

Nutrient removal by NF and RO membranes in a decentralized sanitation system

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Abstract

Decentralized treatment of domestic wastewater offers the possibility of water and nutrient reuse. In a decentralized sanitation system the household wastewater streams are separated in a large diluted stream (gray water) and a small and concentrated stream (black water) containing important nutrients like ammonium and phosphate. Nanofiltration (NF) and reverse osmosis (RO) membranes might be used to recover the nutrients from anaerobically treated black water. The permeate might be used in a water reuse scheme. In case of water reuse the produced permeate should meet guidelines for potable water or meet new guidelines which might be applied in the future for intermediate quality of water, for example toilet flushwater; when this is not possible the permeate should meet guidelines for discharge. The most stringent guidelines apply for ammonium and phosphate. The focus of this paper is to test commercially available NF and RO membranes to remove nutrients from anaerobically treated black water in order to meet the Dutch guidelines. A large number of commercial tubular, capillary and flat sheet NF and RO membranes was tested on laboratory scale on their performance to meet the Dutch guidelines for ammonium and phosphate. The ammonium and phosphate concentrations used were based on the effluent composition of anaerobically treated black water. Ammonium and phosphate rejection were both measured in synthetic single salt and multi-ion mixtures and in anaerobic effluent.

The rejection for ammonium (30–95%) is neither sufficient for discharge nor potable water use. The rejection of phosphate (74–99%) is in most cases almost sufficient to meet the standards for potable water.

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1. Introduction

Water is a valuable product and worldwide fresh drinking water is getting a scarce product. Presently, most drinking water is produced from ground or surface water and after use it is treated in a wastewater treatment plant (WWTP), after which the treated water

is discharged to the surface water. In the current central sewer system wastewater from houses, buildings and industry is transported together and treated in a WWTP. These systems require a lot of space, have a high energy consumption and the options for water and nutrient reuse are limited (Lier and Lettinga, 1999). Furthermore, sewage piping required for transport of wastewater is expensive.

Another approach is to collect and treat wastewater streams close to houses, buildings and industries, called decentralized sanitation. Decentralized collection and

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treatment of wastewater involves separation of wastewater streams produced within houses and buildings. Within a household two main streams can be distinguished, a slightly polluted, but large stream called gray water and a concentrated, but small stream from the toilets called black water. These streams differ in volume and composition. The produced volume of gray water per person per year is 35 m³, the produced amount of black water per person per year is 14 m³. These numbers are based on the Dutch situation (Zeeman and Sanders, 2001).

Black water contains the major part of the produced nitrogen (as ammonium) and phosphate. The produced COD is almost equally distributed over the two wastewater streams (Otterpohl, 2002). More details about the nutrient composition as expected in black water (based on urine composition) is given in Table 1 in Section 2. A general composition of graywater is difficult to give as the characteristics of the graywater depend firstly on the quality of the water supply, secondly on the type of distribution net for both drinking water and the gray wastewater and thirdly on all the activities in the house (Eriksson et al., 2002). The concentrated stream of black water is currently diluted by the large volume of gray water, which results in large WWTPs.

After separation of the two streams, gray water can be treated separately after which it can be reused for several purposes (Christova-Boal et al., 1996; Ottoson and Stenström, 2003). However, certain risks are associated with graywater reuse (Ottoson and Stenström, 2003). The focus of this research is to look at water reuse possibilities and nutrient recovery from black water. The separation of streams fits in the DESAR (Decentralized

Sanitation and Reuse) concept. The DESAR concept with respect to black water separation and treatment is clarified schematically in Fig. 1. The black water with the major part of the nutrients being ammonium and phosphate can be treated in a small aerobic or anaerobic plant. Aerobic treatment of this stream requires oxygen and produces a high yield of biomass. In an anaerobic system a low biomass yield is observed and energy is produced in the form of methane (Tchobanoglous et al., 2003). An anaerobic treatment of black water is therefore preferred. During anaerobic treatment the major part of the nutrients ammonium and phosphate present in black water will be conserved. These nutrients may be concentrated by nanofiltration (NF) or reverse osmosis (RO).

After this concentration step the nutrients can be reused in agriculture as fertilizer. The most favorable option for the produced permeate is reuse; this reuse

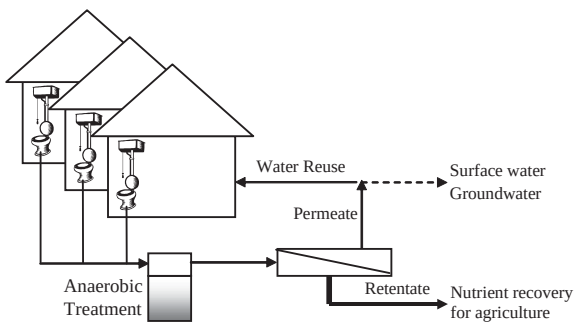


Fig. 1. Schematic overview of the DESAR concept with respect to the separation of black water.

