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MICROFILTRATION/ULTRAFILTRATION OF STORED URINE AND URINE DILUTED WITH WATER

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This thesis is submitted in fulfilment of the requirements of Masters of Science degree in Chemical Engineering, in the Faculty of Engineering at the University of KwaZulu-Natal, South Africa

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DECLARATION

I, J.A Ouma, declare that

- The research reported in this thesis, except where otherwise indicated, and is my original work.
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Co-Supervisor: Dr. Santiago Septien: Signature: ……..

ABSTRACT

Sanitation is a major challenge for developing countries. According to World Health Organization (WHO) and United Nations International Emergency Children's Fund (UNICEF), approximately 2.5 billion people in developing countries lack access to proper sanitation facilities (WHO and UNICEF (2013). This has led to the spread of water borne diseases and reduction of the quality of life of the affected people. The "Reinvent the Toilet Challenge" (RTTC) which is an initiative of the Bill & Melinda Gates Foundation aims is to setup novel sanitation systems and find a hygienic and sustainable disposal route for human waste. Membrane technology such as microfiltration/ultrafiltration, nanofiltration, reverse osmosis and forward osmosis can be used for this purpose.

The main objective of this study was to explore the use of microfiltration/Ultrafiltration membranes to determine the parameters that affect the performance of the membranes when filtering two types of urine: stored urine representing the stored feedstock which could be obtained from Urine Diversion Dry Toilets (UDDT); diluted stored urine representing the feedstock which could be obtained from urinals. This was based on the study of flux, permeability, fouling potential and rejection. This study was limited to stored urine which is more stable than fresh urine.

A stirred Amicon® cell in dead-end filtration mode was used in a range of constant transmembrane pressures (TMP) between 10 and 60 kPa. All the membranes used in this study were similar with the same material and molecular weight cut off (MWCO) of 500 kilo Daltons (kDa). Permeability of the membrane before and after filtration, and after cleaning was determined by measuring flux against transmembrane pressure using deionised water. Fouling potential was determined using the modified fouling index (MFI). Physico-chemical characteristics, including particle size distribution analysis, of diluted and undiluted urine before and after filtration were also determined for the purpose of determining membrane rejection. Three cases were studied during these experiments. Case 1 and case 2 involved filtration of undiluted urine while case 3 using diluted urine (at 1:5 ratio of urine to water). For case 1, the experiment was set to start from low to high transmembrane pressure while in the opposite direction for case 2. Case 3 pressure was operated in a similar manner as case 1.

The results indicated that diluted urine had flux significantly higher than undiluted urine with maximum values of 43 and 26 $L.m^{-2}.h^{-1}$ respectively. Water recovery after a filtration duration of one hour was approximately 40% and 20% for diluted urine and undiluted urine respectively. Permeability of the membranes was lowered significantly, after filtration up to 95%. After cleaning, approximately 80% of permeability was recovered for case 1 and case 3 while approximately 40% was recovered for case 2. Higher membrane resistance due to the cake and irreversible fouling were observed for case 2 (up to 50% higher) compared to case 1 and case 3. It was speculated that particulate matter (larger than 0.1 µm) and colloidal organic matter were the important foulants. According to the modified fouling index, undiluted urine had a higher fouling potential (volume flowrate of 0.089 $L.h^{-1}$) compared to diluted urine (volume flowrate 0.16 $L.h^{-1}$). As expected, the specific cake resistance was lower for undiluted urine compared to diluted urine The permeate obtained after urine microfiltration/ultrafiltration was much less loaded in suspended solids compared to the feedstock, but the concentration of the ionic species remained similar.

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LIST OF ABBREVIATIONS

BMGF	Bill & Melinda Gates Foundation
COD	Chemical oxygen demand
DI	De-ionised
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
PRG	Pollution Research Group
PSD	Particle size distribution
RTTC	Reinvent the Toilet Challenge
TMP	Transmembrane pressure
TS	Total solids
TSS	Total suspended solids
RO	Reverse osmosis
SEM	Scanning Electron microscope
UF	Ultrafiltration
XRD	X-ray diffraction

NOMENCLATURE

CWF	Clean water flux ($L.m^{-2}.h^{-1}$)
C_s	Concentration of accumulated foulants on the membrane surface [$mg.L^{-1}$]
EC	Electrical conductivity [$mScm^{-1}$]
J_p	Permeate flux [$L.m^{-2}.h^{-1}$]
L_p	Membrane permeability [$L.m^{-2}.h^{-1}.kPa^{-1}$]
L_{po}	Initial membrane permeability [$L.m^{-2}.h^{-1}.kPa^{-1}$]
MFI	Modified Fouling Index [$s.l^{-2}$ or $s.m^{-6}$]
R_C	Cake resistance [m^{-1}]
R_f	Fouling resistance [m^{-1}]
R_m	Initial membrane resistance [m^{-1}]
R_t	Total membrane resistance [m^{-1}]
s	Membrane surface area [m^2]
t	Filtration time [s]
T	Temperature [℃]
TMP	Transmembrane pressure
v	Total filtered volume [m^3]
α	Specific cake resistance [m/kg]
μ	Permeate viscosity [Pa.s]
μ_{20}	Permeate viscosity at 20℃ [Pa.s]
$\mu_{(Texp)}$	Permeate viscosity at experimental temperature [Pa.s]
δ_c	Cake thickness [mm]
ε_c	Void fraction of the cake [-]
S_c	Cake surface area per unit mass of solids in the cake [$m^2.kg^{-1}$]

1. INTRODUCTION

This section describes the background, the problem statement, aim and objectives of the study and the significance of the research.

1.1. Background

There are a number of sanitation research programmes funded by the Bill & Melinda Gates Foundation (BMGF) and one of them is the 'Reinvent the Toilet Challenge (RTTC)'. RTTC was launched in the context of millennium development goals (Elledge and McClatchey, 2013). The main objective of this program is to develop a new toilet technology for processing human waste that: is not linked to water, energy, or sewer lines; removes pathogens from human waste and recovers valuable resources such as energy, clean water, and nutrients for agriculture; it should operate at costs affordable in the poor zones in developing countries (Bill & Melinda Gates Foundation, 2011)

The Pollution Research Group (PRG), from the University of KwaZulu-Natal (UKZN), has been granted in the RTTC for a project called "Data acquisition and field support for sanitation projects", aiming to obtain experimental data of a range of excreta streams and undertake treatment process investigations on selected excreta streams. The data will be distributed to the other grantees from the RTTC to support their prototypes design and help them meet their projects criteria.

Human waste (urine and faeces) can be separated at the source using urine diverting dehydration toilets (UDDT). Such type of toilet facility operates without water and has a divider so that the user, with little effort, can divert the urine away from faeces (Kvarnström et al., 2006, Tilley et al., 2008) These kinds of toilets are able to solve problems encountered by other sanitation systems. These include fly breeding, bad smell, ground water contamination, short pit life and pit collapse (Peasey, 2000, Vinnerås, 2001). Depending on the collection and storage/treatment technology that follows, drying material such as lime, ash or earth should be added into the same hole after defecating (Tilley et al., 2008).

Wilsenach and Van Loosdrecht (2003), Maurer et al. (2006) and Vinnerås et al. (2008) suggested that separating urine at the source could contribute significantly to wastewater management and decrease the energy requirement for wastewater treatment. According to Ek et al. (2006), Pronk (2009) and Wang and Qiu (2013), source separation of urine allows collection of nutrients such as potassium, phosphorous and nitrogen which are valuable for agriculture and used for crop production, consequently fighting poverty.

Urine is made up of water up to 95% and can offer an alternative source of water that leads to reduced competition to domestic water (Triger et al., 2012). Such an alternative source can be re-used if subjected to proper treatment where pollutants should be reduced to acceptable levels. One of the methods to achieve this is through membrane filtration processes such as microfiltration, nanofiltration, ultrafiltration, reverse osmosis and forward osmosis (Ek et al., 2006, Fane et al., 2011). Apart from the potential of reuse of water, urine and diluted urine that have undergone membrane filtration can contribute significantly to wastewater management.

