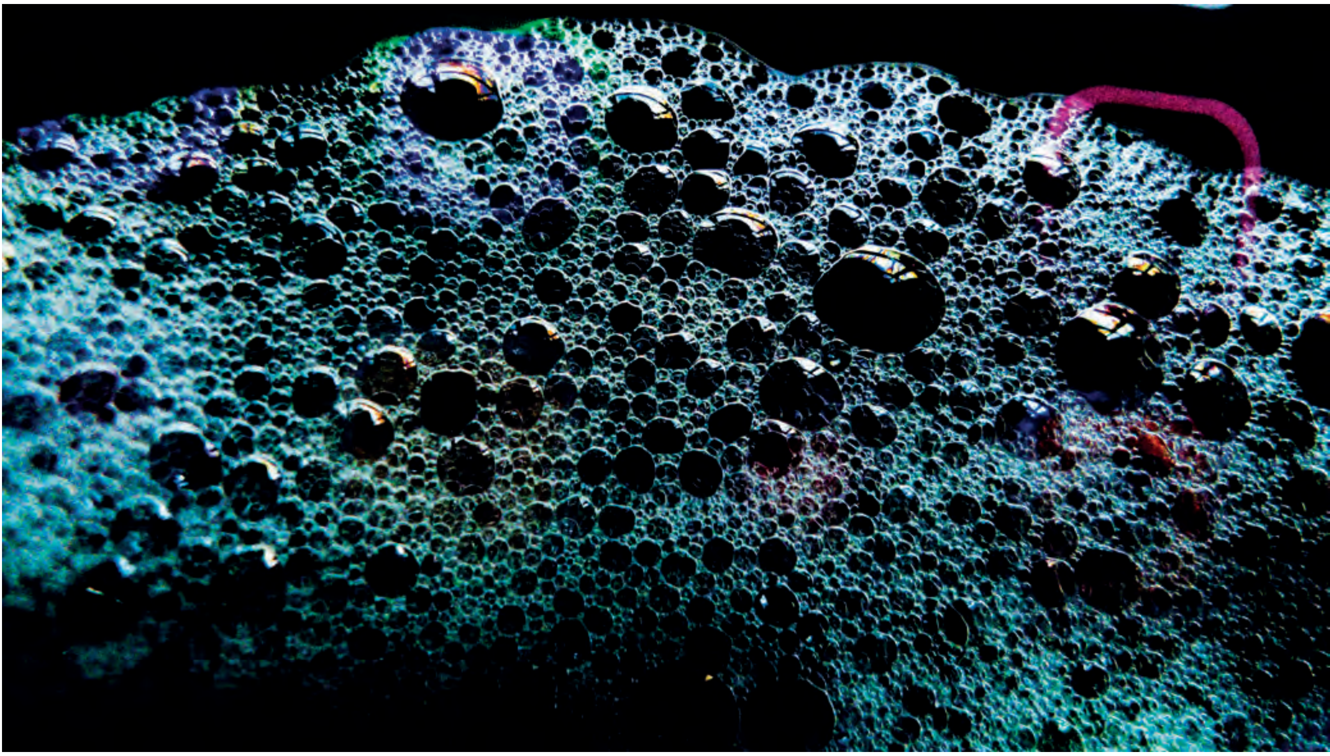
CHAPTER 3

Comparison of three systems for biological grey water treatment



Abstract

Grey water consists of household wastewater excluding toilet discharges. Three systems were compared for the biological treatment of grey water at a similar hydraulic retention time of approximately 12-13 hours. These systems were aerobic treatment in a sequencing batch reactor, anaerobic treatment in an up-flow anaerobic sludge blanket reactor and combined anaerobic-aerobic treatment (up-flow anaerobic sludge blanket reactor + sequencing batch reactor). Aerobic conditions resulted in a COD removal of 90 %, which was significantly higher than 51 % removal by anaerobic treatment. The low removal in the anaerobic reactor may have been caused by high concentration of anionic surfactants in the influent (43.5 mgL^{-1}) and a poor removal of the colloidal fraction of the COD in up-flow anaerobic sludge blanket reactors. Combined aerobic-anaerobic treatment accomplished a COD removal of 89 %, similar to the aerobic treatment alone. Grey water methanization was 32 % for the anaerobic system and 25 % for the anaerobic-aerobic system, yielding a small amount of energy. Therefore, anaerobic pre-treatment is not feasible and an aerobic system is preferred for the treatment of grey water.

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3.1 Introduction

Grey water (i.e., discharges from shower, hand basin, bath, laundry and kitchen) accounts for up to 75 % of the wastewater produced in households (Eriksson et al., 2002). It contains low concentrations of organic compounds (in terms of chemical oxygen demand (COD)), nutrients and pathogens compared to the more highly concentrated black (toilet)water (Otterpohl, 2002). Therefore, it makes sense to collect grey water, treat it separately and re-use it for irrigation, infiltration, washing or other non potable applications.

Currently, most grey water treatment systems installed are based on septic tanks in combination with constructed wetlands, sand filtration or compact aerobic systems such as membrane bioreactors, bio-rotors and biofilters (Jefferson et al., 2001). Upflow anaerobic sludge blanket (UASB) reactors have been successfully applied in domestic wastewater treatment at tropical and semi-tropical conditions (Seghezzo et al., 1998). An important feature of this technology is the advantage of operating at a short hydraulic retention time (HRT) combined with longer sludge retention time (SRT) (Zeeman and Lettinga, 1999), and the possibility to combine the removal of COD with energy production as methane. Only few studies on anaerobic treatment of grey water are available (Abu Ghunmi et al., 2008; Elmitwalli and Otterpohl, 2007). Elmitwalli and Otterpohl (2007) recommended anaerobic treatment as the first treatment step for grey water. They noted a COD removal of around 50 % at 30 °C and an HRT of 6 hours was achieved applying a UASB reactor; in batch tests the maximum anaerobic degradability of grey water was 76 % (Elmitwalli and Otterpohl, 2007).

The process configuration where aerobic and anaerobic conditions are combined for grey water treatment has not been previously investigated. This configuration, however, has the possibility of combining the advantages of anaerobic and aerobic processes, and leading to optimal biological treatment of grey water. Therefore, this study aims at comparing the biological treatment of grey water at lab-scale under anaerobic and aerobic conditions, and under the combination of these at similar overall HRT.

3.2 Experimental Section

3.2.1 Grey water source

Grey water was collected from the 32 houses of the Decentralized Sanitation and Reuse (DeSaR) demonstration project in Sneek, the Netherlands (Hernandez Leal et al., 2007). These 32 houses are equipped with vacuum toilets for the collection of concentrated black water, which is treated on-site. Grey water (the rest of the household wastewater) was collected separately. At the time of this study there was no treatment system on-site yet. Therefore, an autosampler (ASP-Station 2000, Endress + Hauser) was installed to take time proportional samples and store them at 4 °C. The capacity of the autosampler was 80 L. The total amount of water treated was about 5 m^3, therefore we treated 0.5 % of the grey water from this site. These samples were transfered every 1–4 days from Sneek to our lab facilities in Leeuwarden and stored in a cold room (2–10 °C) before the water was treated in lab-scale reactors.

3.2.2 Experimental setup

Three systems were operated at a total HRT of 12-13 hours, based on the design HRT for a UASB reactor Zeeman and Lettinga (1999).

The aerobic system consisted of an SBR of 3.6 L. The anaerobic system consisted of a UASB reactor of 5 L. The combined anerobic-aerobic system consisted of a sequence of an SBR of 3.6 L operated at an HRT of 6 hours and a UASB of 5 L operated at an HRT of 7 hours. Figure 3.2.2 shows the scheme of the setup used in this study. Reactors are labelled after the reactor configuration (SBR or UASB), followed by a number representing the HRT in hours. Reactors SBR12 and UASB12 were operated for 168 days and reactors UASB7 and SBR6 were operated 84 days (from day 84–168).Table 3.1 shows the description of the operating cycles of the SBRs.

The temperature of the reactors was 32 ± 3 °C and it was maintained by means of a water bath connected to the double wall of the reactors.

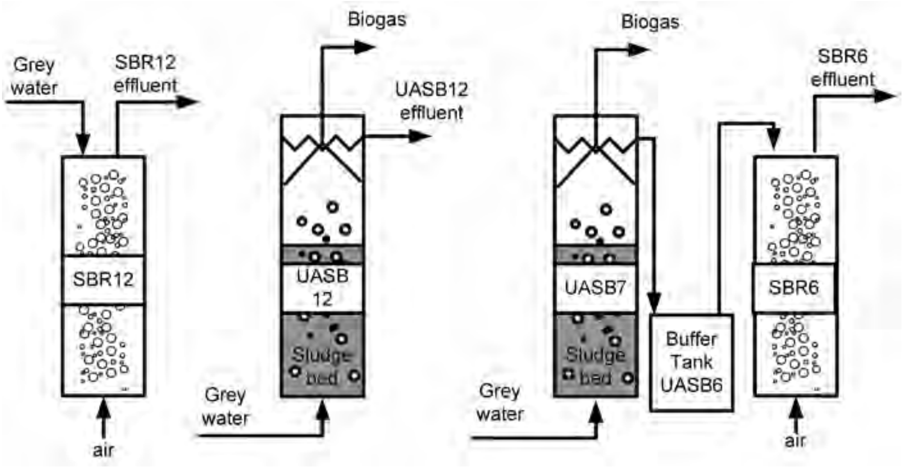

Figure 3.1: Lab-scale reactors set up.

3.2.3 Chemical analysis

Influent and effluent were monitored every 2-3 days over a period of 168 days for total nitrogen, nitrate, total ammonium nitrogen (NH_3-N and NH_4^+), total phosphorus, total and soluble COD and total and volatile suspended solids (TSS and VSS, respectively). These analyses were all conducted according to Standard Methods (APHA et al., 1998), suspended COD was defined by a particle size of >12–25 μm (Schleicher & Schuell 589/1 black ribbon filters) and soluble COD was defined below a particle size of 0.45 μm. Colloidal COD was calculated from the difference of the COD from the black ribbon filtered samples and the dissolved COD.

Table 3.1: Operating cycles for aerobic SBRs.

	SBR12	SBR6
Cycle duration (h)	6	4
Filling (min)	15	10
Reaction time (h)	4.8	3.2
Settling time (min)	45	30
Emptying time (min)	15	10

Effluent from the reactors was collected over periods of 2–3 days, stored at 4–10 °C and then weighed and measured for the above mentioned parameters. This enabled an accurate measurement of flow and the collection of representative samples. Influent and effluent concentrations of anionic surfactants were monitored every 2–3 days for a period of 2 months. Surfactants were measured with cuvette tests based on the MBAS Standard Method (APHA et al., 1998).

Biogas produced in the UASB reactors passed a washing bottle containing sodium hydroxide 15 %w to remove CO_2 and was subsequently measured with gas counters (MGC, Ritter). Dissolved methane in the effluent was calculated according to Henry's law and taken into account in the methane production.

3.2.4 Determination of sludge yield

TSS and VSS concentration in the reactors were measured three times a week for the SBRs and twice a month for UASBs. Sludge yield was determined from a plot of cumulative production of volatile suspended solids versus the cumulative amount of COD removed. The yield was calculated with Equation 3.1 and 3.2. The amount of VSS in the influent was negligible, and therefore it was not used for the calculations.

$$yield = \frac{\Delta VSS_{reactor} + \Sigma VSS_{wasted} + \Sigma VSS_{effluent} - \Sigma VSS_{influent}}{\Sigma COD_{removed}} \tag{3.1}$$

$$COD_{removed} = V_{effluent} \cdot (COD_{in_{total}} - COD_{out_{filtered}}) \tag{3.2}$$

$COD_{in_{total}}$ is the total COD concentration in the influent. $COD_{out_{filtered}}$ is the COD concentration of the effluent filtered through >12-25 μm pore size paper filter (Schleicher & Schuell 589/1 black ribbon filters). Removed COD was calculated as the product of the volume of effluent collected ($V_{effluent}$) and the difference between COD_{in} and $COD_{out_{filtered}}$ measured in the period of collection of that effluent volume. Total effluent COD was not used for the calculation of the yield, since suspended solids in the effluent were considered to be sludge.

SRT was calculated as the ratio between the amount of VSS in the reactor and the sludge production rate (g VSS d^{-1}) over the operational period t, see Equations 3.3 and 3.4.

$$SRT = \frac{VSS_{reactor}}{Sludge\ production\ rate} \tag{3.3}$$

$$Sludge\ production\ rate = \frac{\Sigma VSS_{wasted} + \Sigma VSS_{effluent}}{t} \tag{3.4}$$

The data presented in Table 3.3 have been statistically treated to minimize the influence of outliers in the interpretation. Outliers were defined as values outside the range of the mean ± 2 x standard deviation. For the calculation of yield, SRT, and mass balances all data were taken into account.

3.3 Results and Discussion

3.3.1 Characteristics of grey water

Average concentrations of COD in the influent were similar in the two test periods, i.e., 830 mgL^{-1} (Table 3.2). Of the COD, the suspended fraction accounted for approximately 50 % and the remaining part was equally distributed between the colloidal and dissolved fractions. Grey water in this study had a relatively high concentration of COD compared to other studies previously performed in regions of similar climate and customs. For example, in Germany COD concentrations of 640 mgL^{-1} (Elmitwalli and Otterpohl, 2007) and 420 mgL^{-1} (Nolde, 2005) have been measured. In Sweden concentrations have been reported of 588 mgL^{-1} (Palmquist and Hanaeus, 2005) and at another location in the Netherlands 450 mgL^{-1} (Hernandez Leal et al., 2007). The higher COD concentrations in this study were probably due to the lower volume of grey water produced at this particular site in Sneek (70 $Lp^{-1}d^{-1}$ vs. the Dutch average of 90 $Lp^{-1}d^{-1}$) (Hernandez Leal et al., 2007).

Grey water was found to have a higher temperature than combined wastewater because of the use of warm water in showering, laundry and kitchen. Eriksson et al. (2002) reports temperatures ranging between 18–38 °C. In this study, the temperature was set at 32±3 °C.

Table 3.2: Characteristics (averages with standard deviations) of grey water used in this study (all values are in mgL^{-1}).

	days 1–168 average	days 84–168 average
COD$_{total}$	833 ± 188	827 ± 204
COD$_{suspended}$	411 ± 151	385 ± 167
COD$_{colloidal}$	204 ± 58	227 ± 65
COD$_{soluble}$	224 ± 59	196 ± 52
Anionic surfactants		43.5 ± 6.5
Total N	41.2 ± 27.2	29.9 ± 11.0
NH_4-N	1.0 ± 0.7	0.6 ± 0.4
NO_3-N	0.12 ± 0.08	0.12 ± 0.07
Total P	6.6 ± 2.7	5.8 ± 1.4

3.3.2 General systems performance

Table 3.3 summarizes the operation and average treatment performance of the reactors. For the combined system the table shows the performance of the individual reactors (UASB7 and SBR6) and for the combination (UASB7 + SBR6). Mean VLR was similar for the 3 systems, with a value around 1.6 kg CODm^{-3}d^{-1}. Reactor performances were stable with respect to COD removal and average COD concentrations in the effluent.

Under anaerobic conditions, the removal of COD averaged 51 % in UASB12 and 39% in UASB7, whereas under aerobic conditions 90 % of the COD was removed in SBR12 and 82 % in SBR6. The combined anaerobic-aerobic system achieved a COD removal of 89 % which is similar to the performance of the aerobic reactor operated at an HRT of 12 h. Average concentrations of COD in the effluents of each system were 82, 392 and 100 mgL^{-1} for the aerobic, anaerobic and anaerobic-aerobic system, respectively.

3.3.3 Removal of different COD fractions

Variation in the VLR was due to the variation in the COD concentration of influent, the COD fractions of the influent and HRT in the studied reactors

(Figures 3.2 to 3.5) over the operational period. In the figures, diagonal lines correspond with 100 % removal. The data of the aerobic reactors approached this 100 % removal efficiency for all COD fractions. Furthermore, the data suggest that in theory a further increase of the VLR (i.e., a shorter HRT) might be possible while maintaining a high level of COD removal. It was noted, that at a VLR above 2 kg $\mathrm{CODm^{-3}d^{-1}}$ a COD removal of 90 % can be achieved (Figure 3.2). A higher VLR, however, would also imply higher sludge concentrations and settleability may therefore become a limiting factor.

In reactors UASB12 and UASB7, COD was poorly removed and was mainly accomplished by the removal of suspended COD, which was 79 % for UASB12 and 72 % for UASB7 (Figures 3.3 and 3.4). In another study on grey water, a total COD removal of 52 % was achieved in an UASB operated at HRTs of 10 and 6 h (Elmitwalli and Otterpohl, 2007). The difference between the results of our study and those published by Elmitwalli and Otterpohl (2007) is the higher concentration of COD in our influent and the grey water sampling procedure. The effluent COD in Elmitwalli and Otterpohl (2007) was 310 $\mathrm{mgL^{-1}}$ at an HRT of 10 h and 327 $\mathrm{mgL^{-1}}$ at an HRT of 6 h. Despite of having higher influent COD, in our study the COD removal was lower, leading to effluent COD concentrations of 392 and 528 $\mathrm{mgL^{-1}}$ for UASB12 and UASB7, respectively.

The difference in HRT in the anaerobic reactors strongly affected the removal of the soluble COD. A removal of 30 % was achieved at an HRT of 12 h but only 12 % at an HRT of 7 h. Similarly, 16 % of the colloidal COD was removed at an HRT of 12 h and only 10 % at an HRT of 7 h. The removal of suspended COD remained high at both HRTs, 79 % at 12 h and 72 % at 7 h. Poor COD removal of the anaerobic reactors can be attributed to the limited removal of colloidal COD. It is known that the colloidal fraction of the COD is poorly removed in UASB reactors because it cannot be entrapped or flocculated in the sludge bed, and the HRT is not long enough for its degradation (Elmitwalli et al., 2000).

Table 3.3: Operation and performance of biological reactors for grey water treatment.

	SBR 12 (aerobic system)	SBR6	UASB12 (anaerobic system)	UASB7	UASB7 + SBR6 (anaerobic-aerobic system)
HRT (h)	11.7 ± 1.1	6.1 ± 0.8	12.3 ± 1.8	7.0 ± 2.0	13.17 ± 2.03
VLR (kg CODm^{-3}d^{-1})	1.6 ± 0.5	1.9 ± 0.4	1.7 ± 0.4	2.7 ± 0.8	1.5 ± 0.6
COD removal rate (kg CODm^{-3}d^{-1})	1.5 ± 0.4	1.5 ± 0.4	0.8 ± 0.3	1.1 ± 0.6	1.4 ± 0.5
SLR (kg COD (kg VSS)$^{-1}$ d^{-1})	0.29 ± 0.07	0.6 ± 0.3	0.12 ± 0.04	0.23 ± 0.08	**
Sludge concentration (g VSSL^{-1})	5.5 ± 1.1	3.3 ± 1.1	12.5 ± 2.4	12.7 ± 4.3	**
SRT (d)	15	379	392	97	**
Yield (kg VSS(kg COD)$^{-1}$)	0.12	0.06	0.08	0.18	0.18
COD removal (%)	90 ± 7	82 ± 06	51 ± 13	39 ± 15	89 ± 3
COD effluent (mgL^{-1})	82 ± 47	100 ± 33	392 ± 85	528 ± 180	100 ± 33
Anionic surfactants (mgL^{-1})	1.4 ± 1.2	1.3 ± 1.5	33.4 ± 4.1	35.9 ± 5.3	1.3 ± 1.5
Effluent total N (mgL^{-1})	31 ± 20	26 ± 13	34 ± 17	32 ± 10	26 ± 13
Effluent NH4-N (mgL^{-1})	0.35 ± 0.20	0.4 ± 0.1	4.7 ± 2.1	5.4 ± 2.4	0.4 ± 0.1
Effluent NO3-N (mgL^{-1})	1.5 ± 1.4	22.6 ± 13.5	0.2 ± 0.1	0.2 ± 0.1	22.6 ± 13.5
Effluent total P (mgL^{-1})	4.4 ± 2.4	5.8 ± 1.7	5.3 ± 1.5	6.1 ± 1.7	5.8 ± 1.7
Effluent VSS (mgL^{-1})	45 ± 61	30 ± 26	7 ± 9	21 ± 23	30 ± 26
Removal total N (%)	35 ± 37	26 ± 27	15 ± 33	-1 ± 63	2 ± 56
NH4-N removal (%)	51 ± 47	92 ± 4	*	*	7 ± 86
Total P removal (%)	28 ± 50	31 ± 11	11 ± 28	1 ± 36	3 ± 44
Methane flow (NL d^{-1})	**	**	0.76	0.8	0.8
Methane production (NL m^{-3})	**	**	123	71.5	71.5

[*] No ammonium removal

[**] Not applicable

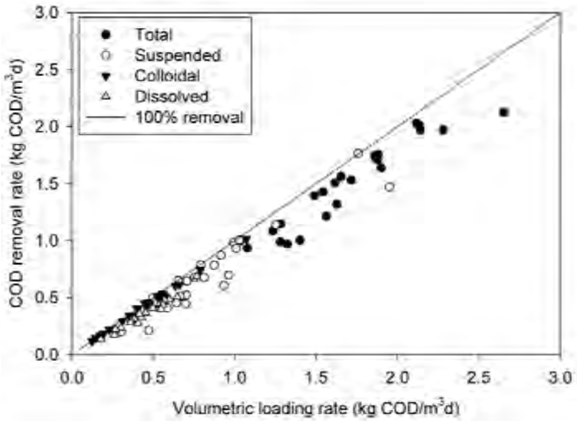

Figure 3.2: COD removal rate vs volumetric loading rate in SBR12

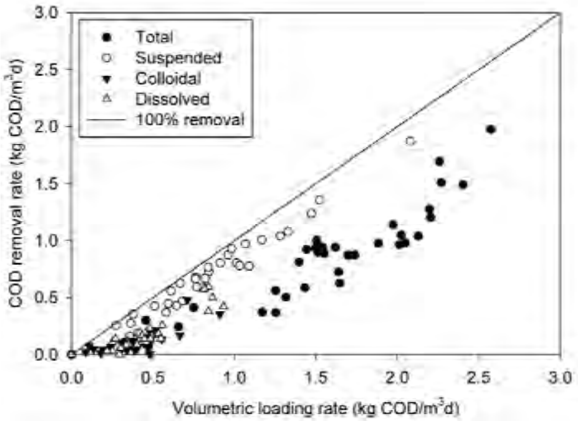

Figure 3.3: COD removal rate vs volumetric loading rate in UASB12

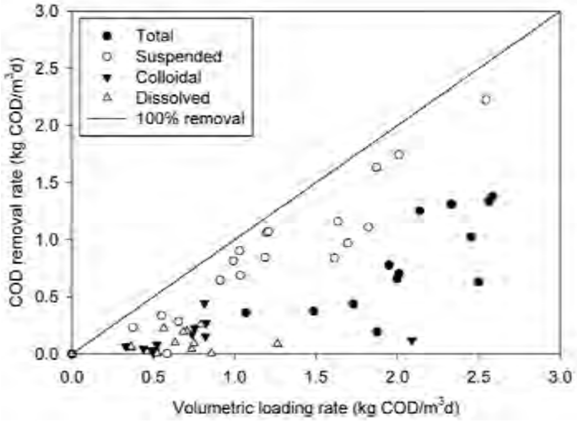

Figure 3.4: COD removal rate vs volumetric loading rate in UASB7

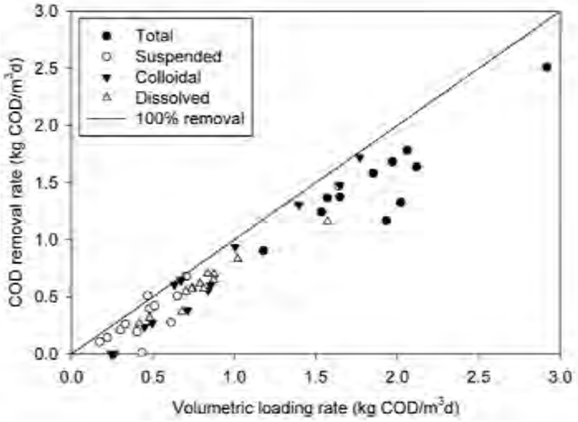

Figure 3.5: COD removal rate vs volumetric loading rate in SBR6

3.3.4 Surfactant effect

The performance of the UASB reactors was most likely affected by the high concentration of anionic surfactants, which constituted about 15 % of the influent COD. The average influent concentration of surfactants was 43.5 mgL^{-1}, of which UASB12 and UASB7 only removed 24 and 17 %, respectively (Figure 3.3.4). In contrast, the aerobic SBR's removed 97 % of the anionic surfactants, leading to average effluent concentrations of 1.4 and 1.3 mgL^{-1} in SBR12 and SBR6, respectively. Anionic surfactants are readily biodegradable under aerobic conditions as opposed to anaerobic conditions, at which they are unlikely to be degraded (Ying, 2006). Removal that occurred in the UASB reactors was probably due to adsorption to the sludge particles. Furthermore, Garcia-Morales et al. (2001) found that acidogenic bacteria in anaerobic sludge were inhibited by linear alkylbenzene sulfonates (LAS, widely used anionic surfactants), with an EC50 of 19 mgL^{-1}. With the concentration of anionic surfactants in the range of 30–50 mgL^{-1}, the inhibition of hydrolysis likely occurred in these UASB reactors, leading to sludge accumulation.

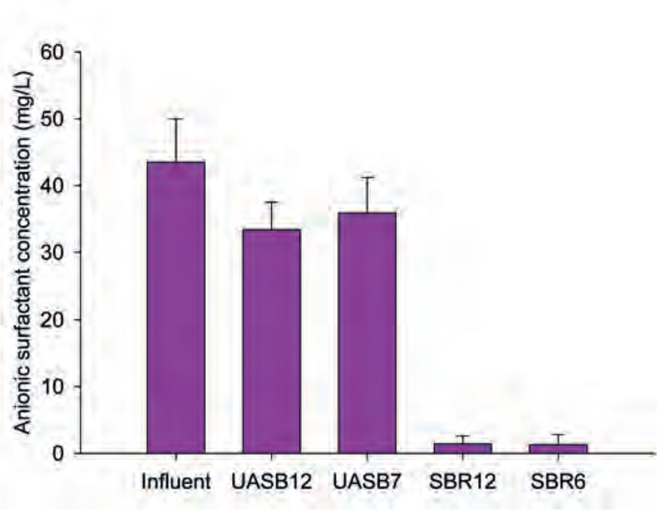

Figure 3.6: Influent and effluent concentrations of anionic surfactants in 4 bioreactors treating grey water.

3.3.5 COD mass balances

Mass balances of COD were done for the anaerobic reactors (Figure 3.3.5). The majority of the influent COD was not converted in the reactors and 55 and 60 % was found in the effluent, respectively for UASB12 and UASB7. Methanization of the influent COD was 32 % in UASB12 and 25 % in UASB6. COD transformed into sludge was determined to be 5 % in UASB12 and 10 % in UASB7. A small percentage (8 and 5 %) could not be accounted for.

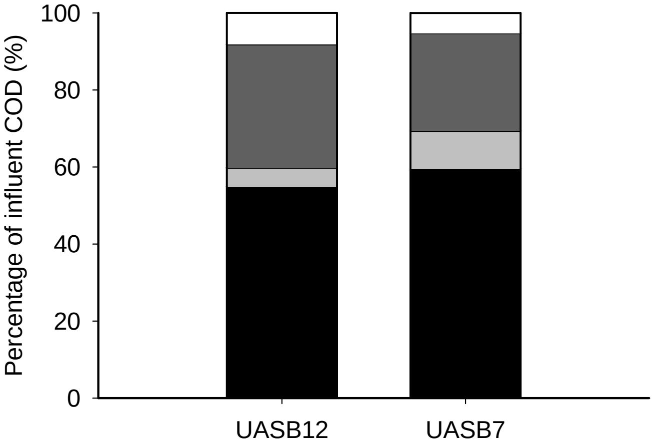

Figure 3.7: COD mass balance on anaerobic reactors UASB12 (period of 168 days) and UASB7 (period of 84 days). Cumulative effluent COD (■), cumulative COD converted into sludge (■), cumulative COD converted into methane (■), cumulative COD not accounted for (□).