Table 1

Urine composition as found in literature, the concentrations of compounds in the mixture tests and the potable water and discharge guidelines for ammonium-N and phosphate-P

Ref.	Urine composition						Mixture tests	Guidelines	
	A	B	C	D	Average	Dilution		Potable ⁽²⁾	Discharge ⁽³⁾
Compound	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	Synthetic mg/L	mg/L	mg/L
NH ₄ -N	3900	5900	9200	2200	5300	265	250 ⁽¹⁾	0.2	2
P-tot (PO ₄ -P)	350	530	1000	205	521	26	25 ⁽¹⁾	2	0.15
K	1200	1830	2200	1013	1561	78	70	12	
Cl	1800	3600	3800	2368	2892	145	130	150	
S-tot	300		1000	200	500	25	25 ⁽¹⁾	150	
Na	1300		4200	960	2153	108	110	120	
Ca	20		170	14.5	68	3	5	150	

A: Jönsson et al. (1997).

B: Fittschen and Hahn (1998).

C: Larsen and Gujer (1996).

D: Kirchman and Petterson (1995).

(1): as NH₄, HPO₄ and SO₄ respectively.

(2): VROM (1999).

(3): Warmer and Dokkum (2002).

however is regulated by guidelines. When reuse is not possible, the produced permeate should meet guidelines for discharge. The most stringent guidelines apply to ammonium and phosphate. Little information is available on the treatment of anaerobic effluent by NF/RO membranes with respect to the rejection of ammonium and phosphate. Kurama (Kurama et al., 2002), tested two NF and RO membranes to remove ammonium from potable water, the concentration found here were in the range of 10 mg/L and are much lower than expected in the anaerobic effluent.

The objective of this study was to test the rejection of ammonium and phosphate with NF and RO membranes. For this, several commercially available, tubular, capillary and flat sheet NF and RO membranes were tested.

2. Experimental

2.1. Salt composition

In this paper, the rejection of ammonium and phosphate salts was tested using concentrations comparable to the concentrations found in effluents after anaerobic treatment. The nutrients in the anaerobic effluent mainly originate from human urine; however they are diluted after flushing the toilet. The concentrations found for pure urine in literature are given in the columns A–D of Table 1. Ammonium and phosphate concentrations are expressed as $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$, respectively. Based on these numbers an average salt composition of pure urine is calculated. The average concentrations are divided by 20 (1.5 L of urine in 30 L of flushing water (= 6 flushes per day $\times$ 5 L per flush)) to find the salt concentrations in diluted black water.

The rejection of ammonium and phosphate was measured in three types of solutions:

- Synthetic single salt solutions (all types of membranes).
- Synthetic mixture of salts (tubular and flat sheet membranes).
- Anaerobic effluent (flat sheet membranes).

In the single salt solutions the rejection of phosphate was measured in a solution of Na_2HPO_4 (0.7 mM), which resulted in a $\text{PO}_4\text{-P}$ concentration of 22 mg/L in accordance with the concentration found in diluted urine (see Table 1). Together with the phosphate rejection some other salts were tested to characterize the membrane. These salts were NaCl (4.0 mM) and CaCl_2 (0.9 mM). The rejection sequence of these salts together with Na_2HPO_4 can be used to characterize the membranes in terms of surface charge.

In the single salt solution the rejection of ammonium was measured in a solution of NH_4Cl (0.01 M) or NH_4HCO_3 (0.01 M), which resulted in a $\text{NH}_4\text{-N}$ concentration of 140 mg/L, which is slightly lower than found in diluted urine.

To gain further insight in the rejection characteristics of the membranes regarding ammonium and phosphate the rejection was also measured in a synthetic mixture of salts with the composition given in Table 1 (Column 8).

The effect of fouling on the rejection of ammonium and phosphate was tested using an anaerobic effluent which originates from an anaerobic sheet reactor treating diluted black water from a school in the North of the Netherlands.

The concentration of ammonium found in this effluent was 194 mg $\text{NH}_4\text{-N/L}$ and for phosphate a concentration of 45 mg $\text{PO}_4\text{-P/L}$ was found. The latter concentration is higher than expected based on the diluted urine composition as given in Table 1.

This difference might be explained by the contribution of faeces to the total phosphate concentration.

The rejection values found for salt mixtures and the anaerobic effluent were used to calculate average permeate values, which were compared with set guidelines for water reuse or discharge. The guidelines for potable water and discharge are also given in Table 1. In the case of water reuse as potable water the ammonium guideline is very stringent (0.2 mg/L), the guideline for phosphate is 2.0 mg/L. Other reuse possibilities might be flush water for toilets or irrigation water. Yet, clear guidelines for these reuse possibilities are not available. In this paper the guidelines for potable water will be used as starting point for other reuse opportunities.