1.2. Problem statement

Stored urine contains high amounts of solids, COD, nitrogen mainly in the form of ammonia, phosphorous, potassium, and chloride. In addition, a variety of microorganisms, which may include pathogens, may also grow in source-separated urine, as the content of biodegradable organic compounds is very high (Udert et al., 2006). Degradation of organic matter and ammonia evaporation cause odours and negative effects in the environment (Troccaz et al., 2013). For these reasons, urine treatment is necessary to reduce water pollution through urine discharge in the environment and to produce fertiliser and /or clean water for reuse.

Several methods of treating source separated urine were outlined by Maurer et al. (2006) and each method depends on the objectives to be met. The methods include: (i) proper storage for disinfection, (ii) acidification and nitrification for stabilization, (iii) evaporation and struvite precipitation for nutrient recycling, (iv) anaerobic ammonium oxidation (anammox) for nutrient elimination to avoid eutrophication discharge of nutrients in surface water, (v) ozonation, nanofiltration and electro dialysis for micro pollutant removal. However, except for storage and evaporation, none of the methods have so far advanced beyond laboratory stage (Maurer et al., 2006). According to Peasey (2000) and Vinnerås et al. (2008), storage by itself does not guarantee elimination of the pathogens and vibrio, such as rotavirus and vibrio cholera which are prevalent in tropical conditions. According to Udert et al. (2006), urine treatment is also necessary in order to prevent the pollution of the environment with micropollutants.

Among the different urine processing technologies, membrane filtration is a promising option because of its affordable cost and relatively simple for operation and maintenance (Ho and Sirkar, 1992, Leslie and Bradford-Hartke, 2013). Microfiltration (MF) and ultrafiltration (UF) membranes are good option to deal with the removal of micropollutants and viruses because of their high rejections of organic compounds and microorganisms (Van der Roest et al., 2002, Baker, 2012, Triger et al., 2012, Leslie and Bradford-Hartke, 2013). These components are usually larger than the pore size of the membranes, accordingly their retention is favoured. It has been demonstrated that MF/ UF is suitable for the treatment of domestic wastewater as the effluent quality can satisfy the requirement for wastewater reuse such as toilet flushing and irrigation (Dama et al., 2002, Udert et al., 2003, Adams, 2012, Leslie and Bradford-Hartke, 2013). It is also a suitable pre-treatment for nanofiltration and reverse osmosis. However, it has not been widely tested on urine.

The loss of flux/permeability due to fouling is one of the main constant problems of using MF/UF membranes, which has to be limited during filtration (Judd, 2006). Fouling also reduces the life span of membranes. It should thus be minimised by determining the best operating conditions of the membranes.

1.3. Aims and objectives of the project

The overall aim of this research was to use pressure driven MF/UF membranes to determine the parameters that affect the performance of the membranes in terms of flux, permeability, fouling potential and rejection while filtering stored urine and urine diluted with flush water in dead-end mode.

The specific objectives were:

- The determination of flux at a different transmembrane pressures (TMP) in the range of 10 - 60 (kPa) during the filtration of undiluted and diluted stored urine. This pressure range was selected according to the manufacturer's specification that the maximum pressure for the membranes is 69 kPa;
- The determination of permeability (volume / area / unit pressure / time) of virgin membrane, after filtration and after being cleaned;
- Exploration of membrane fouling potential from urine feedstock;
- Comparison of the characteristics of the feedstock and the filtrate, and determination of membrane rejections. This study focused on the following characteristics: Chemical Oxygen Demand, Total suspended solids, Total solids, Particle size distribution, Phosphates, Chloride, Electrical conductivity and pH.

1.4. Significance of research

The data obtained will provide a broad guidance for the use of MF/UF membranes to filter stored urine from urine diversion toilets (undiluted urine) and urinals (diluted urine). MF/UF is an important step in concentration of nutrients and recovery of water from stored urine. This is because these membranes are economical and efficient in operation thus they could be used as pre-treatment for further applications (reverse osmosis and nanofiltration) and could also lead to direct use of the permeate.

1.5. Outline of thesis

Chapter 1 presents the background, aims and objectives as well as significance of this study

Chapter 2 critically reviews literature of stored urine and microfiltration/ultrafiltration membranes and gives the state-of- the-art in urine treatment using membranes

Chapter 3 provides details of the materials and methodology used to achieve the objectives of this study

Chapter 4 presents the results of the flux, permeability, membrane hydraulic resistance, fouling potential and physico-chemical analysis and discusses them in details.

Chapter 5 discusses the conclusions of the findings of using MF/UF membranes for treating stored urine and diluted urine.

Chapter 6 gives the outlook for further research in the field of treating stored urine using MF/UF membranes.

2. LITERATURE REVIEW

This literature review focuses on the description of human urine, fresh and stored; cake formation issues during membrane filtration, pressure driven membranes, specifically MF/UF membranes, and their characteristics.

2.1. Fresh urine and stored urine

Human urine is a liquid waste product of the human body, typically yellow in colour, secreted by the kidneys, stored in the bladder and discharged through the urethra (Karak and Bhattacharyya, 2011). Fresh urine refers to urine that has been recently released by a person and has not been hydrolysed (Tilley et al., 2008). According to Pronk (2009), non-hydrolysed urine contains nitrogen in the form of urea, which is not volatile. On the other hand, stored urine is urine that has been hydrolysed naturally over time (Tilley et al., 2008). During storage, urine composition rapidly evolves due to hydrolysis of urea into ammonia and carbon dioxide (Triger et al., 2012, Udert and Wächter, 2012). Urea hydrolysis makes source-separated urine an unstable solution, because ammonia is easily lost by volatilization.

The hydrolysis reaction is as shown in Equation 2-1 (Udert et al., 2003).

$$CO(NH_2)_2 + 2H_2O \rightarrow NH_3 + NH_4^+ + HCO_3^- \qquad \textit{Equation 2-1}$$

Ammonium can turn into gaseous ammonia as seen in Equation 2-2 and Equation 2-3.

$$NH_4^+ + OH^- \leftrightarrow NH_{3(aq)} + H_2O \qquad \textit{Equation 2-2}$$

Dissolved ammonia is in equilibrium with gaseous ammonia according to Equation 2-3.

$$NH_{3(aq)} \leftrightarrow NH_{3(g)} \qquad \textit{Equation 2-3}$$

The comparison in physical and chemical characteristics between fresh and stored urine is shown in Table 2-1.

Table 2-1: Typical chemical characteristics of fresh and stored urine (Udert et al., 2003, Maurer et al., 2006, Pronk et al., 2007a, Von Münch 2009, Etter et al., 2011)

Parameter	Units	Fresh urine	Stored urine
pH		5.5-6.2	8.6-9.1
Total nitrogen	$mg.L^{-1}$	8 830	1 795-9 200
Ammonia/Ammonium NH_4^+ / NH_3	$mg.L^{-1}$	254-463	2 540-8 100
Nitrate/Nitrite NO_3^-+NO_2^-	$mg.L^{-1}$	0.06	0
COD	$mg.L^{-1}$	6 000-10 000	1 650 – 5 200
Potassium, K	$mg.L^{-1}$	1 870-2 737	1980-2 200
Total, P	$mg.L^{-1}$	800-2 000	197-540
Sodium, Na	$mg.L^{-1}$	2 670-3 450	1 900-2 600
Magnesium, Mg	$mg.L^{-1}$	45.4-119	0- <5
Chloride, Cl	$mg.L^{-1}$	6 620-4 970	2 000-3 800
Calcium, Ca	$mg.L^{-1}$	129-233	0- <5
Electrical conductivity, EC	$mS.cm^{-1}$	15.28-22.6	25.0-28.76

Fresh urine is a highly concentrated solution containing about 80% of the excreted nitrogen which is much more than other nutrients (potassium and phosphorous) in the urine (Friedler et al., 2013). Before hydrolysis ammonia concentration is 463 $mgN.L^{-1}$. However, after hydrolysis, 90% of the total nitrogen is turned into ammonia (approx. 8 000 $mgN \cdot L^{-1}$) (Udert et al., 2006).