3.3.6 Sludge yield

The researched aerobic reactors exhibited a sludge yield of only 0.06 and 0.12 kg VSS(kg COD)$^{-1}$ for SBR6 and SBR12, respectively. Figure 3.3.6 shows the yield curve for reactor SBR12. SRT at SBR6 was 378 days which explains the low sludge yield measured in this reactor. In contrast to SBR6, the yield of SBR12 was accompanied by a relatively short SRT of only 15 days. Although this is a good feature of the process, it is not clear why the sludge yield is so low. Based on the total sludge production, the amount of

VSS in the effluent was 43 % for SBR12 and 95 % for SBR6. These figures indicate a need for another reactor configuration to prevent sludge from washing out, e.g. a membrane bioreactor. Nevertheless, both aerobic reactors showed a very low sludge yield, compared to reported average values of 0.30–0.50 (Metcalf and Eddy, 2003).

Anaerobic reactors had a sludge yield of 0.08 (UASB12) and 0.18 kg VSS(kg COD)$^{-1}$ (UASB7). From the total sludge production, 84 and 62 % of the VSS were in the effluent, respectively. Part of the sludge yield cannot be attributed to the formation of biomass, and was caused by the accumulation of slowly biodegradable particulate organic matter in the sludge bed.

The difference between the yields in reactors UASB12 and UASB7 was probably due to lower hydrolysis of slowly biodegradable organic matter in the sludge bed at a higher VLR, and therefore a lower SRT. Nevertheless at an SRT of 97 days and a temperature of 32±3 °C a complete degradation of biodegradable COD was expected (Zeeman and Lettinga, 1999). The combined sludge yield for the anaerobic + aerobic system was 0.18 kg VSS(kg COD)$^{-1}$, which is higher than the aerobic system (0.12 kg VSS(kg COD)$^{-1}$) and the anaerobic one (0.08 kg VSS(kg COD)$^{-1}$). Even though it has a low sludge yield, the anaerobic system cannot be selected for grey water treatment due to the poor COD removal, therefore the aerobic system is preferred.

3.3.7 Nutrient removal

Nutrient removal in all reactors was low and exhibited large variations. This resulted in effluent concentrations of nitrogen in a range of 26–34 mgL^{-1} and effluent phosphorus concentrations of 4.4–6.1 mgL^{-1} (Table 3.3). In spite of the rather long SRT of 15 days in SBR12, nitrification was hardly observed, as can be seen from the low nitrate concentration in the effluent (1.5 mgL^{-1}). Furthermore, differences in influent and effluent total nitrogen and ammonium concentrations strongly indicate that a large fraction of the nitrogen in the influent was organically bound. In sewage, most of the nitrogen is present as ammonium (Elmitwalli, 2000), this is probably because 90 % of the nitrogen in sewage comes from urine (Otterpohl, 2002), which is quickly converted into ammonium. In grey water, most of the nitrogen was organically bound, apparently limited ammonification

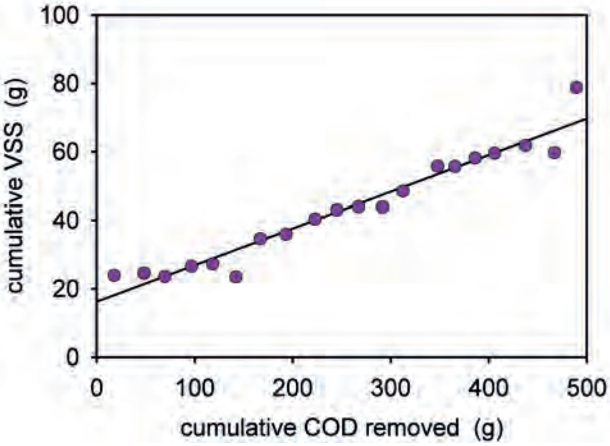

Figure 3.8: Cumulative VSS produced as a function of cumulative COD removed in SBR12 for a period of 168 days.

took place and therefore it was not available for nitrification/denitrification in the SBR12. On the other hand, nitrification in SBR6 was significantly higher, with a mean nitrate concentration of 22.6 mgL^{-1}. The higher nitrification in SBR6 was possibly due to a higher ammonium concentration into SBR6 (5.4 ± 2.4 mgL^{-1}, as opposed to 1.0 ± 0.7 mgL^{-1} into SBR12) and the much longer SRT of 379 days (compared to the SRT of 15 days in SBR12).

Table 3.4 shows the mass of N and P that was removed in the aerobic reactors, along with the estimated mass of N and P required for biomass production (assuming 12 % of VSS is constituted by N and 2 % by P (Metcalf and Eddy, 2003)). In SBR12, nutrient removal could be explained from this biomass production. In SBR6 however, the removal of nutrients could not be attributed to biomass production alone, indicating that a significant fraction of total N was removed with the sludge as non-biomass associated particles.

Table 3.4: Nutrient removal and calculated consumption by sludge production, all values are in g.

	mass of N removed	mass of N in sludge	mass of P removed	mass of P in sludge
SBR12	9.88	8.48	1.15	1.41
SBR6	10.35	3.08	1.02	0.51

3.3.8 Energy production

Whether a combined system is worthwhile from the energetic point of view is an important aspect to consider. With a grey water production of 70 L $p^{-1}d^{-1}$ and a COD of 830 mgL^{-1} as determined in this study, one person produces 58.1 g COD d^{-1} (48 % of the COD load from household wastewater). The energy required for aerobic treatment of grey water treatment was estimated to be 8 kWh $p^{-1}y^{-1}$, based on the energy requirements for aeration of municipal wastewater of 0.31 kWh m^{-3} (Luning, 2006). The methane amount that can be gained from an anaerobic-aerobic system as shown in this study is 5 L $p^{-1}d^{-1}$, which represents 18 kWh $p^{-1}y^{-1}$. For the aerobic post-treatment 4 kWh $p^{-1}y^{-1}$ are required, assuming the energy requirements for the aerobic post-treatment are 50 % of those of aerobic grey water treatment, since 50 % of COD was removed in the UASB reactor. The combined anaerobic-aerobic system, therefore, has a net energy production of 14 kWh $p^{-1}y^{-1}$.

In the context of the whole sanitation concept, black water mixed with kitchen refuse can produce 28 L methane $p^{-1}d^{-1}$, i.e., 101 kWh $p^{-1}y^{-1}$ (Kujawa-Roeleveld et al., 2006). If anaerobic treatment of black water is installed, treatment of grey water with an aerobic system would consume 8 % of the energy production of black water leaving an amount of 93 kWh $p^{-1}y^{-1}$. On the other hand, treatment of grey water with an anaerobic-aerobic system could produce 14 % more methane than by black water treatment alone, to an energy production of 115 kWh $p^{-1}y^{-1}$. However, two UASB reactors are needed instead of one, which makes this treatment option unfeasible, given the limited energy gain. Therefore, the aerobic system is preferred for the treatment of grey water. A combined anaerobic-aerobic system may also have a positive effect on the removal of xenobiotic organic compounds, an aspect that is yet to be investigated.

3.4 Conclusions

- Aerobic treatment of grey water achieved 90 % of COD removal and 97 % removal of anionic surfactants at a HRT of 12 h and a temperature of 32 ± 3 °C.
- The low sludge yield of the aerobic SBR (0.12 kg VSS (kg COD)$^{-1}$) operated at 32 ± 3 °C and an HRT or 12 h makes it an attractive process for the treatment of grey water.
- Anaerobic treatment of grey water at an HRT of 12 hours and a temperature of 32±3 °C reaches 51 % removal of COD, with a grey water methanization rate of 32 % and with a poor removal (24 %) of anionic surfactants.
- A combined anaerobic-aerobic system operated at 32±3 °C and at an HRT of 12 h did not give an advantage, compared to aerobic treatment, with regard to the removal of COD from grey water and sludge yield. However, the benefits of this configuration depend on factors such as gas use and energy input.
- Based on COD removal, sludge yield and energy considerations, treatment of grey water in an aerobic system is preferred over an anaerobic system and a combined anaerobic-aerobic system.

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CHAPTER 4

Occurrence of micropollutants and removal in biological systems

Abstract

Eighteen selected organic micropollutants related to personal care and household chemicals (UV-filters, fragrances, preservatives, biocides, surfactants) were measured in grey water from 32 houses and in effluents of three different biological treatment systems (aerobic, anaerobic and combined anaerobic + aerobic). All selected micropollutants were detected in grey water samples in the low $\mu g L^{-1}$ range. Generally, lower concentrations were measured after biological treatment and removal efficiencies were higher under aerobic conditions than under anaerobic conditions. However, most of the micropollutants were still detected in biologically treated grey water. The most persistent compounds were the fragrance tonalide, and the UV-filters 2-phenyl-5-benzimidazolesulfonic acid and ethylhexyl methoxycinnamate. Estimated estrogenic potential of the effluent ranged between 0.07 and 0.72 ngL^{-1} of 17β-estradiol equivalents. Depending on the application of the effluent and its environmental risk, physical-chemical processes may be required to increase the removal efficiency of these compounds from grey water.

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4.1 Introduction

The water crisis the world is facing is the main driving force to develop approaches that more efficiently use freshwater resources . The concepts of decentralized sanitation and reuse (DeSaR) provide opportunities to minimize the production of wastewater and increase its reuse (Ledin et al., 2001). Grey water is the effluent from washing activities in the household (kitchen sinks, laundry, hand basins, showers and baths). Due to its substantial amount (up to 75% of domestic wastewater) and lower concentration of pollutants compared to black water (discharge from toilets), after appropriate treatment grey water has a high potential for reuse in applications such as irrigation, toilet flushing, laundry and infiltration (Eriksson et al., 2003). Until now, grey water treatment technologies focused on parameters such as BOD and COD, nutrients and pathogens. Only a few studies have dealt with the characterization of other substances, such as organic micropollutants, which in grey water are present at low concentrations (in the range of $\mu g L^{-1}$). Eriksson et al. (2003) identified almost 200 micropollutants in grey water, and these may have a negative impact on plants, animals, humans and the environment if they persist in recycled water or if discharged to water bodies.

These micropollutants, manufactured in large quantities, can be found in almost all household and personal care products and therefore usually end up in grey water. Because biological treatment is usually the first step in the treatment of grey water, it is essential to study the fate of these substances in grey water treatment systems. The aim of our study was to determine the occurrence of micropollutants in grey water and measure their removal in three different biological treatment systems.

4.1.1 Selection of study micropollutants

When referring to grey water, the micropollutants of main concern are not pharmaceuticals but ingredients of household and personal care products. In our study we selected a number of micropollutants based on their persistence to biodegradation, tendency for bioaccumulation (based on $\log K_{OW}$ values) and potential harmful effects (toxicity, estrogenicity, carcinogenicity, etc.) of these substances in the environment. The selected compounds also represent the different groups of personal care ingredients such as fragrances, UV filters, biocides, preservatives and surfactants. The list with selected micropollutants is shown in Table 1.3 including a description of their application, logK_{OW}, water solubility and aerobic biodegradability data. Information about their ecotoxicological effects is shown in Tables 1.8 and 1.9. The structures of the compounds can be found in Figure 1.1 (Chapter 1).

Fragrance ingredients, such as galaxolide and tonalide, are extensively used in formulations of personal care products. In Europe, the production of galaxolide and tonalide ranges from 1000–5000 tons/year (Heberer, 2003). Endocrine disrupting (antiandrogenic) effects of galaxolide and tonalide have been proven in vitro and in vivo (Schreurs et al., 2004).

UV filters are compounds used to protect the skin against solar radiation. The amount of sunscreens sold in The Netherlands was 950 tons/year (in 2000) (Balk et al., 2001). Due to the higher incidence of skin cancer in the last decades, the European Union has promoted the use of sunscreen products. Currently it is estimated that consumers use only half of the necessary amount (Europa press-releases, 2009) and an increase of the use of these compounds, therefore, is expected. In 1999, amongst the most used UV-filters in Germany were benzophenone-3 (BP3), 2-phenyl-5-benzimidazolesulfonic acid (PBSA), octrocrylene, 2-ethylhexyl-4-methoxycinnamate (EHMC), 4-methylbenzylidene-camphor (4MBC), 2-ethylhexyl salicylate (2EHS) and 4-tert-Butyl-4'-methoxy-dibenzoylmethane (avobenzone) (Balk et al., 2001). The endocrine disrupting potency of these compounds has been proven in different species in vivo and in vitro (Fent et al., 2008; Heneweer et al., 2005; Kunz and Fent, 2006). Although median effect concentrations (EC50) are usually higher than concentrations measured in the environment, these compounds are highly bioaccumulative and risks cannot be excluded.

Parabens, alkyl esters of p-hydroxybenzoic acid, are commonly used as preservatives in personal care products in concentrations up to 0.8%. In Denmark, the annual consumption of parabens was estimated at 216 tonnes (in 2006) (Eriksson et al., 2008b). Major concerns of these compounds are their endocrine disrupting effects (Golden et al., 2005). Parabens are readily biodegradable compounds, yet they are still detected in effluents from wastewater treatment plants and in receiving water bodies (Andersen et al., 2007; Gonzalez-Marino et al., 2009; Lee et al., 2005).

Triclosan has been used as a biocide in diverse applications, mostly in personal care products but also in textiles and plastics; its consumption in Europe in 2006 reached 450 tons/year (European Comission, 2009a). Triclosan has been proven to affect thyroid systems in frogs and rats (Zorrilla et al., 2009).

4.2 Materials and methods

4.2.1 Grey water source and treatment systems

Grey water was collected from a residential area with 32 houses in Sneek, the Netherlands (Hernandez Leal et al., 2007). An autosampler (ASP-Station 2000, Endress + Hauser) collected time proportional samples and stored them at 4 °C. The collected grey water was transported to the lab facilities twice per week and stored in a 150 L tank placed in a cold room (4–10 °C).

Grey water treatment was done in three lab-scale reactor systems located at the lab facilities of TTIW Wetsus (Leeuwarden, the Netherlands). These systems are described in detail in Chapter 3 and consist of an aerobic sequencing batch reactor, an anaerobic up-flow sludge blanket reactor and a combination of the afore mentioned reactors (anaerobic + aerobic). The total hydraulic retention time of each of these systems was 12 hours. The effluents were collected in tanks (storage capacity of 6–10 days) placed in a cold room (4–10 °C).

4.2.2 Sampling

A total of 22 samples of grey water and the three different effluents were collected between January and August 2008, at a frequency of approximately every 10 days. Samples were collected in previously cleaned glass bottles (hot water, deionized water, acetone and ethylacetate and heated at 350 °C for 10 hours) and stored at -30 °C until analysis.

4.2.3 Chemicals

Tonalide, galaxolide, benzophenone-3 (BP3), 4-methylbenzylidene-camphor (4MBC), octocrylene, ethylhexyl methoxycinnamate (EHMC) and avobenzone were purchased from CHEMOS GmbH (Germany); hexylcinnamic aldehyde (HCA), 2-phenyl-5-benzimidazolesulfonic acid (PBSA), 2-ethylhexyl salicylate (2EHS) and bisphenol-A were purchased from Aldrich (Germany); benzalkonium chloride (BaCl) was purchased from Sigma-Aldrich (Germany); triclosan, ethylparaben, propylparaben and butylparaben were purchased from Fluka (Germany); methylparaben from SUPELCO (Germany) and nonylphenol-mixture of isopolymers from ACROS organic (Germany).

4.2.4 Analytical methods

Sample preparation

A scheme of the sample preparation procedure prior to analysis with thermal desorption gas chromatography mass spectrometry (TD-GC/MS) is shown in Figure 4.1. Compounds were adsorbed on stir bars coated with polydimethyl siloxane and were desorbed on a 5% phenyl methyl siloxane column in a thermal desorption unit connected to the GC-MS system. Acetic anhydride was added to the sample prior to the adsorption to the stir bars in order to derivatize the hydroxyl groups in parabens, triclosan, and nonylphenol. This was noted to significantly improve the sensitivity of the analysis of these compounds.

A scheme of sample preparation procedure prior to analysis with liquid chromatography tandem mass spectrometry (LC-MS/MS) is shown in Figure 4.2. Briefly, 5 mL of sample was filtered through a glass fiber filter. The filter was washed with 5 mL of acetonitrile (ACN). Then, 1.8 mL of this ACN was evaporated to dryness and reconstituted with 100 μL of ACN and 100 μL of 200 mM of NH_4COOH + 2%HCOOH and 1.8 mL of the filtered sample.

GC/MS analyses

TD-GC/MS with stir sorptive extraction (SBSE) was used to measure parabens, fragrances, bisphenol-A, 4MBC, 2EHS, EHMC, octocrylene and triclosan. The equipment used for this measurement was a Gerstel TD

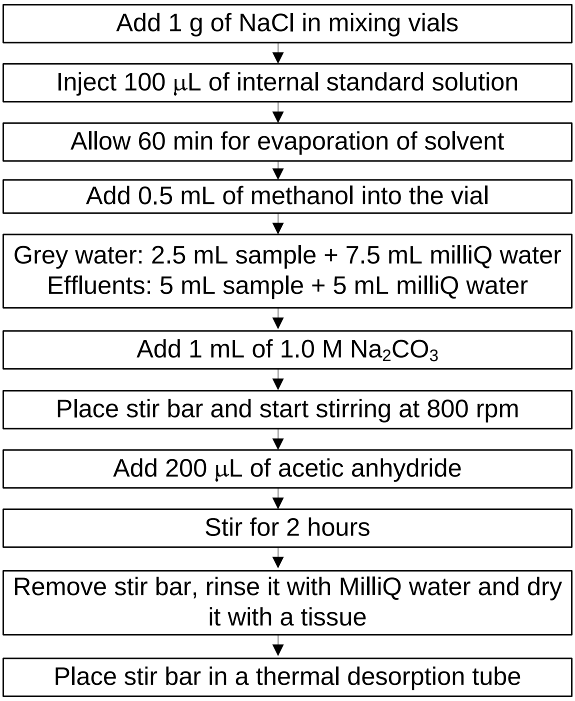

Figure 4.1: Sample preparation procedure for analysis with GC-MS with stir bar sorptive extraction

Unit, an Agilent 6890N GC and an Agilent 5975 inert XL mass selective detector. The responses for calibration and quantification of GC-MS compounds were corrected with the responses of internal standards. Parabens, triclosan and BPA were corrected with bisphenol-A-d16 (CHEMOS, Germany); tonalide, galaxolide, HCA, 2EHS, octocrylene, 4MBC and EHMC were corrected with tonalide-d3 (Dr. Ehrenstorfer GmbH, Germany) and nonylphenol was corrected with benzophenone-d5 (CHEMOS, Germany).

The analytes were desorbed from the stir bars in a thermal desorption unit and then trapped into a cooled injection system (CIS) unit. Then, temperature was raised gradually and the analytes were transferred into the GC column. Initial temperature of the TD unit was 30 °C and it was increased to 280 °C at 720 $°\mathrm{C\,min^{-1}}$ and held at this temperature for 5 min-

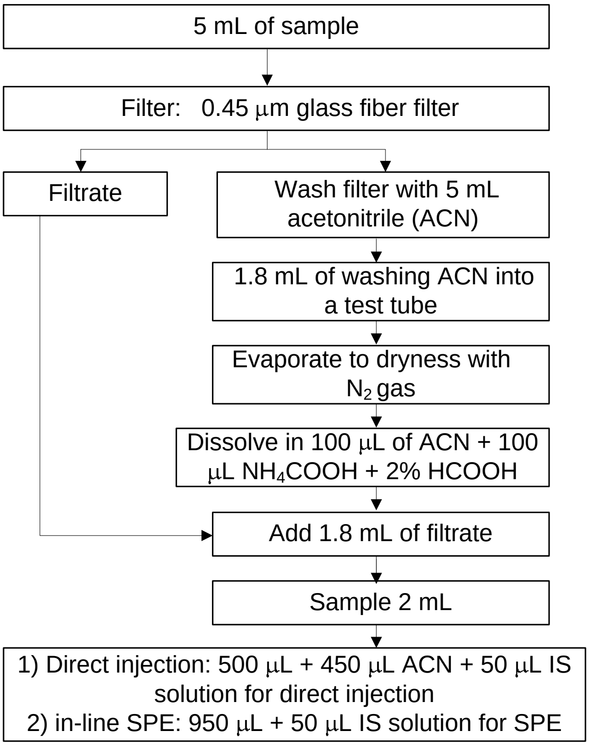

Figure 4.2: Sample preparation procedure for analysis with LC-MS/MS in direct injection and inline SPE

utes. During desorption, CIS unit was kept at a temperature of -50 °C. After desorption, the temperature was increased to 300 °C at 12 °Cs^{-1} and held at this temperature for 10 minutes. The analytical GC column (HP-5ms, 30m x 0.25mm x 0.25μm, Agilent) was kept at a temperature of 60 °C for the first 2 minutes and then ramped into 280 °C at 15 °Cmin^{-1} and held at this temperature for 5 minutes. The analytes were detected at selected ion mode and the ions are presented in Table 4.1.

To determine the recoveries, the matrix samples were spiked with the analytes at different concentrations. Grey water samples were spiked at concentrations between 2 and 25 μgL^{-1} and the other two matrices at 1

Table 4.1: Ions selected for monitoring in GC/MS analysis.

Compound	**SIM (m/z)**
Methylparaben*	121
Ethylparaben*	121
Propylparaben*	138
Butylparaben*	138
EHMC	178
2EHS	120
4MBC	254
Octocrylene	249
Galaxolide	243
Tonalide	243
Hexyl cinnamic aldehyde	129
Nonylphenol*	135
Triclosan*	288
Bisphenol-A*	213
Tonalide-d3	246
Bisphenol-A-d16*	224
Benzophenone-d5	187

* Acyl-derivatives of the analytes

to 10 μgL^{-1} depending on the analyte. The samples were analyzed as described above and all the measurements were done in triplicates.

LC-MS/MS analysis

Liquid chromatography with tandem mass spectrometry (LC-MS/MS) was used to measure PBSA, BaCl, BP3 and avobenzone. Concentrations in the range of 2.5–250 μgL^{-1} were measured by directly injecting the samples to the LC-MS/MS system (Agilent 1200 series LC, 6410 TripleQuad LC/MS). Concentrations in the range of 0.001–2.5 μgL^{-1} were measured by first concentrating the samples using in-line solid phase extraction (SPE). The LC separations were performed on the LC (Agilent Technologies 1200 series) consisting of a binary pump, a vacuum degasser, a thermostated autosampler and a thermostated column oven. Analytes were separated on Eclipse XDB-C18, Rapid Resolution HT column (4.6 x 50 mm, 1.8 μm, Agilent) equipped with a guard column (Agilent Eclipse XDB-C18, 4.6 x 12.5 mm, 5 μm). In a direct injection method, the eluent flow rate was 0.5 mLmin^{-1},

Table 4.2: LC elution program of direct injection method.

Time (min)	% acetonitrile	% HCOOH (0.1%)
0	5	95
12	100	0
16.5	100	0
17	5	95
26.5	5	95

Table 4.3: LC Elution program of in-line solid phase method.

Time (min)	% acetonitrile	% HCOOH (0.1%)
0	5	95
6	5	95
18	100	0
26.5	100	0
27	5	95
34	5	95

injection volume was 2 μL and the column oven was kept at 30 °C. The column elution program is presented in Table 4.2.

In addition to the direct injection, samples were concentrated using SPE. The LC was equipped with a quaternary pump and a column-switching valve that allowed the SPE to be done in-line with the analytical separation. SPE was performed with an Oasis HLB extraction cartridge (2.1 x 20 mm). The analytes were loaded into the cartridge at a flow rate of 0.5 mL min^{-1} using aqueous solution (10 mM NH4COOH + 0.1% HCOOH) and eluted with the gradient run of the analytical column at flow rate of 0.5 mL min^{-1} (Table 4.3). Column oven was kept at 30 °C and injection volume depended on the sample matrix. Samples from the aerobic effluents was injected at a volume of 175 μL and grey water samples as well as the anaerobic effluent samples was inject at a volume of 58 μL.

Mass spectrometry

The flow from the LC column was transferred to a triple-quadrupole mass spectrometer (Agilent Technologies 6410 TripleQuad LC/MS) equipped with an electrospray ionization source. Nitrogen was used as the desolvation gas at the source at a flow rate of 10 L h^{-1}. Nebulizer pressure was kept at 50 psi and the capillary voltage was 4000 V. The source temperature was 320 °C. Nitrogen was used as the collision gas. Positive ions of the analytes were acquired in multiple reaction monitoring mode. The optimized MS/MS parameters are presented in Table 4.4.

Table 4.4: The optimized MS/MS parameters for LC analytes.

Compound	Precursor ion (m/z)	Product ion (m/z)	Fragmentor voltage (V)	Collision energy (eV)
PBSA	275.1	194.2	190	33
BP3	229.1	151.0	115	15
Avobenzone	311.2	135.0	115	18
BaCl (1)*	304.3	91	140	32
BaCl (2)*	332.3	91	140	35

* Benzalkonium chloride was present at two homologs

Quality parameters

For all three matrices (grey water, aerobic matrix and anaerobic matrix), recoveries were determined by spiking them with a stock solution containing all the analytes and determined as described above. For all the matrices, the spiking level was 100 μgL^{-1} when the direct injection method was used. For in-line SPE method, grey water and anaerobic matrix samples were spiked at a level of 1 μgL^{-1} and the aerobic effluent at a level of 0.5 μgL^{-1}. Recovery samples were done at triplicates. Limit of quantifications (LOQ) were determined using a method called the Target RSD (Vial et al., 2003). The LOQ was determined at RSD 10%.

4.3 Results and discussion

4.3.1 Recoveries and limits of quantification

Methyl-, ethyl-, propyl- and butylparaben and bisphenol-A were very well recovered in all matrix samples, which are grey water, aerobic effluent and anaerobic effluent (Table 4.5). Triclosan, galaxolide, tonalide, HCA, 2EHS and 4MBC were relatively well recovered (50–100%) in all matrices, except the recovery of triclosan in grey water (38% recovery) and tonalide and galaxolide in the anaerobic matrix (36% and 50%, respectively). In general, a slightly lower recovery was achieved in the anaerobic matrix.

Although the recovery for nonylphenol was rather low, it was consistently around 20–30% in all matrices. EHMC showed a rather high recovery of 83% in grey water, but significantly lower in the effluents (32% for aerobic and 38% for anaerobic matrix).

Table 4.5: Recoveries (rec.) and limits of quantification (LOQ) of micropollutants in grey water, aerobic and anaerobic matrices

	Grey water matrix		Aerobic matrix		Anaerobic matrix	
	rec. (%)	LOQ (μgL^{-1})	rec. (%)	LOQ (μgL^{-1})	rec. (%)	LOQ (μgL^{-1})
Methylparaben	63	3.19	111	0.90	78	1.29
Ethylparaben	77	1.04	129	0.31	108	0.37
Propylparaben	86	0.23	126	0.08	115	0.09
Butylparaben	88	0.09	125	0.03	118	0.03
EHMC	83	0.10	32	0.13	38	0.11
2EHS	94	0.09	70	0.06	63	0.06
4MBC	87	0.09	100	0.04	61	0.07
PBSA	70	0.06	65	0.02	70	0.06
BP3	49	0.06	83	0.01	47	0.06
Avobenzone	28	0.14	65	0.12	28	0.14
Octocrylene	38	0.53	29	0.34	59	0.17
Galaxolide	83	0.24	77	0.13	36	0.28
Tonalide	84	0.24	70	0.14	47	0.21
HCA	95	0.21	79	0.13	50	0.20
BaCl	70	1.42	26	2.3	79	1.27
Nonylphenol	20	0.41	23	0.17	28	0.14
Triclosan	38	0.21	98	0.04	64	0.06
Bisphenol-A	96	0.08	110	0.04	131	0.03

Because of the high limits of quantification (LOQs) for methyl and ethylparaben in grey water, these coumpounds could not be quantified in any of the grey water samples. The recoveries of octocrylene were low and varied significantly, and it was difficult to obtain a calibration curve with a correlation factor of at least 0.99. This resulted in rather high LOQs and in combination with the low recoveries (Table 4.5) implied that octocrylene could only be determined semi-quantitatively in the grey water and effluent samples.