Discharge guidelines will become important if reuse is not possible or desirable. The guidelines set for discharge are based on the Dutch situation (and differ per location) and are given as total-nitrogen and total-phosphate. The guideline for phosphate is very stringent compared to nitrogen. The main focus in the following sections will be on the rejection of phosphate and ammonium with NF and RO membranes.

2.2. Analyses

In the experiments with the single salt solutions, concentrations in the feed/concentrate and permeate were measured by conductivity. In the mixture and the anaerobic effluent the ions were measured separately. Phosphate was measured by spectrophotometry or later on with ion chromatography (IC). Sulphate was measured by IC. Potentiometric titrimetry or IC was used for chloride. ICP-AES was used to analyze calcium, sodium, and potassium. Ammonium was measured by an auto-analyzer including spectrophotometric measurements at 660 nm, later on Dr. Lange kits were used.

Hydrocarbonate concentrations were derived after the titration with HCl and later on HCO_3^- concentrations were measured in a TOC analyzer.

2.3. Data analysis

Measuring the rejection of ammonium and phosphate is sufficient to estimate the permeate concentration as a function of rejection ($R = 1 - C_p/C_f$), the recovery ($S = Q_p/Q_f$) and the feed concentration C_f (Mulder, 1996):

$$\bar{C}_p = \frac{C_f}{S} [1 - (1 - S)^{(1-R)}] \quad (1)$$

In this formula, $\bar{C}_p$ is the average permeate concentration (mg/L), C_f the feed concentration (mg/L), S the recovery ($= Q_p/Q_f$) (–), and R the measured rejection ($= 1 - C_p/C_f$) (–).

Based on measured rejections, a recovery of 90% (0.9) and an assumed feed concentration of 194 mg/L for $\text{NH}_4\text{-N}$ and 47 mg/L for $\text{PO}_4\text{-P}$, permeate concentrations are calculated and compared with the guidelines for discharge and reuse.

2.4. NF and RO membranes

In a decentralized sanitation system it is desirable that the total process is simple and robust requiring as little maintenance as possible. A direct treatment of the anaerobic effluents is therefore desirable. Anaerobic effluents have a quite high turbidity and this can cause fouling problems in spiral wound modules. It is known that the tubular and capillary membrane geometry is less susceptible towards fouling than spiral wound modules (Frank et al., 2001).

For this reason tubular or capillary membranes might be used directly after an anaerobic treatment without any further pre-treatment. The tubular NF and RO membranes tested were AFC30, AFC40, AFC80, AFC99, kindly supplied by PCI membranes.

Tubular membranes have a low fouling tendency but have the disadvantage of a low packing density. Capillary membranes combine the advantage of tubular membranes (low fouling tendency) with the advantage of spiral wound modules (a high packing density) (Frank et al., 2001). The capillary NF membrane tested was NF50 together with some capillary membranes with an experimental top-layer, kindly supplied by X-Flow BV, The Netherlands.

Tubular and capillary membranes have the advantage of being less susceptible towards fouling, but another important parameter in this project is the removal of ammonium and phosphate to meet set guidelines, therefore a number of flat sheet NF and RO membranes with high flux and rejection were tested as well. The flat sheet NF membranes NF90 and 200, together with the flat sheet RO membranes BWLE, XLE and BW30 were kindly supplied by Dow FilmTec. The NF membrane ESNA LF (low fouling), was supplied by Hydranautics. The specifications of the membranes, as supplied by the manufacturers are given in Table 2.

2.5. Test units

Tubular (12.7 mm diameter) and capillary (1.5 mm diameter) membranes were tested in an experimental set up from Norit Membrane Technology (The Netherlands).

Average trans-membrane pressures (TMP) were 2 bar for capillary membranes and 4 bar for tubular

Table 2

Membrane specifications of the membranes used in this research. The specifications are based on the membrane data supplied by the membrane manufacturers

Membrane	Permeability (L/m ² h bar)	Stabilized salt rejection		Conditions	
		NaCl (%)	CaCl ₂ (%)	Concentration (ppm)	Pressure (bar)
AFC30	6.8		53	5000	25
AFC40	7.2		40	5000	25
AFC80		80			
AFC99	2.0	99			
NF50	13	35		3500	6
ESNA LF	6.1		80	500	5.2
NF90	10.2	85–95		2000	4.8
NF200	7.6		35–50	500	4.8
BWLE	4.6	99.2		2000	10.3
XLE	7.1	99		500	6.9
BW30	3.2	99.2		2000	15.5

membranes. Cross flow velocities varied between 2 and 3 m/s. Flat sheet membranes (area 38 cm²) were tested in a stirred cell, pressurized by nitrogen at 20°C. Applied pressure was 3 bar for single salt solutions and 4 bar for the mixture. Membrane flux was recorded automatically. All membranes were rinsed with demineralized water for 30 min, after which the salt solutions were permeated through the membrane for 1–8 h depending on the permeability of the membrane.