The main differences between fresh and stored urine are the urea content and the pH. Fresh urine contains urea that is hydrolysed to ammonia and carbon dioxide with time, hence it is significantly reduced or absent in stored urine. Stored urine has also a higher pH than fresh urine due to the conversion of urea into ammonia which leads to the formation of OH^-. Furthermore, in fresh urine, long-chain organic acids, creatinine, amino acids and carbohydrates are the main organic compounds (Ronteltap et al., 2010). In stored urine, most of these compounds are already broken down by fermentation.

Compounds such as magnesium and calcium are not found in stored urine although they are available in fresh urine probably because they are precipitated out with time. Nitrates and nitrites are neither available in fresh nor stored urine because they are in the form of ammonia. COD level is lower after storage compared to fresh urine probably due to degradation. Electrical conductivity of stored urine is higher than that of fresh urine because storage increases the electrolyte composition of urine.

2.2. Concepts of membrane filtration

Filtration is defined as the separation of two or more components from a fluid stream based primarily on size differences (Cheryan, 1998). A membrane is a material that allows some components to pass through it more readily than others (Judd, 2006). Membrane filtration is a process used in the water industry to improve the quality of water for use, reuse, or discharge to the environment (Fane et al., 2011). Membranes range from finely porous structures to nonporous, and can remove contaminants such as bacteria and protozoa down to ions.

2.2.1 Pressure driven membranes

Pressure driven membranes are divided into four main types based on their pore size: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) with decreasing pore size respectively. A microfiltration filter has a pore size in the order of 0.1 µm, so during filtration of wastewater, microorganisms and large particles of 0.1 to 10 µm are removed, but viruses remain in the filtrate (Mukiibi and Feathers, 2009). Ultrafiltration uses a finely porous membrane in the order of 0.01 µm to separate water and micro-solutes from macromolecules. An ultrafiltration membrane would be able to remove most of the particles, macromolecules and some viruses (Fane et al., 2011, Baker, 2012). Nanofiltration membrane can reject molecules with minimum size between 1 to 10 nm such that all particles and viruses cannot pass (Koyuncu and Cakmakci, 2010). NF membranes also remove divalent ions. Reverse osmosis is the filtration processes in which the permeate is virtually free of solids and solutes (Leslie and Bradford-Hartke, 2013). After a solution passes through a reverse osmosis filter, it is essentially pure water. In addition to organic molecules and viruses, reverse osmosis also removes most minerals which are present in the water except dissolved gases and some monovalent ions.

One of the major problems in pressure-driven membrane processes is the reduction of the flux during the operation of the membrane. Membrane fouling is one of the main phenomena responsible for this (Field, 1995, Listiarini et al., 2009). Nevertheless, membranes offer many advantages over conventional solid-liquid separation techniques. The technology is very compact, does not rely on gravity separation and provides consistent product quality over a range of pollutant loading rates (Leslie and Bradford-Hartke, 2013). During MF and UF, all ions can pass through the membrane, so no ionic species accumulation in any side occurs and therefore the osmotic pressure is caused by colloids since osmotic pressure is a colligative property. (Adams, 2012, Leslie and Bradford-Hartke, 2013). On the other hand, during NF and Forward osmosis (FO), the osmotic pressure is mainly caused by salts that are accumulated on the retentate side, leading to the increase of the osmotic pressure on this side with respect to the other one. Osmotic pressure is the pressure difference between the solutions on either side of the membrane that is opposed to the flow of the feed

The differences in membrane filtration in terms of pore size, operating pressures and contaminant removal are summarised in Table 2-2. These membranes have different rejection mechanisms. Microfiltration and ultrafiltration have similar mechanism of separation which is based on molecular sieving through fine pores (Baker, 2012). NF membranes use electrical repulsions as a separation mechanism (Muro et al., 2012). On the other hand, RO uses a mechanism of solution-diffusion. According to this theory, solutes permeate the membrane by dissolving in the membrane material and diffusing down a concentration gradient. Separation occurs because of the solubility and mobility differences of the solutes in the membrane (Ho and Sirkar, 1992, Baker, 2012).Thus in RO process, the water is very soluble and mobile in the membrane compared to the solute.

The Molecular Weight Cut off (MWCO) is defined as the lower limit of a solute molecular weight for which the rejection is 95-98% (Boerlage et al., 2003). In theory, compounds having a molecular weight greater than MWCO of the membrane will be retained by the membrane while compounds with molecular weight less than the MWCO will pass the membrane as a permeate (Muro et al., 2012). However, this assumes that the pores of the membrane are mono sized. In practice there is a pore size distribution, thus there will be a range of rejections. MWCO in respect to the type of membrane is shown in Figure 2-1.

Table 2-2: Pressure-driven membrane processes (Xin, 2004, Thor and Fløgstad, 2006, Muro et al., 2012)

Process	Operating Pressure (kPa)	Pore size range (µm)	Specific retained solutes	Removal Efficiency
MF	50-200	0.1-1.0	Bacteria, fat, oil, grease, colloids, organic microparticles	80-90%
UF	200-500	0.01-0.1	Proteins, pigments, oils, sugar, organic microparticles	90%
NF	1 000-2 000	0.001-0.01	Pigments, sulfates, divalent cations and anions, sodium chloride	100%
RO	5 000-6 000	<0.001	Salts, sodium chloride and inorganic ions	100%

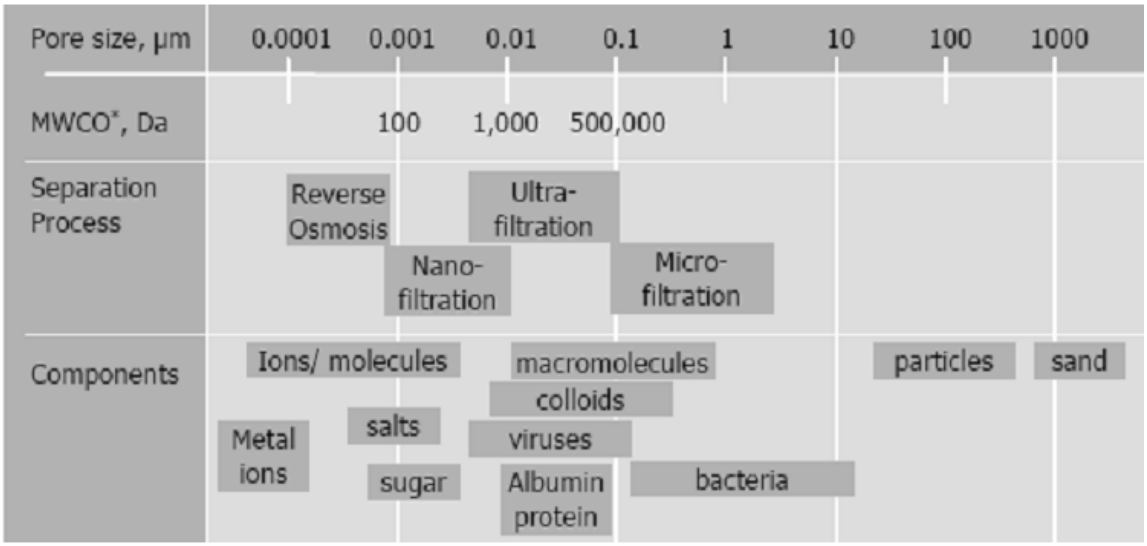


Figure 2-1: Classification of pressure driven membrane processes in terms of Molecular Weight Cut-off (Pillay, 2011)

2.2.2 Membrane fouling

Fouling consists in the build-up of material (foulants, such as adsorbed macromolecules, gels, or deposited particles) on the membrane surface or within the material. The foulants remain trapped on the membrane and do not diffuse back to the bulk stream. Fouling can originate from a physical and/or chemical phenomena(Ho and Sirkar, 1992, Zhao, 2000). The properties of foulants and their interactions with the membrane determine the fouling and cleaning process (Al-Amoudi and Lovitt, 2007).

