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Bisphenol A Retention in the Direct Ultrafiltration of Greywater

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Abstract

Decentralised treatment is an increasing trend in the attempts to manage water more wisely in light of water restrictions, overconsumption and drought. Greywater is a fraction of household wastewater that offers the potential to be treated locally to be reused for garden irrigation, car washing and toilet flushing. In this paper the performance of submerged and direct ultrafiltration (UF) of synthetic greywater is investigated with regards to organic trace contaminant, namely Bisphenol A (BPA), and fouling. The synthetic greywater solution consisted of inorganic particulates (kaolin), organic fibres (cellulose), protein (casein), surfactant (sodium dodecyl sulphate, SDS), humic acid (HA), calcium, sodium chloride electrolyte and sodium bicarbonate buffer.

Results indicate that UF can remove 30-45% of BPA. This removal is attributed to partitioning of the compound to the membrane material, suspended and dissolved solids as well as the fouling layer. Humic acid and calcium were the main contributors to fouling, which also affected BPA retention. Fouling increased with an increase in HA concentration, which calcium contributed most to fouling at a concentration of about 0.5 mM. At higher concentration of calcium aggregation appeared to reduce fouling significantly.

The implications of this study are that trace contaminant-solute interactions play an important role for retention potential and this relationship offers room for optimization by selecting particulate additives with a high affinity for target compounds. This is of particular importance if such contaminants are a concern (which is dependent on the product water application) and in the absence of biological treatment which is in this case not desired. The separation of greywater into fractions of low and high strength is of advantage if this can eliminate the presence of humic substances.

Keywords: Greywater, graywater, direct ultrafiltration, recycling, bisphenol A (BPA), trace contaminant.

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1 INTRODUCTION

1.1 Greywater origin and characteristics

Greywater is wastewater from the kitchen, bathroom (sink, bath and shower), laundry and any other non-toilet household wastewater. Due to the lack of urine and faeces in greywater, it is generally better accepted for recycling than blackwater which contains toilet waste. In the context of water restrictions, drought and water shortage greywater is considered for recycling for irrigation or in house purposes following decentralized treatment. Given the decentralized nature of the likely application such treatment needs to reliable and robust. Greywater characteristics vary significantly depending on the lifestyle and product selection of the household participants and fluctuations in a decentralized system can be severe, allowing significant periods of zero wastewater production to high flow of low strength greywater. The maintenance of some treatment systems, biological in particular, would give difficulties in light of fluctuating quantity and quality of the influent. Other treatment processes such as conventional filtration technology focuses primarily on particulate and biological contaminants.

Greywater accounts for about 65-75% of water used in a household and the major contributors to this greywater load are summarized in Table 1. Greywater is generally characterised as a mixture of suspended solids (SS, particulates and colloids) and turbidity, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total dissolved solids (TDS), on occasion total organic carbon (TOC) and the nutrients nitrogen (N) and phosphorous (P). A summary of greywater characteristics compared to blackwater is presented in Table 2. Due to the variation in greywater types, the fluctuations in quality are large and hence considerable overlap exists between black- and greywater. Ramon *et al*. [1] have in fact argued that the wastewater would be better classified as a function of pollution load rather than origin and hence suggesting the notion of low (bath, shower & washbasin) and high (kitchen, washing machine & dishwasher) strength greywater. This indicates that for research a variation of parameters over an expected concentration is justified.

The pH range of greywater (5–10.9) is more alkaline than domestic wastewater (5.9–7.7). The higher alkalinity of greywater originates mainly from laundry effluent. The highest values for suspended solids also originated from the laundry and kitchen, due to the presence of sand and clay from clothes or rinsing vegetables. COD, BOD, and TOC values differ widely within

the greywater sources mostly due to a strong dependence on chemical products used. Proteins, carbohydrates and fats are common constituents [2]. The nitrogen concentration is lower, because urine as the main nitrogen source in domestic wastewater is not present in greywater, while most nitrogen originates from household cleaning products and from the kitchen sink. Proteins, which have a high nitrogen content, are also common ingredients in shampoos, the most commonly used compounds being keratin and milk proteins. Phosphate originates mainly from laundry detergents. Overall greywater does not containing the right nutrient and trace element ratio required for biological treatment or a membrane bioreactor [3]. Surprisingly, no data on surfactant concentrations in domestic wastewater and greywater could be identified, even though those are predominant household chemicals. Low concentrations of metals have been recorded in greywater by Erikson [4].

Pathogens occur in greywater in much lower quantities than in domestic wastewater. The presence of total and faecal coliforms in greywater is probably related to the introduction of faecal bacteria into the system during body hygiene and laundry of potentially contaminated items such as nappies. As ultrafiltration (UF) removes pathogens from water reliably and biodegradation or biofouling is not of interest in this study, the influence of pathogens in these short term experiments will not be investigated. Based on these observations from literature, a model greywater composition (synthetic greywater) has been identified and will be described in the materials and methods section of this paper.

1.2 Trace organic greywater contaminants

In addition to the bulk constituents, another major concern are trace contaminants like endocrine disrupting chemicals (EDCs) in wastewater [5]. The organic contaminants which would predominate through the use of detergents, washing powders and personal care products has to date not been considered. No data is available with regards to the presence of trace organic compounds in greywater. The presence of such compounds would depend on the many constituents in personal care products and detergents as well as their degradation products. The level of concern with regards to such contaminants is bifold. While detergents are rarely a concern if the recycled water is used for toilet flushing, in irrigation applications, which is a common use of treated and untreated greywater in households, organic contaminants are posing a number of concerns. Firstly, additives to detergents play an important role in the transport of

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contaminants in soils and waterways, which is facilitated through rainfall and runoff, and secondly the potential of some contaminants to accumulate in soil, organisms and vegetation is to date poorly understood. Sumpter and Johnson [6] outline the issue of endocrine disrupting chemicals, such as Bisphenol A, in detail. Of particular interest to this study is the issue of 'pseudopersistence' the low level but continuous release of compounds as well as mixtures and degradation products. In wastewater treatment the sorption of compounds to sludge and in the land application, the sorption to soil are important [7]. Similar interactions apply in greywater treatment where particulates and organic molecules will interact to some extend with trace organic contaminants which will affect the removal potential. In the environment, degradation following a number of pathways is important and some products may be more persistent than parent compounds. Degradation pathways are biological, hydrolysis and photochemical [8] with the proportion of each depending on chemical characteristics of the compounds as well as the nature of the environment.