The anaerobic effluent was permeated through the membranes for 5–6 h at 5 bar under extensive stirring.

3. Results and discussion

3.1. Transport of solutes in NF and RO membrane filtration

Transport and selectivity of NF membranes are mainly but not exclusively determined by two effects: steric/hydrodynamic effects and charge repulsion. The first effect is caused by the relative size of the ions to the membrane pores, the second effect is caused by the charged nature of the membrane and electrolytes (Garcia-Aleman and Dickson, 2004). In case of RO membranes the pore size becomes smaller and diffusion dominates over convection. The solution-diffusion model describes the transport sufficiently well (Wijmans and Baker, 1995).

In case of charged NF membranes Donnan effects frequently contribute or even sometimes dominate the separation performance. When a charged membrane is placed in an ionic solution, an equilibrium occurs between the membrane interface and solution (Schaep et al., 1998). The concentration of the co-ion (with the same charge as the membrane) in the membrane is lower than in solution, because the co-ion is excluded to a certain extent by the membrane (Donnan exclusion). The counter-ion concentration (opposite charge as the fixed membrane charge) is higher in the membrane than in solution.

The electro-chemical (Donnan) potential develops to counteract the transport of counter-ions and co-ions to the membrane phase. During operation the effect of the Donnan potential is then to repel the co-ion and because of electroneutrality requirements the counter-ion is rejected as well and salt retention occurs (Schaep et al., 1998).

By this mechanism salt rejection increases with membrane charge (Mukherjee et al., 2005). By a known salt composition, using the simple Donnan-equilibrium consideration, information can be obtained about the charge of the membrane. The Donnan equilibrium is only valid to describe ion transport between the bulk and the membrane in case of sufficiently high water fluxes (Schaep et al., 1998).

In case of an NF membrane with a negative surface charge the rejection sequence will be $R(1-2, \text{monovalent positive-divalent negative}) > R(1-1, \text{monovalent positive-monovalent negative}) > R(2-1, \text{divalent positive-monovalent negative})$ in case of equivalent salt concentrations. In case of a positive surface area the rejection sequence would be $R(2-1) > R(1-1) > R(1-2)$.

These sequences were found for negatively and positively charged membranes by Peeters (Peeters et al., 1998), using Na₂SO₄ as (1-2 salt), NaCl as (1-1) salt and CaCl₂ as (2-1) salt. A third class of membranes was found that does not follow one of the above-mentioned sequences; in this case the rejection sequence cannot be explained by Donnan exclusion only. In this case influence of sieving and diffusion may play also a role in the separation process.

Information about the membrane charge is important as charge characteristics play a significant role in the transport of water and solute molecules through the membrane. Additionally, the interaction of colloids and charged molecules with the charged membrane plays a role in membrane fouling (Childress and Elimelech, 2000).

3.2. Phosphate and ammonium rejection in single salt solutions

The rejection of phosphate and ammonium in single salt solution was measured to (i) determine the membrane charge and rejection mechanisms and (ii) get an indication of the performance of the tested NF/RO membranes to remove phosphate and ammonium.

3.2.1. Phosphate rejection

In diluted urine phosphate is present and therefore Na₂HPO₄ was used instead of Na₂SO₄ as a (1-2) salt. The measured rejections of Na₂HPO₄, NaCl and CaCl₂ for the tubular membranes (AFC30 and 40) and the flat sheet NF membranes (ESNA LF and NF200) nicely follow the rejection sequence $R(\text{Na}_2\text{HPO}_4) > R(\text{NaCl}) > R(\text{CaCl}_2)$ as can be seen from Table 3 rejections given in bold. These membranes also show the highest water flux and information from Donnan equilibrium can now be obtained, considering the above-mentioned arguments.

The obtained rejection sequence of these membranes is a strong indication that these membranes are negatively charged. The negative charge of NF200 is confirmed by a zeta potential of –16.5 mV measured by Her et al. (2000) and Cho et al. (1998). The rejection sequence for AFC30 and 40 was found previously (Linde and Jönsson, 1995). Based on the salt rejection the ESNA LF is assumed to be negative. This negative charge is confirmed by zeta-potential measurements measured by different authors (Cho et al., 1998; Lee et al., 2004; Park et al., 2005).