Recoveries and LOQs for LC-MS/MS compounds shown in Table 4.5

correspond to the in-line SPE mode (with the exception of BaCl, for which direct injection was used for all measurements). With this method lower LOQs could be achieved compared to the direct injection method. With the method of direct injection, recoveries were above 90% for all compounds except for BaCl in the aerobic matrix, which had a consistent low recovery of 30% (data not shown). BaCl could not be analyzed with in-line SPE and therefore the LOQ for this compound was rather high (2.3 μgL^{-1}). As a result, BaCl could not be quantified in any of the aerobic sample.

4.3.2 Occurrence of micropollutants in grey water

In this study, 22 samples were measured per matrix, the results are shown in Tables 4.6 and 4.7. The most prevalent compounds in grey water were triclosan, EHMC, BaCl and nonylphenol.
The majority of the studied micropollutants were detected in grey water samples, with the exception of methyl- and ethylparaben. Propylparaben was present at concentrations of 2.9±1.4 μgL^{-1} and butylparaben at 0.86±0.86 μgL^{-1}. In general, parabens in this study presented lower concentrations than those found by Andersen et al. (2007) in grey water produced by showers and hand basins, with average concentrations of 6.9±9.7 μgL^{-1} of methylparaben, 3.0±0.24 μgL^{-1} of ethylparaben, 3.6±4.8 μgL^{-1} of propylparaben and 1.7±3.9 μgL^{-1} of butylparaben. Parabens are ingredients of hand soap, showering and bathing products (e.g. personal care), more likely to be present in hand basin and shower discharges rather than in laundry and kitchen discharges. Lower concentrations of parabens in this study, therefore, might have been due to the dilution effect of laundry and kitchen wastewater.

Most studied UV-filters were found at the highest concentration during the summer months (Table 4.6). The UV-filter EHMC was found at concentrations of 15.5±13.2 μgL^{-1} and 2EHS at 2.1±1.3 μgL^{-1}(4.6). These concentrations are significantly higher than those reported in literature for sewage, which range from <3 ngL^{-1} to a maximum of 19 μgL^{-1} for EHMC (Balmer et al., 2005; Loraine and Pettigrove, 2006; Rodil et al., 2009) and 28±1 ngL^{-1} for 2EHS (Negreira et al., 2009). On the other hand, 4MBC concentrations averaged at 1.7±2.0 μgL^{-1} and BP3 concentrations were 1.0±1.0 μgL^{-1}, which were at the same level as in sewage from Switzerland (Balmer et al., 2005; Buser et al., 2005).

Table 4.6: Micropollutant concentrations in grey water, aerobic, anaerobic and anaerobic + aerobic effluents, all concentrations are in μgL^{-1}; refer to the text for abbreviations of compounds (av= average, SD= standard deviation, min= minimum concentration, max= maximum concentration, LOQ= limit of quantification), n = 22, n>LOQ= number of samples with concentrations greater than the limit of quantification, NA= non applicable, nd = below LOQ.

compound	grey water					aerobic				
	av	SD	min	max	n>LOQ	av	SD	min	max	n>LOQ
Preservatives										
Methylparaben	nd	NA	nd	nd	0	2.8	0.12	2.6	3.2	22
Ethylparaben	nd	NA	nd	nd	0	0.84	0.05	0.80	0.98	22
Propylparaben	2.9	1.4	nd	5.5	21	0.21	0.18	nd	0.34	2
Butylparaben	0.86	0.86	0.19	4.4	22	0.04	0.00	nd	0.05	19
UV-filters										
EHMC	15.5	13.2	3.9	67.7	22	7.9	6.3	nd	23	11
2EHS	2.1	1.3	nd	4.7	17	0.31	0.05	0.28	0.44	22
4 MBC	1.7	2.0	nd	8.9	20	0.11	0.01	0.10	0.13	22
PBSA	2.3	3.5	0.1	15.3	20	3.0	4.9	0.1	8.5	22
BP3	1.0	1.0	0.3	4.9	21	0.14	0.19	0.03	0.70	11
Avobenzone	3.5	5.0	0.3	17.4	21	0.48	0.63	0.12	2.9	20
Octocrylene*	38	33	nd	146	14	3.5	NA	nd	3.5	1
Fragrances										
Galaxolide	10.7	3.8	5.7	19.1	22	2.1	0.87	1.4	5.7	22
Tonalide	2.2	1.7	nd	5.8	19	1.5	0.18	1.3	2.0	22
HCA	3.8	3.1	0.6	11.5	22	0.26	0.06	0.19	0.38	22
Surfactants/biocides										
BaCl	10.2	5.6	2.1	20.7	19	nd	nd	nd	nd	0
Nonylphenol	7.5	7.1	0.8	38	22	0.85	0.75	nd	3.5	21
Triclosan	15.6	6.8	6.3	35.7	22	0.35	0.32	0.1	1.5	22
Plasticizer										
Bisphenol-A	0.74	0.21	0.42	1.2	22	0.07	0.06	nd	0.25	18

* Semi-quantitative values

Table 4.7: Micropollutant concentrations in grey water, aerobic, anaerobic and anaerobic + aerobic effluents, all concentrations are in μgL^{-1}; refer to the text for abbreviations of compounds (av= average, SD= standard deviation, min= minimum concentration, max= maximum concentration, LOQ= limit of quantification), n = 22, n>LOQ= number of samples with concentrations greater than the limit of quantification, NA= non applicable, nd = below LOQ..

compound	anaerobic					anaerobic + aerobic				
	av	SD	min	max	n>LOQ	av	SD	min	max	n>LOQ
Preservatives										
Methylparaben	1.61	0.52	nd	3.3	13	2.5	0.65	nd	3.0	20
Ethylparaben	1.42	0.05	nd	1.5	10	0.85	0.04	nd	0.9	17
Propylparaben	0.72	0.54	nd	1.9	20	0.11	0.01	nd	0.1	3
Butylparaben	0.28	0.10	nd	0.5	10	0.04	0.02	nd	0.1	15
UV-filters										
EHMC	3.80	3.6	nd	11.8	16	11	13.75	nd	33	8
2EHS	1.34	0.6	0.6	2.9	21	0.3	0.08	0.3	0.6	22
4MBC	0.30	0.19	0.05	1	21	0.09	0.02	nd	0.12	20
PBSA	2.29	3.6	0.2	14.9	22	3.1	4.80	0.1	20.7	22
BP3	0.63	0.4	0.2	2.0	22	0.05	0.04	0.03	0.14	6
Avobenzone	1.27	1.1	0.2	5	22	0.2	0.14	0.1	1	21
Octocrylene*	12.85	13	2.3	56	21	8.5	6.12	nd	13	2
Fragrances										
Galaxolide	9.97	5.1	3.6	20	21	1.9	0.61	nd	2.7	21
Tonalide	1.62	0.7	0.9	3.7	21	1.3	0.42	nd	1.9	19
HCA	0.45	0.2	nd	0.8	15	0.2	0.07	0.2	0.5	22
Surfactants/biocides										
BaCl	7.66	2.8	4	17	21	nd	NA	nd	nd	0
Nonylphenol	13.1	6.6	4.1	30.6	21	1.4	0.98	0.2	4.1	22
Triclosan	5.51	3.2	1.5	11.9	21	0.5	0.27	0.2	1.2	22
Plasticizer										
Bisphenol-A	0.72	1.1	0.26	4.7	21	0.1	0.12	nd	0.5	15

* Semi-quantitative values

Due to the input of flushing water for toilets and storm water, sewage is generally more diluted than grey water. Higher concentrations are, therefore, expected in grey water. Other factors, however, may have a higher impact on the concentrations of certain micropollutants, such as the increased consumption of particular personal care products in a drainage area.

From the fragrance materials analyzed, galaxolide was found at the highest concentrations (10.7±3.8 μgL^{-1}), probably since it is one of the most used fragrance materials (Heberer, 2003). The production of galaxolide is 4 times higher than that of tonalide (Heberer, 2003), which is consistent with the concentration of tonalide found in grey water (2.2 ±1.7 μgL^{-1}) . The fragrance HCA was found at a concentration of 3.8±3.1 μgL^{-1}, which is slightly lower than that determined by Simonich et al. (2002) for sewage (12.8±7.27 μgL^{-1}).

Concentrations of BaCl were 10.2±5.6 μgL^{-1}. Other studies detected BaCl in sewage at concentrations of 4.9–170 μgL^{-1} Martinez-Carballo et al. (2007) and 2.7–36.6 μgL^{-1} (Ferrer and Furlong, 2001). Even though nonylphenol has been prohibited for commercial use in Europe, this compound was detected in all grey water samples at a concentration of 7.5±7.1 μgL^{-1}. A possible cause of the occurrence of these compounds in household wastewater is imported textiles (Swedish Chemical Agency, 2009).

The average concentration of triclosan in grey water was 15.6±6.8 μgL^{-1}, i.e. much higher than previously reported values for sewage (i.e. from <0.05 to 5.2 μgL^{-1} (Gonzalez-Marino et al., 2009; Lee et al., 2005; Loraine and Pettigrove, 2006; Oppenheimer et al., 2007)). The reason could be that grey water does not contain either toilet water or storm water to dilute the waste stream or the more frequent use of soaps with antibacterial effect within the 32 houses in the drainage area.

In grey water, bisphenol-A was present at an average concentration of 0.74±0.21 μgL^{-1}, i.e. in the same range as found in sewage in previous studies (Jonkers et al., 2009; Lee et al., 2005; Vethaak et al., 2005).

4.3.3 Removal of micropollutants in the biological treatment systems

Table 4.8 summarizes the removal of micropollutants from grey water by the different treatment systems. The removal is presented qualitatively, classifying the removal in three categories: well removed (>80%) represented with ++, moderately removed (removal between 50 and 80%) represented by + and poorly or not removed (<50%) represented by −. Only a few compounds were well removed in all the systems, and in general, aerobic conditions were found to be more favorable for the removal of micropollutants. Only a few micropollutants exhibited a low removal in all the treatment systems.

Table 4.8: Assessment of micropollutant removal from grey water. Removal higher than 80% (++), between 50 and 80% (+), less than 50% (−), possible removal mechanisms are mentioned as adsorption (A), biodegradation (B) and volatilization (V)

Compound	Aerobic	Anaerobic	Anaerobic + aerobic	Possible removal mechanism
4MBC	++	++	++	A
HCA	++	++	++	A, B
Propylparaben	++	+	++	A, B
Butylparaben	++	+	++	A, B
2EHS	++	−	++	A
Octocrylene	++	+	+	A
BP3	++	−	++	A
Avobenzone	++	+	++	A
Nonylphenol	++	−	++	A, B
Triclosan	++	+	++	A, B
BaCl	+	−	+	−
Bisphenol-A	++	−	++	A, B
Galaxolide	++	−	++	A, V
PBSA	−	−	−	−
Tonalide	−	−	−	A, V
EHMC	−	+	−	A, B

Micropollutants well removed in all biological systems tested

The UV-filter 4MBC and the fragrance HCA were well removed in all three biological systems tested in this study. In the aerobic system, the removal was 93%, and in the anaerobic + aerobic system the removal was 95% for both compounds. The UV-filter 4MBC presented similar or higher removal efficiencies than reported for domestic wastewater treatment plants (WWTPs), where removal ranged from 18–97% (Balmer et al., 2005; Buser et al., 2005). High removal values for 4MBC and HCA are consistent with a high adsorption capacity and a good aerobic biodegradability reported for these micropollutants (Table 1.3).

Under anaerobic conditions removal was slightly lower (82% for 4MBC and 88% for HCA), which most likely can be attributed to their adsorption to the anaerobic sludge, as their chemical structure probably does not allow for anaerobic biodegradation (US-EPA, 2009).

Micropollutants well removed under aerobic conditions but poorly under anaerobic conditions

Eleven micropollutants showed a good removal under aerobic conditions but a poor removal under anaerobic conditions. These were propyl- and butylparaben, 2EHS, octocrylene, BP3, avobenzone, nonylphenol, triclosan, BaCl, bisphenol-A and galaxolide. Aerobic removal efficiencies were more than 90% for propyl- and butylparaben, octocrylene, triclosan, bisphenol-A. Removal of 2EHS, BP3, avobenzone, nonylphenol, BaCl and galaxolide ranged between 77 and 90%.

Elimination of propyl- and butyl-paraben, 2EHS, nonylphenol, triclosan and bisphenol-A probably occurred through combined adsorption to sludge and biodegradation, given the properties of high hydrophobicity and ready biodegradability of these micropollutants (Table 1.3). According to literature, removal of galaxolide in WWTPs varied in a wide range from no removal to complete removal (Onesios et al., 2009). The most likely removal mechanism for galaxolide is adsorption (given the high $\log K_{OW}$). Since galaxolide is a volatile compound, it could also have been stripped out from the aerated reactors.

The most likely removal mechanism of octocrylene and avobenzone was adsorption, because these micropollutants have a high $\log K_{OW}$ and are poorly biodegradable under both aerobic and anaerobic conditions. High removal of octocrylene has been reported in WWTPs with three or four treatment stages (Balmer et al., 2005; Buser et al., 2005). Balmer et al. (2005) estimated that up to 99% removal was due to sorption to organic matter. There is limited information available on the occurence of avobenzone from wastewater, and there is no information on its removal during biological treatment.

The reasons for the high removal efficiency of BP3 are not clear. Balmer et al. (2005) estimated that a removal of BP3 of only about 5% can be expected based on adsorption to organic matter. Besides, biodegradability estimations based on BP3's chemical structure indicate primary biodegradation can take days or weeks (US-EPA, 2009). Yet, the removal of BP3 at an HRT of 12 hours was 87% in the aerobic system and 95% in the combined anaerobic + aerobic system. One of the possibilities is that the long term and constant exposure of sludge to BP3 had caused the development of microorganisms capable of degrading it.

Micropollutants not removed during biological treatment

No removal was measured for the UV-filter PBSA in any of the biological treatment systems. PBSA is a very hydrophilic compound with a $\log K_{OW}$ of -0.16 and a poor biodegradability (US-EPA, 2009). Therefore, removal in these treatment systems could not be expected. From the studied fragrances, tonalide was the most persistent, with a 32% removal in the aerobic and the anaerobic system and 54% for the combined anaerobic + aerobic treatment. Adsorption to sludge was the most likely removal mechanism. Even though the UV filter EHMC has been reported to be readily biodegradable, the conditions in the biological systems used for this study apparently were not favorable to achieve a high removal of EHMC. The exact removal efficiencies cannot be estimated, because EHMC concentrations could only be measured in some of the effluent samples.

4.3.4 Overview of micropollutants in grey water and biological treatment effluents

Figure 4.3 shows an overview of the selected micropollutants in the four different matrices. The concentrations in each matrix were normalized, based on the compound present at the highest average concentration in the matrix. In grey water the dominant compounds were triclosan, EHMC, galaxolide, benzalkonium chloride and nonylphenol, with average concentrations in the range of 7.5-15.6 μgL^{-1}.

The removal of micropollutants from grey water was the highest in the aerobic system and in the combined anaerobic + aerobic system (Figure 4.3). Micropollutant concentrations after anaerobic treatment indicated their overall poor removal. The micropollutant concentrations of the aerobic and the combined anaerobic + aerobic effluent were similar, with the UV filters EHMC and PBSA present at the highest concentrations in their effluents. In the aerobic effluent, EHMC was present at 7.9 μgL^{-1} and PBSA at 3.0 μgL^{-1}. In the combined anaerobic + aerobic effluent, EHMC was present at a concentration of 11 μgL^{-1} and PBSA at 3.1 μgL^{-1}. According to literature, the combination of redox conditions, as applied in the combined anaerobic + aerobic system, can enhance the removal of certain organic compounds. In our case, however, there is no clear indication that the combination of redox conditions improved the removal of the selected micropollutants.

4.3.5 Possible effects

Even though a significant removal of micropollutants was achieved during aerobic biological treatment, most of them were still detected in the effluent samples, with the UV-filters EHMC and PBSA, the preservative methylparaben and the fragrances galaxolide and tonalide being the most prevalent ones (Figure 4.3). Unfortunately, for many ingredients of personal care products there is an incomplete set of data regarding benchmark doses such as no observed effect levels (NOEL) (Ternes and Joss, 2006).

As mentioned above, some xenobiotics mimic the effects of natural hormones and their endocrine disrupting effects have been measured in vivo and in vitro. Relative estrogenic potencies (compared to 17β-estradiol)

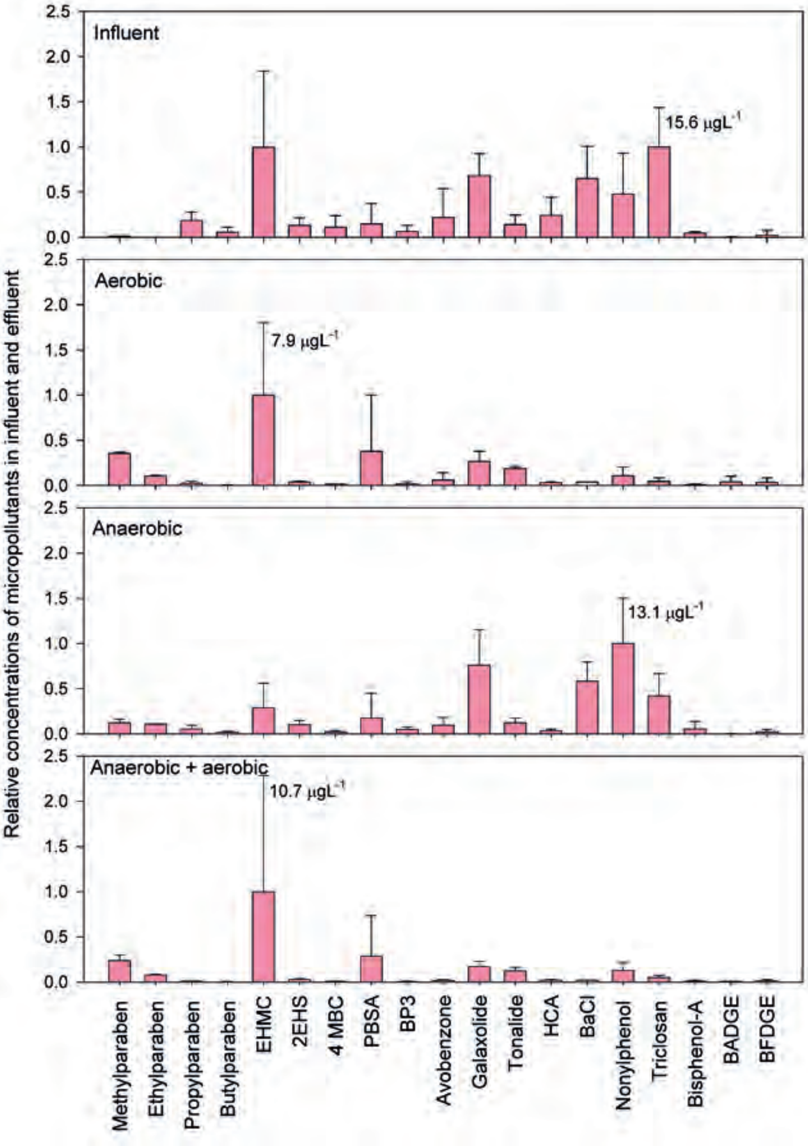

Figure 4.3: Profile of micropollutants in grey water, and aerobic, anaerobic and anaerobic + aerobic effluent. The highest concentration of micropollutants in each matrix was normalized to 1. Highest concentrations of micropollutants are in parentheses. Actual concentrations are given in Table 4.6 and 4.7.

Table 4.9: Estrogenic potency of grey water and effluent expressed in 17β-estradiol equivalents (ngL^{-1}), IC_{50} = 57.2 ngL^{-1}. All values calculated based on YES assay data from literature (Miller et al., 2001)

	average	min	max
Grey water	0.70	0.12	2.64
Aerobic	0.07	0.01	0.21
Anaerobic	0.72	0.20	2.01
Anaerobic + Aerobic	0.09	0.01	0.26

have been determined for BP3, 4MBC, EHMC (in MCF7 cells) (Heneweer et al., 2005), methyl-, ethyl-, propyl- and butylparaben, bisphenol A and nonylphenol (yeast estrogen screen (YES) bioassay) (Miller et al., 2001). Considering additive estrogenic potencies of these compounds in water samples, the total estrogenic potency of grey water and effluents can be calculated (Table 4.9). Since results from different bioassays are not comparable, only the results of YES bioassays were considered for the estimation of estrogenic potency, as there were more micropollutants of which YES data were available. This can result in an underestimation of the estrogenic potency. However, the calculated value is based on in-vitro assays (generally more sensitive than in-vivo tests) and effects such as bioavailability and bioaccumulation in aquatic organisms are not taken into account. The estrogenic potency of grey water and anaerobic effluent were equivalent to a concentration of 0.7 ngL^{-1} of 17β-estradiol. The treatment of grey water in an aerobic system and in a combined anaerobic + aerobic system resulted in 0.07 and 0.09 ngL^{-1} 17β-estradiol equivalents, respectively. The median effective concentration (EC_{50}) of 17β-estradiol measured with YES bioassay is 55 ngL^{-1} (Miller et al., 2001). Based on this bioassay, the estrogenic potency of aerobically treated grey water is 1000 times less than the EC_{50}. According to this calculation, the risk of exposure to estrogenic compounds is less from raw grey water than it is from raw sewage, where concentrations of 17β-estradiol are in the range of 0.5–224 ngL^{-1} (Koh et al., 2008).

For tonalide, the effect concentration for most sensitive aquatic organism in toxicity studies was determined to be 3.5 μgL^{-1} (tested on fathead minnow) (Knacker et al., 2006). Maximum concentrations of tonalide in the effluents were around 1-1.5 μgL^{-1} for aerobic and combined anaerobic

+ aerobic effluent. Considering the discharge of this effluent directly in surface water, the final concentration of tonalide would be attenuated. Based on this NOEL, tonalide concentrations in the effluent do not represent a high risk. Considering the application of this effluent as irrigation water, the risk would be minimized due to the adsoption of tonalide to soil. This has been observed in a full-scale project in Braunschweig, Germany where treated wastewater was used for irrigation. The irrigation water contained 0.10±0.05 μgL^{-1} and samples taken from different wells in the area were below the LOQ of 0.025 μgL^{-1} (Ternes et al., 2007). A predicted no effect concentration (PNEC) for EHMC was 0.4 μgL^{-1}. Direct discharge of effluent into surface waters (considering a dilution factor of 10) may result in concentrations higher than this PNEC, especially in summer periods and may pose a risk to aquatic organisms.

For applications of household reuse, such as toilet flushing, laundry and perhaps showering and bathing, the quality of treated grey water should meet high standards regarding pathogens, for which disinfection will be required. Regarding xenobiotics, their presence in reuse water may pose a risk as they may accumulate. Advanced treatment, e.g. ozonation or activated carbon adsorption, is therefore recommended based on the precautionary principle.

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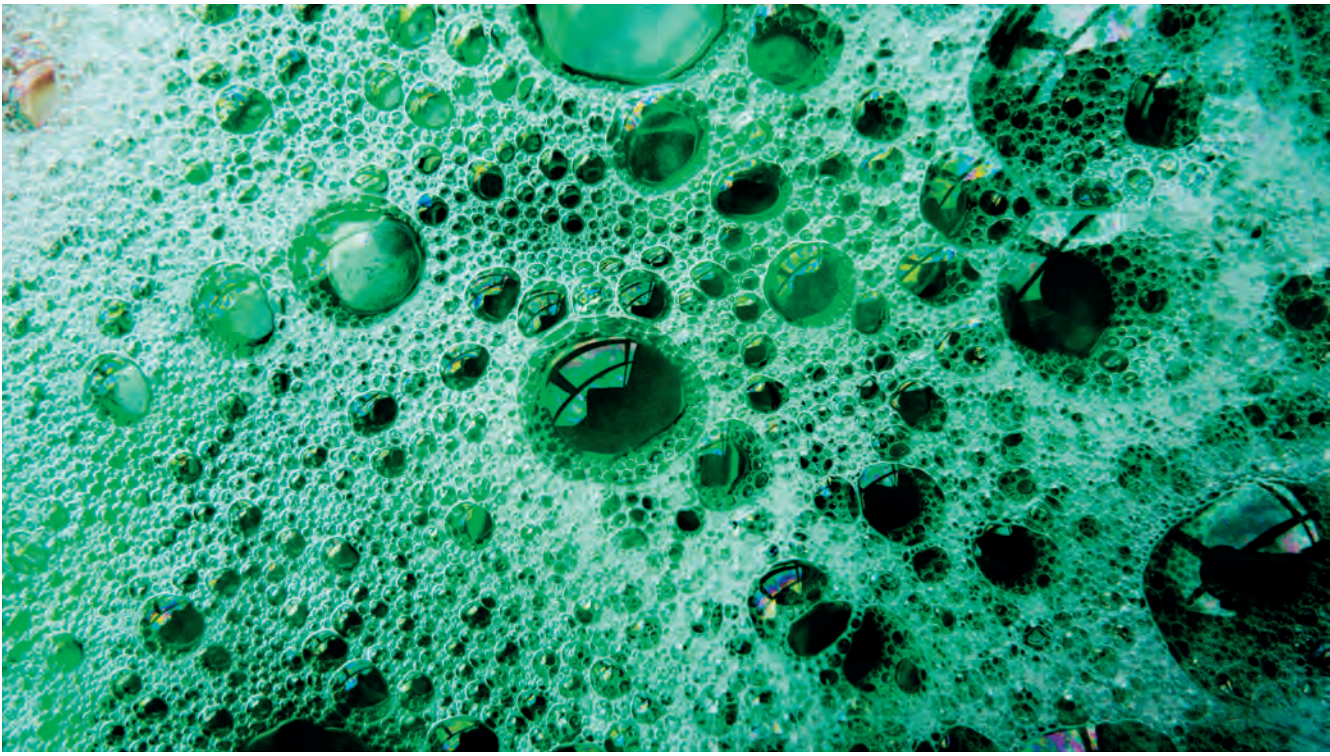
CHAPTER 5

Removal of micropollutants via activated carbon and ozonation



Abstract

The removal of 18 micropollutants of personal care and household products from MilliQ and aerobically treated grey water via ozone and activated carbon was tested at lab-scale. Four parabens, bisphenol-A, hexylcinnamic aldehyde, 4-methylbenzylidene camphor (4MBC), benzophenone-3 (BP3), triclosan, galaxolide, ethylhexyl methoxycinnamate were effectively removed ($> 99\%$) from milliQ water spiked with 100-1600 μgL^{-1} after 45 min of ozonation at a dosing rate of 1.22 mgL^{-1}min^{-1}. After 60 min, the removal efficiency of benzalkonium chloride was 98 %, tonalide and nonylphenol 95 %, octocrylene 92 % and 2-phenyl-5-benzimidazolesulfonic acid (PBSA) 84 %. Ozonation of aerobically treated grey water at an applied ozone dose of 15 mgL^{-1}, reduced the concentrations of octocrylene, nonylphenol, triclosan, galaxolide, tonalide and 4-methylbenzylidene camphor to below limits of quantification, with removal efficiencies of at least 79 %. Complete adsorption of all studied micropollutants onto powdered activated carbon (PAC) was observed in batch tests with milliQ water spiked with 100-1600 μgL^{-1} at a PAC dose of 1.25 gL^{-1} and a contact time of 5 min. Three granular activated carbon (GAC) column experiments were operated to treat aerobically treated grey water. The operation of a GAC column with aerobically treated grey water spiked with micropollutants in the range of 0.1-10 μgL^{-1} at a flow of 0.5 bed volumes(BV)h^{-1} showed micropollutant removal efficiencies higher than 72 %, during the operation time of 1728 BV, no breakthrough of TOC or micropollutants was observed. Removal of micropollutants from aerobically treated grey water was tested in a GAC column at a flow of 2 BVh^{-1}. Bisphenol-A, triclosan, tonalide, BP3, galaxolide, nonylphenol and PBSA were effectively removed even after a stable TOC breakthrough of 65 % had been reached. After spiking the aerobically treated effluent to micropollutant concentrations of 10-100 μgL^{-1}, efficient removal to below limits of quantification continued for at least 1440 BV. Both ozonation and adsorption are suitable techniques for the removal of micropollutants from aerobically treated grey water.