Bisphenol A was selected as a trace organic contaminant for this study due to its broad abundance in wastewater. BPA is known to quickly biodegrade and to adsorb to suspended solids and sediment in water. Vilchez *et al.* [9] recorded concentration of BPA from 0.02 to 0.50 mg/L in wastewater, while Zafra *et al.* [10] recorded concentrations ranging from 0.01 to 2.50 mg/L. The pKa value of BPA is between 9.6 to 10.2 [11] which means that the molecule is neutral up to about pH 10 and then has a negative charge. The strong interaction with solids is an indication that solute-solute interactions may be important for this compound.

1.3 Greywater treatment

Greywater treatment allows the reuse of locally available water and prevents the dilution of blackwater. It reduces the dilution of trace contaminants excreted by humans in the blackwater may increase the removal potential in sewage treatment for such compounds. Ramon *et al*. [1] have conducted experiments of low strength greywater treatment using UF and nanofiltration (NF). Depending on the membranes used UF removed 45-70% of COD as well as 92-97% of turbidity. As expected NF achieved >90% dissolved organic removal in addition to about 50% TDS removal. Nghiem *et al.* [12] have investigated the removal mechanism of BPA in NF. The retention was pH dependent with retention of about 40% at pH 6 when BPA is neutral and near 100% at pH 11 when BPA is negatively charged. In a more applied study, Wintgens *et al*. [13]

recorded retentions of nonylphenol (NP) and bisphenol A (BPA) in NF ranging between 70% and 100% and in a UF project, Schäfer *et al*. [14] found that particle-contaminant interaction like the adsorption of natural hormones onto activated sludge and other particulates enhanced the retention of the hormones. Estrone retention in pure water ranged between 0-20% depending on the membrane type, in solution containing NOM and kaolin retention was found between 10-30% and the highest retention was found during filtration of activated sludge (50–65%) where retention by the cake deposit may also have influenced retention.

With regards to wastewater treatment and recycling most studies are applying a processes referred to as membrane bioreactor (MBR). In this process biological degradation and UF are combined. Fouling is a major issue in this process due to the generally high pollutant load. For example, Lodge *et al*.[15] have compared wastewater with greywater in UF following biological treatment and found similar fouling behaviour reasoning that the difference could be explained with a higher SS concentration in wastewater in that case. Yean *et al*. [16] used a MBR containing a submerged hollow fibre membrane for the treatment of household wastewater (including toilet waste), but this study mainly focused on nitrogen removal. The MBR was found to enhance nitrogen removal efficiency (83%) compared to other biological nitrogen removal processes. Submerged UF membranes have been gaining more attention in water treatment applications since they are less energy consuming than crossflow and dead-end filtration membranes and they require little space [17, 18], which makes them also an interesting option for decentralized greywater recycling applications. Since nutrient deficiency in terms of both macro- and micronutrients which greywater exhibits potentially retard the efficacy of biological processes [3], including MBR, it might be of advantage to treat greywater purely by UF if sufficient organic matter can be removed.

In this study the direct UF as a physical separation process is studied to explore the potential of this direct treatment in absence of biological processes. The effect of selected greywater compounds on the retention of a model trace organic contaminant, Bisphenol A, is investigated. Due to the design of the experiments of a relatively short term nature in the absence of microorganisms, retention of trace organics can be assumed to be due to sorption rather than degradation. The core interest of this study is to evaluate treatability of greywater on site with a physical membrane filtration technology that requires little maintenance.

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1.4 Ultrafiltration membrane fouling

Different fouling mechanisms have been described in UF in many studies. While Jiang *et al*. [19] found pore blocking and cake formation the most important fouling mechanism in a MBR pilot plant, other studies have investigated colloidal, biological as well as organic fouling and their control [17, 20, 21]. While the mechanisms of particulate fouling are reasonably well understood, the interaction of particles with organic matter which is the case in most real life applications and organic fouling in general remains a challenge. Bulk organic matter such as natural organics, effluent organics and compounds like humic acid (HA) have been known for its fouling potential in membrane processes for quite some time which was confirmed by Oschmann *et al*. [22]. Previous studies showed that membrane fouling by such bulk organics is affected by many factors, including the hydrodynamic and operating conditions, the characteristics of the organics and the membranes, and the solution chemistry (in particular pH, ionic strength and presence of multivalent ions) of the feed [23-25]. Naceur *et al*. [26] found an increase in DOC retention in a microfiltration process due to adsorption of HA onto modified Algerian clay. Lin *et al*. [27] also investigated the effects of HA characteristics on UF performance and found the hydrophilic fraction exhibits the worst flux decline despite little solute rejection and the molecules with the largest molecular weight (6.5 to 22.6 kg/mol) exhibit the worst fouling. Ruohomäki *et al*. [28] found HA retention of 50-95 % during UF when coagulants were used. Pre-coagulation with NaCl, KCl, $AlCl_3$ and $FeCl_3$ affected retention positively, while no severe fouling occurred. This indicates that particle interactions are important both with respect to fouling as well as retention. Further, calcium is an important parameter due to its complexation by humic materials [29, 30]. Calcium and bulk organics are both present in greywater and are hence expected to play a major role in the fouling behaviour. Yuan *et al*. [31] observed significant effect on fouling only for large molecular weight cut off membranes during UF of HA. The rate and extent of HA fouling was found to increase at low pH, high ionic strength, and in the presence of calcium. Aoustin *et al*. [32] discovered a strong effect of calcium concentration on HA retention in UF where aggregation due to calcium increased retention of bulk organics and reduced fouling.