According to Zhao (2000) , Judd (2006) and Ramaswamy et al. (2013) fouling occurs because of various reasons such as :

(1) Formation of a dynamic surface layer of filter cake on the active side of the membrane, by accumulation of the rejected particles.

(2) Fouling within the membrane structure due the adsorption of foulants.

(3) Fouling by pore blocking. The deposition of materials on the surface of the membrane can obstruct the pore entrance.

Judd (2006) classified these mechanisms as: complete blocking, standard blocking, intermediate blocking and cake filtration, shown in Figure 2-2 below.

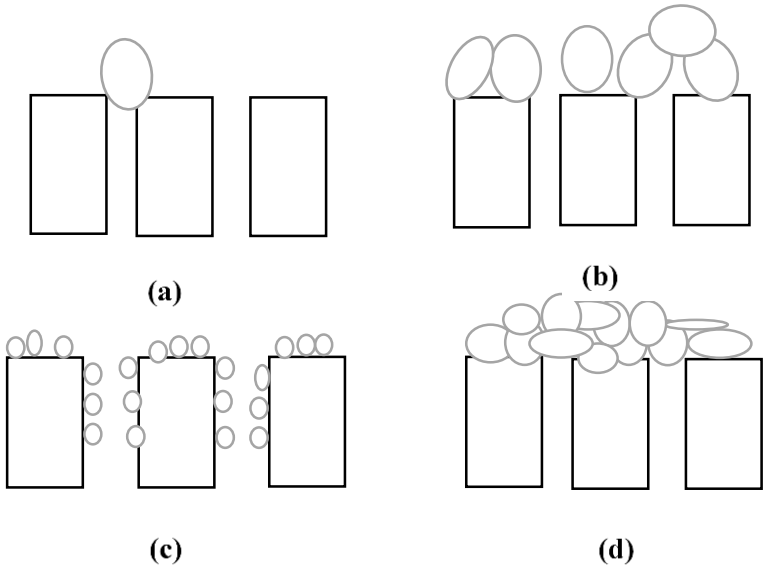


Figure 2-2: Types of fouling : (a) complete blocking, (b) standard blocking, (c) intermediate blocking (adsorption) and (d) cake filtration (Judd, 2006)

Cake formation and pore blocking can occur if the solute molecules are large enough to be retained by the membrane while adsorption can occur if the solute molecules are small enough to access inside pores of the membrane where they are adsorbed on the wall. The fouling phenomena changes the effective pore size distribution of the membrane (Field, 1995). The loss of effective membrane surface porosity is dependent upon the size of the depositing molecules and the pore size.

Membrane fouling can be broadly categorised into reversible and irreversible phenomena. Reversible fouling is caused by the cake formation layer which is readily removed from the membrane by physical and/or chemical cleaning. On the other hand, internal fouling, caused by adsorption of matter within the membrane, and pore blocking are considered irreversible as they cannot be removed by conventional cleaning methods (Madaeni et al., 1999).

Membrane materials also influence fouling. In general, hydrophobic membranes (polysulfide, polypropylene, and polytetrafluoroethylene) have a greater fouling tendency to natural organic matter than hydrophilic membranes (cellulose acetate, polyacrylonitrile, polyethersulphone). The disadvantages of hydrophilic membranes is that they are less thermally and chemical resistant (Ramaswamy et al., 2013).

Techniques to reduce fouling depend on the type of foulants. Cake formation can be reduced by operating below the critical flux/pressure (which is the flux at which an increase in pressure does not result in an increase in flux but rather remains constant or declines) and back pulsing (flushing the cake off the membrane surface using water). Pore blocking can be reduced by using a membrane with smaller pores and adsorption by using hydrophilic membranes (Ramaswamy et al., 2013).

In general, the occurrence of fouling affects the performance of the membrane as it prolongs the time for processing, increases the energy and cleaning costs, decreases separation efficiency, and, may lead to irreversible clogging and replacement of the membrane in the long term (Madaeni et al., 1999, Adams, 2012)

2.2.3 Flux and membrane resistances

Flux is used to describe the volumetric flow of a liquid through a defined surface area of membrane (Judd, 2006). Membrane resistance physically means the resistance to the water flow through the membrane. The filtration flux resistance through a uniform membrane surface can be described by the general form of Darcy's law (Ping Chu and Li, 2005), as seen in Equation 2-4.

$$J_P = \frac{\Delta p}{\mu(R_m + R_f + R_c)}$$ *Equation 2-4*

Where:

Jp Permeate flux [L.m^{-2}.h^{-1}]

Δp TMP [kPa]

μ Viscosity of water [Pa.s]

R_m Initial membrane resistance [m^{-1}]

R_f Membrane resistance due to fouling [m^{-1}]

R_c Membrane resistance due to cake layer formation [m^{-1}]

The total resistance, R_t, on the surface of the membrane is given by Equation 2-5.

$$R_t = R_m + R_f + R_c$$ *Equation 2-5*

Flux can change as a function of temperature because of the viscosity dependence to temperature. Usually authors correct the flux at 20°C, which is the reference value used in literature to normalize their results (Judd, 2010, Pillay, 2011), as shown in Equation 2-6.

$$J_{20} = \frac{J_T}{1.024^{(T-20)}}$$ *Equation 2-6*

Where:

J_{20} Flux corrected to 20 °C [L.m^{-2}.h^{-1}]

J_T Flux at the experimental temperature [L.m^{-2}.h^{-1}]

T Experimental temperature [◦C]

2.2.3.1 Initial membrane resistance

R_m is the intrinsic hydraulic resistance of the membrane. In the case of flux of pure water across the membrane, R_f and R_c are equal to zero, therefore, Equation 2-4 can be written as Equation 2-7.

$$Jp = \frac{\Delta p}{\mu(R_m)}$$ *Equation 2-7*

As demonstrated by Ping Chu and Li (2005), R_m can be determined by performing a clean water flux profile on a clean membrane, i.e. measuring the flux at different TMP. The slope of the plot flux versus TMP gives the initial membrane permeability as shown in Figure 2-3. Thus, R_m is calculated using Equation 2-8.

$$Lpo = \frac{1}{\mu \cdot Rm}$$ *Equation 2-8*

Where:

Lpo Initial membrane permeability [L.m^{-2}.h^{-1}.kPa^{-1}]

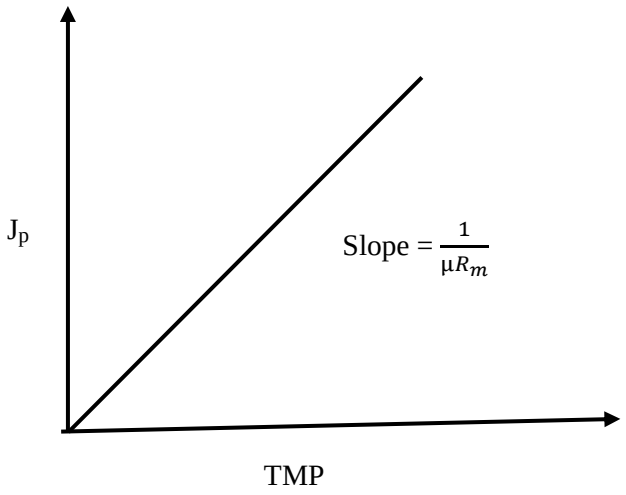


Figure 2-3: Plot of flux versus transmembrane pressure for the determination of permeability

2.2.3.2 Fouling resistance

The membrane resistance due to irreversible fouling, R_f, is caused by solute adsorption onto the membrane pores and walls (Drioli and Giorno, 2010). Fouling resistance can be calculated through the experimental methodology proposed by Pillay (2011). The water flux across the fouled membrane, previously cleaned to remove the cake, is measured at constant TMP. Then using Equation 2-9, R_f is deduced since R_m is already known.

$$J_{P(T)} = \frac{TMP}{\mu_{(20°C)} * (R_m + R_f)}$$ *Equation 2-9*

2.2.3.3 Cake resistance

The membrane resistance due to the cake, R_C ,is caused by the deposited cake layer, which is removable after membrane cleaning (Drioli and Giorno, 2010). It is determined by measuring clean water flux across the fouled membrane before cleaning. Using the permeability obtained and knowing R_m and R_f, the cake resistance is then estimated by Equation 2-4**Error! Reference ource not found.**.