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5.1 Introduction

The presence of micropollutants, such as pharmaceuticals and ingredients of personal care products, in the environment has proven to cause harmful effects in the aquatic environment (Ternes and Joss, 2006). The major source of these micropollutants is domestic wastewater. In grey water, it has been shown that micropollutants are present in the low μgL^{-1} range (Eriksson et al., 2003; Palmquist and Hanaeus, 2005).

The occurrence of 18 selected compounds (3 fragrances, 2 surfactants, 4 preservatives, 7 UV-filters, a plasticizer and a biocide) and their removal during biological treatment in three different systems were studied in Chapter 4. Partial removal of micropollutants occurred in biological treatment due to biodegradation and sorption, but a considerable number of micropollutants were still present in treated grey water, which poses potential risks depending on its final use. Physical-chemical posttreatment, therefore, was recommended for the reuse application of remaining micropollutants in biologically treated grey water.

Ozonation and adsorption onto activated carbon are very effective techniques to reduce the load of micropollutants from wastewaters at acceptable costs of 0.05–0.20 €/m^3 (investment and operation) (Joss et al., 2008).

The oxidation by ozone of some micropollutants from personal care products has been demonstrated in previous studies. Table 5.1 shows an overview of the studies done on some of the micropollutants studied in Chapter 4. The fragrances galaxolide and tonalide were effectively removed from the effluent of sewage treatment plants to below detection limits (Rosal et al., 2010; Ternes et al., 2003). Triclosan, bisphenol-A and nonylphenol are as well removed to a high extent by ozonation (Rosal et al., 2010; Snyder et al., 2006; Zhang et al., 2008). For the UV-filters benzophenone-3 (BP3), ethylhexyl methoxycinnamate (EHMC), octocrylene and 4-methylbenzylidenecamphor (4MBC), ozonation was not as effective with removal efficiencies ranging from 0 to 27 % (Li et al., 2007; Rosal et al., 2010). Although Snyder et al. (2006) reported a removal higher than 83 % for BP3.

Table 5.1: Overview of ozonation tests for the removal of personal care products from sewage. AOD = applied ozone dose; C_0 = initial concentration; NR = not removed

	Type of water	**Scale**	**AOD** mgL^{-1}	**C_0** ngL^{-1}	**Removal**
Tonalide	STP effluent	pilot plant	5	100	>50 % [a]
	STP effluent	lab-scale	16.3	188	72 % [b]
Galaxolide	STP effluent	pilot plant	5	730	>93 % [a]
	Tertiary effluent	pilot plant	7.3	1170	>99 %[c]
	STP effluent	lab-scale	16.3	1486	83 %[b]
Triclosan	STP effluent	lab-scale	16.3	246	78 %[b]
	Tertiary effluent	pilot plant	7.8	47	>99 %[c]
Bisphenol-A	STP effluent	lab-scale	$\sim$ 15	246	>96 %[d]
Nonylphenol	STP effluent	lab-scale	$\sim$ 15	800	87 %[d]
BP3	STP effluent	Lab-scale	16.3	123	NR[b]
	Tertiary effluent	pilot plant	7.3	6	>83 %[c]
	Tertiary effluent	full scale	5-6	311	20 %[e]
EHMC	STP effluent	lab-scale	16.3	234	NR[b]
	Tertiary effluent	full scale	5-6	60	27 %[e]
Octocrylene	STP effluent	lab-scale	16.3	114	20%[b]
	Tertiary effluent	full scale	5-6	68	16 %[e]
4MBC	STP effluent	lab-scale	16.3	55	NR[b]
	Tertiary effluent	full scale	5-6	938	24 %[e]

[a] Ternes et al. (2003)
[b] Rosal et al. (2010)
[c] Snyder et al. (2006)
[d] Zhang et al. (2008)
[e] Li et al. (2007)

Activated carbon can be used to remove many different organic compounds from water (Snyder et al., 2003). The performance of this process depends on the properties of the activated carbon, such as pore size and surface area, and the characteristics of the solute (shape, size and hydrophobicity). Adsorption onto activated carbon is particularly effective in the removal of hydrophobic substances,with a log$K_{OW} > 2$, as it is the case for most of micropollutants selected for this study (see properties of micropollutants in Chapter 1).

Most studies on the removal of micropollutants with activated carbon have been conducted on surface water. Bisphenol-A spiked at 500 ngL^{-1} was removed from surface water with an efficiency higher than 99 % using a powdered activated carbon (PAC) dose of 15 mgL^{-1}, and a contact time of 4 h (Yoon et al., 2003). The treatment of river water spiked with 5 mgL^{-1} of PAC and a contact time of 4 h removed triclosan, BP3 and galaxolide by 89, 93 and 56 %, respectively (Westerhoff et al., 2005). Rossner et al. (2009) tested a PAC dosing range of 0.3-10 mgL^{-1}. With a PAC dose of 10 mgL^{-1} removal of >99 % of 28 compounds from river water was achieved, BP3 and triclosan amongst them.

Choi et al. (2005) showed that the treatment of surface water by granular activated carbon (GAC) columns to produce drinking water can be very effective to decrease the relatively high concentrations of nonylphenol (500 μgL^{-1}) and bisphenol-A (200 μgL^{-1}), operating at an empty bed contact time (EBCT) of 15 min. Bisphenol-A breakthrough occurred after 7678-19597 bed volumes, depending on the type of carbon that was used. Stackelberg et al. (2007) studied 113 compounds at relevant concentrations in a full-scale surface water treatment plant including GAC filtration with a contact time of 1.5-3 min. Concentrations of bisphenol-A were reduced from 45 to 14 ngL^{-1}, tonalide from 73 to less than 1 ngL^{-1} and galaxolide from 105 to 14 ngL^{-1}. Rapid small scale column tests carried out at a drinking water treatment plant showed that compounds such as triclosan and BP3 did not reach 5 % of breakthrough after 55,000 bed volumes (BV) treated, as opposed to ibuprofen with 4280 BV or diclofenac with 9810 BV (Snyder et al., 2007).

The aim of this chapter is to evaluate the removal of selected micropollutants during treatment with activated carbon and ozone, to provide a general comparison of the two technologies and indicate their suitability for the posttreatment of grey water. It is not the purpose of this chapter to provide specific details of kinetics of ozonation or adsorption of the specific compounds, but rather give a general view of the feasibility of these processes to remove organic micropollutants from biologically treated grey water.

5.2 Materials and Methods

5.2.1 Chemicals

Tonalide, galaxolide, benzophenone-3 (BP3), 4-methylbenzylidene-camphor (4MBC), octocrylene, ethylhexyl methoxycinnamate (EHMC) and avobenzone were purchased from CHEMOS GmbH (Germany); hexylcinnamic aldehyde (HCA), 2-phenyl-5-benzimidazolesulfonic acid (PBSA), 2-ethylhexyl salicylate (2EHS) and bisphenol-A were purchased from Aldrich (Germany); caffeine and benzalkonium chloride (BaCl) were purchased from Sigma-Aldrich (Germany); triclosan, ethylparaben, propylparaben and butylparaben were purchased from Fluka (Germany); methylparaben from SUPELCO (Germany) and nonylphenol-mixture of isopolymers from ACROS Organic (Germany).

5.2.2 Analytical methods

Chemical oxygen demand (COD) and total organic carbon (TOC) were measured according to Standard Methods (APHA et al., 1998). Yellow color analysis, measured in color units (CU), was done spectrophotometrically (based on the platinium cobalt method) following Standard Method 2120 C (APHA et al., 1998).

Analysis of organic micropollutants was done with gas and liquid chromatography (GC/LC) coupled with mass spectrometry (MS). Thermal desorption gas chromatography (TD-GC-MS) with stir sorptive extraction (SBSE) was used to measure parabens, fragrances, bisphenol A, 4MBC, 2EHS, EHMC, octocrylene and triclosan. The equipment used for this measurements was a Gerstel TD Unit, an Agilent 6890N GC and an Agilent 5975 inert XL mass selective detector. Compounds were adsorbed on stir bars coated with polydimethyl siloxane and were desorbed on a 5 % phenyl methyl siloxane column in a thermal desorption unit connected to the GC-MS system. Acetic anhydride was added to the sample prior to the adsorption to the stir bars in order to derivatize the hydroxyl groups in parabens, triclosan, and nonylphenol. More details about the analytical method used to determine these micropollutants with TD-GC-MS can be found elsewhere (Vieno, 2010a).

Liquid chromatography with tandem mass spectroscopy (LC-MS/MS) was used to measure PBSA, BaCl, BP3, caffeine and avobenzone. Concentrations in the range of 2.5–250 μgL^{-1} were measured by directly injecting the samples to the LC-MS/MS system (Agilent 1200 series LC, 6410 Triple-Quad LC/MS). Concentrations in the range of 0.001–2.5 μgL^{-1} were measured by first concentrating the samples using inline solid phase extraction (SPE). A detailed description of the analytical method for determination of these compounds can be found elsewhere (Vieno, 2010b).

5.2.3 Aerobically treated grey water

Grey water was treated in a sequencing batch reactor with a hydraulic retention time of 12 h and a temperature of 25 °C. More details about the operation of the reactor can be found in Chapter 3. The treated grey water was filtered through a membrane with a pore size of 0.20 μm. The average composition of this treated grey water is shown in Table 5.2.

Table 5.2: Average composition of aerobically treated grey water used in this study, standard deviation is shown in parentheses

	Units	Average
TOC	mgL^{-1}	12.9 (5)
COD	mgL^{-1}	33.3 (11.5)
Color	CU	58.2 (16)
pH	(-)	8.4 (0.12)

5.2.4 Ozonation tests

A three liter reactor glass reactor was used for ozonation experiments. Figure 5.1 shows a schematic representation of the ozonation setup. Ozone was produced from pure oxygen with an Anseros ozone generator (COM-AD-02). An ozone analyzer (Anseros Ozomat GM) was used to measure ozone concentration in the gas phase of the inlet and outlet from the reactor. For this purpose two valves were installed to divert the inlet or outlet gas flow into the analyzer. The ozone concentration in the inlet was measured before each ozonation started, this concentration was assumed constant throughout the experiment, when the analyzer was connected to the outlet flow of the reactor. Ozone consumption could be measured by the difference of inlet and outlet concentrations. Flow rate of ozone was maintained at 20 Lh^{-1} (measured with a gas counter Ritter TG05/5 and regulated by a valve), as it was the ideal flow rate for ozone analysis. Water samples were taken with a syringe and a long needle inserted in the reactor through an opening on the top of it.

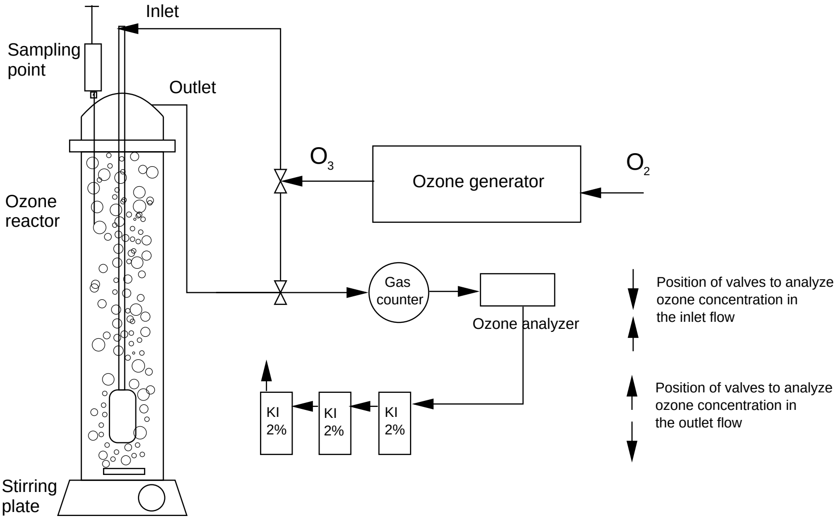

Figure 5.1: Schematic of the ozonation setup used for this study

MilliQ water was spiked to reach a concentration of about 1 mgL^{-1} of each compound, by adding 0.7 mL of an acetone spiking solution with 1 %w of each of the selected micropollutants. Three liters of spiked milliQ were treated with an ozone dosing rate of 1.22 $mgL^{-1}min^{-1}$ and samples were taken after 1, 3, 5, 15, 30, 45, 60, 90, 120 and 210 min and prepared for analysis (cumulative applied ozone dose (AOD) of 0-266 mgL^{-1}).

Experiments were done with aerobically treated effluent and MilliQ without any addition of micropollutants and with aerobically treated effluent and MilliQ spiked at relevant concentrations (10-100 μgL^{-1}, depending on the solubility of the compounds). Samples were taken after 5, 10 and

15 min of ozonation, corresponding to AODs of approximately 5, 10 and 15 mgL^{-1}. Ozonation tests were run for 60 min to observe the curves of ozone consumption.

5.2.5 Powdered activated carbon batch tests with milliQ water spiked at 1 mgL^{-1}

All activated carbon experiments were done with granular activated carbon (GAC) type NRS Carbon EA 0.5-1.5 (Norit), recommended for removal of organic micropollutants from wastewater. This carbon is thermally activated with a total surface area of 950 m^{2}g^{-1}, an apparent density of 410 kg m^3 and a iodine number of 850. Powdered activated carbon (PAC) tests were done using the same GAC ground to an average particle size of 114 μm.

Adsorption of micropollutants onto activated carbon was tested with a multiflask test. Fifteen 100 mL Erlenmeyer flasks were filled with 80 mL of MilliQ spiked with 1 mgL^{-1} and 0.1 g of PAC. Flasks were placed in a shaker with a water bath at 25 °C. Two flasks were sacrificed for micropollutant analysis after 5, 10, 15, 30, 60 and 120 minutes. The blanks were sacrificed after 60 and 120 min.
Activated carbon was removed by centrifugation at 15300 rpm for 15 min. The supernatant was prepared for micropollutant analysis.

5.2.6 Granular activated carbon column experiments

Column experiments were carried out in three identical set-ups. Double-walled PVC columns (height 40 cm, internal diameter 3.3 cm, see Figure 5.2) were filled with 29 g of GAC, giving a bed volume (BV) of 70.6 mL. A temperature of 25 °C was maintained with a water bath. The columns were operated at a down-flow mode according to Table 5.3. Once columns 2 and 3 reached a stable TOC removal efficiency, column 2 was used to test the removal of a PBSA solution (12.4 mgL^{-1}) in MilliQ and column 3 was spiked with a cocktail of 18 micropollutants at a concentration 100 times the normal concentrations in treated grey water.

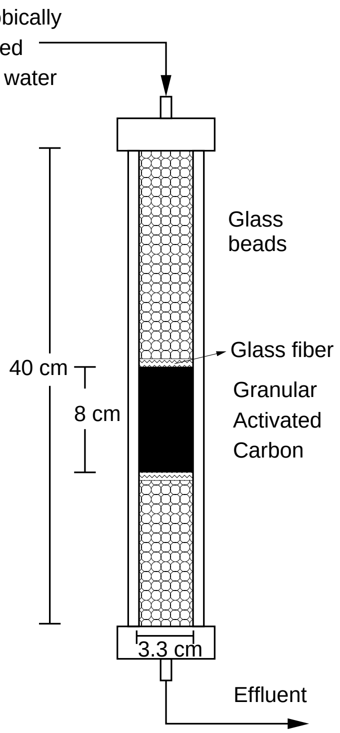

Figure 5.2: Schematic representation of granular activated carbon column set-up

5.3 Results and discussion

5.3.1 Ozonation

The removal of the 18 selected micropollutants from spiked milliQ by ozonation is shown in Figure 5.3. During the first minutes of ozonation, both gas-liquid equilibration of ozone in the liquid phase and reaction with micropollutants were taking place. Experiments done with milliQ water alone, showed that it takes about 7 minutes to reach equilibration of ozone in the liquid phase (Figure 5.4).

Complete removal (> 99 %) of the four parabens, bisphenol-A, HCA, 4MBC and BP3 was observed after 15 min of ozonation (total ozone consumption of 8.3 mgL^{-1}). After 20 min, the same removal was achieved for triclosan,

Table 5.3: Operational conditions of granular activated carbon columns

Column	**period (in BV)**	**Influent type**	**flow (BVh^{-1})**
1	0-1728	SBR effluent spiked at 0.1-10 μgL^{-1}	0.5
2	0-2976	SBR effluent	2
2	2976-6434	MilliQ with 12.4 mgL^{-1} of PBSA	2
3	0-2160	SBR effluent	2
3	2160-5040	SBR effluent	4
3	5040-6480	SBR effluent spiked at 10-100 μgL^{-1}	4

galaxolide and caffeine. EHMC and avobenzone were removed to > 99 % only after 30 min. After 45 min of ozonation 2EHS was completely removed (> 99 %), and the removal of BaCl was 98 %, tonalide and nonylphenol 95 %, octocrylene 92 % and PBSA 84 %. During the first 10 min of ozonation, the curve of tonalide had a different pattern from the rest of the compounds and during this time the concentration of tonalide can be considered constant (differences may be connected to the different dilutions made for analysis at different ozonation times) and oxidation of the compound only happened once the liquid was saturated with ozone. The reasons of this behavior of tonalide can not be explained.

5.3.2 Ozone consumption by MilliQ and aerobically treated grey water

Figure 5.4 shows the difference between the AOD and the actual consumption of ozone in aerobically treated grey water and spiked MilliQ water and aerobically treated grey water with micropollutants to achieve concentrations in the range of 10-100 μgL^{-1}.

The curve of ozone consumption by spiked MilliQ (TOC = 2.2 mgL^{-1}) completely overlaps with the ozone consumption by MilliQ water alone, indicating that the ozone needed to oxidize micropollutants at the μgL^{-1} level is very low. The same can be observed for effluent (TOC = 15.6 mgL^{-1}) and spiked effluent (TOC = 17.4 mgL^{-1}). The addition of micropollutants caused only a subtle increase in the ozone consumption. The consumption of ozone, therefore, depends primarily on the presence of the background organic carbon in treated grey water.

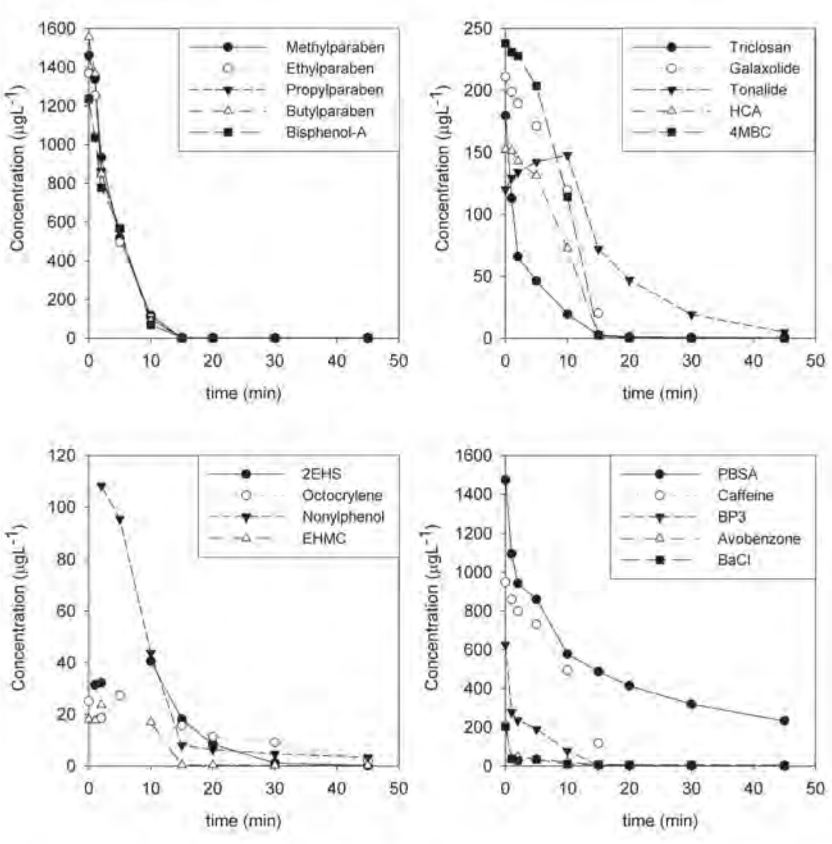

Figure 5.3: Removal of micropollutants by an ozone dose of 1.22 $mgL^{-1}min^{-1}$ in MilliQ water spiked with 1 mgL^{-1} of micropollutants

Removal of micropollutants from biologically treated grey water by ozone

The removal of micropollutants was studied in aerobically treated grey water. Figure 5.5 shows the results for PBSA, BP3, octocrylene, nonylphenol, triclosan, tonalide, 4MBC and galaxolide. The other micropollutants all were below limits of quantification (LOQs) in the aerobically treated grey water. In general, all micropollutants were effectively removed at an AOD

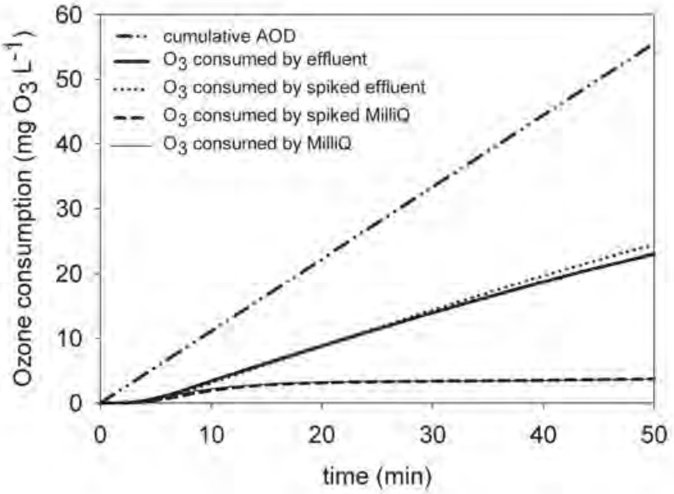

Figure 5.4: Differences between applied ozone dose and consumption by different water matrices

of 15 mgL^{-1} (removal efficiencies higher than 79 %). The removal of PBSA from aerobically treated grey water was 84 % at an AOD of 15 mgL^{-1}, higher than what was observed during ozonation of millipore water at the same AOD (56 %). BP3 was removed up to 94 % after applying 15 mgL^{-1} of ozone, in accordance with the experiment on MilliQ water and the results of Snyder et al. (2006) and contradicting the results of Li et al. (2007) and Rosal et al. (2010). Octrocrylene concentration decreased from 1166 ngL^{-1} to the LOQ of 155 ngL^{-1}, showing a removal efficiency of at least 87 %, higher than the previously reported removal efficiencies of 16-20 % (Li et al., 2007; Rosal et al., 2010). Nonylphenol was removed by >79 % at an AOD of 15 mgL^{-1}, to a final concentration of <113 ngL^{-1}. A similar removal efficiency was previously reported by Zhang et al. (2008). Triclosan was present at 48 ngL^{-1} and was removed to below the LOQ of 7 ngL^{-1} (removal efficiency of at least 87 %) at an AOD of 10 mgL^{-1}, similar to other studies (Rosal et al., 2010; Snyder et al., 2006). At an AOD of 15 mgL^{-1}, the synthetic musks galaxolide and tonalide were removed to below LOQs of 91 ngL^{-1} and 40 ngL^{-1}, respectively. Removal efficiencies for these musks were at least 87 % for galaxolide and 79 % for tonalide, which are in the range of removal previously shown by Rosal et al. (2010)

and Ternes et al. (2003). The UV-filter 4MBC was present in aerobically treated grey water at a concentration of 405 ngL^{-1} and was removed by >98 % at an AOD of 10 mgL^{-1} to a concentration below 10 ngL^{-1}, unlike the previously reported poor removal efficiencies of 0-24 % (Li et al., 2007; Rosal et al., 2010).

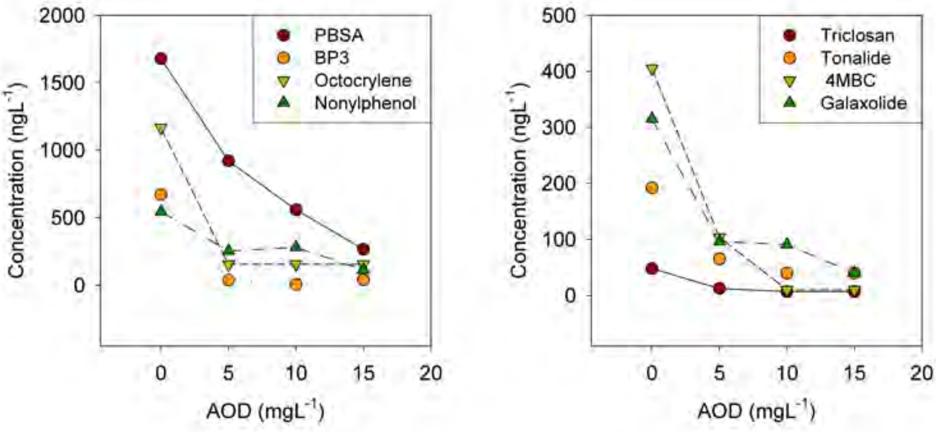

Figure 5.5: Removal of micropollutants from aerobically treated grey water at three different applied ozone doses

The removal efficiency of micropollutants was much higher from milliQ than aerobic effluent spiked at 10-100 μgL^{-1}(data not shown). For example, a PBSA initial concentration of about 30 μgL^{-1} can be removed from MilliQ water by 98 % with an AOD of 5 mgL^{-1}. The same PBSA concentration in treated grey water can only be removed by 25 % with an AOD of 5 mgL^{-1}. With an AOD of 15 mgL^{-1}, the removal efficiency of PBSA was only 70 %. These results are consistent with what was observed from the ozone consumption curves (Figure 5.4).

5.3.3 Batch tests with powdered activated carbon

The addition of powdered activated carbon to milliQ with a mixture of micropollutants at 1 mgL^{-1} resulted in a removal higher than 94 % for all compounds after only 5 minutes of contact time (data not shown). The application at relevant concentrations and on a real wastewater matrix must, however, confirm the results of this feasibility test.

5.3.4 Continuous GAC column operation

Figure 5.6 shows breakthrough curves at 25 °C for TOC in the three GAC columns tested, the curves were similar for color (data not shown). During the operational period of 1728 BV of column 1, only 20 % of breakthrough was measured. Column 2 seemed to have achieved a stable TOC removal of about 65 % after 2976 BV, and therefore the column was stopped for further testing with a PBSA solution to investigate whether a background TOC saturated column was capable of removing PBSA (see section 5.3.4). Column 3 was operated for a longer period (6480 BV) and TOC reached a breakthrough of over 90 %.