Another group of contaminants in greywater are surfactants. Surfactants have mainly been studied in the context of micellar enhanced UF, where a surfactant is added to the feed,

which is later removed in form of micelles containing the pollutant [33, 34]. Only very few fouling studies can be found [35, 36] and Archer *et al*. [36] found an increase in flux in the critical micelle concentration (cmc) region during NF of an anionic surfactant. Hence micelle formation, much alike to aggregate formation is beneficial to membrane productivity in several studies. In our previous work, Nghiem *et al*. [37] found that sodium dodecyl sulphate (SDS) alters the attachment of deposits to UF membranes significantly.

Proteins are also a core constituent of greywater. Most protein fouling studies, driven by the dairy industry, use bovine serum albumin (BSA) as a model compound [38-40] and a small number of studies has been conducted on casein fouling [41]. Huisman *et al*. [38] found that protein–membrane interactions influence the fouling behaviour in the initial stages of filtration. In the high-fouling regime (later stages of filtration), protein–protein interactions dictate the overall performance and Jones *et al*. [39] found adsorption of the protein onto the membrane is greatest near the isoelectric point (IEP) of the protein (pH 4.7 for BSA). At higher pH values adsorption decreases due to increased electro-static repulsion between the protein molecules. Su *et al*. [40] found pore blocking and adsorption into the pores the main fouling mechanism during filtration of BSA. Seeing the concentrations of protein in such studies is significantly higher than what can be expected in greywater, the direct applicability of those studies is questionable and hence the foulant concentration will be investigated.

In this study the influence of greywater foulants and their impact on BPA retention is examined in a systematic manner. BPA retention is presented as a function of a wide pH range in order to understand the impact on BPA characteristics for a number of synthetic greywater solutions. The impact of particle, calcium, casein, surfactant sodium dodecyl sulphate and humic acid as greywater model compounds are investigated. The effect of biological matter or biofouling is not investigated here as the greywater treatment is intended as a physical treatment with the possible need to prevent biological actitivity.

2 MATERIALS AND METHODS

2.1 Submerged Direct Ultrafiltration Set-Up

The filtration system used is shown in Figure 1. The membrane is submerged in a feed container of a volume of 2.25 L that is magnetically stirred. The peristaltic pump used in this

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study was a Masterflex Laboratory Standard (L/S) equipped with a digital variable-speed console drive. Masterflex Norprene L/S 25 tubing with an inner diameter of 4.8 mm was used. The pump had a variable flow rate range from 10 to 1000 mL/min. For all experiments presented in this paper the permeate flow was set at 60 mL/min. Further equipment consists of a DIN 16007 pressure gauge supplied by Dobbie and a PC-351 magnetic stirrer, with a maximum stir rate of 1200 rpm supplied by Industrial Equipment & Control Pty Ltd.

2.2 UF Membranes

A ZeeWeed®-1 (ZW-1) UF module supplied by Zenon Environmental, was used in this study. This module operates in an "outside-in" configuration, where a negative pressure provided by the pump induces a flow of water from outside to the inside of the membrane fibres. The ZeeWeed® membrane module is installed directly in the feed tank and works under dead end filtration conditions. The nominal pore size is 0.04 µm and the membrane surface area 0.047 m^2. The module is 17.5 cm high and 5.8 cm in diameter.

2.3 Filtration and Cleaning Protocol

The experiments were run with a synthetic greywater solution for 5-6 h on a set flow rate of 50 mL/min. The objective of this protocol is short term testing without biological processes occurring. When biofoouling and biogegradation were of interest a different experiment would have to be designed. A volume of 2250 mL of feed solution was prepared 16–18 h prior to the experiment and stirred for at least one hour at 1200 rpm. The solution was stored over night at 4°C and stirred for a further 30 min before the start of the experiment. Stirring was continuous at the maximum setting during the experiment. pH adjustments were carried out immediately before the experiment. The transmembrane pressure (TMP) was observed every 30 min as a fouling indicator. Feed and a permeate samples were taken every hour for turbidity, pH and conductivity measurements. These samples were then returned into the feed beaker. Other samples (20 mL) were taken every 1-1.5 h for calcium, UV_{254} absorption, TOC and BPA analysis. The UV_{254} measurements were undertaken immediately, the rest of the samples were stored at 4 °C until time of measurement.

Cleaning was conducted at the end of each experiment and consisted of the following protocol; 15 minutes aeration of the membrane in the feed beaker (removal of particles from the

membrane); 15 min soaking in 0.5 g/L SDS solution (removal of HA, organics); 15-30 min soaking in 10 mL/L bleach solution (concentration 0.35% HOCl) during constant aeration (removes HA, organics and desorbs BPA). The membrane is rinsed after every step with purified water with a quality of >18MΩ/cm, then purified water is filtered and if the TMP pressure is +/- 1 kPa, the same as during purified water filtration prior to all experiments, then the cleaning procedure is considered as successful. The cleaned module is stored in purified water.

2.4 Analytical Methods

A Hach – Model 2100N analyser was used for turbidity measurements. Conductivity was measured with an Alpha 200 conductivity meter (CHK engineering). A Micro 2 pH/Ion Meter was used to determine pH. A Shimadzu UV1700 ParmaSpec UV-Visible spectrophotometer was used to measure absorbance. Samples were analyzed undiluted for absorbance at 254 nm for HA, which is the wavelength used for organics analysis, and at 280 nm for casein.

Total organic carbon (TOC) was measured using a Shimadzu TOC-V_{CSH} analyser. Analysis was conducted in non-purgeable organic carbon (NPOC) mode. Samples were kept at 4°C until analysed, and a calibration was conducted before each analysis using potassium hydrogen phthalate to produce standards of 0, 2.5, 5 and 10 mg/L. TOC vials were cleaned by rinsing with tap water and then soaking overnight in 1M NaOH. Vials were rinsed three times with deionised water, baked in an oven over night at 250°C, and stored in clean glass beakers and covered with aluminium foil to prevent contamination.

A Varian AA- 300 Plus Atomic Absorption Spectrometer was used to measure the calcium concentration in the samples. The optimal working range of the instrument for calcium is 0.01–3 mg/L. The instrument runs with an oxidizing nitrous oxide – acetylene flame, a lamp current of 10 mA, a wavelength of 422.7 nm and a slit width of 0.5 nm. Prior to the analysis a calibration with a 0.5, 1, 2, 3 mg/L standard solution prepared from a 1000 mg/L Ca^{2+} solution has been implemented.