Table 3

Rejection of the salts Na_2HPO_4 (0.001 M), NaCl (0.004 M) and CaCl_2 (0.001 M) with a selection of tubular (NF and RO), capillary (NF) and flat sheet (NF and RO) membranes

Type	Membrane	Na_2HPO_4 (%)	NaCl (%)	CaCl_2 (%)	Permeability ($\text{L}/\text{m}^2 \text{ h bar}$)
Tubular NF	AFC30	95	54	20	7
	AFC40	97	40	13	8
Tubular RO	AFC80	94	72	71	3
	AFC99	96	96	99	2
Cap. NF	NF50	74	49	91	13
Flat sheet NF	ESNA LF	98	90	64	7
	NF90	98	87	92	5
	NF200	97	67	16	5
Flat sheet	BWLE	97	83	81	5
RO	XLE	98	93	92	5
	BW30	99	96	95	3

The other NF membranes (AFC80 and NF90) from Table 3 show a less pronounced difference between the CaCl_2 and NaCl rejection. In this case influence of sieving and diffusion may play also a role in the separation process.

A different behavior is found for the NF50 membrane, the membrane with the highest water flux. From this it can be assumed that the transport of solutes mainly takes place by convection. Based on the high rejection of CaCl_2 a positive membrane can be expected, but the rejection of NaCl is lower than the rejection of Na_2HPO_4 , which is not in accordance with the expected rejection sequence of positive membranes. Consequently size effects are also important as HPO_4^{2-} as hydrated ion is bigger than Cl^- . To support this argument, the diffusion coefficients and hydrodynamic radii of the different ions are given in Table 4.

The RO membranes show almost no difference in rejection among the tested salts and show the lowest water fluxes. In this case solute transport takes not place by convection, but by solution-diffusion.

The tested membranes can be divided in 4 groups. The first group consists of the negative membranes where the rejection of salts is dominated by Donnan exclusion (AFC30, AFC40, ESNA LF and NF200). A second group of membranes are the NF90 and AFC80 membranes, where both charge and size effects play a role in the separation of salts. The third group contains the NF50 membrane, which is a rather open membrane where rejection is obtained by positive charge effects and size effects. The RO membranes are the fourth group: separation here occurs by solution-diffusion. Separation of phosphate is obtained by charge effects in case of negative membranes and in other cases size effects will play a roll as well. Urase (Urase et al., 1996) found

Table 4

Diffusion coefficients in water and hydrodynamic radii for several ions

	D ($10^{-9} \text{ m}^2/\text{s}$) ^a	r (nm) ^b
NH_4^+	1.957	0.11
Na^+	1.334	0.16
Ca^{2+}	0.92	0.23
HCO_3^-	1.185	0.18
Cl^-	2.032	0.11
HPO_4^{2-}	0.439	0.49
NO_3^-	1.902	0.11

^aFrom Lide (1995).

^bCalculated with Stokes–Einstein equation (Atkins, 1990), based on given diffusion coefficients.

phosphate rejections above 99% using other NF membranes. The measured water permeabilities are in most cases in agreement with the data given by the manufactures (Table 2).

3.2.2. Ammonium rejection

The ammonium found in diluted black water is formed after the decomposition of urea:

$\text{CO}(\text{NH}_2)_2 + 3 \text{H}_2\text{O} \leftrightarrow 2\text{NH}_4^+ + \text{CO}_2 + 2\text{OH}^-$ (Jönsson et al., 1997).

Under the circumstances given (pH 7–8), HCO_3^- will be formed from CO_2 and OH^- , which will balance the presence of ammonium. In order to show the influence of the presence of HCO_3^- as the counter-ion of ammonium, the rejection of ammonium was measured in solutions of NH_4Cl and NH_4HCO_3 . Furthermore the rejection of NaCl was measured in the same series of experiments; concentration used was 0.01 M.

The separation sequence of these monovalent (1-1) salts cannot be explained by the Donnan theory. In this case, the rejection sequence can be explained by differences in size, which are reflected by the differences in diffusion coefficients (see Table 4). In case of negative membranes the rejection of ammonium and sodium is determined by the negative co-ion. It can be seen that HCO_3^- has a bigger hydrated radius resulting in a lower diffusion coefficient than Cl^- . A higher rejection of NH_4HCO_3 compared to NaCl is expected. When the co-ion (same charge as membrane) is the same as it is the case with NH_4Cl and NaCl , the size of the counter-ion can determine the rejection sequence. In this case it can be seen that $\text{Na}^+ > \text{NH}_4^+$ and a higher rejection of NaCl is expected. Based on these considerations the expected rejection sequence with these three mono-valent salts for negatively charged membranes would be $R(\text{NH}_4\text{HCO}_3) > R(\text{NaCl}) > R(\text{NH}_4\text{Cl})$. Looking at the results in Table 5, AFC30, AFC40, ESNA LF and NF200, clearly follow this sequence, which are also the negative membranes as determined in the previous section rejections given in bold.

The other NF membranes (AFC80 and NF90) follow in principle the same sequence but a less pronounced difference between NH_4HCO_3 and NaCl is found.