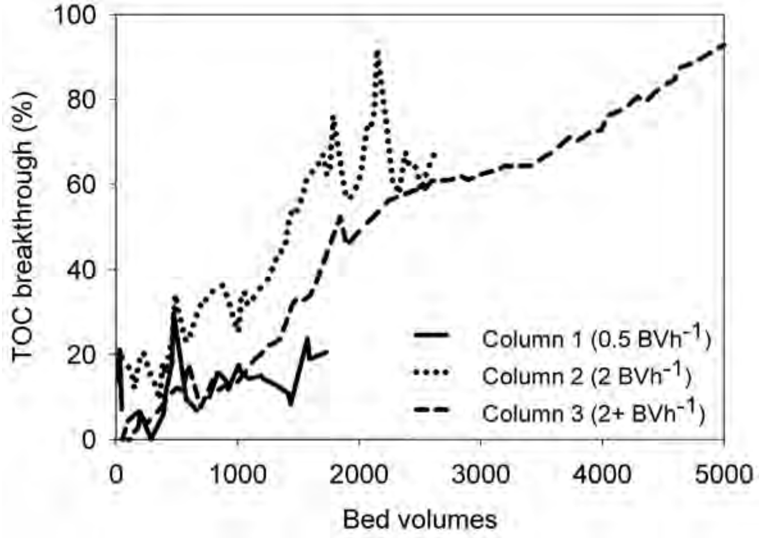

Figure 5.6: Breakthrough curves for total organic carbon aerobically treated grey water at 25 °C

Removal of micropollutants from spiked aerobic effluent in a GAC column operated at low flow

Column 1 was operated at a low flow (0.5 BVh^{-1}) and micropollutants were added aiming at concentrations similar to those in grey water (0.1-10 μgL^{-1}). Given the low solubility of most compounds (see properties in Chapter 1), the addition of a spiking solution did not always result in the intended concentration. Therefore, some compounds were below detection limits in the spiked influent.

Table 5.4 shows the influent and effluent concentrations of micropollutants during treatment with a GAC column at a low flow of 0.5 BV^{-1}. When one or none of the effluent samples were above LOQ, removal was calculated based on the LOQ. No trend was observed in the removal of micropollutants, the table represents the entire operational period of 1728 BV.

Influent micropollutant concentrations ranged between 22 and 4367 ngL^{-1}. The removal efficiencies for methylparaben, octocrylene and EHMC should be considered as an indication only, and no strong conclusions can be drawn because only 2 or 3 samples were above the LOQ in the influent.

In general, these results indicate the effectiveness of the treatment with GAC, with removal efficiencies higher than 67 %. Removal efficiencies of ethyl-, propyl- and butylparaben, triclosan, caffeine, BP3, PBSA and 4MBC from spiked effluent was 90 % or higher. Despite of their high $\log K_{OW}$, the removal efficiencies of tonalide, galaxolide and nonylphenol were lower: 67 %, 79% and 84 %, respectively.

Removal of micropollutants in GAC columns at real concentrations in aerobically treated grey water

Although in Chapter 4 17 out of the 18 selected micropollutants were detected in aerobically treated grey water in levels from 40 ngL^{-1} to 7.9 μgL^{-1}, concentrations of some these micropollutants were below LOQs in the filtered aerobically treated grey water used for this study. In this section we present the results for a few micropollutants.

Table 5.4: Influent and effluent concentrations from GAC column 1 treating spiked aerobically treated grey water at a flow of 0.5 BV^{-1}. All concentrations are expressed as ngL^{-1}, n = 10; except for PBSA, caffeine and BP3 where n = 14, n* = n>LOQ

		Influent			Effluent			Removal
	LOQ	Mean	S.D.	n*	Mean	S.D.	n*	%
Methylparaben	20	189	176	2	53	44	3	72
Ethylparaben	11	189	336	5	16	6	2	92
Propylparaben	10	866	552	9	16	4	3	98
Butylparaben	3	663	455	9	9	3	4	99
Bisphenol-A	10	579	463	8	196	65	2	66
Triclosan	6	2032	2184	10	102	122	5	95
Galaxolide	20	886	832	10	184	62	2	79
Tonalide	6	215	230	8	70	122	5	67
2EHS	6	22	11	5	25	NA	1	>95
Octocrylene	50	591	201	2	189	NA	1	>92
Nonylphenol	150	1685	1351	9	269	69	4	84
4MBC	1	252	296	9	23	17	5	91
EHMC	31	351	376	3	70	NA	1	>91
PBSA	6	4367	1517	14	442	821	14	90
Caffeine	8	1519	781	14	112	173	14	93
BP3	1	285	242	14	14	38	14	95

Figure 5.7 shows the influent and effluent concentrations for bisphenol-A, triclosan, tonalide, galaxolide and nonylphenol during the first 5000 BV of column 3. Most compounds were effectively removed to below LOQs. Removal efficiencies of these micropollutants were stable even though the GAC column was already saturated with TOC. This indicates a higher affinity of the carbon to these specific compounds than the background organic carbon and a longer life time of the GAC (i.e. lower treatment costs) than based on background TOC.

Bisphenol-A was present in the influent at an average concentration of 88 ngL^{-1} and was removed by at least 85 %. Triclosan was measured at an average concentration of 17 ngL^{-1} and was removed by at least 88 %, with the effluent of the column containing less than 2 ngL^{-1}. Tonalide was present in the influent at a concentration of 29 ngL^{-1} and was removed by >52 % to below 14 ngL^{-1}. BP3 was removed by 71 %, with an av-

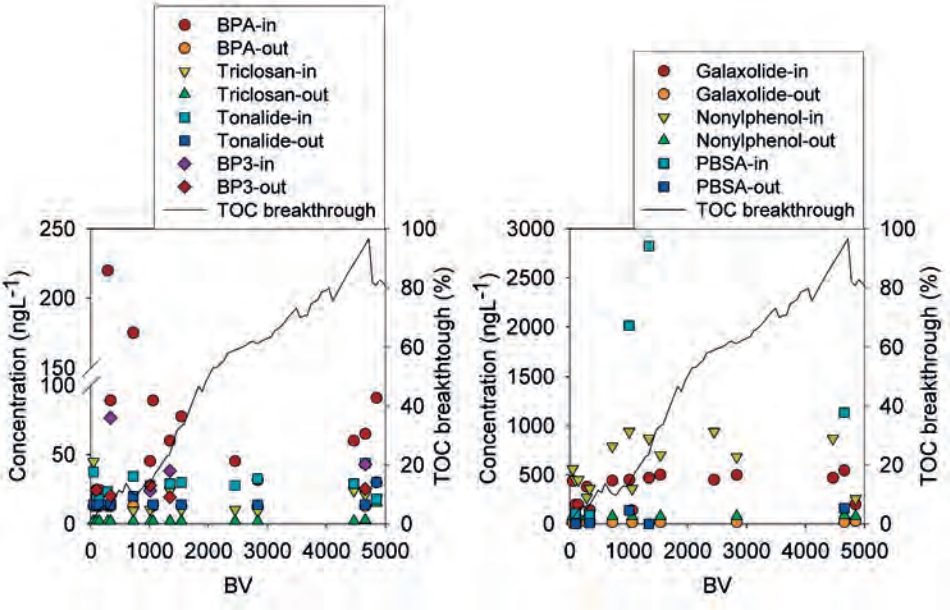

Figure 5.7: Concentrations of micropollutants in the influent (aerobically treated grey water) and effluent of a GAC column operated at 2-4 BVh^{-1} (column 3) and 25 °C; the solid line is the TOC breakthrough line

erage concentration in the effluent of 25 ngL^{-1}. Galaxolide, nonylphenol and PBSA were present in the influent at higher concentrations (Figure 5.7, right side), with influent concentrations of 387, 813 and 1243 ngL^{-1}, respectively. Their removal efficiencies in the GAC column were >95 %, >52 % and 93 %, respectively, and effluent concentrations were <14 ngL^{-1} for galaxolide, <76 ngL^{-1} for nonylphenol and 81 ngL^{-1} for PBSA.

In order to further test the capacity of the GAC column to remove micropollutants even when saturated with background TOC, after 5000 BV, the influent of the GAC column 3 was spiked with a cocktail of micropollutants to achieve micropollutant concentrations approximately 100 times higher than in aerobically treated grey water. Figure 5.8 indicates that despite the fact that the column was saturated with TOC and the aerobically treated grey water was spiked with relatively high concentrations of micropollutants, the GAC column still had the capacity of removing these compounds to below LOQs for at least an additional 1440 BV. The GAC column could not be operated long enough to provide breakthrough times for micropollutants.

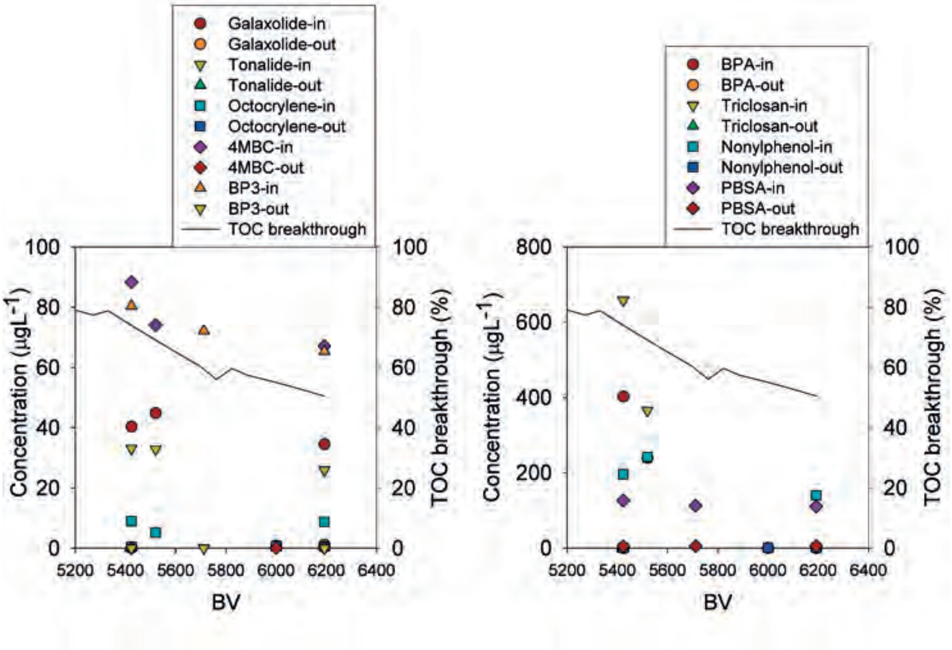

Figure 5.8: Concentrations of organic micropollutants in and out of a GAC column (column 3) after spiking influent with 100x the real concentrations of micropollutants operated at 4 BVh^{-1} and 25 °C; the solid line is the TOC breakthrough line.

Removal of PBSA at high concentrations in a GAC column saturated with TOC

The UV-filter PBSA was not removed during biological treatment (see Chapter 4), therefore, a test was done solely on this compound to observe its removal in a GAC column. Firstly, the column 2 was operated with aerobically treated effluent for about 3000 BV. At that point a stable TOC breakthrough of approximately 60-65 % was achieved (Figure 5.6), indicating saturation of the activated carbon with the background TOC of the influent. Thereafter, the influent was changed to a solution of 12.4

mgL^{-1} of PBSA in milliQ water. Figure 5.9 shows that a saturated column removed 80 % of the influent concentration of PBSA for about 2800 BV before the removal decreases to 45 %. Complete breakthrough did not occur during the operational period. The removal of PBSA is possible in a GAC column saturated with TOC. However, the tested concentrations were extremely high (about 12000 times the concentration in effluent) and 80 % removal leads to a final concentration of PBSA of 2.5 mgL^{-1}, which is still very high. Tests at the low μgL^{-1} level should provide more insight about the real situation, regarding removal and amount of BV until breakthrough, of grey water treatment.

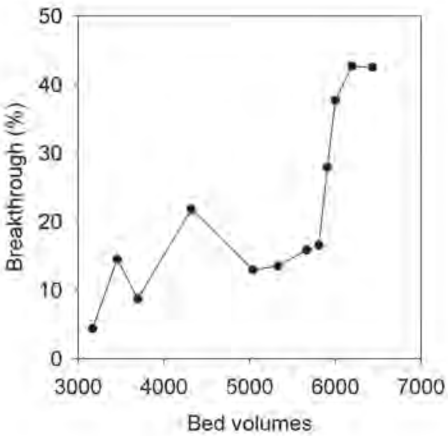

Figure 5.9: Breakthrough curve of PBSA in a GAC column saturated with TOC operated at 2 BVh^{-1}.

5.4 Outlook

Both ozonation and adsorption onto activated carbon are effective techniques to remove organic micropollutants from aerobically treated grey water. The removal of UV-filters PBSA, octocrylene, 4MBC and BP3, the fragrances tonalide and galaxolide, the biocide triclosan and the surfactant nonylphenol were compared in both treatment processes for non-spiked aerobically treated grey water. Based on these compounds both processes showed similar removal efficiencies for all compounds except for PBSA which showed a slightly higher removal with activated carbon.

All tested compounds were susceptible for ozonation, with the UV-filter PBSA and the fragrance tonalide being the slowest reacting compounds. The ozonation tests were performed in a batch process. The performance of the ozonation can be optimized to increase the utilization of the ozone applied as was shown by Ternes et al. (2003) in a bubble column, where most ozone applied was consumed by the wastewater.

The application of an ozone dose of 15 mgL^{-1} has been regarded as an affordable post-treatment process with costs of 0.05–0.20 €m^{-3} (investment and operation) (Joss et al., 2008). The advantage of ozonation is that it is also a disinfection step, a feature required for reuse applications that imply direct human contact, e.g., household reuse applications.

Adsorption on activated carbon was an effective process for the removal of all tested micropollutants. The cost implications cannot be assessed because breakthrough times of micropollutants were not achieved in the GAC columns operated in this study. However, the capacity of adsorption of a GAC column saturated with background TOC can allow for longer life time before carbon regeneration has to be performed, which will considerably decrease the operational costs below values of 0.05–0.20 €m^{-3} estimated by Joss et al. (2008).

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CHAPTER 6

Bioflocculation of grey water for improved energy recovery

Abstract

Bioflocculation of grey water was tested with a lab-scale membrane bioreactor in order to concentrate the COD. Three concentration factors were tested based on the ratio of sludge retention time (SRT) and hydraulic retention time (HRT): 3, 8 and 12. COD concentration factor was up to 7.1, achieving a final concentration of 7.2 gL^{-1} of COD. Large fractions of suspended COD were recovered in the concentrate (57 %, 81 % and 82 % at SRT/HRT ratios of 3, 8 and 12, respectively) indicating a strong bioflocculation of grey water. A maximum of 11% of COD mineralization of grey water was measured at the longest SRT tested (1 d). The integration of bioflocculation of grey water in decentralized sanitation concepts may increase the overall production of methane by 73 %, based on the biogas produced by black water only. Therefore, bioflocculation is a promising grey water pre-treatment step for energy recovery within decentralized sanitation concepts.

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6.1 Introduction

The concept of Decentralized Sanitation and Reuse (DeSaR) proposes the separation of wastewater streams into black water (urine and faeces with flush water) and grey water (discharges of hand basins, laundry, shower, bath and kitchen basin), for a more specific treatment of each stream in order to gain resources of what otherwise would be waste. Black water is a small stream rich in organic matter and nutrients; grey water is a large part of the household wastewater with much lower concentration of organic matter and nutrients. Within the scope of DESAR until now, black water has been considered for the recovery of organic matter (i.e. as energy and soil conditioner) and nutrients (i.e. as fertilizer) and grey water has been considered an alternative source of fresh water.

Anaerobic treatment is regarded as the core technology for decentralized sanitation concepts (Kujawa-Roeleveld and Zeeman, 2006). With anaerobic treatment of black water about 60 % of the chemical oxygen demand (COD) can be converted into biogas, either with an Upflow Anaerobic Sludge Blanket (UASB) reactor or a continuous stirred system (de Graaff et al., 2008; Kujawa-Roeleveld et al., 2006; Meulman et al., 2008; Wendland et al., 2007). Though present at low concentrations (in the range of 200-1000 mg/L), the COD load in grey water represents half of the total COD load of household wastewater (Otterpohl, 2002). Therefore, the anaerobic pre-treatment of grey water has been suggested to recover a part of this COD load (Abu Ghunmi et al., 2008; Elmitwalli and Otterpohl, 2007; Hernández Leal et al., 2010). However, anaerobic treatment of grey water performed poorly, removing only about 50 % of the influent COD (Abu Ghunmi et al., 2008; Hernández Leal et al., 2010) and a limited methanization rate of 25 %, probably caused by a rather large fraction of colloidal COD present in grey water and the high concentration of inhibitory surfactants (Chapter 3). The recovery of this COD as methane, therefore, remained a challenge for anaerobic treatment and aerobic treatment was preferred with the disadvantage of mineralizing COD (Chapter 3).

Bioflocculation of wastewater has recently gained attention, as it provides the opportunity of concentrating organic matter as unstabilized sludge by means of adsorption and immobilization, as also demonstrated in the A-step from the AB-process (Boehnke et al., 1997). This unstabilized sludge can be then processed anaerobically to produce methane rather than mineralize it (Akanyeti et al., 2010; Verstraete et al., 2009). The bioflocculation process utilizes a small fraction of the COD to produce exopolymers that act as flocculants for colloidal and soluble COD to create bigger particles or flocs. Short sludge retention time (SRT) must be applied in order to prevent extensive mineralization; likewise the hydraulic retention time (HRT) must be short to achieve a sufficiently high concentration of COD, necessary for efficient anaerobic treatment (Akanyeti et al., 2010).

In their study Akanyeti et al. (2010) showed that sewage, treated in a high-loaded membrane bioreactor (MBR), can be concentrated up to 10 times leading to a concentrate with up to 93 % of suspended COD. Bioflocculation could be a good option for the pre-treatment of grey water, to concentrate the organic load and afterwards recover the COD as methane together with black water and kitchen waste in a UASB, as schematically shown in Figure 6.1. Ideally, the concentrate of grey water should contain as much COD as black water (10 gL^{-1}), so it can easily be treated in the same UASB reactor. Therefore it is the objective of this study to assess the feasibility of bioflocculation of grey water in a high-loaded MBR as a pre-treatment step for anaerobic methane production and energy recovery.

6.2 Materials and Methods

6.2.1 Grey water source

Grey water was collected from the 32 houses of the DESAR demonstration project in Sneek, the Netherlands (Hernandez Leal et al., 2007). The grey water was collected from a storage tank at the demonstration site. Grey water was transported to the experimental hall in Leeuwarden and placed in a cold room (2–10°C) before the water was fed into the influent tank (at ambient temperature). The influent tank was continuously stirred during the experiments.

6.2.2 Experimental setup

The lab-scale MBR used for this study is described in detail by Akanyeti et al. (2010). In short, the system is a submerged MBR with an effective

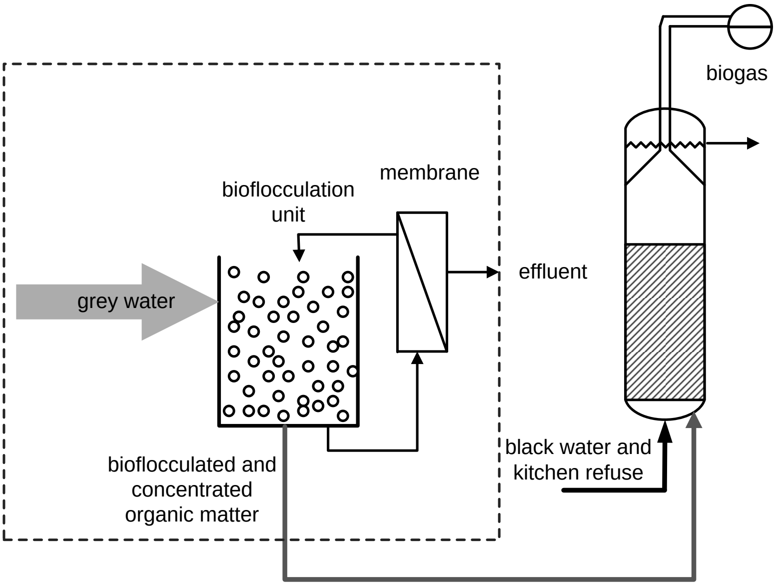

Figure 6.1: Bioflocculation of grey water as pre-treatment

volume of 2.5 L with two flat sheet polyvinylidenefluoride (PVDF) membranes with a pore size of 0.1 μm and an area of 0.232 m^3 each (see Figure 6.2). The MBR was aerated with PVC pipes installed in the bottom part of the reactor both to provide scouring to the membrane surface and to supply oxygen to the microorganisms. The resulting oxygen concentration was always within the range of 6–8 mgL^{-1}. A pressure sensor (Endress and Hauser) was used to measure transmembrane pressure (TMP).

Three experiments were set with different SRT/HRT as described in Table 6.1. Steady state was assumed after a minimum of 3 times the SRT. Experiments lasted for 3 days each, after steady state. HRT was defined by the permeate flow and SRT by the concentrate flow. Permeate and concentrate were continuously collected at ambient temperature in containers and 24 h samples of permeate, concentrate and grey water were taken every day. In this way, samples representing the whole operation period could be collected and measured.

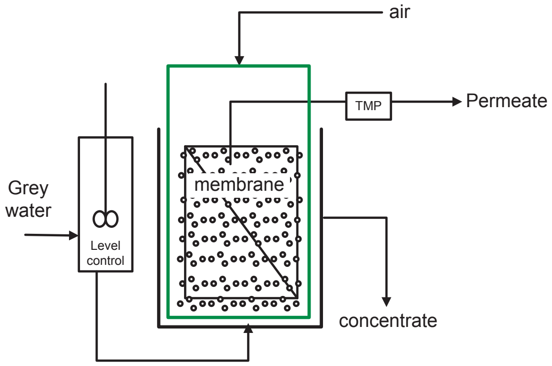

Figure 6.2: Bioflocculation set up

Table 6.1: Experimental setup for bioflocculation

Experiment	**1**	**2**	**3**
SRT (d)	0.2	0.4	1.0
HRT (h)	1.6	1.3	1.9
SRT/HRT	3.4	8.0	12.0
Volumetric loading (kg COD m^{-3} d^{-1})	9.2	10.8	12.7

Twice a day the membranes were physically cleaned with pressurized water, the rinsing water was collected and analyzed for total COD to account for the cake in the mass balance.

6.2.3 Anaerobic biodegradability test

One concentrate sample (SRT/HRT=1) was tested for biochemical methane potential (BMP), calculated as the percentage of COD of a sample converted into methane. Serum bottles of 220 mL were filled with 1 g of volatile suspended solids (VSS) of granular anaerobic sludge from a paper mill effluent treatment plant (Janssen et al., 2009). The BMP test was conducted in duplicate for the undiluted sample (substrate to inoculum ratio of 0.015), 50 % diluted with medium and 50 % diluted with water (substrate to inoculum ratio of 0.0075). The headspace of the bottles was flushed with nitrogen gas and closed with rubber stoppers and crimp caps and placed on a shaker (100 rpm) at a temperature of 30°C. During the degradation of grey water the gas pressure was monitored by a hand held pressure meter (GMH 3150, Greisinger electronic GmbH) and at the end of the test gas composition was measured by gas chromatography for CH_4, CO_2 and H_2 in duplicate.

6.2.4 Chemical analyses

Samples of grey water, permeate and concentrate were analyzed for total nitrogen (TN), total phosphorous (TP), total and soluble COD (<45 μm) and total suspended solids (TSS) and VSS. These analyses were all conducted according to standard methods (APHA et al., 1998), suspended COD was defined by a particle size of >12–25 μm. Additionally, anionic surfactants were determined with cuvette tests based on the MBAS standard method (APHA et al., 1998).
The parameters of COD, TSS and anionic surfactants were measured three times (three combined samples of 24 hours) for every experiment, TN and TP were measured once, the last day of the experiment.

6.3 Results and Discussion

6.3.1 Characteristics of grey water and concentrate

COD concentrations were similar in the first two experiments, with a total COD value of about 600 mgL^{-1} (Table 6.2). The grey water used for experiment 3, however, contained higher concentrations of total COD of about 1000 mgL^{-1}. The nutrient concentrations show the opposite trend with a nitrogen concentration of 32 mgL^{-1} in experiment 1 and 13 mgL^{-1} in experiments 2 and 3, and phosphorous concentration of 9 mgL^{-1} in experiment 1 and 5–6 mgL^{-1} in experiments 2 and 3. The concentrations of anionic surfactants showed similar concentrations in all experiments (Table 6.2). The different trends in the measured parameters showed that the fluctuations in the grey water characteristics are not related to dilution by use of more water, but probably to the different activities in the households prior to the collection of grey water for the experiments. Hernández Leal et al. (2010) reported an average grey water concentration of about 830±200 mgL^{-1} in a period of six months in the same demonstration project. In the study of Hernández Leal et al. (2010), grey water was taken from an autosampler working time proportionally collecting 200 mL samples from the piping over long periods. By the time of this study a storage tank of 5 m^3 was in place and the sampling was done by collecting about 200 L of grey water at once.

Table 6.2: Characteristics of grey water and concentrate in the different SRT/HRT tested (all values are in mgL^{-1}). CODt = total COD, CODss = suspended COD, CODsol = soluble COD, CODcol = colloidal COD, TSS = total suspended solids, TN = total nitrogen, TP = total phosphorous, AS = anionic surfactants.

	CODt	**CODss**	**CODcol**	**CODsol**	**TSS**	**TN**	**TP**	**AS**
SRT/HRT = 3								
Grey water	603	158	209	236	53	32.3	9.1	57
	(112)	(19)	(24)	(88)	(12)			(12)
Concentrate	1501	862	355	284	173	92	16	81
	(220)	(150)	(89)	(102)	(126)			(11)
SRT/HRT = 8								
Grey water	598	237	159	203	46	13.6	5.1	40
	(44)	(125)	(83)	(39)	(22)			(4)
Concentrate	2511	2040	223	248	816	66	8	73
	(366)	(285)	(50)	(65)	(285)			(14)
SRT/HRT = 12								
Grey water	1014	481	244	289	254	12.9	6.2	53
	(119)	(122)	(142)	(87)	(109)			(18)
Concentrate	7233	5947	876	410	3372	85	34	130
	(1312)	(783)	(507)	(100)	(564)			(53)

Total COD concentrations achieved in the bioflocculation process were 1501 mgL^{-1} for an SRT/HRT of 3, 2511 mgL^{-1} for an SRT/HRT of 8 and 7233 mgL^{-1} for an SRT/HRT of 12 (Table 6.2). For all experiments COD, TSS and TN had similar concentration factors, all lower than the theoretical concentration factor determined by the ratio SRT/HRT (assuming 100 % membrane retention and zero mineralization, see Figure 6.3).

The COD concentration factor during the experiment at an SRT of

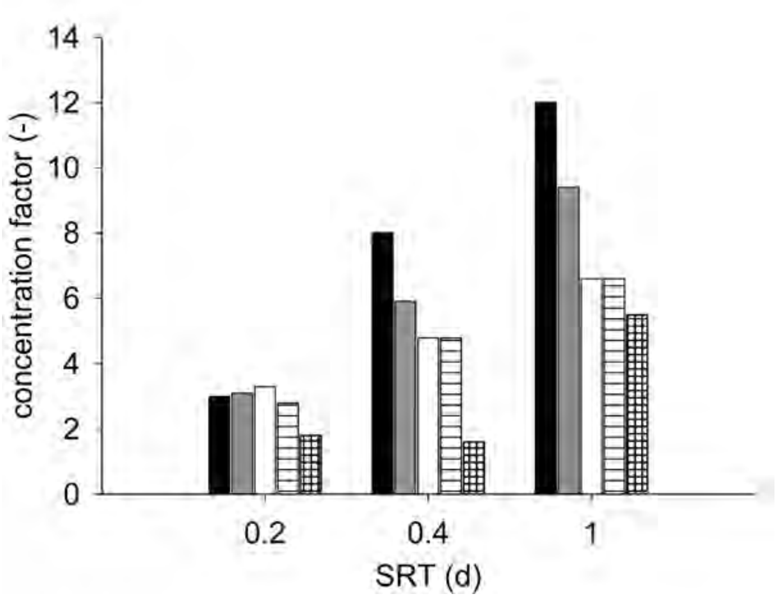

Figure 6.3: COD concentration factor compared to the ratio of SRT/HRT. Ratio SRT/HRT (■), total COD concentration factor (▩), total suspended solids (□), total nitrogen (⊟), total phosphorous (⊞). The amount of COD in the cake was considered in this graph and included in the concentrate, the other parameters were not measured in the cake and therefore are not included in this graph

.