A Shimadzu HPLC-UV system was used to determine the BPA concentration in the UF permeate samples. A reverse phase C-18 drug discovery Supelco column was used for the analysis. For the Bisphenol A analysis the pump operated at 1 mL/min and the wavelength of the UV detector was set to 280 nm. The injection volume was 50 µL and analysis time 25 min.

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Eluent A contains 80% acetonnitrile and 20% water and eluent B contains 20% acetonnitrile and 80% water buffered at pH 4.3 using 25 mM KH_2PO_4. BPA was analysed in feed solutions prior to the addition of greywater compounds and in permeate samples. The interference with organic compounds such as HA was investigated and was not identified as a problem in permeate samples.

2.5 Greywater Compostion

The following model components were selected to constitute the synthetic greywater solutions used in the experiments. The synthetic greywater composition for each experimental series is given in Table 4.

Kaoline was chosen as a representative of suspended inorganic solids. Kaolin is a form of natural clay and contains a mineral content of ~97% Kaolinite (Al_2O_3-$2SiO_2$-$2H_2O$). Kaolinites have hydrophilic surface OH groups, the average particle size of kaolin is ~3.4 µm, the specific surface area is 10–20 m^2/g and the density is $4000 \cdot 10^6$ mg/m^3 [42].

Cellulose is an organic fibre and one of many polymers found in nature. Cellulose is insoluble in water and made of 2000-14000 repeat units of the monomer D-glucose. Cellulose is found in plants as microfibrils (2-20 nm diameter and 100 - 40 000 nm long). The Cellulose used in the experiments had an average particle size of ~20µm, consists of 40.54% C and a density of $1500 \cdot 10^6$ mg/m^3.

Humic Acid (HA) was chosen to represent the dissolved organic loading in the experiments. HA is a component of natural organic matter that is present in all natural waters and also in wastewater [43]. The structure of HA changes with solution pH and salt concentration [42]. The HA used in the experiments was Sigma Aldrich HA. The recorded elementary composition in literature is 60 % C, 4.47 % H, 34.5 % O, 0.96 % N [44]. The measured carbon concentration is lower at about 35–40 % (20mg/L HA ≅ 6.22 mg/L TOC).

Sodium dodecyl sulphate (SDS) ($CH_3(CH_2)_{11}OSOO_3Na$), also known as sodium lauryl sulphate, is an ionic detergent that is commonly found in household products such as shampoos [45]. The molecule has a tail of 12 carbon atoms, attached to a sulphate group, giving the molecule the amphiphilic properties required of a detergent. SDS has a high foaming capacity

and a critical micelle concentration (CMC) of 8.1 mM in water (25°C), while the CMC decreases in the presence of salt from 3.82 mM (0.02 M NaCl) to 0.0083 mM (0.4 M NaCl) [46].

Casein was chosen to represent the nitrogen and protein fraction of the greywater solution. Proteins are commonly used in shampoos, the most commonly used proteins being keratin and milk proteins. Casein is the major protein in milk ~80% of the total protein content. The nitrogen content of milk is distributed among caseins (76%), whey proteins (18%), and non-protein nitrogen (NPN) (6%). The principal casein fractions are alpha (s1) and alpha (s2)-caseins, ß -casein**,** and kappa-casein**.** The molecular weight is between 19000 and 25000 g/mol depending on the fraction. Most, but not all, of the casein proteins exist in a colloidal particle known as the casein micelle**.** Colloidal calcium phosphate (CCP) acts as a cement between the hundreds or even thousands of submicelles that form the casein micelle. Binding may be covalent or electrostatic. Calcium plays an important role in stabilizing the casein micelle. The removal of Ca^{2+} leads to reversible dissociation of casein without micellular disintegration, while Ca^{2+} also leads to aggregation.

BPA is a common name for 2,2-(4,4-dihydroxydiphenyl) propane which is used in polycarbonate plastics and epoxy resins. The structure of BPA and physicochemical characteristics are summarised in Table 3. BPA is one of the most produced chemicals worldwide and it is known to have endocrine disrupting potential [47].

The chemicals used for preparing the synthetic greywater solution are analytical grade chemicals. The chemicals used were sodium chloride (BDH Chemicals), sodium bicarbonate, calcium chloride and kaolin (Ajax Finechem), cellulose, HA, sodium dodecyl sulphate (SDS), casein, Bisphenol A (BPA) (all Sigma Aldrich). 1 M HCl and 1M NaOH were used for pH adjustment.

For stock solutions, 50g/L of casein was prepared in 1M NaOH solution and 1g/L of BPA was prepared in pure methanol. These solutions were kept at 4°C and were used to prepare the experimental solution. The surfactant used for cleaning is the same surfactant (Sigma Aldrich SDS) as used in the synthetic greywater solution. The used bleach is common household bleach (Home Brand Regular Bleach, Woolworth Australia). The active constituent is 3.5% sodium hypochlorite.

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3 RESULTS AND DISCUSSION

3.1 BPA Retention

Synthetic greywater was spiked with 1 mg/L BPA to examine trace contaminant removal efficiency. The experiment was conducted as a function of pH to investigate the impact of compound speciation, namely the dissociation at a pH of about 10, on retention. The speciation of BPA as a function of pH is shown in Figure 2. At low and neutral pH BPA exists predominantly in its neutral form HO-$C_{15}H_{14}$-OH, while above pH 10.1 the negatively charged specie HO-$C_{15}H_{14}$-O^- predominates. Speciation has been shown to be important in the nanofiltration (NF) of BPA where retention increased significantly at pH 11 over pH 6 presumably due to charge repulsion [12]. For estrogens speciation affects adsorption to the membrane and subsequently retention, while during initial stages of filtration retention is high at low pH (due to adsorption), retention is low at high pH if the pore size is sufficiently large [48]. After adsorption at equilibrium is reached, adsorbing compounds (low pH) are retained substantially less than charged species (high pH) [12, 49].