The exception is again NF50, the highest rejection is found for NaCl , this can be contributed to the positive membrane charge as in size Na^+ is bigger than NH_4^+ . The rejection of NH_4HCO_3 is almost equal to NH_4Cl .

The RO membranes show almost no difference in rejection among the tested salts as mentioned earlier.

The rejection of ammonium is determined by charge effects in case of negative membranes, as the presence of

HCO_3^- ion as negative co-ion (same charge as membrane) plays an important role. In case of RO membranes the rejection of ammonium is determined by solution-diffusion.

The difference in rejection between ammonium and phosphate for the negatively charged membranes can be explained by the fact that the co-ion hydrogen-phosphate ion (HPO_4^{2-}) is larger than the co-ion bicarbonate ion (HCO_3^-) and the fact that the hydrogen-phosphate ion has a larger negative charge which implies that it is stronger repelled by the negatively charged membrane. In the case that charge plays a less pronounced role, the difference can be explained by differences in the ion diffusion coefficients.

3.3. The removal of phosphate and ammonium in a salt mixture and in the anaerobic effluent

The rejection of ammonium and phosphate might change in the presence of other salts and/or organics. Therefore, ammonium and phosphate rejection was measured in a mixture of salts and in the anaerobic effluent.

3.3.1. Tubular membranes

The removal of ammonium and phosphate was measured in the mixture of salts with the composition shown in Table 1. The results for the tubular membranes are presented in Table 6. The results from this table can be compared with the results from the single salt experiments (Tables 3 and 5). The rejection of phosphate in the mixture hardly changed in comparison with the rejections in the single salt solution.

The rejection of ammonium decreased for all tested tubular membranes when it was measured in a mixture of salts. This can mainly be explained by the higher total salt concentration in the mixture that causes a larger concentration difference over the membrane. The salt flow through the membrane will increase and at equal water flow this results in a lower rejection. A second effect of a higher salt concentration is that the Donnan

Table 5
Rejection of the salts NH_4Cl (0.01 M), NH_4HCO_3 (0.01 M) and NaCl (0.01 M) with a selection of tubular (NF and RO), capillary (NF) and flat sheet (NF and RO) membranes

Type	Membrane	NH_4HCO_3 (%)	NaCl (%)	NH_4Cl (%)
Tubular NF	AFC30	79^a	54^b	45
	AFC40	72^a	40^b	31
Tubular RO	AFC80	77	72 ^b	46
	AFC99	87	96 ^b	98
Cap. NF	NF50	29	49	21
Flat sheet NF	ESNA LF	92	89	48
	NF90	92	90	54
	NF200	87	65	54
Flat sheet RO	BWLE	94	91	90
	XLE	92	90	90
	BW30	94	95	94

^a NH_4HCO_3 concentration: 0.006 M.

^b NaCl concentration: 0.005 M.

Table 6
Measured rejections (as ions) of ammonium and phosphate in the mixture of salts with tubular NF and RO membranes

	Ammonium mix	Phosphate mix
<i>NF</i>		
AFC30	43	N/A ^a
AFC40	39	N/A ^a
<i>RO</i>		
AFC80	53	99
AFC	99	96

^aBelow detection limits.

Table 7

Measured rejections (as ions) of ammonium and phosphate in the mixture of salts and in the anaerobic effluent with flat sheet NF and RO membranes

Membrane	Ammonium		Phosphate	
	Mixture	Anaerobic effluent	Mixture	Anaerobic effluent
ESNA LF	86	82	94	94
NF90	89	90	91	98
NF200	73	61	96	98
BWLE	86	90	91	98
XLE	93	93	93	98
BW30	29	93	92	98

exclusion becomes less effective, which results in a higher concentration of the co-ion in the membrane and a lower rejection.

3.3.2. Flat sheet NF and RO membranes

The effect of fouling on the rejection of ammonium and phosphate was measured with an anaerobic effluent as the feed solution. Due to practical reasons the tests were performed with the flat sheet membranes only. The rejections of ammonium and phosphate measured in the salt mixture and the anaerobic effluent are shown in Table 7. Samples were taken from the total amount of permeate that was produced; this was also done in the experiments with the salt mixtures. Comparing these results with the earlier obtained results it can be seen that only the ammonium rejection (as NH_4HCO_3) decreased using the NF 200 membrane. The rejection of ammonium decreased from 73% in the salt mixture till 61% in the anaerobic effluent. This decrease might be explained by the higher salt concentration and the effect of fouling.

For the other membranes no distinct differences in ammonium and phosphate rejection are found between the single salt solution, the mixture and the anaerobic effluent. Despite the decrease in flux (Fig. 2A, B) for most of the membranes the rejection did not change. It should be noted that these experiments were conducted for only 5 h and that it is difficult to predict the long-term performance. The decrease in flux was measured during the experiment; J_0 is the flux at the beginning of the experiment with anaerobic effluent. The decrease in flux was calculated by dividing the flux at $t = t$ by the flux at time $t = 0$.