0.2 d, the SRT/HRT and the concentration factor were similar. At longer SRTs of 0.4 and 1 d, the difference between SRT/HRT and the concentration factor is larger, the concentration factor being about 22–25 % lower than SRT/HRT; this difference can be related to COD mineralized or transferred through the membrane (see section 6.3.3).

High concentrations of total nitrogen were detected in the concentrate, 92 mgL^{-1} at and SRT/HRT of 3, 66 mgL^{-1} at an SRT/HRT of 8 and 85 mgL^{-1} at an SRT/HRT of 12. This indicates that the major fraction of the influent total nitrogen was contained in the concentrated stream (69 % of the total nitrogen of the influent at an SRT/HRT of 3, 85 % at an SRT/HRT of 8, 51 % at an SRT/HRT of 12) unlike the results from Akanyeti et al.

(2010) where the major fraction of nitrogen in the influent was conserved in the permeate. Most of grey water's total nitrogen was organically bound (ammonium was less than 3 % of TN) and apparently was retained by the membrane or its cake. In the case of sewage most of TN is present as ammonium which easily passed through the membrane (Akanyeti et al., 2010).

6.3.2 COD distribution in different fractions

A large fraction of suspended COD was measured in the concentrate in all bioflocculation experiments. This fraction increased from 26 % in the influent to 57 % in the concentrate at an SRT/HRT of 3, from 39 to 81 % at an SRT/HRT of 8 and from 47 to 82 % at an SRT/HRT of 12 (Figure 6.4). As a result, most of the concentrate COD is in particulate form and its removal and eventual degradation in a UASB could be achieved. The colloidal fraction of grey water has been shown to be poorly removed in anaerobic treatment systems (Elmitwalli and Otterpohl, 2007; Hernández Leal et al., 2010). The colloidal fraction in the concentrate was considerably reduced in comparison to grey water, which was reduced from 35 to 24 % at an SRT/HRT of 3, from 26 to 8 % at an SRT/HRT of 8 and from 24 to 12 % at an SRT/HRT of 12 (Figure 6.4).

The strong decrease in colloidal COD in the concentrate along with a strong increase of its suspended fraction (Figure 6.4), indicates that bioflocculation of the colloidal COD indeed took place. The concentration of soluble COD was also reduced in the concentrate compared to the grey water either by bioflocculation or biomass formation.

6.3.3 Mass balances

Mineralization was estimated as the closure of the COD mass balance. The main part of grey water's COD was collected in the concentrate (Figure 6.5), which accounted for 61, 53 and 55 % of the total COD at SRTs of 0.2, 0.4 and 1 d, respectively. The fraction of the COD in the cake was 15 % at an SRT of 0.2, 19 % at an SRT of 0.4 and 11 % at an SRT of 1 d.

Only a low amount of mineralization was observed (Figure 6.5), which increased with the increase in SRT. At an SRT of 0.2 d, mineralization was

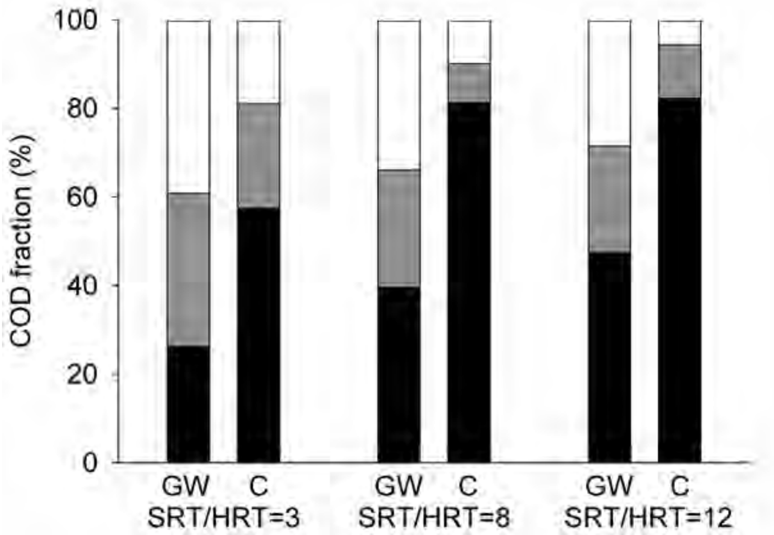

Figure 6.4: COD fractions of grey water (GW) and concentrate (C) at different SRT/HRTs. Suspended COD (■), Colloidal COD (▨), Soluble COD (□)

3 %, at an SRT of 0.4 d, 5 % and at an SRT of 1 d 11 %. These low mineralization rates indicate that concentration of grey water's COD can be done by bioflocculation without significant loss of COD.

Based on the results of the bioflocculation tests, an SRT of 0.4 d (SRT/HRT of 8) is sufficient to achieve over 80 % of suspended COD in the concentrate and limited COD mineralization. For an SRT/HRT ratio of 12 with a SRT of 0.4 d, the HRT should be reduced from 1.4 to 0.9 h or even less if a higher concentration factor is desired. The increase of flux, however, represents a practical limitation of a submerged MBR (as used in this study) because there is no sufficient membrane area to provide the flux needed (Akanyeti et al., 2010). Hence, a new reactor configuration (e.g., with an external membrane) would be required.

6.3.4 Surfactant concentrations

Anionic surfactants were not as strongly concentrated as COD. The concentrations of anionic surfactants in the concentrate ranged from 73 to

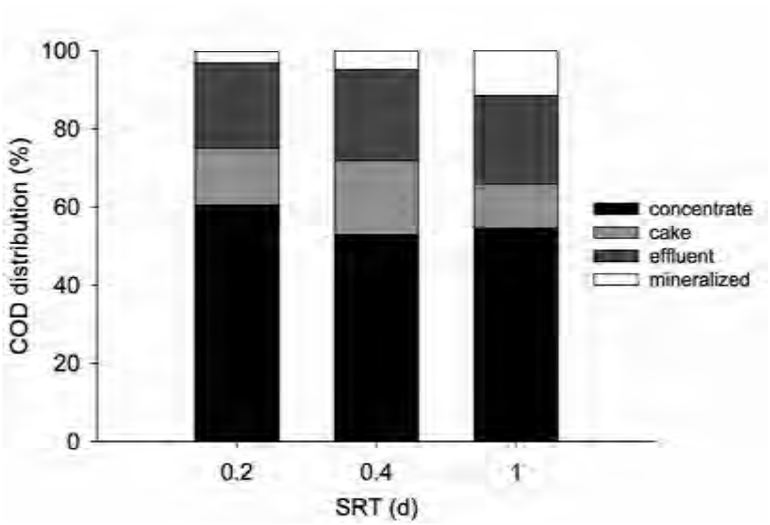

Figure 6.5: Total COD mass balances on bioflocculation experiments at different SRTs.

130 mgL^{-1} (Table 6.2). Anionic surfactants are generally persistent under anaerobic conditions and it has been shown that anionic surfactants may inhibit anaerobic processes (Garcia-Morales et al., 2001; Ying, 2006). Therefore, the partial degradation of anionic surfactants will be a desired feature of the bioflocculation. The concentrate contained 19–34 % of anionic surfactants and the permeate contained 33–41 % (Table 6.3). The missing fraction was considered biodegraded or adsorbed by the cake, and accounted for 30–48 % of the anionic surfactants from grey water. Given the high aerobic biodegradability of anionic surfactants and the longer retention time of the cake in the reactor, biodegradation of these surfactants very likely occurred. Although only about a third of the anionic surfactants remained in the concentrate, the surfactants may still inhibit the anaerobic digestion based on the EC50 of 19 mg/L determined by Garcia-Morales et al. (2001). Considering that this concentrate would be mixed with black water and kitchen waste to be treated in a UASB, there will be a dilution effect on this concentration of about 50 % (considering SRT/HRT of 12).

Table 6.3: Percentage of anionic surfactants in concentrate, permeate and biodegraded/adsorbed during bioflocculation of grey water at different sludge retention times (SRTs)

SRT	**d**	**0.2**	**0.4**	**1**
Concentrate	%	34	23	19
Permeate	%	35	41	33
Biodegraded/adsorbed	%	30	36	48

6.3.5 Permeate characteristics

The permeate accounted for 22–23 % of the total grey water COD at all the SRTs tested (Figure 6.5). COD concentrations in the effluent ranged from 160–240 mgL^{-1} with a concentration of nutrients ranging from 2.5–4 mgL^{-1} of total nitrogen and 1.1–3.8 mgL^{-1} of total phosphorous (Table 6.4). A COD:N:P ratio of 100:20:1 is necessary for biological treatment (Metcalf and Eddy, 2003). Based on this, the permeate with a COD:N:P of 100:2.4:1.4 is significantly short of nitrogen.

Table 6.4: Characteristics of permeate from bioflocculation unit (all values are in mgL^{-1}), standard deviations are shown in parentheses. CODt = total COD, TN = total nitrogen, TP = total phosphorous, AS = anionic surfactants.

SRT/HRT	**3**	**8**	**12**
CODt	166(30)	159 (23)	238 (59)
TN	4.0	4.8	2.5
TP	2.3	1.1	3.8
AS	26.7(2)	18.8 (0.3)	19.2 (10)

Nevertheless, in the study of aerobic grey water treatment (Chapter 3) a COD:N:P ratio of 100:4.8:0.8 was applied and a COD removal of 90 % was achieved by taking up only 25 % of the nitrogen. Anionic surfactant concentrations in the permeate are still high, these surfactants are readily biodegradable under aerobic conditions (Ying et al., 2002). Hence, aerobic treatment is recommended for the permeate. The addition of nutrients should be considered, in case of nutrient deficiency.

6.3.6 Membrane fouling

Membrane fouling occurred quickly during all the bioflocculation experiments (Figure 6.6). The profile is similar for experiments done at SRT/HRT of 3 and 12 with a steep slope in TMP, however at an SRT/HRT ratio of 8 fouling seems to occur at a slower rate without an obvious reason. Though the fouling layer developed fast, the flux recovered completely after just physical cleaning, with water at high pressure. The development of a cleaning strategy, therefore, is key to the good performance of this process. Furthermore, the energy consumption of a high loaded MBR should be considered in the total energy balance.

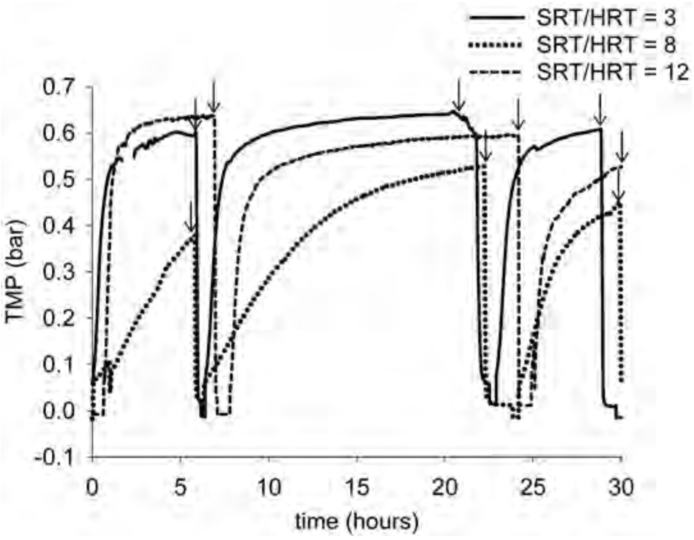

Figure 6.6: Transmembrane Pressure (TMP) profile of bioflocculation of grey water at different SRT/HRT ratios,the arrows indicate the occassions in which the membrane was cleaned.

6.3.7 Optimization of bioflocculation of grey water

Optimization of the bioflocculation process by increasing the SRT/HRT ratio will probably lead to higher concentration factors. By keeping HRT around 1 h and the SRT at 1 day a theoretical concentration factor of 24 with a COD concentration factor of possibly 15-20 could be achieved, assuming low mineralization rates as shown in this study. As mentioned above another reactor configuration might be needed. Settleability of the concentrate should be assessed to evaluate the possibility of using a settler instead of a membrane and potentially minimize the operational costs. An effluent free of particles, however, seems an attractive feature within a water reuse scheme.

6.3.8 Integrating bioflocculation to the DESAR concept

Based on the results of the highest concentration factor at an SRT/HRT = 12, a concentrate with a COD of 7.2 gL^{-1} can be achieved, which is in the range of concentrated black water collected with vacuum toilets (Table 6.5). Grey water has an anaerobic biodegradability of 70–74 % (Abu Ghunmi, 2009; Elmitwalli and Otterpohl, 2007). The grey water concentrate had a biodegradability of 88±5 %, significantly higher than that of grey water. This was perhaps due to the partial degradation of compounds (e.g., anionic surfactants) that are not biodegradable anaerobically.

Table 6.5: Characteristics of black water from vacuum toilets (Meulman et al., 2008), bioflocculated grey water (at SRT/HRT = 12) and the mix of them

	Units	**Black water**	**Bioflocculated grey water**	**Mix**
Volume	($Lp^{-1}d^{-1}$)	5	5.5	11.5
CODtotal	(gL^{-1})	16	7.2	11.3
COD_{SS}	(gL^{-1})	12	5.9	9.1
Surfactants	(mgL^{-1})		130	62

The calculated characteristics of the mix of concentrated grey water and black water (Meulman et al., 2008) indicate the production of 10.5 $Lp^{-1}d^{-1}$ of a stream with a total COD of 11.3 gL^{-1} (Table 6.5). From black water 16.8 L $CH_4p^{-1}d^{-1}$ can be produced at a COD load of 80 $gp^{-1}d^{-1}$ and a methanization rate of 60 % (0.35 L CH_4(g COD)$^{-1}$) (Kujawa-Roeleveld et al., 2006). Grey water concentrate, with a load of 39.9 $gp^{-1}d^{-1}$ and a methanization rate of 88 %, as measured in this study, can potentially yield 12.3 L $CH_4p^{-1}d^{-1}$, increasing the methane production by 73 % in comparison with only treating black water. Also, the amount of excess sludge produced in a UASB reactor and therefore its volume will depend on its hydrolysis efficiency. The quality of the sludge could be affected by the components in grey water, a topic that needs to be further investigated.

The methane produced by grey water concentrate is equivalent to 160 $MJp^{-1}y^{-1}$ ($35.6\ MJ(Nm^3CH_4)^{-1}$). Considering an efficiency of 85 % of combined heat and power generators, of which 40 % is electricity and 60 % heat, the grey water concentrate can yield 15.1 kWh $p^{-1}y^{-1}$. With a grey water flow of 25.5 $m^3p^{-1}y^{-1}$, the electricity gained is 0.59 kWh m^{-3}, which can cover the electricity costs for fouling control (0.2-0.3 kWh m^{-3}) and have a surplus of 0.29-0.39 kWh m^{-3} of electricity. The possibility of applying a settler instead of a membrane as a separation step should be investigated, as it would further increase the energy efficiency of the system.

6.4 Conclusions

Bioflocculation of grey water was successfully demonstrated where grey water can be concentrated for the recovery of energy. A large fraction of suspended COD can be obtained in the concentrate with low mineralization rates. Anionic surfactants are partially degraded, but they may still affect the anaerobic degradation of the concentrate. The permeate produced from the bioflocculation process contains COD in the range of 200 mgL^{-1} and treatment in a compact biological unit would be necessary before reuse or discharge. By adding the grey water concentrate to the anaerobic treatment of black water, methane production can be potentially increased by 73 %. Therefore, it is possible to recover grey water's COD for energy production within the decentralized sanitation concept without the need for an extra anaerobic reactor and without mixing wastewater streams.

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CHAPTER 7

Concluding discussion

Hernández Leal, L., Temmink, H., Zeeman, G and Buisman, C.J.N.

7.1 Introduction

Grey water constitutes a large fraction of the household wastewater: up to 75 % if normal flushing toilets are installed, and over 90 % with vacuum toilets. Compared to concentrated toilet water, grey water is much less polluted and therefore, after proper treatment, has a great potential for reuse. The goal of this thesis was to provide the necessary information to define a suitable treatment system for grey water, with special focus on removing organic micropollutants.

A thorough characterization was presented in Chapter 2. The biological treatment of grey water was studied in Chapter 3 and 6. Chapter 4 described the presence of micropollutants and their removal during biological treatment. Although micropollutants were removed to a large extent during aerobic grey water treatment, many were still detected in the effluent. Therefore, in Chapter 5 we showed the feasibility of removing these micropollutants by ozonation and activated carbon adsorption.

In this chapter, the reuse possibilities of grey water and their implications in terms of treatment, infrastructure, behavior and product development are briefly discussed. Based on the results obtained in this thesis, key aspects for grey water treatment are described. Furthermore, preliminary results of ecotoxicological evaluation of treated grey water will be presented. A concept for grey water treatment is defined and discussed.

7.2 Prospects for grey water reuse

The value of reused water is perhaps not as appreciated in countries with abundant water sources (e.g., The Netherlands) as it is in countries with water scarcity, such as Egypt, Jordan and Israel. Nevertheless, in The Netherlands the search for alternative drinking water sources is under serious consideration. Main drivers for this search are emerging environmental problems like the pollution and salination of aquifers, resulting in increased costs to produce drinking water (Stuyfzand and Raat, 2010). The costs (in particular environmental costs) of producing drinking water can be reduced by minimizing its demand by water reuse.

The Netherlands as a whole, does not face serious water scarcity. However, the provinces of Zeeland and Groningen depend on neighboring provinces for fresh water. Furthermore, on the Wadden islands fresh water is a scarce resource, especially during summer time. As a result, these islands are dependent on the main land for water supply, for which a pipeline was connected. This solution has been identified as undesirable and within the project "cradle to cradle islands" one of the objectives is to reach water independence by the year 2020. For this purpose, measures are planned to minimize water demand, increase water reuse and desalinate seawater. A demonstration project has recently started in a holiday house on Ameland. One of the aims of this project is to show that savings in energy and water can be achieved without reducing the level of comfort (Sombekke, 2010).

Standards for grey water reuse were suggested by Li et al. (2009) and are presented in Table 1.2 in Chapter 1. There are different factors to consider when selecting the appropriate water reuse applications, including water quality, technology available, matching supply and demand, infrastructure requirements, economic feasibility and environmental considerations (Asano et al., 2007). Some of these factors are briefly discussed in the following subsections.

7.2.1 Household reuse

Health risks associated with grey water are lower than those of combined domestic wastewater. Domestic wastewater has a concentration of 10^7-10^8 *E. coli* per 100 mL, whereas grey water has a concentration of 10^4-10^5 *E. coli* per 100 mL (Mara and Kramer, 2008). Nevertheless, if grey water is to be reused in the household, the main problem will be the risks of exposure to pathogens from the recycled water. High quality and well-disinfected reclaimed water must be maintained to ensure public protection (Asano et al., 2007).

In the UK, household reuse had a higher acceptance if applied within single households (Bixio et al., 2006). However, the collection of grey water from neighbourhoods or apartment buildings would increase the economic feasibility of grey water treatment and reuse (Asano et al., 2007).

Major infrastructure components in household reuse systems are dual reticulation systems. A risk of such an infrastructure is the possibility of accidental cross-connections. The installation of dual-reticulation systems for potable and non-potable water (for laundry, garden and toilet flushing) in the Netherlands has been banned due to one negative experience of cross connection with the drinking water supply (Bixio et al., 2006; Oesterholt et al., 2007). For future implementation of dual-reticulation systems, it must be guaranteed that no cross-connections will occur. Rebuilding trust between stakeholders, however, will be a major challenge for the application of household water reuse in the Netherlands.

Grey water production of 70-90 $Lp^{-1}d^{-1}$ is higher than the demand of non-potable water for laundry (17.2 $Lp^{-1}d^{-1}$) and toilet flushing (36 $Lp^{-1}d^{-1}$, or 6 $Lp^{-1}d^{-1}$ if vacuum toilets are installed). Reusing treated grey water for toilet flushing and laundry, can reduce the drinking water consumption by 42 %, if normal toilets are installed, or only 18 % if vacuum toilets are installed. To close the water balance within the household, treated grey water should be reused also for showering (52.3 $Lp^{-1}d^{-1}$). There are several examples worldwide in which treated grey water is reused for toilet flushing and garden watering (Anderson, 2003). However, there are no documented cases of direct water reuse for showering in Europe. This reuse application would require a thorough evaluation of the risks and public acceptance. In Windhoek, Namibia, the percentage of wastewater used for production of drinking water has been up to 35 % in periods of serious drought. The treatment applied to this water, however, is a very extensive and costly multibarrier system (du Pisani, 2006).

Traces of micropollutants from personal care and household products in the reuse water may be present in recycled grey water. The risks associated with the exposure to these micropollutants should be assessed. Even though most ingredients of personal care are not toxic to humans, in closed systems, they will accumulate and perhaps be transformed into more toxic compounds. The risks are higher with the discharge of organic pollutants from uncommon household activities, for example the discharge of paint, specialized cleaning agents, antifreeze, etc. A change of behavior by users will be necessary to prevent these toxic substances from entering the closed water cycle.

Awareness would be needed to prevent these chemicals from entering the recycling system. Grey water reuse in single households would increase awareness about what substances are put down the sink. Furthermore, the development of personal care and household products with high biodegradability must be boosted to prevent accumulation of micropollutants in recycling systems and in the environment. Some products have already earned a “cradle-to-cradle” certificate (MBDC, 2010).

7.2.2 Water reuse for irrigation

In countries like The Netherlands, irrigation is seasonal and water reuse in this type of application will require large tanks to store water during winter time, which is highly unpractical and costly. However, in countries where irrigation is required around the year, such as in dry areas of the world, grey water reuse is feasible.

The use of grey water for irrigation of greenhouses has been proposed by Mels et al. (2010) within a larger concept called the Greenhouse Village, a neighbourhood with the goal of self-sufficiency with regard to energy and water. Grey water reuse for green house irrigation, as proposed in the Greenhouse Villate concept, may require desalination or irrigation strategies to prevent sodium accumulation (flushing with fresh water). The limit of sodium in greenhouse irrigation water is 2 mmol while grey water contains 6 mmol of sodium. Sodium can be removed at a small scale by a capacitive deionization system (van Limpt, 2010).

Regarding micropollutants the attenuation capacity of the soil plays an important role. Short term studies showed that micropollutants are immobilized and slowly degraded in soil (Ternes and Joss, 2006). However, many of the micropollutants studied in this thesis are highly accumulative, and long term studies would better show the effects of reusing treated grey water on crops, soil and soil organisms. It may be required to remove micropollutants before treated grey water is applied for irrigation.

7.2.3 Industrial reuse

Industry is a major water user. In particular power plants, oil refineries and manufacturing facilities could use reclaimed water as cooling water. Additional treatment is usually necessary to meet the specific requirements for the industrial process (Asano et al., 2007). To prevent scaling or corrosion of piping systems, total dissolved solids, chlorides and dissolved oxygen are parameters that need to be strictly controlled.

Asano et al. (2007) have made an overview of experiences with water reuse in industrial applications, e.g., in pulp and paper, and textile industries. Paper industry is water intensive and reclaimed water can be used for the production of brown paper. An example of this is a newspaper manufacturing plant in Los Angeles, California.

In The Netherlands, the effluent of the municipal wastewater treatment plant (WWTP) from 55,000 Terneuzen inhabitants is reused by industry for the production of demineralized water after treatment with an membrane bioreactor (MBR) and reverse osmosis (RO)(Marjarnaa, 2009). In contrast to the estuary water, otherwise used for the production of process water, treated wastewater had much lower salt concentrations. This allowed for lower pressures in the RO treatment, which considerably reduced the costs. Furthermore, the effluent of the WWTP was consistent in quality, an advantage for the operation of the RO treatment. The production process of demineralized water, however, had to be adapted to cope with fouling problems (e.g., using fouling resistant membranes).

In The Netherlands, industrial water use accounts for about 20 % of the total drinking water consumption. Municipal water use accounts for only about 8 %. Therefore in theory, it is possible to find an application for grey water reuse in the industrial sector. The main problem in this case will be the coordination of the point of generation of recycled grey water and the point of use. In new urban developments, it can be studied whether a housing state can be built close to a water intensive industry. However, people generally do not prefer to live close to industrial areas.

7.2.4 Indirect potable reuse

Nowadays, with all the technology available, it is possible to produce high-quality recycled water which would comply with drinking water standards. The main constraint on wastewater recycling for drinking water is the public perception of drinking water that once contained human excreta (Asano et al., 2007). Grey water , however, contains minimum amount or no human excreta. In areas of extreme water scarcity, where sewage is considered as an alternative drinking water source, grey water should be a better alternative in terms of acceptance and treatment costs.

A more accepted water reuse application is the indirect potable reuse, by recharging aquifers or discharging into a water reservoir from which water is to be drawn for drinking water treatment. The advantage of aquifer recharge is the capacity for storage and the extra treatment provided by the filtration, sorption of metals and organic compounds and the biodegradation of slowly biodegradable compounds (Ternes and Joss, 2006). Indirect potable reuse has been demostrated in England (augmentation of surface water), Belgium (artificial recharge of an unconfined aquifer in dune water catchment), Austria (direct infiltration in a subsoil aquifer system) and Germany (soil aquifer treatment) (Ternes and Joss, 2006). In The Netherlands, groundwater recharge is mostly done with surface water in the dunes, where water will be stored for a period of 60 days before extraction.

Unplanned indirect water reuse often occurs as eventually treated wastewater reaches water bodies from where drinking water is produced. In some cases (e.g., in France, UK, USA) during summer periods, WWTP effluents account for 70-95 % of low flow surface water (Ternes and Joss, 2006). A better wastewater management is required to prevent nutrients and organic micropollutants from reaching water bodies. A promising approach is the separation at source and specific treatment of wastewater streams. The targeted treatment of concentrated toilet water facilitates the recovery of energy and nutrients and the efficient destruction of pharmaceuticals and hormones (de Graaff, 2010). As a consequence, the load of nutrients, hormones and pharmaceuticals into receiving waters will be decreased. Grey water can be reused or discharged for eventual indirect reuse at a lower risk than sewage. Recharge of aquifers or augmentation of surface waters with grey water can be done locally. In this way water supply and demand can be matched locally, instead of discharging treated water faraway from its point of use.

7.3 Key aspects to consider in a grey water treatment concept

Grey water contains roughly 700-800 mgL^{-1} of COD, about 30 mgL^{-1} of total nitrogen and 7 mgL^{-1} of total phosphorus. Since grey water is the result of washing activities, surfactants are important constituents of grey water, especially anionic surfactants which are present in the range of 10-70 mgL^{-1}. Based on these constituents of grey water, biological treatment is a suitable treatment step.

Poor COD removal (about 50 %), low methane production and poor removal of organic micropollutants lead to the conclusion that anaerobic treatment is not a suitable choice for grey water (pre) treatment. On the other hand, aerobic treatment, with a high COD removal efficiency of 90 %, a low sludge yield (0.12 kg VSS/kg COD) and a fair removal of micropollutants, is a preferred option for the biological treatment of grey water. The combination of anaerobic + aerobic treatment achieved 89 % COD removal. However, the overall sludge production was higher (0.18 kg VSS/kg COD) and the micropollutant removal was lower than aerobic treatment alone. These factors along with the low methane production (72 NLm^{-3}) did not make the combined system worthwhile.