In this situation with a number of suspended and dissolved solutes in the synthetic greywater, the BPA retention is constant between pH 4-9 and then decreasing until there is no retention at pH 12 (see Figure 3). This trend is identical for both calcium concentrations investigated. The retention at low and medium pH is surprisingly high for UF with about 40% at low and 30% at high calcium concentration. The retention of BPA is presumably attributed to the adsorption of BPA on particulate or organic matter, which is then retained by the membrane or due to adsorption on the membrane itself (which is evident by the high retention in purified water). Those mechanisms were also recorded by Wintgens *et al.* [13].

An identical trend is shown in Table 5 where permeate BPA concentration is constant between pH 4-9 and then a steep increase in BPA concentration between pH 9-12 is observed. At high pH values (>9) a release of the adsorbed fraction to the liquid phase takes place, shown in lower retention and higher BPA permeate concentrations. Adsorption to the membrane, organics and particulates of BPA occurs at pH values below the pK_a value (pK_a of BPA is between 9.6 to 10.2 [11]), while desorption is starting to occur at pH values in the range of the pKa value and above, until there is no further adsorption observed at pH 12. Clara *et al.* [47] reported the same effect during adsorption of BPA and other EDCs onto sewage sludge. The pH dependence of

BPA speciation shows a similar trend to the pH dependence of BPA retention with retention decreasing dramatically at high pH. As expected adsorption is low were charge repulsion is higher (negatively charged membrane and BPA at high pH).

To distinguish between BPA adsorption onto the membrane and adsorption onto particulate matter, purified water containing 1 mg/L BPA was filtered for one hour at each pH value from 4–12 (see also Table 5 and Figure 3). The retention is similar (about 30%) to results obtained at high calcium concentration (4 mM). This indicates that adsorption on the membrane is a strong component, although the difference of adsorption to the membrane and partitioning into organic and inorganic solutes is difficult to distinguish. In the presence of organic matter the membrane surface properties change [50, 51] and hence adsorption would be expected to vary also. Further, in the presence of organic matter the adsorption of trace organics on particulate matter varies, in the case of kaolin and natural organics the estrone adsorption increases [14]. Organic matter adsorbs to inorganic particles in the aqueous environment and trace organic contaminants tend to partition into some bulk organics through an affinity process. Calcium plays a bridging role between negatively charged organic matter and negatively charged particulates as well as membranes. It hence substantially influences the aggregation and stability of such mixtures and the surface charge of the resulting particulates. Examining similar solutes for the adsorption of estrone (at a lower concentration of 100 ng/L) the measured adsorption was 114-176 ng/g for hematite, kaolin, bentonite and cellulose. Adsorption onto natural organic matter or HA was 1750 ng/g and on activated sludge 6 ng/g [14]. Those values are affected significantly by the available surface area as well as solute concentration, however, one would expect that the presence of organic matter increases adsorptive interactions. The role of calcium in these interactions remains unclear. Seeing that calcium interacts at charge moieties of the molecules, one would expect hydrophobic interactions to increase as those charged groups are occupied.

BPA was also spiked in the experiments containing casein to examine the influence of organics. The BPA permeate concentration and the BPA retention at different casein concentrations are shown in Figure 4. Casein concentration has no significant influence on BPA retention, the retention is stable at about 40-45% in all experiments (see Figure 3) which indicates that additional BPA is probably retained due to interaction with casein in addition to adsorption onto particles, HA and the membrane as described above. Further work is required to

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determine the extent of such interactions. Casein concentration does not appear to be limiting the uptake of BPA and has therefore no influence on retention.

Membrane fouling complicates the observations further. If pores are blocked, a 'dynamic membrane' may form and retain more solutes than in a clean state. This was shown to have a significant effect in the UF of activated sludge (biologically inactive) where retention increased significantly [14]. In the following section the fouling of UF membranes for different synthetic greywater solutions (with varying composition) is examined and related to BPA retention.

3.2 Transmembrane Pressure increase during Greywater Filtration

The transmembrane pressure, which is the driving force of filtration, increases when the membrane fouls as the permeate flow is set constant. Figure 5 and Figure 6 show transmembrane pressure increase for a range of greywater mixtures to evaluate the main contributors to membrane fouling and explain some of the effects observed in BPA retention.

Figure 5 investigates the impact of calcium and HA on fouling. The first column shows negligible fouling by particulates in the absence of HA. The addition of 20 mg/L HA in the fourth set shows a significant amount of pressure increase, while this decreases if either particles (column 2) or calcium (column 3) are removed. Those results indicate the importance of the interplay of the different solutes and the fact that it is HA and calcium that act as a glue to hold the particle cake to the membrane. Very interestingly, if the calcium concentration is increased to 4mM the pressure increase is inhibited as in the absence of HA. This phenomenon is similar to those observed by Waite [52] and Aoustin [32] and can be attributed to aggregation at a sufficiently high calcium concentration that results in a looser deposit.

It is interesting to note the correlation between pressure increase and hence fouling and BPA retention. The retention of BPA is 10% higher when the pressure increase is the most significant at the 0.5 mM (or 20 mg/L) calcium concentration. BPA due to its molecular dimensions (see Table 3) of about 1 nm should not be retained by a membrane with a nominal pore size of about 40 nm. It is hence evident that the retention of such a small contaminant has to be due to adsorption to the membrane, a solute or due to capture in a membrane deposit.

Figure 6 shows the impact of some organic molecules on fouling. All experiments contain kaolin and cellulose as in previous tests. In the first column the HA concentration is

increased from 20 to 80 mg/L as shown in Figure 5, which more than doubles the transmembrane pressure. The addition of SDS does not influence fouling in the presence of calcium but causes an increase of fouling in the absence of calcium. Most likely those changes affect micelle formation and hence permeability of the boundary layer. Casein increases pressure, but decreases substantially in the absence of HA. Those results indicate that even in the presence of substantial amount of other organics and particulates, HA and calcium are the main determinants in membrane fouling. To investigate those effects in a more systematic and controlled manner, the concentrations of each compound are varied. Those results are shown in Figure 7.