In general, it can be said that the rejection of ammonium and phosphate with the flat sheet NF and RO membranes did not change significantly in the different mixtures, but that a flux decrease was found during the filtration of the anaerobic effluent. This

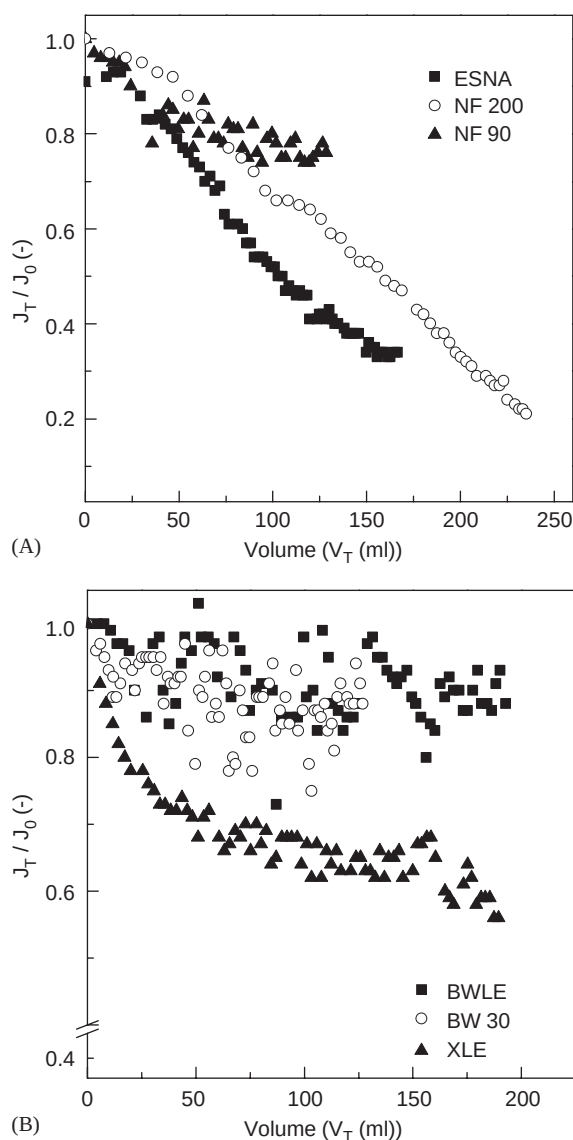


Fig. 2. Relative flux decline (J_T/J_0) observed during the filtration of anaerobic effluent with (A) NF membranes and (B) RO membranes.

implies that in practice more membrane area is required to treat a certain volume.

The rejection of ammonium (80–90%) and phosphate is substantial (>90%) for most of the tested membranes. Question is, whether these obtained rejections are sufficient to meet any set quality guideline for water reuse or water discharge. Based on the measured ammonium and phosphate rejections in the mixture of salts and the anaerobic effluent, an average permeate concentration can be estimated with the process parameters and Eq. (1) given in Section 2.3. The results

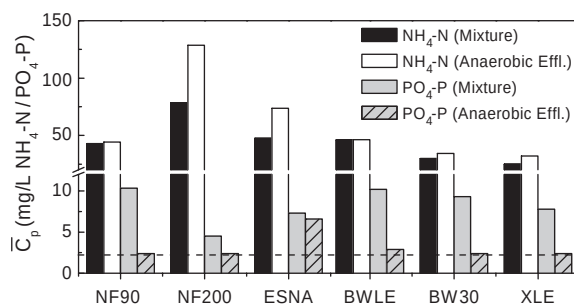


Fig. 3. Calculated (Eq. (1)) average permeate concentrations based on rejection measurements in the salt mixture and anaerobic effluent for ammonium (C_f 194 mg/L $\text{NH}_4\text{-N}$) and phosphate (C_f 47 mg/L $\text{PO}_4\text{-P}$) with flat sheet NF and RO membranes. (---: Discharge guideline for total-N and the potable water guideline for phosphate.)

for the flat sheet NF and RO membranes are shown in Fig. 3.

The results in Fig. 3 show that the removal of phosphate with NF and RO membranes is almost sufficient to meet the potable water guidelines for phosphate.

The higher feed concentrations and the lower rejections of ammonium make it difficult to meet the guidelines for nitrogen discharge as can be seen from the same figure.