Shan (2004) and Fane et al. (2011) stated that cake resistance can also be determined from Carman Kozeny equation, Equation 2-10.

$$R_c = \frac{K(1-\varepsilon_C)^2 {S_c}^2 \delta_c}{{\varepsilon_c}^3}$$ *Equation 2-10*

Where:

δ_c Cake thickness [mm]

ε_c Void fraction of the cake [-]

S_c Cake surface area per unit mass of solids in the cake [$m^2.kg^{-1}$]

K is a constant reported to be 5 by Grace (1953). However, this equation will not be used in this thesis because the parameters are not easy to determine.

2.2.4 Modified fouling index and specific cake resistance

The modified fouling index (MFI) indicates the membrane fouling potential with a particular feed stream and is often used to predict fouling (Le-Clech et al., 2003, Listiarini et al., 2009). It expresses the amount of time needed to filter a given amount of feed sample. A longer time indicates a higher fouling potential (Boerlage et al., 2003) . The units for MFI are $s.L^{-2}$ or $s.m^{-6}$. It is often estimated by measuring the volume of the sample obtained with respect to time at a constant TMP, then plotting the graph time/ volume *(t/V)* versus time *(t)* as shown in Figure 2-4. MFI is determined from the gradient of the linear section of the plot. The first section of the graph presents filtration with pore blocking while the second section presents cake filtration without compression and the third section is cake filtration with compression.

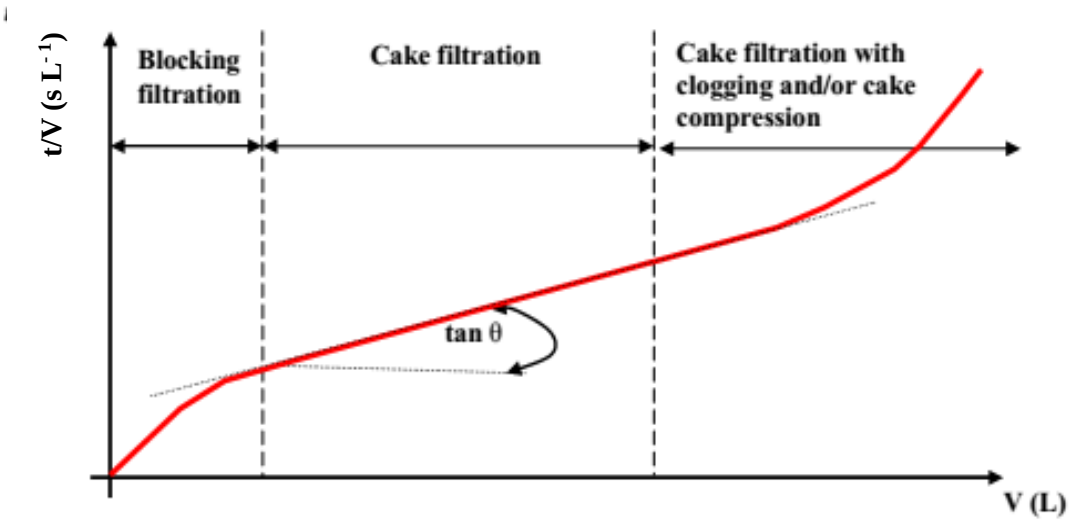


Figure 2-4: Filtration time divided by the filtrate volume (t/V) as a function of the filtrate volume (V) (Boerlage et al., 2003)

Specific cake resistance, *α,* is another indicator of fouling. It describes the way that the cake has been built on the membrane and indicates the cake porosity or particle size (Boerlage, 2001, Chang and Kim, 2005). A decrease in cake porosity or a decrease in particle diameter size leads to an increase in specific cake resistance (Madaeni, 1999, Chang and Kim, 2005). Its unit is $m.kg^{-1.}$

The relationship between specific cake resistance (α) and the MFI is given by Equation 2-11 . Knowing the MFI and the other parameters, specific cake resistance can be deduced using this equation.

$$MFI = \frac{\alpha C_s \mu}{2A^2 * TMP}$$ *Equation 2-11*

Where:

C_s Concentration of accumulated foulants on the membrane surface [mg.L^{-1}]

A Membrane surface area [m^2]

In most of the cases, the value of C_s cannot be experimentally determined (Pillay, 2011). As a consequence, only the value of the product of αC_s can be deduce from the MFI. Nonetheless, Madaeni (1999) and Shan (2004) reported that the value of C_s can be approximated to the total suspended solids concentration of the sample.

2.2.4.1 Cake resistance and specific cake resistance

Specific cake resistance,α, is further related to the cake resistance,R_C, on the basis of the dry mass per unit area of the membrane surface formed by the filter cake according to Equation 2-12 (Chang and Kim, 2005).

$$\alpha = \frac{R_c}{W}$$ *Equation 2-12*

Where;

W Mass of cake deposited per unit area of the membrane [kg.m^{-2}]

Mass of the cake deposited on the membrane,M_c (kg), is related to the filtrate volume (V) and concentration of the solids (C_S) in the feed according to Equation 2-13.

$$M_c = WA = C_S V$$ *Equation 2-13*

Combining Equation 2-12 and Equation 2-13 gives the relationship between the resistance due cake, specific cake resistance and the mass of cake build up as in Equation 2-14.

$$R_C = \frac{\alpha C_S V}{A}$$ *Equation 2-14*

2.2.4.2 Compressible and incompressible cakes

According to Boerlage et al. (2003), MFI of MF/UF membranes is based on the cake filtration theory. According to this theory, dead-end filtration at constant pressure takes place in 3 stages i.e. pore blocking, cake filtration with compression and cake filtration without compression as in Figure 2-4 above. A compressible cake is a cake whose porosity and resistance are dependent on the applied pressure while an incompressible cake is a cake independent of the applied pressure (Boerlage et al., 2003, Taheri et al., 2013). Compressible cakes are characterized by a decrease in void volume i.e. cake porosity and an increase in specific cake resistance as the applied pressure is increased (Ho and Sirkar, 1992). The specific cake resistance is constant for incompressible cakes but for compressible cake it changes with the applied pressure.

The degree of cake compressibility is often estimated by determining the compressibility index, n. The value of compressibility index lies between 0 for an incompressible cake to a value of up to 1 for compressible cakes, so the higher the n, the more compressible the cake is (Boerlage et al., 2003).

The value of compressibility index, n, can be estimated by assuming that the specific cake resistance is a power law function of the applied pressure as shown in Equation 2-15 (Boerlage et al., 2003). This is achieved by calculating the specific cake resistance at different pressure points then plotting the logarithm of α vs the logarithm of ΔP. The slope of this plot gives the value of the compressibility index (Boerlage et al., 2003).

$$\alpha = \alpha_0 \Delta P^n \qquad \textit{Equation 2-15}$$

Where;

α_0 Constant related to the size and shape of the particles forming the cake

n Compressibility index

2.2.5 Methods of membrane cleaning

Membrane cleaning is necessary in order to remove reversible fouling and to regain permeability. Lim and Bai (2003) describe the following methods for membrane cleaning:

- Backwashing with de-ionized (DI) water by reversing the flow;
- Sonication in an ultrasonic bath;
- Chemical cleaning;
- Combination of these methods.

During a chemical cleaning, the membrane is soaked in different chemical solutions. Firstly, NaOH is used to remove any biological material growth, secondly HCl for scaling elimination, and finally NaOCl to remove any remaining substances. This type of cleaning is called a cleaning in place (CIP) (Legierse, 2013). Another chemical cleaning method consists of using a hypochlorite solution (1 000 $mg.l^{-1}$), whose pH is adjusted to 12 by adding NaOH, for membrane soaking during 2 hours, then followed by a citric acid solution washing (0.5%) (Waeger et al., 2010).