Fouling increases with an increase of particle concentration (see Figure 7A). While the initial increase is steep, this levels out after about 100 mg/L. The initial increase can be explained with an increase in the particle deposit on the membranes, while the leveling off can be explained with the fact that the membrane is mounted vertically and after a certain amount of deposit, gravity will limit the cake thickness. The calcium contribution to fouling (Figure 7B) peaks at about 20 mg/L and then drops steadily, presumably as it's contribution to aggregation of solutes increases. The fouling contribution of casein is small (Figure 7C), despite the relatively high concentration. In the presence of HA this contribution is identical but HA adds 10 kPa to the transmembrane pressure. Sodium dodecyl sulphate (SDS) has little to contribute to fouling and effects are comparable to casein (Figure 7D). HA is the main contributor (note the different y-axis scale) to fouling with a direct correlation between concentration and pressure increase. HA is also added in the lowest concentration compared to other compounds (Figure 7E).

The implications of these findings are that separation of greywater from different origins may be sensible with regards to cleaning. HA in greywater would mostly originate from kitchen waste and hence contribute mostly to what Ramon *et al.* [1] describe as high strength greywater. If low strength greywater is treated then a very economic performance can be expected. Further work is required to determine the effects of common surfactants and personal care products on the cleaning capacity of membranes.

4 CONCLUSIONS

The fouling and retention of trace contaminants during short term experiments of direct ultrafiltration of synthetic greywater was investigated. Fouling studies with particulates (kaolin and cellulose), organics (humic acid, sodium dodecyl sulphate, casein) in an electrolyte matrix

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with varying concentrations of calcium and bisphenol A (BPA) as a trace contaminant was investigated. Fouling in such systems is mostly determined by humic acid in combination with a small concentration (0.5 mM) of calcium.

BPA retention was measured as 30-45% in short term experiments and occurs due to adsorption onto the membrane and onto particulate or organic matter at a solution pH below the pK_a of BPA and decreases at pH values around and above the pK_a. The BPA retention is slightly higher in the experiments containing low calcium concentration. Casein concentration does not have an effect on the BPA retention.

Further work is in progress to investigate the partitioning of trace compounds on other solutes, the fouling layer and the membrane. Understanding of such interactions will contribute significantly to the potential direct ultrafiltration has in producing chemicals free product water which is important if greywater is introduced into the environment.

5 ACKNOWLEDGEMENTS

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Table 1: Sources of wastewater and their pollutants [53, 54]

Wastewater source	Share of Water usage (%)	Pollutants
Kitchen	6 - 9	Oils, bacteria, dishwashing detergent
Bathroom, showers and hand basins	28 - 36	Soaps, shampoos, body-fats, hair, soils (occasionally lint, fabric fibres, skin, urine and faeces)
Laundry troughs and washing machines	12 - 17	Detergents, bleaches (occasionally oil, pains and solvents)
Toilet- flushing	23 - 32	Urin, faeces, toilet paper, cleaning products

Table 2: Composition of domestic wastewater and greywater [2, 4, 54-56]

	Blackwater	Greywater
pH [-]	5.9 – 7.7	5 -10.9
Total solids [mg/L]	200 - 1200	113 - 2410
Total dissolved solids (TDS) [mg/L]	100 - 850	137 - 1260
Suspended solids (SS) [mg/L]	24 - 608	3.1 - 330
BOD5 [mg/L]	28 - 400	33 - 1460
TOC [mg/L]	42 - 290	30 - 880
COD [mg/L]	45 - 1000	3.8 - 1380
Nitrogen [mg total N/L]	20 - 117	0.28 - 74
Phosphorus [mg total P/L])	3.2 - 30	0.0062 - 74
Surfactant [mg/L]	-	-

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Table 3 Physico-chemical characteristics of Bisphenol A (BPA). Mwd Calculations made with trial Chemoffice ultra 2005 without energy minimisation and without consideration of the van der Waals radius, pK_a and log K_{ow} were determined using software (Pallas 3.0 [57]), Dipole moment and structure was determined using software (Hyperchem [58]), EC50 for induction of vitellogenin in fish (concentration for 50% of maximum possible response) and relative potency to estradiol (E2) adapted from Sohoni *et al*. [59].

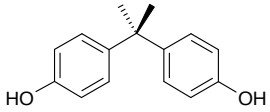
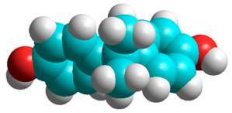
Formula	**MW** (g/mol)	**Molecular Widh X** (nm)	**Molecular Width Y** (nm)	**Molecular Length Z** (nm)	**Solubility in Water** (mg/L)	**pK_a**	**Log K_{ow}**	**Dipole Moment** (Debye)
$C_{15}H_{16}O_2$	228	0.383	0.587	1.068	129	10.1	3.32	1.411
Structure				**3D Structure Model**			**EC50** (µg/L)	**Relative Potency to E2**
							50	0.0004

Table 4: Concentrations of compounds used in various greywater UF experiments

Experimental Series	NaCl [mM]	$NaHCO_3$ [mM]	$CaCl_2$ [mM]	HA [mg/L]	Kaolin [mg/L]	Cellulose [mg/L]	SDS [mg/L]	Casein [mg/L]	BP A [mg/L]
1. f (Ca^{2+})	10	1	0-4	20	100	100	-	-	-
2. f (HA)	10	1	0.5	0-80	100	100	-	-	-
3. f (particles)	10	1	0.5	20	0-200	0-200	-	-	-
4. f (SDS)	10	1	0.5	20	100	100	0-570	-	-
5. f (pH)	10	1	0.5	20	100	100	-	-	1
6. f (Casein)	10	1	0.5	-	100	100	-	0-400	-

Table 5: Permeate BPA concentration after 1 h of filtration of synthetic greywater and purified water containing an initial concentration of BPA of approximately 1 mg/L (Ca^{2+} 0.5-4 mM, HA 20 mg/L, kaolin and cellulose 100mg/L, NaCl 10mM, $NaHCO_3$ 1mM).

pH (-)	**0.5 mM Ca^{2+}**	**4 mM Ca^{2+}**	**Purified Water**
	Permeate concentration (mg/L)	**Permeate concentration (mg/L)**	**Permeate concentration (mg/L)**
4	0.64	0.70	0.78
6	0.61	0.71	0.76
8	0.63	0.72	0.78
10	0.79	0.80	0.79
12	1.08	1.21	1.07

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FIGURE CAPTIONS

Figure 1: Experimental set-up of submerged UF rig for greywater recycling and ZW1 membrane module.