A single NF or RO membrane filtration unit does not remove ammonium sufficiently to meet the guidelines; a possible solution is to put a number of units in series. In this case, the permeate of the first unit is the feed for the second unit etc. It can be calculated that at least three RO units with rejections $>94\%$ are necessary to meet the discharge guideline of total-nitrogen. However, this results in a complicated system with a low recovery that is not desirable within decentralized sanitation. A higher recovery can be obtained by a system in which two membrane units are used and the concentrate of the second unit is returned to the feed of the first unit as is presented by Bruggen et al. (2001). However, the calculated average permeate concentration will be too high to meet any guideline. Furthermore within DESAR, only small volumes of wastewater, in this case black water, will be treated. Van der Bruggen calculated that low feed flows results in exceptional high prices (Bruggen et al., 2001). A reasonable price of 0.2 Euro/ m^3 of treated water is obtained treating more than 1000 m^3/h . To produce this amount of black water 600,000 persons (1000 m^3/h divided by $1.67 \times 10^{-3} \text{ m}^3/\text{h}$ ($= 40 \text{ L/person/day}$)) are necessary which is not the amount of persons meant for DESAR concepts.

Consequently, the possibilities for reuse of black water are limited by the high feed concentration of ammonium. In theory it is possible to reduce the

Table 8

Measured rejection (as total salt) of KNO_3 (0.004 M) and the calculated C_p concentration, based on Eq. (1) and with a C_f of 250 mg/L $\text{NO}_3\text{-N}$

	R (%)	C_p (mg/L)
<i>NF</i>		
ESNA LF	82	73
NF90	63	123
NF200	49	149
<i>RO</i>		
BWLE	69	110
XLE	78	86
BW30	84	66

ammonium concentration by per example an aerobic treatment step. In this case the ammonium will be converted into nitrate, which implies conservation of the nutrient nitrogen. Advantageous is also the fact that the potable guideline for nitrate (25–50 mg/L) is less stringent than the guideline for ammonium (0.2 mg/L).

In order to test the effluent from aerobically treated black water the rejection of nitrate as KNO_3 was measured in a single salt solution with the flat sheet NF and RO membranes. The results (Table 8) are presented as the measured rejection and the calculated average permeate concentration based on Eq. (1) of nitrate.

The average permeate concentration for nitrate is calculated with a feed concentration of 194 mg $\text{NO}_3\text{-N/L}$ as total-N, assuming a total conversion of $\text{NH}_4\text{-N}$ in $\text{NO}_3\text{-N}$.

Notable is the lower rejection of nitrate compared with the ammonium rejection measured with the same membranes given in Table 8. In case of negatively charged membranes (the NF membranes) this difference can be explained by the fact that the co-ion nitrate is smaller than the co-ion bicarbonate. These size effects might also play a role in the rejection differences between ammonium and nitrate of the RO membranes. Furthermore, it can be seen that the obtained rejection in single salt solutions is not sufficient to meet the guideline for nitrate in potable water.

An option to increase the possibility for water reuse is to decrease the amount of ammonium or nitrate in the feed water. This can either be done by a biological process in which the ammonium is converted into elemental nitrogen or physical–chemical processes like precipitation or ion exchange. The reduction of ammonium by one of these techniques provides an opportunity to reuse the black water by removing the remaining ammonium with NF or RO membranes. Other reuse possibilities for the treated black water are as flush water for the toilets or as irrigation water, but no clear

guidelines are yet available. It can be expected that these guidelines will be focused on the microbial quality of the water; in this case NF and RO membranes are an absolute barrier for bacteria and viruses and reuse of black water will be possible.

4. Conclusions

The aim of this paper was to look at the possibility of water reuse for black water. In this paper anaerobic treatment of black water is assumed. After this treatment the major part of the nutrients like ammonium and phosphate will remain in the effluent. The guidelines for reuse (as potable water) are rather stringent for ammonium (0.2 mg/L) while they are less stringent for phosphate (2.0 mg/L). In case reuse is not possible the produced water should meet the guidelines for discharge, which are very stringent for phosphate (0.15 mg/L) and less stringent for ammonium (2.0 mg/L).

The removal of ammonium and phosphate was tested with NF and RO membranes in three different types of solutions. The results in the single salt solutions showed that the rejection sequence of Na_2HPO_4 , NaCl and CaCl_2 can be used to determine the surface charge of the NF and RO membranes. The presence of the relative large bicarbonate as the counter-ion of ammonium plays an important role in the rejection of ammonium in single salt solutions. Results showed rejections for ammonium between 80% and 90% and phosphate above 90%. The results within the salt mixture and anaerobic effluent showed that the guideline for water reuse as potable water regarding phosphate is almost met. This is not the case for ammonium.

A possible conversion of ammonium to nitrate is not a solution as was shown by the test results with flat sheet NF and RO membranes. Further research will be focused on the reduction of ammonium by complete conversion of ammonium into elemental nitrogen in a biological process or physical-chemical techniques such as ion-exchange and precipitation to make reuse of black water possible.

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