Clean water flux (CWF) is usually measured before and after cleaning in order to determine the extent of fouling and to check the success of the cleaning method (Ramaswamy et al., 2013).

2.3. Microfiltration / Ultrafiltration

MF/UF refers to the filtration processes that use porous membranes to separate macro-solutes with diameters between 0.01 and 10 µm (Baker, 2012, Leslie and Bradford-Hartke, 2013). In general, microfiltration membranes fall between ultrafiltration membranes and conventional filters. The typical pore size of microfiltration membranes is 0.1 to 2 µm and typical applied pressure is 1 to 4 bars (Shan, 2004). Transition from MF to UF is not clear and several authors state that MF and UF are basically the same. Udert et al. (2003) indicated that molecular weight cut-off of MF membrane is 100 kDa while 500 kDa for Pillay (2011). Muro et al. (2012) reported that the MWCO of MF is in the range of 100-500 kDa and UF in the range of 20-150 kDa.

These membranes separate components by size exclusion. According to Baker (2012), all compounds larger than the largest pores are completely rejected by the membrane. The solutes with a size comprised in the range of the membrane pore sizes distribution are partially rejected. Compounds much smaller than the smallest pores will pass through the membrane while some of it can be absorbed within the pores, thus rejected. Thus, separation of solutes by a microporous membrane is mainly a function of their sizes and the membrane pore size distribution.

In UF, the amount of foulants deposited within the membrane pores is lower compared to that on the surface because UF membranes have smaller pore size compared to MF. In MF, there is greater deposition within the pores and internal fouling appears to dominate within large pores (Baker, 2012)

The wide pore size range of the MF/UF membranes have enabled them to have large applications in the dairy industry as well in wastewater treatment. One of their main industrial applications is in the sterilization and clarification of beverages and pharmaceuticals in the food and pharmaceutical industries (Xin, 2004). In the dairy industry, MF has been used to remove bacteria and somatic cells from skim milk and cheese brine (Adams, 2012). MF/UF has been widely used in the treatment of domestic wastewater and the effluent quality can satisfy the requirement for wastewater reuse (Shan, 2004). MF and UF membranes can be used as a clarifier to remove micron-sized particles such as microorganisms and suspended solids; reducing effluent turbidity and providing partial or full disinfection.

2.3.1 Membrane materials

There are mainly two different types of membrane materials: polymeric and ceramic. Comparison between ceramic and polymeric membranes is outlined by Ho and Sirkar (1992), and Madaeni (1999). Polymeric membranes are relatively inexpensive to manufacture, but are damaged by chemical agents and high temperatures. Consequently, they are difficult to clean and exhibit short lifetimes (approximately 1 year in an industrial setting). Ceramic membranes, on the other hand, can be cleaned with a wide variety of chemical agents, heat-sanitized with temperatures in excess of 100°C, and may last up to 10 years without a need for replacement. They can also operate at higher pressures than the polymeric membranes. However, their use in wastewater treatment is limited due to their relative high production cost. This can be ten times higher than their polymeric counterparts (Judd, 2006, Pillay, 2011). Another difference between both types of membrane materials is their geometry: ceramic membranes exist almost exclusively in tubular conformations, whereas polymeric membranes can be found in different types of geometry (Baker, 2012). It is important to note that the lifetime of any membrane is affected by the operating conditions (temperature, pH and fouling). High temperature, an extreme pH and aggressive particles shorten the lifetime. Frequent cleaning also shorten the lifetime as the chemical conditions used during cleaning are harsh (Ramaswamy et al., 2013).

MF/UF polymeric membranes have been successfully used in the wastewater treatment field as RO pre-treatment of secondary clarifier effluent (Bhattacharya et al., 2013). According to Judd (2006), only a number of materials are suitable for polymeric membrane in the context of wastewater treatment: polyvinylidene difluoride (PVDE), polyethersulphone (PES), polyethylene (PE) and polypropylene (PP). These materials encompass the characteristics required for a good operation in wastewater treatment context: to be mechanically, chemically and thermally strong and to exhibit relative resistance to membrane fouling.

2.3.2 Dead-end filtration and cross flow filtration

According to Baker (2012), during dead-end filtration, the fluid flow is forced through the membrane under the effect of pressure. There are two types of filtration which can be employed in a dead-end unit: dead-end microfiltration with constant flux or with constant pressure drop. The former keeps the permeate flux constant while in the later, the permeate flux decreases with time as fouling increases (Munir, 2006). Figure 2-5 illustrates dead-end filtration.

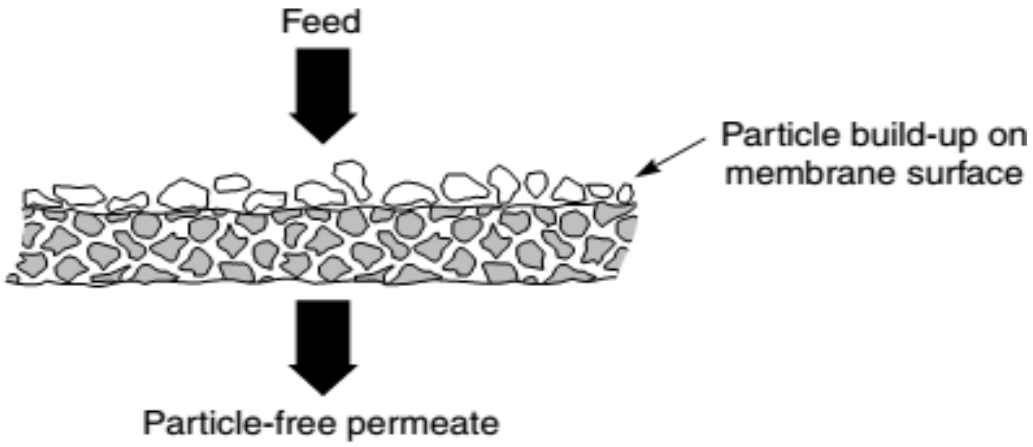


Figure 2-5: Dead-end filtration (Baker, 2012)

In cross-flow systems, the feed solution is circulated across the surface of the membrane filter, producing two streams: a clean particle-free permeate and a concentrated retentate containing the particles (Baker, 2012). This filtration mode is depicted in Figure 2-6.

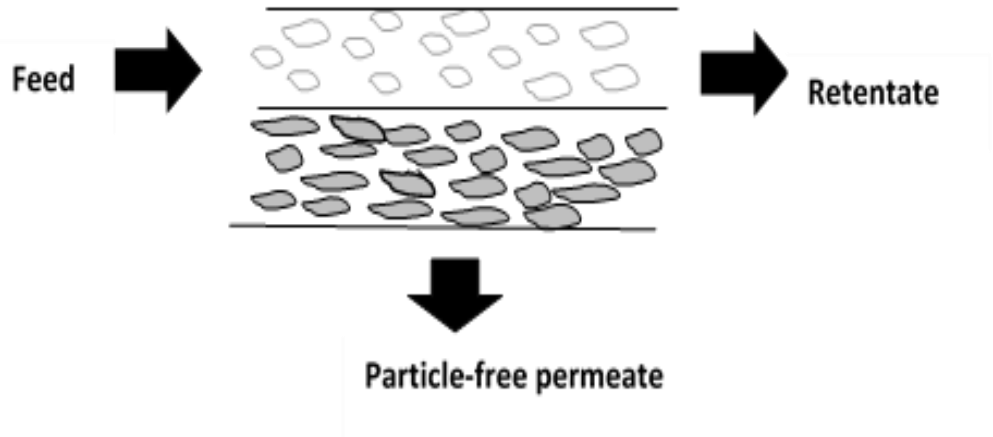


Figure 2-6: Cross flow filtration (Baker, 2012)

Most MF/UF applications operate in dead-end flow filtration (Gekas and Hallström, 1990), and only a few operate in cross flow mode. An important criterion of decision between both filtration configurations is the amount of solid to be retained by the membrane. For higher solid concentrations in the feed stream, it is preferable to operate in cross flow filtration (Noble and Stern, 1995) to limit fouling.