Figure 2: pH dependence of BPA speciation (calculated based on a pKa value of 10.1 [57]).

Figure 3: BPA retention as a function of pH in synthetic greywater (Ca^{2+} 0.5-4 mM, HA 20 mg/L, kaolin and cellulose 100mg/L, NaCl 10mM, $NaHCO_3$ 1mM) and purified water

Figure 4: Permeate BPA concentration and retention as a function of casein concentration (pH 6.8-8.0, HA 20 mg/L, Ca^{2+} 0.5mM, kaolin and cellulose 100 mg/L, NaCl 10mM, $NaHCO_3$ 1mM)

Figure 5: Transmembrane pressure Δp as a function of greywater composition (all experiments contained NaCl 10mM and $NaHCO_3$ 1mM, pH 8)

Figure 6: Transmembrane pressure Δp as a function of greywater composition (all experiments contained kaolin and cellulose 100 mg/L, NaCl 10mM and $NaHCO_3$ 1mM, pH 8). Note that scale is 2.5 times larger than Figure 5.

Figure 7: Transmembrane pressure Δp as a function of contaminants concentration for A: Particles, B: Calcium, C: Casein, D: Sodiumdodecyl sulphate, E: Humic acid. (all experiments contained NaCl 10mM and $NaHCO_3$ 1mM)