After filtration to remove suspended solids, the aerobically treated effluent contained COD concentrations of 48 mgL^{-1} ($\text{BOD}_5 < 10\ \text{mgL}^{-1}$), total nitrogen of 26 mgL^{-1}, total phosphorus of 3.5 mgL^{-1} and 1.4 mgL^{-1} of anionic surfactants. This does not meet the reuse standards suggested by Li et al. (2009). Furthermore, micropollutants were still detected in the aerobically treated grey water, and therefore a physical-chemical treatment step was recommended. Ozonation and granular activated carbon (GAC) showed good results for the removal of micropollutants (Chapter 5). The effluent after ozonation with an applied ozone dose of 15 mgL^{-1} contained 39 mgL^{-1} of COD ($\text{BOD}_5 < 10\ \text{mgL}^{-1}$), 3.5 mgL^{-1} of total nitrogen, 2.3 mgL^{-1} of total phosphorus and 0.4 mgL^{-1} of anionic surfactants. A GAC column, even when saturated with background TOC, can remove micropollutants. The effluent of a GAC column will therefore be similar to the biologically treated grey water regarding COD, color and nutrients. Anionic surfactants and other micropollutants, however, will be removed. The concentration of anionic surfactants will probably be <1 mgL^{-1} (suggested limit for reuse applications, see Table 1.2 in Chapter 1). In the studied grey water, neither ozonation nor adsorption could reduce the concentration of nutrients to the recommended limits defined for reuse in recreational impoundments and an additional treatment step would be necessary (e.g., sand filtration). In other cases, grey water may contain lower nutrient concentrations and the suggested guidelines for reuse would be met by biological treatment alone. Except for pathogens, which were not measured in this thesis, aerobic effluent after treatment with ozone or activated carbon, complies with recommended standards for urban reuse. Ozonation and activated carbon adsorption are regarded as affordable techniques for wastewater posttreatment with a cost of 0.05-0.20 €m^{-3} (Joss et al., 2008). The advantage of applying ozonation as posttreatment is that ozone oxidizes micropolluntants and disinfects water at the same time, and from that perspective it may be a more suitable posttreatment.

From this thesis, key elements to include in the grey water treatment concept are biological (aerobic) treatment and posttreatment with either ozonation or activated carbon. Though not addressed in this thesis, removal of pathogens must be included in the treatment concept.

7.4 Preliminary results on ecotoxicological quality of treated grey water

Ecotoxicity links the information of chemical and physical quality of an effluent to the actual impact on organisms exposed to it. This is valuable when assessing the risks of reuse or discharge of treated grey water. A preliminary ecotoxicological study was done to evaluate acute effects (on midge larvae and daphnids) and chronic effects (on daphnids) of grey water, biologically treated grey water (aerobic treatment and combined anaerobic + aerobic treatment), ozonated aerobically treated grey water and aerobically treated grey water treated with activated carbon (Soeter et al., 2010).

Grey water was acutely toxic to both tested organisms while biologically treated grey water had an effect on the survival of daphnids (48h survival test). Biologically treated grey water had negative effects on the population growth rate and delayed the first day of reproduction (21d test).

Additionally, the treatment with a combined anaerobic + aerobic system caused negative effects on growth and cumulative reproduction. Aerobic treatment alone produced a better ecotoxicological effluent quality than the combination of anaerobic + aerobic, giving another argument to avoid the implementation of such system.

The exposure of daphnids to ozonated aerobically treated grey water with ozone had a neutral effect, except for a slight stimulation of the cumulative reproduction. Activated carbon treated grey water had a slight negative effect on daphnid survival (48h test), an early first day of reproduction and slight stimulation of population growth rate (21d test). These results indicate that based on ecotoxicological tests, ozonation of aerobically treated grey water produces a slightly better effluent than the treatment of aerobically treated grey water with activated carbon.

7.5 Proposed grey water treatment concept

Although grey water contains low concentrations of COD compared to concentrated black water, grey water contains approximately 50 % of the COD discharged by households (Otterpohl, 2002). The bioflocculation system presented in Chapter 6, demonstrated the potential for COD recovery from grey water as methane. By using this system, the methane production can potentially be increased by 73 %, based on the methane production from concentrated black water. For reasons of energy recovery, the proposed treatment concept for grey water is based on bioflocculation as pretreatment, followed by an aerobic polishing step and a physical/chemical step (Figure 7.1).

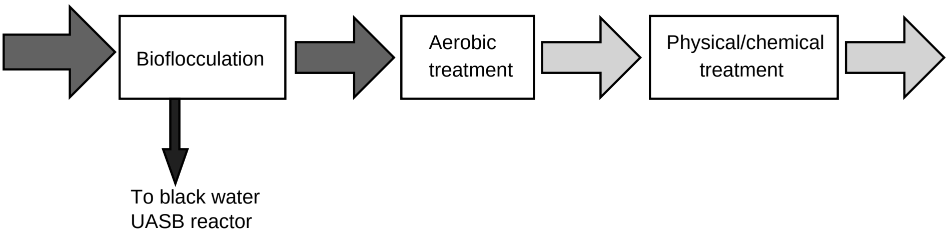

Figure 7.1: Proposed treatment scheme for grey water

7.5.1 Bioflocculation of grey water

Bioflocculation of grey water was tested in a highly loaded MBR. It may be possible to achieve similar results operating a highly loaded activated sludge system and a settler. This type of system is currently applied in the DeSaR demonstration project in Sneek (The Netherlands) for the treatment of grey water and it removes about 42 % of the COD. No information is available regarding the mineralization rate in this system (Gorter, 2010). The sludge produced in this highly loaded system is then processed further in another aerobic step instead of recovering the COD in the upflow anaerobic sludge blanket (UASB) reactor, as proposed in Figure 7.1. In a bioflocculation system with membrane separation, as tested in Chapter 6, the removal of COD is over 70 %, which is much higher than achieved only with a settler. The energy required for membrane filtration in the MBR, however, is higher than the energy required by the system with a settler. A more detailed analysis will have to be done to evaluate if the cost savings by avoiding the application of an MBR will make up for the lower energy recovery as methane from a highly loaded activated sludge system. For single household reuse, bioflocculation is recommended to be done in an MBR as it is more compact and the high effluent quality may require fewer treatment units to achieve reuse quality.

The grey water sludge produced in the bioflocculation system was proven to have a high anaerobic biodegradability (88 %), and in principle energy recovery within decentralized sanitation concepts can be increased by 73 % (see Chapter 6). This is assuming the collection of black water with vacuum toilets and the treatment of concentrated black water together with grey water sludge in a UASB reactor as successfully applied by de Graaff (2010) and Meulman et al. (2008). Further investigation is needed to evaluate the impact of adding grey water sludge into the black water treating UASB. The stability of the flocs formed in the grey water sludge should be assessed and observed if the solids indeed can be captured in the sludge bed of the UASB.

Regarding (hydrophobic) micropollutants, with total retention of suspended and colloidal particles, a large fraction of them would be adsorbed in the retained grey water sludge. Grey water sludge will be mixed with black water, concentrating in one stream most of the hormones, pharmaceuticals and personal care products. More hydrophilic compounds, such as PBSA, will most likely be present in the permeate. The fate of micropollutants should be studied in further detail. The removal of micropollutants from sludge needs to be studied, as it may be required before reusing it in agriculture. Further testing of the permeate (chemical and ecotoxicological) should be done to assess the risks related to its reuse.

7.5.2 Aerobic post-treatment

Thanks to the membrane separation at the bioflocculation step, the effluent is solids free and theoretically free of pathogens, with a COD concentration of 160-240 mgL^{-1}, total nitrogen of 2.5-4.8 mgL^{-1} and total phosphorus of 1.1-3.8 mgL^{-1}. Treatment in a trickling filter, for example a down flow hanging sponge reactor (Tandukar et al., 2005), would remove remaining biodegradable COD, most of the nutrients and would provide additional removal of micropollutants. After this step, the effluent may already meet standards for restricted grey water reuse (see Chapter 1, Table 1.2) and discharge into receiving bodies, which up until now do not include threshold values for micropollutants. For unrestricted grey water reuse a disinfection step, such as UV-radiation, would be necessary.

7.5.3 Post-treatment/disinfection step

The need for further post-treatment should be evaluated with respect to the quality of the effluent from the biological treatment and the (re)use option. If a higher micropollutant removal is required, ozone or activated carbon treatment can be applied. An advantage of ozone treatment over GAC treatment is perhaps the double effect of destruction of micropollutants by oxidation and the disinfection of the treated grey water. We do not know to which extent pathogens are removed in a GAC column. A downside of ozone treatment is the possible production of more toxic compounds, that will end up deteriorating the quality of the effluent. However, preliminary ecotoxicological results indicate that ozonation produced an effluent with neutral effects on daphnids. This aspect should be investigated further.

The proposed treatment concept can achieve the defined standards for unrestricted water reuse (see Chapter 1, Table 1.2). The reuse of grey water in the household for laundry and toilet flushing may require the removal of micropollutants, which can be done with ozone to also provide disinfection. For applications such as showering and bathing, and drinking in areas with extreme water scarcity, an extra disinfection step should be included at the point of use. This can be an in-line UV-radiation unit installed in the shower head and in the kitchen water tap.

7.6 Fate of micropollutants

The removal of micropollutants from grey water was studied in this thesis. Whether these compounds were biodegraded or were adsorbed to sludge could not be assessed, because concentrations in sludge were not measured. Physical/chemical properties and biodegradability data of the compounds give an indication of the possible removal mechanism, but the determination of micropollutants in sludge is required to confirm the hypotheses.

The problem of micropollutants should also be addressed closer to the source, which is product development. As mentioned above, there are already personal care and household products in the market which are biodegradable and are able to match consumers' demands just like regular products. However, the variety is generally low and the prices higher than for regular products. Through policy and regulations, this type of products should be supported. This will eventually lead to a wider variety and competitive prices of products which are easily biodegradable. As a result, consumers will be able to choose for a better option in personal care and household products, with a lower negative impact on the environment at the same level of comfort.

7.7 Outlook

Separation at source of wastewater streams presents several advantages for the management of carbon, nutrient and water resources (Otterpohl, 2002). From a technological point of view, grey water reuse can be realized at a community level or in single households. Advantages for the separation of black and grey water, their targeted treatment and reuse are much clearer in areas with water scarcity problems. In countries with abundant water, separation at source of black and grey water provides advantages for environmental protection and recovery of energy and nutrients.

This thesis has shown that grey water treatment can be done to achieve high quality effluent using combined biological and physical-chemical processes. But it is important to define the treatment extent according to the reuse application. Producing drinking water quality for non potable applications, such as laundry, toilet flushing and gardening, is simply economically and environmentally unsustainable. A differentiation of the extent of treatment should be deployed for different applications. The highest quality of non potable reuse would be for showers and hand basins. The second non potable water quality would be for reuse for laundry, toilet flushing and water for other washing purposes (e.g., car washing). For applications such as irrigation, infiltration, industrial reuse and discharge, a third quality of water will be required, as this water undergoes further treatment either by natural attenuation or in a industrial water pretreatment plant.

To guarantee a steady high quality water at all times, a multibarrier system would be required. The first barrier is to keep grey water separated from toilet water. In this way the treatment can be simplified, as there will be less COD, hormones, pharmaceuticals and pathogens. The total sanitation concept including grey water reuse at community level is shown in Figure 7.2. Grey water is collected at community level and treated in a bioflocculation system with an MBR, which will provide the second barrier for pathogens. The permeate can be further treated in an aerobic post-treatment step (trickling filter, constructed wetland) for the removal of remaining COD and nutrients. Up to this point, grey water treatment can be optimized to meet standards for infiltration, irrigation, industrial reuse or discharge. Reuse as irrigation water may be done directly after aerobic post-treatment or after a desalination step. Micropollutant removal would be desired for household reuse and an ozonation unit can be implemented, offering a third barrier for pathogens. Thereafter the disinfected water can be stored for non potable reuse, such as laundry, toilet flushing, car washing, etc. For showers and hand basins, a forth barrier can be installed as point-of-use disinfection with inline UV-lamps. Black water is collected in vacuum toilets together with kitchen waste, and grey water sludge from the bioflocculation system is mixed with this stream for its treatment in a UASB for recovery of energy. Further treatment of this stream is done for the recovery of nutrients, removal of pathogens and micropollutants and then it can be safely discharged.

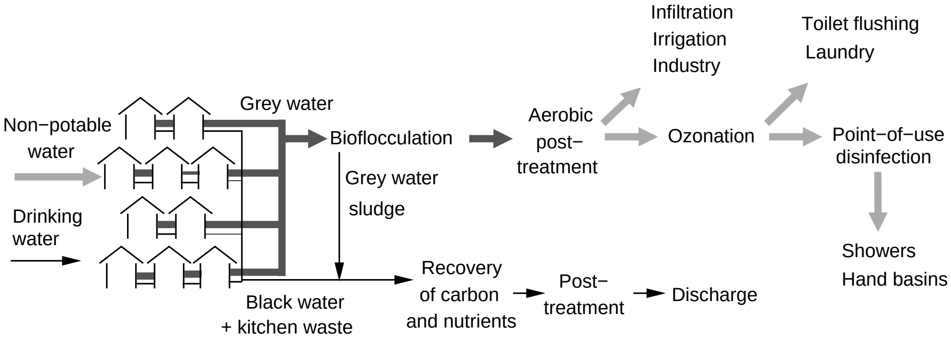

Figure 7.2: Total concept for household wastewater management at community level with different treatment levels for different reuse applications

The reuse of grey water within single households avoids the transport of a large amount of water to other locations for treatment and reuse. Furthermore, grey water reuse in single households has a higher acceptance than at community level. The grey water treatment concept proposed before (see Figure 7.1) could be implemented at single household scale. The total sanitation concept would then look as in Figure 7.3. The bioflocculation step can, perhaps, be adapted in a way that the grey water concentrate or sludge can be collected with the vacuum sewer, together with the concentrated black water and kitchen waste.

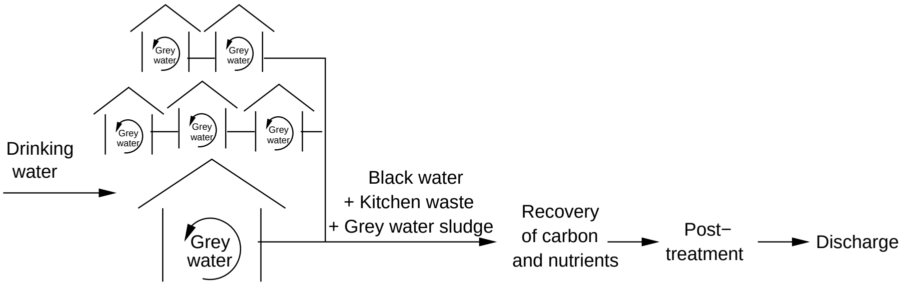

Figure 7.3: Total concept for household wastewater management

Although it has been mentioned that people would sooner reuse their own wastewater than that of others (Bixio et al., 2006), acceptance will be a major challenge within this single-house reuse concept. Within this single-house reuse concept, dual reticulation systems outside the household can be avoided. However, single-house treatment units must be developed at an affordable price. Furthermore, a single household treatment system should be robust and easy to operate. Additionally, as supply and demand are never fully matched, storage capacity will be needed. This type of concept demands a much higher involvement and responsibility of water users than in the current situation. The user will be forced to be more aware of what type of products are put into the house water cycle. The use of biodegradable personal care and household products may have to become a habit.

Drinking water demands could be theoretically reduced from 127.5 $Lp^{-1}d^{-1}$ to 15.6 $Lp^{-1}d^{-1}$ (water used for drinking and cooking). This reduction in drinking water demand will have an impact on drinking water infrastructure and the water treatment costs. Environmental costs of an overexploitation of groundwater and surface water resources will be saved. Additionally, the size of transport and treatment infrastructure of sewage will be reduced to deal with only concentrated black water. Because there is no mix with storm water, emergency discharges of sewage into surface waters would be avoided.

Depending on the reuse application, further investigation is necessary to define the risks of exposure to the constituents of treated grey water (micropollutants, pathogens, salts, etc.). Treated grey water (eco)toxicological testing can provide useful information about the risks of exposing humans, plants and aquatic or soil organisms to grey water reuse. The accumulation of micropollutants and salts in the grey water cycle should be addressed and strategies should be defined to cope with it.

Summary

Grey water is household wastewater originating from laundry, hand basins, kitchen sinks, showers and baths, thus household wastewater without the input of toilets. Grey water is a substantial amount of the household wastewater, up to 75% with normal flushing toilets, and over 90% with vacuum toilets. It is also less polluted than (concentrated) toilet water and therefore grey water, after proper treatment, has a great potential for reuse.

Chapter 1 describes general aspects of grey water including its characteristics, treatment, reuse and concerns about organic micropollutants. Characteristics of grey water vary significantly depending on factors such as water source, water consumption, climate and cleaning habits. For example, COD concentrations can vary in the range of 100-681 $\mathrm{mgL^{-1}}$. Treatment of grey water is required before any reuse application for which suggested standards are presented. Organic micropollutants are an increasing environmental concern. Over 900 (organic) micropollutants can potentially be present in grey water. The presence of these micropollutants in recycling systems may have an effect on human health and the environment. Based on their persistence to biodegradation, potential for bioaccumulation and toxic effects, ingredients of personal care and household products were selected. These micropollutants are: the fragrances galaxolide, tonalide and hexylcinnamic aldehyde; the UV-filters benzophenone-3 (BP3), 4-methyl benzylidenecamphor (4MBC), octocrylene, ethylhexyl methoxycinnamate (EHMC), avobenzone, 2-phenyl-5-benzimidazolesulfonic acid (PBSA) and 2-ethylhexyl salicylate (2EHS); the preservatives methyl-, ethyl-, propyl- and butylparaben; the biocide triclosan; the surfactants nonylphenol and benzalkonium chloride (BaCl), and the plasticizer bisphenol-A.

Grey water from a neighborhood of 32 houses in Sneek, The Netherlands was thoroughly characterized for COD, anaerobic biodegradability, surfactants, nutrients, cations and anions (**Chapter 2**). COD concentrations were 724 ± 150 $\mathrm{mgL^{-1}}$, of which 34% was suspended COD, 25% colloidal and 38% soluble COD. The maximum anaerobic biodegradability of grey water of 70 ± 5% indicates the possibility of recovering the COD as methane. Surfactants were an important fraction (15%) of grey

water's COD. Anionic surfactants were present at concentrations of 41.1 ± 12.1 $\mathrm{mgL^{-1}}$. At these concentrations anionic surfactants may have an inhibitory effect on anaerobic treatment. Nutrient concentrations in grey water were 26.3 ± 12 $\mathrm{mgL^{-1}}$ of total nitrogen, and 7.2 ± 4.2 $\mathrm{mgL^{-1}}$ of total phosphorus. Metals were present in concentrations below the suggested limits for irrigation. The relatively high concentrations of sodium, however, may restrict grey water reuse for irrigation of sodium tolerant crops.

In **Chapter 3** biological grey water treatment was investigated in three lab-scale systems: aerobic, anaerobic and the combination of anaerobic + aerobic. The total hydraulic retention time (HRT) was 12-13 hours and the systems were tested at 32°C. Aerobic treatment achieved 90% of COD removal and 97% removal of anionic surfactants. The low sludge yield of 0.12 kg VSS $\mathrm{(kg\ COD)^{-1}}$ makes aerobic treatment an attractive process for the treatment of grey water. Anaerobic treatment achieved only 51% of COD removal, with a methanization rate of 32% and a poor removal of anionic surfactants (24%). Poor performance in the anaerobic system was because of the presence of inhibitory anionic surfactants and a relatively large fraction of colloidal COD in grey water, which cannot be retained in the UASB. The combined anaerobic + aerobic treatment of grey water did not provide an advantage regarding COD removal efficiency and it produced a higher sludge yield (0.18 g VSS/g COD) than the aerobic treatment alone. Grey water methanization in the combined treatment was 24%, yielding a low amount of energy. Based on COD removal efficiency, sludge yield and energy considerations, treatment of grey water in an aerobic system was preferred over an anaerobic system and a combined anaerobic + aerobic system.

The occurrence of organic micropollutants and their removal in three biological treatment systems are described in **Chapter 4**. All selected micropollutants were found in grey water in the low $\mu\mathrm{gL^{-1}}$ range. The most prevalent compounds were the UV-filter EHMC (15.5 $\mu\mathrm{gL^{-1}}$), the biocide triclosan (15.6 $\mu\mathrm{gL^{-1}}$), the fragrance galaxolide (10.7 $\mu\mathrm{gL^{-1}}$) and the surfactant BaCl (10.2 $\mu\mathrm{gL^{-1}}$). Generally, lower concentrations were measured after biological treatment. The UV-filter 4MBC and the fragrance HCA were well removed (>80%) in all three biological systems. Most micropollutants showed good removal efficiencies under aerobic conditions but poor removal efficiencies under anaerobic conditions. Aerobic removal efficiencies for propyl- and butylparaben, octocrylene, triclosan and bisphenol-A were higher than 90%. For the fragrance galaxolide, the UV-filters 2EHS and avobenzone, the surfactants nonylphenol and BaCl, the biocide triclosan and the plasticizer bisphenol-A, the removal efficiencies under aerobic conditions were between 77 and 90%. No removal was observed for PBSA in any of the biological systems, poor removal efficiencies (<54%) were observed for the fragrance tonalide and the UV-filter EHMC. From the three biological systems, the aerobic one was the one with highest micropollutant removal efficiencies. The most prevalent micropollutants in aerobically treated grey water were the UV-filters EHMC (7.9 μgL^{-1}) and PBSA (3 μgL^{-1}), and the fragrance galaxolide (2.1 μgL^{-1}).

Organic micropollutants were only partially removed during biological treatment. Physical-chemical treatment, therefore, was required to remove remaining concentrations of micropollutants. In **Chapter 5** ozone and activated carbon treatment were studied to remove micropollutants from aerobically treated grey water. At an applied ozone dose of 15 mgL^{-1}, most micropollutants were eliminated to below the limits of quantification (LOQs). Tests were conducted to compare the ozone consumption in both aerobically treated grey water and MilliQ water spiked to concentrations in the range of 10-100 μgL^{-1}. Results indicate that most of the ozone consumption is due to background organic carbon in treated grey water. The granular activated carbon (GAC) columns were operated at 0.5 and 2 bed volumes (BV) per hour to treat aerobically treated grey water. The GAC column operated at 0.5 BVh^{-1} removed most micropollutants from treated grey water spiked with 0.1-10 μgL^{-1} to below LOQs, during the operational period of 1728 BVs. At 2 BVh^{-1} the GAC column was effective in removing micropollutants from treated grey water to below LOQs. Even after the GAC column was saturated with background organic carbon, removal of micropollutants continued to be efficient. After spiking treated grey water with micropollutants to concentrations of 10-100 μgL^{-1}, the GAC column continued to remove micropollutants to below LOQs for at least 1440 BVs. From the results obtained in these tests, it was concluded that both ozonation and activated carbon adsorption are suitable techniques for the removal of micropollutants from aerobically treated grey water.

Within new sanitation concepts up until now, grey water had been considered as an alternative source of water and concentrated black water was considered a source of energy and nutrients. But grey water, though relatively low in COD concentration, accounts for 50% of the total COD load from the household wastewater. Theoretically, grey water can also be used as a source of energy. **Chapter 6** describes the bioflocculation of grey water in a highly loaded membrane bioreactor with the purpose of concentrating grey water for improved energy recovery within decentralized sanitation concepts. Three concentration factors based on the ratio of sludge retention time (SRT) and HRT were tested: 3, 8 and 12. The main part of grey water's COD (66-76%) was conserved in the concentrate. Of the remaining COD, 21-23% was transferred to the permeate and a small fraction (3-11%) was mineralized. A grey water concentrate with a large fraction of suspended COD was obtained, 57% at an SRT/HRT of 3, 81% at an SRT/HRT of 8, and 82% at an SRT/HRT of 12. Biodegradability tests on the grey water concentrate showed that 88% of the COD can be converted into methane. The integration of grey water bioflocculation within decentralized sanitation concepts would result in an overall increase of methane production of 73%, based on the methane production from concentrated black water.

Within this thesis, the treatment of grey water was studied with the purpose of reuse. In **Chapter 7** the different options for grey water reuse are discussed briefly. These reuse applications are in the household, for irrigation, in industry and indirect potable reuse. The main issue with household reuse, is the risk of exposure to pathogens and toxic components of reused grey water. Water reuse for irrigation purposes can only be done in countries were the demand for irrigation water is continuous, e.g. dry regions. The main challenge of grey water reuse in industry is the distance between the source of grey water and the industry. This application may only be practical in new housing states built close to a water intensive industry. Indirect potable reuse after groundwater infiltration or surface water augmentation is perhaps the most accepted form of water reuse. Preliminary ecotoxicological results of grey water and effluents of 4 different treatments (aerobic, anaerobic + aerobic, aerobic + ozone and aerobic + activated carbon) were presented in this chapter. Based on the results obtained in this thesis, a treatment concept for grey water is proposed based on different reuse water qualities. This consists of a bioflocculation pretreatment step, an aerobic post-treatment and depending on the quality of the treated grey water, an additional post-treatment and an point-of-use disinfecting step. The quality of the effluent achieved with this treatment should meet recommended reuse standards. Several aspects should be further investigated in this treatment concept, such as the fate of micropollutants, the effects of exposing the public and environment to treated grey water, and issues of acceptance of treated grey water as a non potable water source within the household. Nevertheless, the separation and specific treatment of grey water provide opportunities for reducing the consumption of drinking water while also protecting the environment.

Samenvatting

Grijs water is huishoudelijk afvalwater zonder het toiletwater, dus afvalwater afkomstig van wasmachine, spoelbak, gootsteen, douche en bad. Grijs water vertegenwoordigt een aanzienlijk volume van het huishoudelijke afvalwater, tot 75 % in het geval van normale toiletten en tot 90 % in het geval van vacuümtoiletten. Ook is het minder vervuild dan (geconcentreerd) toiletwater en daarom is grijs water, na behandeling, een veelbelovende bron voor waterhergebruik.

In **Hoofdstuk 1** werden algemene aspecten van grijs water beschreven zoals samenstelling, behandeling, mogelijkheden tot hergebruik en maatschappelijke ongerustheid over organische microverontreinigingen. De samenstelling van grijs water kan significant verschillen door verschillende factoren zoals herkomst van het water, mate van waterconsumptie, klimaat en schoonmaakgewoontes. De concentraties chemisch zuurstof verbruik (CZV) kunnen bijvoorbeeld variëren van 100 - 681 mgL^{-1}. Volgens aanbevolen kwaliteitseisen voor hergebruik van water is de behandeling van grijs water nodig voor alle toepassingen. De milieuzorgen over organische microverontreinigingen zijn de laatste jaren toegenomen. Meer dan 900 (organische) microverontreinigingen kunnen potentieel in grijs water aanwezig zijn. De aanwezigheid van deze microverontreinigingen in hergebruikt water kunnen een effect op de menselijke gezondheid en het milieu hebben. Voor onderzoek in dit proefschrift werden bestandsdelen van persoonlijke verzorgingsmiddelen en huishoudelijke producten voor onderzoek geselecteerd op lage biologische afbreekbaarheid, mogelijke biologische accumulatie en toxische effecten. De geselecteerde bestandsdelen zijn de geurstoffen galaxolide, tonalide en hexylcinnamaldehyde, de UV-filters benzofenon-3 (BP3), 4-methylbenzylidene kamfer (4MBC), octocryleen, ethylhexyl methoxycinnamaat (EHMC), avobenzon, 2-fenyl-5-benzimidazol sulfonzuur (PBSA), en 2-ethylhexyl salicylaat (2EHS), de conserveringsmiddelen methyl-, ethyl-, propyl- en butylparabeen, de biocide triclosan, de oppervlakteactieve stoffen nonylfenol en benzalkonium chloride (BaCl) en de weekmaker bisfenol-A.

Grijs water van 32 huishoudens in Sneek, Nederland, werd uitgebreid geanalyseerd op CZV, anaërobe biologische afbreekbaarheid, oppervlakteactieve stoffen, nutriënten, kationen en anionen in **Hoofdstuk 2**. CZV concentraties waren 724±150 mgL^{-1}, hiervan was 34 % in suspensie, 25 % colloïdaal en 38 % in oplossing. De maximale anaërobe biologische afbreekbaarheid van het onderzochte grijs water was 70±5 %, wat aangeeft dat de mogelijkheid bestaat om een groot deel van het CZV terug te winnen als methaan. Oppervlakteactieve stoffen vormen een belangrijke fractie (15 %) van het CZV van het grijs water. Anionische oppervlakteactieve stoffen waren aanwezig in concentraties van 41.1±12.1 mgL^{-1}. Bij deze concentraties kunnen anionische oppervlakteactieve stoffen een negatief effect op anaërobe behandeling hebben. De concentraties van nutriënten in grijs water waren 26.3±12 mgL^{-1} voor totaal stikstof en 7.2±4.2 mgL^{-1} voor totaal fosfor. Metalen waren aanwezig beneden de aanbevolen kwaliteitseisen voor hergebruik als irrigatiewater. De relatief hoge concentratie natrium kan beperkingen opleveren voor het hergebruik van behandeld grijs water voor irrigatie van natrium-intolerante gewassen.