2.3.3 Techniques to improve membrane filtration

The MF/UF process can be optimized through the steps provided by Wakeman and Williams (2002):

- Firstly, by feed pre-treatment involving either physical or chemical processes. Physical processes usually include pre-filtration or centrifugation to remove suspended solids that may blind the membrane, while chemical processes may involve precipitation, coagulation or flocculation.

- Secondly, by selecting an appropriate membrane material with low interactions with the solutes. This should limit membrane fouling, and enhance foulants removal during cleaning.

- Thirdly, by flow and mechanical manipulations during the operation which can be achieved by back flushing, pulsing and shocking.

2.4. Use of membranes in urine treatment

Membranes are used to treat urine for the purposes of reuse water and nutrient recovery. The objective of the treatment may be to concentrate nutrients and/or to purify the urine (Leslie and Bradford-Hartke, 2013).

Ek et al. (2006), investigated the possibilities of using polyamide reverse osmosis membranes to concentrate stored urine. These authors used a 0.5 mm sieve, 5 µm cartridge filters and UF membrane of molecular cut-off weight of 100 kDa as pre-treatment. These authors did not provide details on the performance of UF membranes but concluded that pre-treatment with UF membranes resulted in better performance of RO membranes. They were able to concentrate up to 98% of total nitrogen and 99.9% of total phosphorous.

Another urine filtration work using membranes was done by Pronk et al. (2006) who used NF membranes to separate pharmaceutical and estrogenic compounds from source-separated urine and to produce a nitrogen enriched permeate as liquid fertilizer. They used crossflow filtration mode at a constant pressure of 20 bars with 3 types of NF membranes; DSS, NF270 and N30F with MWCO of 150-300,300 and 400 Daltons respectively. These authors found that NF270 membranes showed the best performance in retaining micropollutants, up to 92%.Theyconcluded that nanofiltration be used to produce a permeate which contains most of the nitrogen and a greatly reduced proportion of micropollutants.

Triger et al. (2012), researched on UF of stored urine for its safe reuse. These authors are the only ones who have conducted until now researches exclusively on UF of urine. They investigated the properties of different UF membranes (pore size and materials) during stored urine filtration. The experimental set-up was dead-end mode with a constant pressure of 0.3 bars. These authors found that membrane fouling during ultrafiltration of stored urine is mainly due to the retention of crystals, which are normally formed during storage, and soluble organic matter.

2.4.1 Challenges of using membranes for urine treatment

According to Leslie and Bradford-Hartke (2013), membrane treatment of urine may be more feasible if the scale is increased to incorporate many households rather than a single one, but this would require urine storage. The spontaneous hydrolysis of urea in stored urine is unfavorable for micropollutants removal using nanofiltration as the rejection decreases with the increase of pH (Pronk et al., 2006). Furthermore, the precipitates which are formed as a consequence of urea hydrolysis can lead to scaling on the membranes (Udert et al., 2003). RO membranes should require the use of physical / chemical pre-treatment to prevent the accumulation of salts and precipitates on the surface (Leslie and Bradford-Hartke, 2013). This could be achieved by MF/UF.

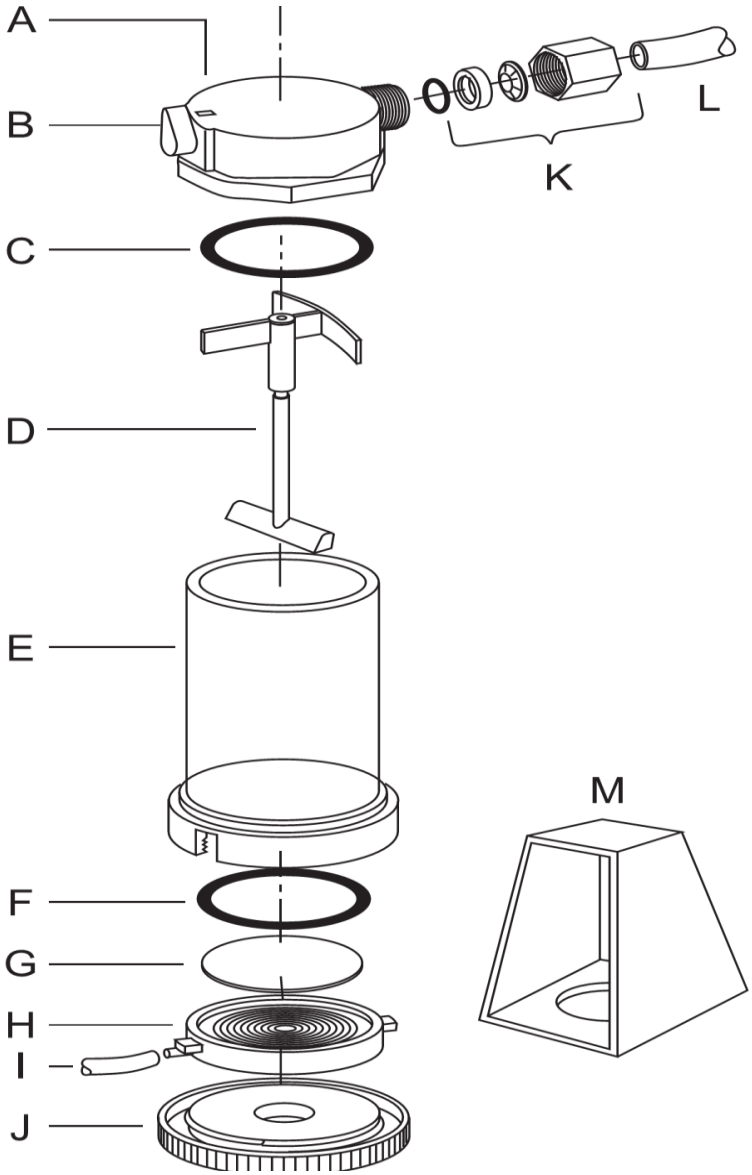
3. MATERIALS AND METHODS

This chapter describes the procedure during filtration experiments and the chemical analyses that were undertaken over the course of this research study. Filtration of the feed stock was done in dead-end filtration mode and fouling was estimated from the permeability of the membranes with clean water before and after filtration experiments. Specifically, the first test was clean water flux test on the virgin membrane, followed by urine flux test, then clean water flux test on the used membrane and finally clean water flux test on the used membrane after cleaning. Physico-chemical analyses on the feedstock and the permeate were also performed.

3.1. Equipment and apparatus

- Amicon® stirred cell (Millipore model 8400)
- Compressed air
- Glass beaker
- Magnetic stirrer (MMS-3000)
- Mass balance (Adam HCB602H)
- Pressure gauge (0-60 kPa)
- Pressure regulator ×2 (0-1 000 kPa)
- Mercury glass thermometer (0 to 100◦C)
- Computer
- Microfiltration/Ultrafiltration polyethersulphone membranes with an effective surface area of 0.00418 m^2 and a diameter of 76 mm (Millipore). These were selected based the specifications of the amicon cell

Amicon® stirred cells (from Millipore) are designed for rapid concentration or purification of macromolecular solutions through MF/UF in a lab scale. The cell volumes can vary from 3 to 400 mL. In this study, the amicon cell of 400 ml capacity was selected because it was readily available. The Amicon® cell, and its parts are shown in Figure 3-1.