Figure 1

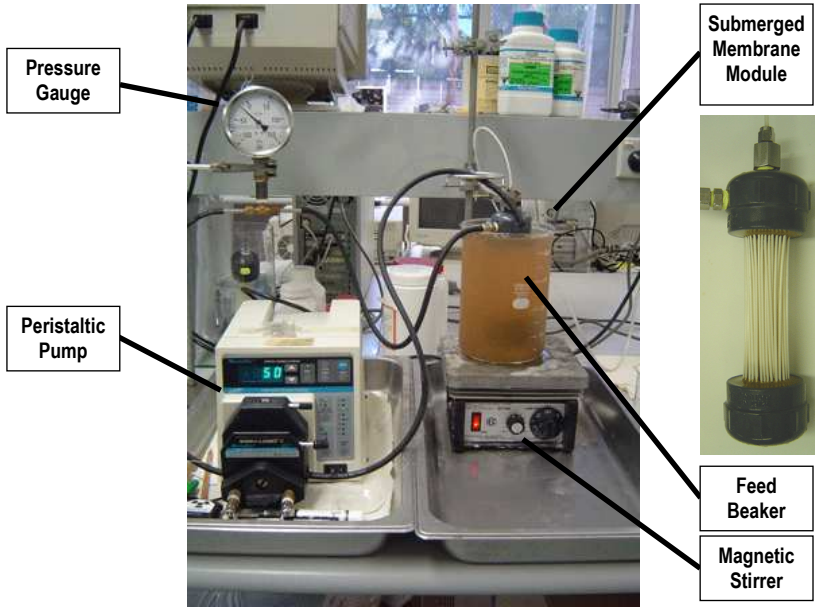

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Figure 2

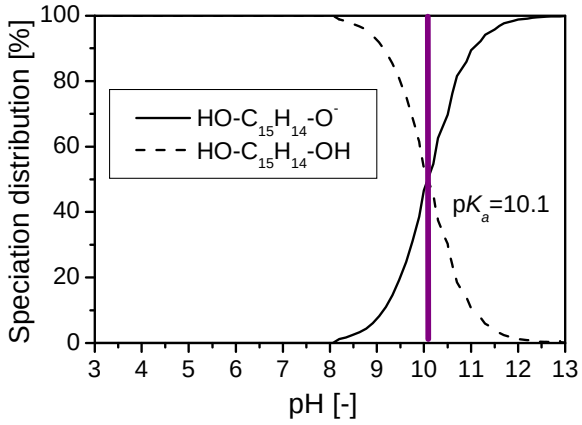

Figure 3

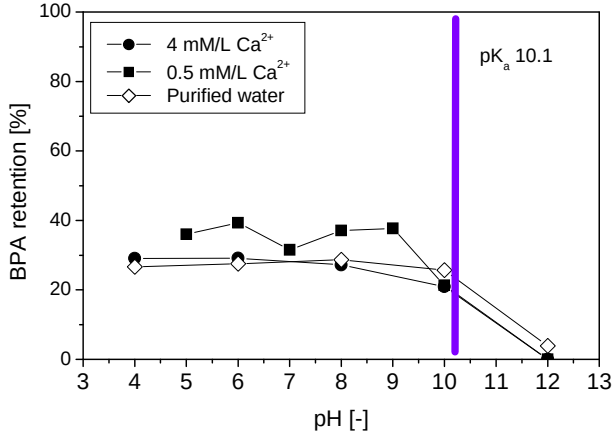

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Figure 4

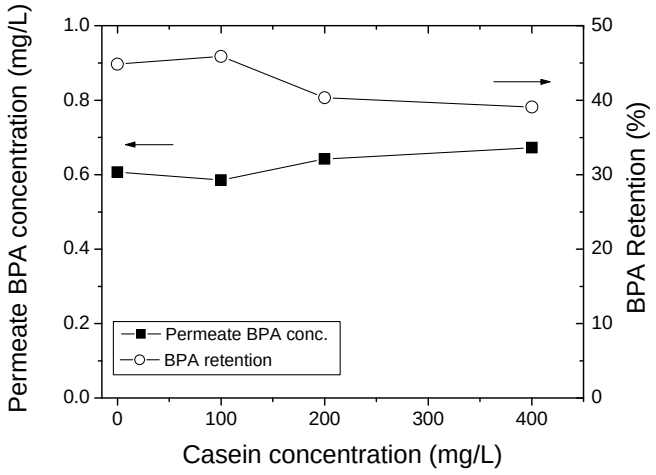

Figure 5

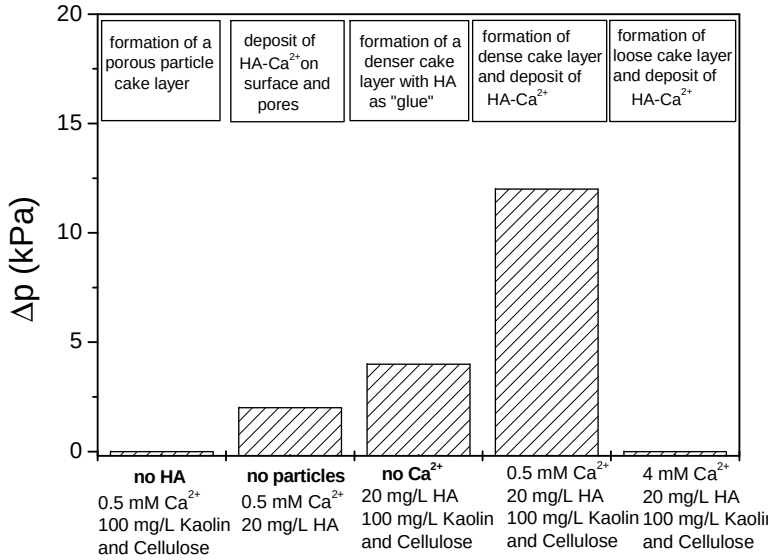

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Figure 6

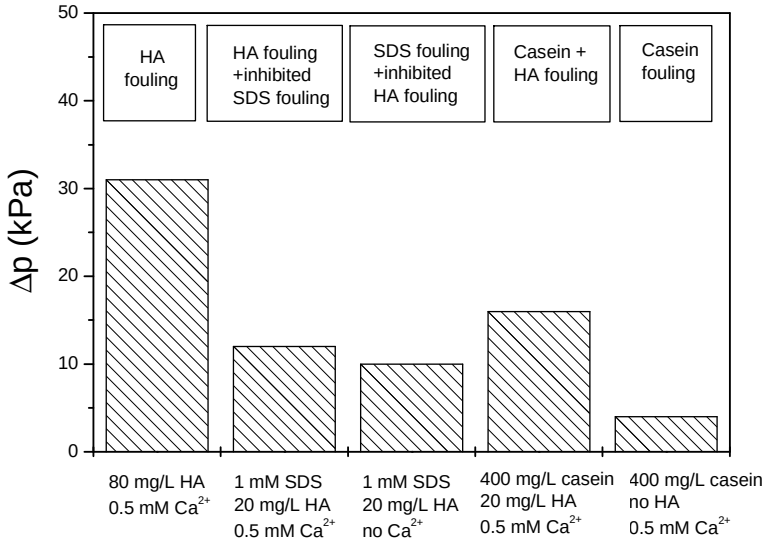
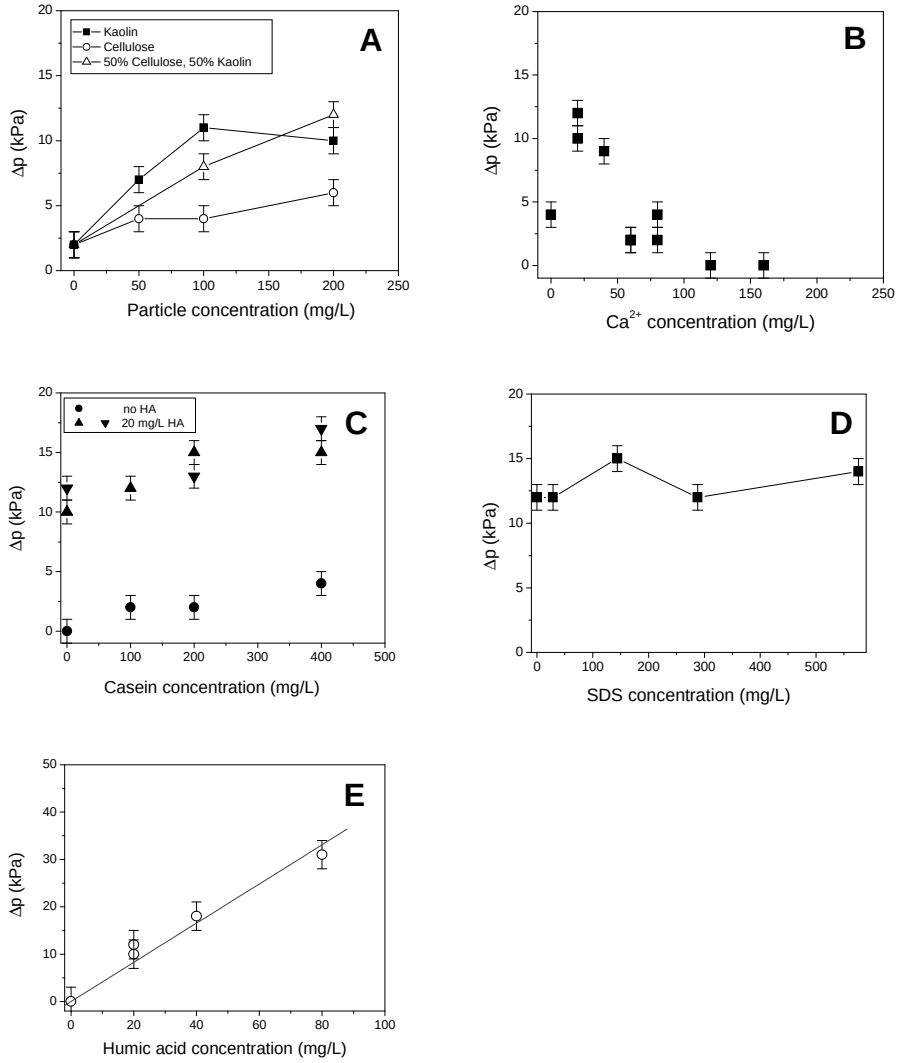
Figure 7