In **Hoofdstuk 3** werden drie systemen voor biologische grijs water behandeling onderzocht op laboratoriumschaal: aërobe behandeling, anaërobe behandeling en gecombineerde anaërobe en aërobe behandeling. De totale hydraulische verblijftijd (HRT) was 12-13 uur en de temperatuur was vastgesteld op 32 °C. Aërobe behandeling leidde tot 90 % verwijdering van CZV en 97 % verwijdering van oppervlakteactieve stoffen. Gecombineerd met een lage slibproductie van 0.12 g $VSS(g\ CZV)^{-1}$, is aërobe behandeling een aantrekkelijk proces voor grijs water behandeling. Anaërobe behandeling leidde tot 51 % verwijdering van CZV waarvan 32 % werd omgezet in methaan; oppervlakteactieve stoffen werden slecht verwijderd (24 %). De lage efficiëntie van de anaërobe behandeling werd toegeschreven aan de aanwezigheid van anionische oppervlakteactieve stoffen die negatieve effecten hebben op anaërobe activiteit en aan een relatief grote fractie van colloïdaal CZV in grijs water, dat niet kan worden binnengehouden in de Upflow Anaërobe Slib Bed (UASB) reactor. De gecombineerde anaërobe en aërobe behandeling van grijs water was niet gunstiger wat betreft de verwijdering van CZV en de slibproductie was met 0.18 g $VSS(g\ CZV)^{-1}$ hoger dan bij alleen aërobe behandeling Het percentage methaan geproduceerd uit grijs water voor de gecombineerde behandeling was 24 % wat een lage energieopbrengst geeft. Gebaseerd op de CZV verwijdering, slibproductie en energiebalans, is aërobe behandeling van grijs water verkozen boven anaërobe behandeling of gecombineerde anaërobe en aërobe behandeling.

De aanwezigheid van organische microverontreinigingen en de verwijdering hiervan in 3 biologische zuiveringssystemen werd beschreven in **Hoofdstuk 4**. Alle geselecteerde microverontreinigingen werden gevonden in grijs water in de lage μgL^{-1} range. De meest voorkomende componenten waren de UV filter EHMC (15.5 μgL^{-1}), de biocide triclosan (15.6 μgL^{-1}), de geurstof galaxolide (10.7 μgL^{-1}) en de oppervlakteactieve stof BaCl (10.2 μgL^{-1}). Meestal werden lagere concentraties gemeten na biologische behandeling. De UV-filter 4MBC en de geurstof HCA werden goed verwijderd (>80 %) in alle drie de biologische systemen. De meeste microverontreinigingen werden goed verwijderd onder aërobe omstandigheden maar slecht verwijderd onder anaërobe omstandigheden. Onder anaërobe omstandigheden werden propyl- en butylparabeen, octocryleen, triclosan en bisfenol-A goed verwijderd (>90 %). De geurstof galaxolide, UV filters 2EHS en avobenzon, de oppervlakteactieve stoffen nonylfenol en BaCl, de biocide triclosan en de weekmaker bisfenol-A werden onder aërobe omstandigheden verwijderd van 75 tot 90 %. In alle drie de biologische systemen werd PBSA niet verwijderd en werden slechte verwijderingen (<54 %) gemeten voor de geurstof tonalide en de UV filter EHMC. Van de drie biologische systemen werden de microverontreinigingen het beste verwijderd onder aërobe omstandigheden. De meest resistente microverontreinigingen in aëroob behandeld grijs water waren de UV filters EHMC (7.9 μgL^{-1}) en PBSA (3 μgL^{-1}) en de geurstof galaxolide (2.1 μgL^{-1}).

Organische microverontreinigingen werden slechts gedeeltelijk verwijderd tijdens de biologische behandeling. Daarom is fysisch-chemische nabehandeling nodig om de resterende microverontreinigingen te verwijderen. In **Hoofdstuk 5** werden ozon en actief kool onderzocht op de toepasbaarheid voor verwijdering van microverontreinigingen uit aëroob biologisch behandeld grijs water. Met een ozondosis van 15 mgL^{-1} werd de meerderheid van de microverontreinigingen verwijderd tot onder de detectiegrens. Tests werden uitgevoerd om het ozonverbruik te vergelijken tussen aëroob behandeld grijs water en MilliQ water waaraan microverontreinigingen werden toegevoegd tot een concentratie tussen 10-100 μgL^{-1}. De resultaten gaven aan dat het ozon grotendeels werd verbruikt door het aanwezige organische koolstof in behandeld grijs water en niet door de microverontreinigingen. Het korrelvormige actief kool (GAC) werd in kolommen gepakt en aëroob behandeld grijs water werd door de kolommen geleid met bedsnelheden (BV) van 0.5 en 2 per uur. De GAC kolommen gevoed met aëroob behandeld grijs water met een verhoogde concentratie microverontreinigingen van 0.1-10 μgL^{-1}, bedreven met een BV van 0.5 per uur, verwijderden de meeste microverontreinigingen tot onder de detectiegrens voor een operationele periode van 1728 BV's. Ook bij een BV van 2 per uur verwijderden de GAC kolommen de microverontreinigingen tot onder de detectiegrens. Na verzadiging met het aanwezige organische koolstof uit het grijs water werden nog steeds de microverontreinigingen efficiënt verwijderd. Ook met aëroob behandeld water met verhoogde concentraties microverontreinigingen (10-100 μgL^{-1}) bleven de GAC kolommen microverontreinigingen verwijderen tot onder de detectiegrens gedurende meer dan 1440 BV's. Uit de resultaten van dit onderzoek kan worden geconcludeerd dat behandeling met ozon en adsorptie aan actief kool beide geschikte technieken zijn voor het verwijderen van microverontreinigingen uit aëroob behandeld grijs water.

Bij nieuwe sanitatieconcepten is tot op heden grijs water beschouwd als alternatieve bron voor hergebruik van water en zwart water als bron voor terugwinning van energie en nutriënten. Grijs water, hoewel verdund, bevat echter de helft van de energie in CZV van het huishoudelijke afvalwater. Theoretisch gezien kan grijs water ook als geschikte bron van energie gebruikt worden. **Hoofdstuk 6** beschreef biologische vlokvorming van afvalstoffen aanwezig in grijs water in een hoogbelaste membraan bioreactor met als doel de energie te concentreren en deze energie terug te winnen in decentrale sanitatieconcepten. Drie concentratiefactoren met een ratio tussen slibverblijftijd (SRT) en hydraulische verblijftijd (HRT) van 3, 8 en 12 werden onderzocht. Het grootste deel van het CZV in grijs water (66-76 %) kon worden geconcentreerd in slibvlokken. Van het overgebleven CZV kwam 21-23 % in het permeaat terecht en een kleine fractie (3-11 %) werd afgebroken. Het grijs water concentraat dat werd verkregen bevatte aan grote fractie gesuspendeerd CZV, 57 % bij een SRT/HRT ratio van 3, 81 % bij een SRT/HRT ratio van 8 en 82 % bij een SRT/HRT ratio van 12. Van het CZV aanwezig in het geconcentreerde grijs water werd 88 % biologisch afgebroken tot methaan. De integratie van biologische vlokvorming van grijs water in decentrale sanitatieconcepten leidt tot een toename in de methaanproductie van 73 %, ten opzichte van methaanproductie uit alleen zwart water.

In dit proefschrift werd de behandeling van grijs water bestudeerd met het oog op het hergebruik van het behandelde grijs water. In **Hoofdstuk 7** werden de verschillende opties voor grijs water hergebruik behandeld. Het hergebruik van grijs water is mogelijk in het huishouden, voor irrigatie, in industrie en voor indirect drinkwaterhergebruik. Het voornaamste aandachtspunt voor hergebruik van grijs water binnen het huishouden is het risico op verspreiding van pathogene micro-organismen en giftige stoffen. Grijs water hergebruik voor irrigatie kan alleen worden toegepast in gebieden waar een continue watervraag is, bijvoorbeeld in gebieden met een droog klimaat. De grote uitdaging voor hergebruik van grijs water in de industrie is de grote afstand tussen de bron van het grijs water en de industrie. Het lijkt uitsluitend praktisch mogelijk voor nieuwbouwwijken die dicht bij een water intensieve industrie liggen. Hergebruik als drinkwater na infiltratie in het grondwater of naar het oppervlaktewater is waarschijnlijk de meest acceptabele vorm van grijs water hergebruik. De eerste ecotoxicologische effecten van grijs water na vier verschillende behandelingsmethoden (aëroob, anaëroob + aëroob, aëroob + ozon en aëroob + actief kool) werden in dit hoofdstuk beschreven. Met de resultaten beschreven in dit proefschrift werd een behandelingsconcept voor grijs water voorgesteld gebaseerd op verschillende voorwaarden voor hergebruik. Het concept bestaat uit een voorbehandeling door biologische vlokvorming en een aërobe nabehandeling. Afhankelijk van de voorwaarden voor hergebruik, kunnen er dan verschillende nabehandelingstappen worden uitgevoerd en een desinfectiestap op de plek waar het water zal worden gebruikt. De kwaliteit van het water kan dan aan de voorwaarden voor hergebruik voldoen. Verschillende aspecten moeten verder worden onderzocht in dit behandelingsconcept, zoals het lot van de microverontreinigingen, de effecten van behandeld grijs water op mens en milieu, en de acceptatie van het hergebruik van behandeld grijs water als een bron van niet-drinkbaar huishoudelijk water. Desalniettemin bieden de gescheiden inzameling en behandeling van grijs water kansen voor het reduceren van de drinkwaterconsumptie terwijl ook het milieu beter wordt beschermd.

Resumen

Aguas grises consisten del agua residual doméstica originada del lavado de ropa, manos, duchas, bañera y fregadero, es decir, el agua residual doméstica sin el agua de sanitarios. Las aguas grises son un porcentaje substancial del agua residual doméstica, 75 % en el caso de sanitarios comunes de descarga de agua (6 L/descarga) y más del 90 % en el caso de sanitarios de canalización con vacío. Las aguas grises está menos contaminadas que las aguas (concentradas) de los sanitarios y por este motivo, las aguas grises, una vez tratadas apropiadamente, tienen un gran potencial para la reutilización.

El **Capítulo 1** describe los aspectos generales de las aguas grises, incluyendo sus características, tratamiento, reutilización y cuestiones de microcontaminantes orgánicos. Las características de las aguas grises varían significativamente dependiendo de factores tales como la fuente del agua, el consumo de agua, clima y hábitos de limpieza. Por ejemplo, concentraciones de demanda química de oxǵeno (DQO) pueden variar en el rango de 100 a 681 $\mathrm{mgL^{-1}}$. El tratamiento de aguas grises es necesario previo a cualquier aplicación de reutilización, para el cual se presentan estándares propuestos en la literatura. Por otro lado, los microcontaminantes orgánicos son una cuestión ambiental que ha ganado importancia en los últimos años. Más de 900 microcontaminantes (orgánicos) pueden estar presentes en aguas grises. La presencia de estos microcontaminantes en sistemas de reciclaje puede afectar a la salud humana y del medio ambiente. En base a sus propiedades de biodegradabilidad, potencial de acumulación y sus efectos tóxicos, se seleccionaron ingredientes de productos de higiene personal y productos de limpieza. Estos compuestos son: las fragancias galaxolide, tonalide y aldehido hexilcinámico; los filtros solares benzofenona-3 (BP3), 4-metil benzilidencanfor (4MBC), octocrileno, metoxicinamato de etilhexilo (EHMC), avobenzona, ácido 2-fenil-5-benzimidaxolsulfonico (PBSA) y 2-etilhexil salicilato (2EHS); los conservadores metil-, etil, propil- y butilparabeno; el bactericida triclosán; los surfactantes nonifenol y el cloruro de benzalkonio (BaCl), y el plastificador bisfenol-A.

Aguas grises de un área residencial en Sneek, Países Bajos, fue carac-

terizada en términos de DQO, biodegradabilidad anaerobia, surfactantes, nutrientes, cationes y aniones (**Capítulo 2**). La concentración de DQO fue 724±150 mgL^{-1}, de la cual un 34 % estuvo presente en forma suspendida, 25 % coloidal y 38 % soluble. La máxima biodegradabilidad anaerobia de 70±5 % indica la posibilidad de recuperación de la DQO en forma de metano. Una fracción importante de la DQO en el agua gris (15 %) estuvo compuesta de surfactantes. La concentración de surfactantes aniónicos fue de 41.1±12.1 mgL^{-1}. A estas concentraciones, los surfactantes aniónicos pueden inhibir el tratamiento anaerobio. Las concentraciones de nutrientes en aguas grises fueron 26.3±12 mgL^{-1} de nitrógeno total y 7.2±4.2 mgL^{-1} de fósforo total. Las concentraciones de metales estuvieron dentro de los límites sugeridos para irrigación. Sin embargo, la concentración de sodio fue relativamente alta, lo que puede restringir el uso de las aguas grises sólo para la irrigación de plantas tolerantes al sodio.

En el **Capítulo 3** se investigaron tres sistemas para el tratamiento biológico de aguas grises: aerobio, anaerobio y la combinación de anaerobio + aerobio. El tiempo de residencia (HRT) total fue de 12-13 horas y los sistemas fueron operados a 32°C. El tratamiento aerobio alcanzó una remoción de DQO del 90 % y una remoción de surfactantes aniónicos del 97 %. La baja producción de lodos de 0.12 kg VSS $(\text{kg DQO})^{-1}$, hace del tratamiento aerobio un proceso atractivo para el tratamiento de aguas grises. Con el tratamiento anaerobio solo se logró una remoción de DQO del 51 %, con una tasa de metanización de 32 % y una limitada remoción de surfactantes aniónicos (24 %). El pobre desempeño del sistema anaerobio se debió a la presencia de surfactantes aniónicos y a la relativamente alta fracción de DQO coloidal, la cual no fue retenida en el reactor. El tratamiento de agua gris combinado anaerobio + aerobio no demostró tener ventajas respecto a la remoción de DQO y la producción de lodos en este sistema (0.18 kg VSS$(\text{kg DQO})^{-1}$) fue más alta que en el sistema aerobio. La metanización de aguas grises en el sistema de tratamiento combinado fue del 24 %, dando lugar a una producción de energía muy baja. En base a la remoción de DQO, producción de lodos y consideraciones de energía, se recomienda hacer el tratamiento de agua gris en un sistema aerobio.

La presencia de microcontaminantes orgánicos en aguas grises y su remoción en tres sistemas de tratamiento está descrita en el **Capítulo 4**.

Los 18 microcontaminantes estudiados estuvieron presentes en aguas grises a niveles de μgL^{-1}. Los compuestos más prevalecientes fueron el filtro solar EHMC (15.5 μgL^{-1}), el bactericida triclosán (15.6 μgL^{-1}), la fragancia galaxolide (10.7 μgL^{-1}) y el surfactante BaCl (10.2 μgL^{-1}). En general, el tratamiento biológico redujo las concentraciones de microcontaminantes. El filtro solar 4MBC y la fragancia HCA fueron removidos eficientemente (>80 %) en los tres sistemas biológicos. La mayoría de los microcontaminantes mostraron altas eficiencias de remoción en condiciones aerobias pero bajas en condiciones anaerobias. Bajo condiciones aerobias, se registraron altas eficiencias de remoción (>90 %) para propil-, butilparaben, octocrileno, triclosán y bisfenol-A. Las eficiencias de remoción para la fragancia galaxolide, los filtros solares 2EHS y avobenzona, los surfactantes nonilfenol y BaCl, el bactericida triclosán y el plastificador bisfenol-A variaron entre 77-90 %, en estas condiciones. El filtro solar PBSA no fue removido en ninguno de los tres sistemas biológicos, y bajas eficiencias de remoción (<54 %) se registraron para la fragancia tonalide y el filtro solar EHMC. De los tres sistemas biológicos estudiados, el más eficiente para la remoción de microcontaminantes fue el aerobio. Los microcontaminantes más prevalecientes en el efluente del sistema aerobio fueron los filtros solares EHMC (7.9 μgL^{-1}) y PBSA (3 μgL^{-1}), y la fragancia galaxolide (2.1 μgL^{-1}).

Los microcontaminantes fueron removidos sólo parcialmente en el tratamiento biológico. Por eso se requiere un tratamiento físico-químico para eliminar el remanente de estos microcontaminantes. En el **Capítulo 5** se estudiaron la ozonización y la adsorción con carbón activado para la remoción de microcontaminantes de aguas grises tratadas en el sistema aerobio. A la dosis de ozono aplicada de 15 mgL^{-1}, la mayoría de los microcontaminantes fueron eliminados a niveles por debajo del límite de cuantificación. Se realizaron pruebas para comparar el consumo de ozono en aguas grises tratadas en el sistema aerobio y en agua milliQ con concentraciones de microcontaminantes en el rango de 10-100 μgL^{-1}. Los resultados indican que, en su mayoría, el consumo de ozono es debido al carbono orgánico presente en la matriz del agua gris tratada. Columnas con carbón activado granulado (GAC) fueron operadas a 0.5 y 2 volúmenes de lecho (BV) para el tratamiento de agua gris tratada en el sistema aerobio. Aguas grises tratadas a la que se le agregaron XOCs (0.1-10 μgL^{-1}) fueron tratadas en una columna GAC a 0.5 BVh^{-1}, logrando remover microcontaminantes a niveles por debajo de los límites de cuantificación durante todo el periodo operacional (1728 BVs). Otra columna GAC, operada a 2 BVh^{-1} y con aguas grises tratadas en el sistema aerobio, logró remover microcontaminantes a niveles por debajo de los límites de cuantificación. Incluso después de la saturación del carbón activado con materia orgánica, la remoción de microcontaminantes continuó siendo efectiva. Después de inyectar concentraciones de microcontaminantes (10-100 $\mu\mathrm{gL}^{-1}$) a esta columna, la remoción permaneció igual por al menos 1440 BVs. De los resultados obtenidos en estas pruebas se concluye que tanto la ozonización como la adsorción en carbón activado son técnicas apropiadas para la remoción de microcontaminantes de aguas grises.

Dentro de los nuevos conceptos de saneamiento existentes a la fecha, las aguas grises se han considerado como fuente alternativa de agua y las aguas negras como fuente de energía y nutrientes. Pero las aguas grises, aunque contiene bajas concentraciones de DQO, engloba el 50 % de la carga total de DQO doméstica. En teoría, las aguas grises se puede utilizar también como una fuente de energía. El **Capítulo 6** describe la biofloculación de agua gris en un bioreactor de membrana de alto gasto con el fin de concentrar las aguas grises y así mejorar la recuperación de energía en conceptos descentralizados de saneamiento. Se realizaron pruebas a tres diferentes factores de concentración basados en la tasa entre el tiempo de residencia de lodos (SRT) y el HRT: 3, 8 y 12. Gran parte de la DQO (66-76 %) se retuvo en el concentrado, 21-23 % de la DQO se transfirió al permeado y una pequeña fracción (3-11 %) se mineralizó. Un gran porcentaje de la DQO en el concentrado estuvo compuesto de DQO suspendido, 57 % a un SRT/HRT de 3, 81 % a un SRT/HRT de 8 y 82 % a un SRT/HRT de 12. Pruebas de biodegradabilidad del concentrado mostraron una conversión a metano de 88 % en base a la DQO. La integración de la biofloculación de agua gris en los conceptos de saneamiento descentralizados resultaría en una ganancia adicional de metano del 73 %, basado en la producción de metano de agua negra concentrada.

Por último, en esta tesis se estudió el tratamiento de aguas grises con el fin de su reutilización. En el **Capítulo 7** se discuten brevemente las opciones para la reutilización de aguas grises. Estas opciones son reutilización doméstica, irrigación, en industria y la reutilización potable indirecta. La cuestión principal en el caso de reutilización doméstica es el riesgo de exposición a patógenos y compuestos tóxicos. La reutilización para la irrigación es factible en países donde la demanda de agua de irrigación es continua, e.g., regiones áridas. El mayor reto para la reutilización de agua gris en la industria es la distancia entre la fuente de las aguas grises y la industria. Esta aplicación es factible en la planeación de nuevas áreas urbanas, donde nuevos vecindarios pueden construirse cerca de la industria. La reutilización indirecta como agua potable de las aguas grises tratadas (después de su paso por un acuífero o un lago) es quizá la opción más aceptada de reutilización de agua tratada. En este capítulo se presentan resultados ecotoxicológicos preliminares del agua gris y efluentes de 4 tratamientos diferentes (aerobio, anaerobio + aerobio, aerobio + ozone y aerobio + carbono activado). Con los resultados obtenidos en esta tesis, se propone un concepto de tratamiento para agua gris basado en diferentes niveles de calidad de agua para diferentes aplicaciones. Este consiste en el tratamiento del agua en una unidad de biofloculación, posterior tratamiento aerobio y, dependiendo de la calidad del efluente del tratamiento aerobio, un tratamiento adicional resultaría necesario (además de un paso de desinfección en el punto de uso). La calidad del efluente alcanzada con este tratamiento debe cumplir con los estándares recomendados para la reutilización. El destino de los microcontaminantes, los efectos de exposición del público y medio ambiente a las aguas grises tratadas y aspectos de aceptación del agua tratada como fuente de agua no-potable en la vivienda, son cuestiones que deben investigarse a fondo. Sin embargo, la separación y tratamiento específico de las aguas grises ofrecen oportunidades para la reducción del consumo de agua potable y al mismo tiempo, para la protección del medio ambiente.

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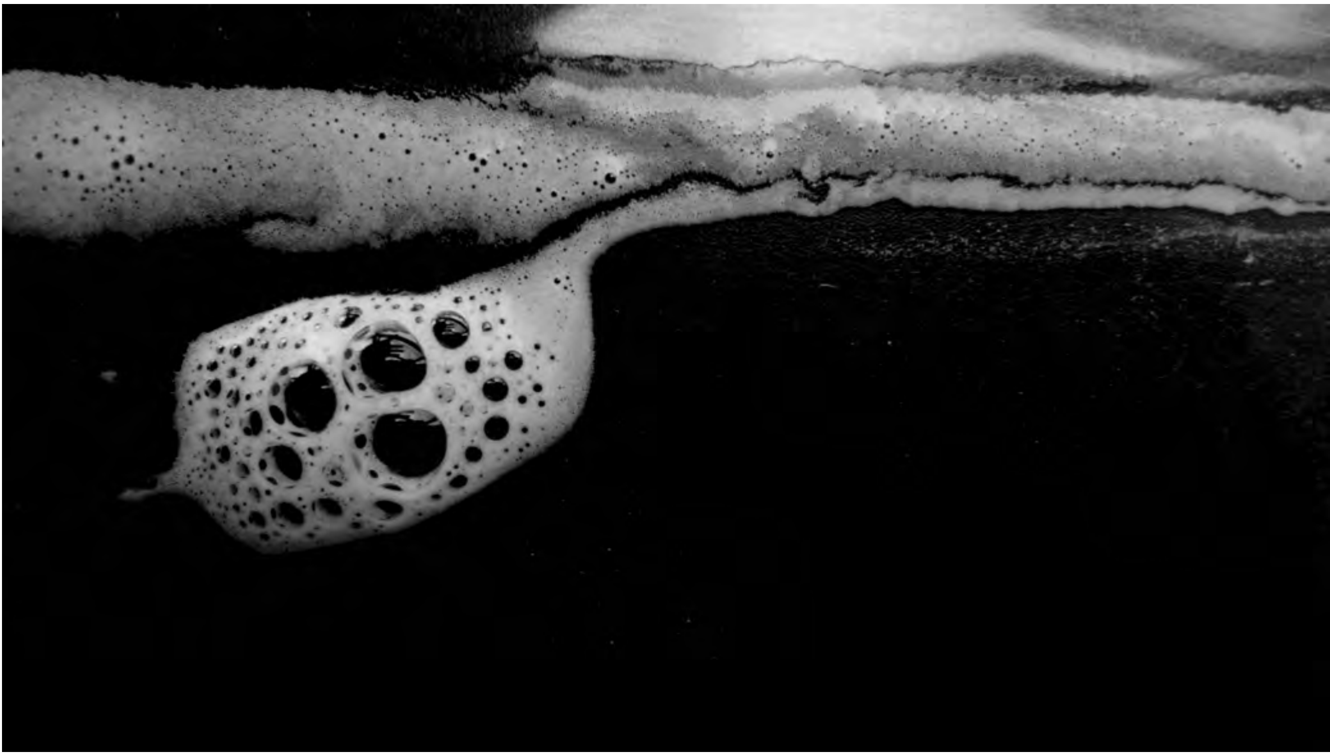

To my astonishment here I am writing the last pages of my PhD thesis. After countless trips to Sneek and even more frustrations with analytical methods, this project has come to an end. It has been a long roller-coaster ride and I am glad I was not alone.

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Getting started in Leeuwarden was not very easy for me. Soon after I arrived I realized that I had to meet more people outside the research world. The Irish Pub was a great opportunity to meet new people. Thank you Baukje, Jeff, Sanne, Chantel, Margie, Damien's, Chantal, Natalia, Jordi, Claire, and all the others, thank you very much for the time we shared (during the good and the bad shifts). Getting to know you has made my Leeuwarden experience much more exciting. Through you I also got to meet more people whom I appreciate very much too: Allerd, and Andrea (thank you for inviting me to the Film festival as a translator, that was fun!).

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Lucía Hernández Leal
August 2010

About the author

Lucía Hernández Leal was born on 11th August 1978, in Monterrey, México. In December 1999, she graduated from Chemical Engineering at Tecnológico de Monterrey, México. From 2000 to 2002 she worked as a process engineer at Nylon de México, in the polymerization plant. In 2002, she moved to Germany to pursue a double degree program at the Hamburg University of Technology (TUHH) and the Northern Institute of Technology (NIT). Within the Master Program, in 2003 she did a 5-month internship at the Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ), in the sector project ecosan. In January 2005, she completed her Master of Science in Environmental Engineering at the TUHH and the Professional Master on Technology Management at the NIT Hamburg (2005). In March 2005 she began with her PhD project at the Sub-department of Environmental Technology from Wageningen University, conducting the research at Wetsus, Centre of Excellence for Sustainable Water Technology. Since April 2010 she works at Wetsus as postdoc and scientific project manager of the theme “Separation at source”.

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CERTIFICATE

The Netherlands Research School for the
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born on 11 August 1978 in Monterrey, Mexico

has successfully fulfilled all requirements of the
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Wageningen, 10 September 2010

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Prof. dr. Rik Leemans	Dr. Ad van Dommelen

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The SENSE Research School declares that **Ms. Lucía Hernández Leal** has successfully fulfilled all requirements of the Educational PhD Programme of SENSE with a work load of 43 ECTS, including the following activities:

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- Environmental Research in Contex
- Research Context Activity: "Co-organizing two-day Symposium on Sensible Water Technology at Wetsus, Leeuwarden (12- 13 April 2007)
- Basic Statistics

Other PhD and MSc courses

- Ecotoxicology module 1: effects
- Techniques for writing and presenting a scientific paper
- Environmental risk assessment of micropollutants
- Modern Analytical techniques

Oral Presentations

- Advanced Sanitation IWA international conference, 12-13 March 2007, Aachen, Germany
- Sanitation Challenge IWA international conference, 19 – 21 May 2008, Wageningen, The Netherlands
- Sensible water technology (SENSE meeting), 12 April 2007, Leeuwarden, The Netherlands
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SENSE Coordinator PhD Education and Research

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