A	Cap Assembly
B	Pressure Relief Valve
C	O-Ring
D	Stirrer Assembly
E	Body
F	O-Ring
G	Membrane
H	Membrane holder
I	Elastomeric Tubing
J	Base
K	Tube Fitting Assembly
L	Tubing Plastic
M	Stand Assembly

Figure 3-1: The Amicon® stirred cell (Millipore, 2008)

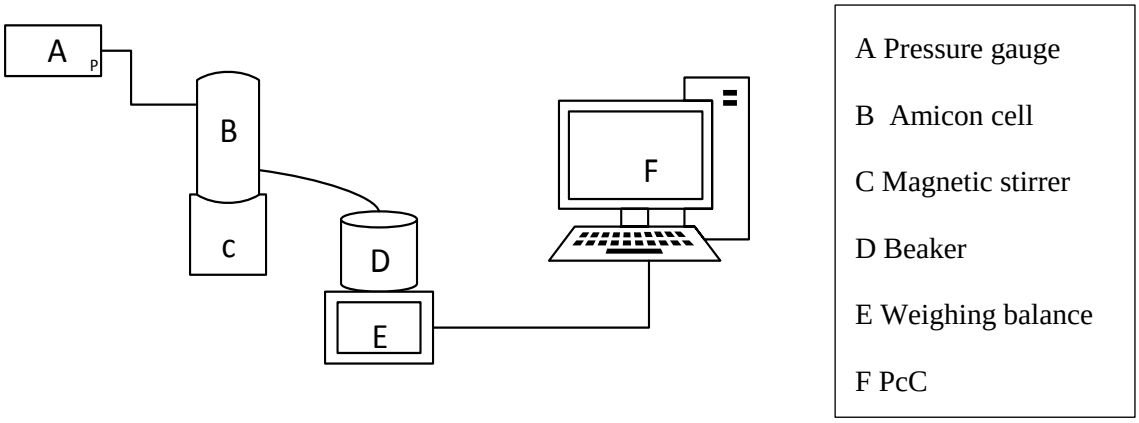
3.2. Feedstock

The feedstock in this study was stored urine collected from a storage tank located in Newlands KwaMashu Research Centre in Durban, South Africa. The urine from the storage tank is issued from UDDTs installed within Durban Municipality. For some of the experiments, the sample was diluted with distilled water by a factor of 5, as most urinals use around 4 L of water for flushing (Tilley et al., 2008), while an adult excretes an average of 1 to 1.5 liters of urine per day (Tilley et al., 2008, Karak and Bhattacharya, 2011). The characteristics of the feed urine sample is presented in section 4.3

3.3. Experimental setup

Filtration experiments were carried out using an Amicon cell in dead-end configuration and microfiltration/ultrafiltration polyethersulphone (PES) disc membranes 76 mm diameter (PBVK07610) from Millipore. The disc membranes had a molecular weight cut-off (MWCO) of 500 kDa and an effective area of 0.00418 m^2. Polyethersulphone was selected as the membrane material because of its hydrophilic character, wide pH of operation, suitability for aqueous solutions, acceptable mechanical strength and low fouling propensity (Baker, 2012, Ramaswamy et al., 2013). The pressure was controlled using two pressure regulators and a pressure gauge. The permeate was collected in a beaker placed on a digital balance (Adam HCB602H) which was connected to a PC for data acquisition using LabVIEW software. A detailed experimental procedure is presented in Appendix A. The experimental setup is depicted in Figure 3-2.

During operation, the filtration cell was continuously stirred by a magnetic stirrer in order to maintain a homogenous solution and limit cake formation on the membrane. The temperature of the permeate was measured every minute for temperature correction to 20℃ as recommended by (Judd, 2010). The formula for temperature correction is presented in section 2.2.3 .A data acquisition system (LabVIEW) was used to continuously log data during filtration experiments.



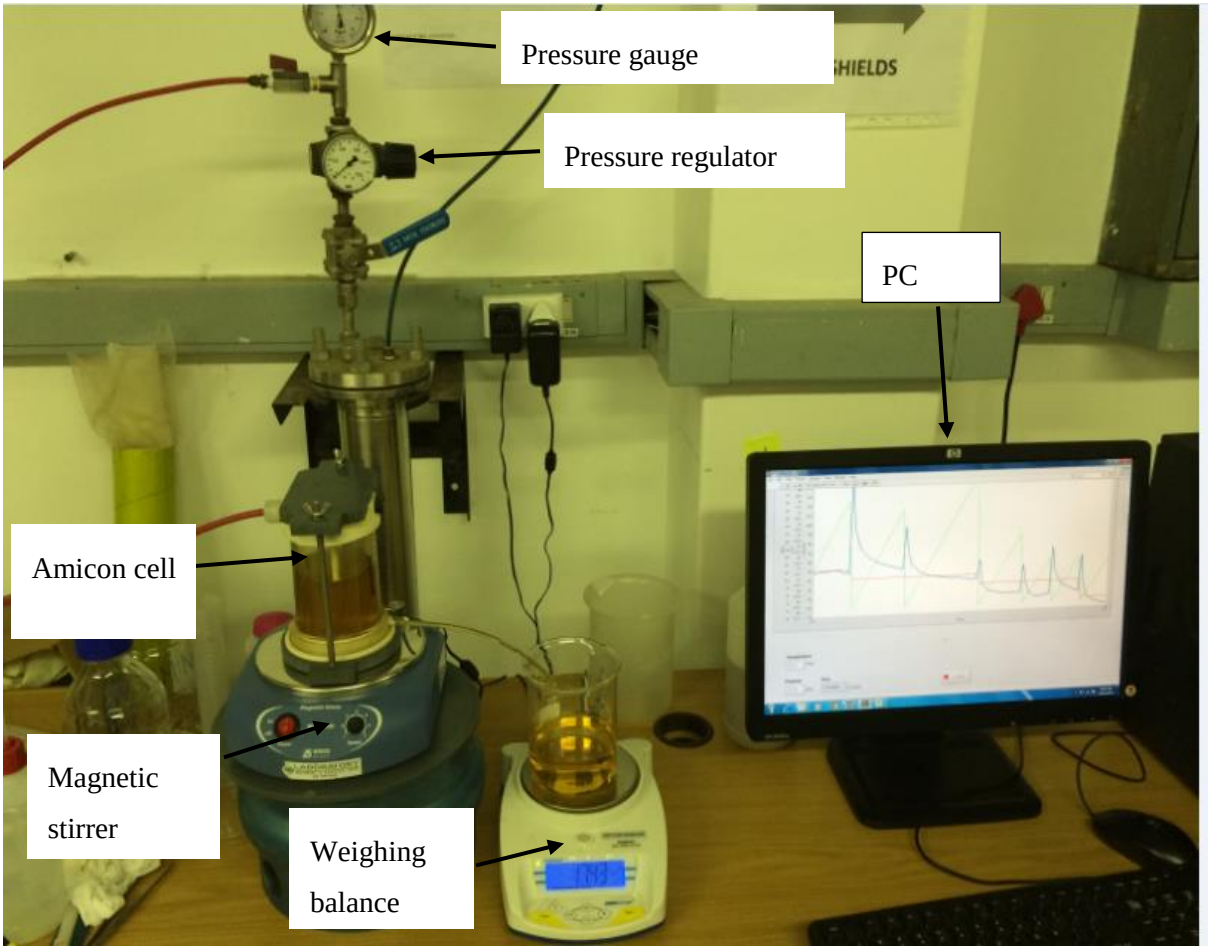


Figure 3-2: Experimental setup

3.4. Experimental methods during urine filtration

Filtration parameters such as flux, permeability, resistance, modified fouling index (MFI) and specific cake resistance were determined.

For each experiment, 350 mL of feedstock was added in the Amicon® cell. Filtration of the feedstock at each TMP step was set to last 10 min. The permeate was measured in grams then calculated to flux in $L.m^{-2}.h^{-1}$.

Three filtration cases were tested. In case 1, filtration experiments with stored urine were performed by increasing TMP in the range 10 to 60 kPa with 3 membranes. In case 2, the same experimental procedure was carried out with 2 membranes, but by decreasing the TMP from 60 to 10 kPa. In case 3, experiments with diluted urine were performed with TMP set from 10 to 60 kPa, with 3 membranes. On each membrane, replicates were done for each measurement, i.e. a total of 6 repetitions for case 1, 4 repetitions for case 2 and 6 repetitions for case 3.

Prior to any filtration experiments, the virgin membrane was conditioned by soaking in the milli distilled water for at least 1 hour with the shiny side up while changing the water at least 3 times. For each experimental case, the flux of deionised water using the virgin membrane was measured so as to determine the permeability of the membrane before fouling. This was followed by the measurement of permeate flux during urine sample filtration. Then, the water flux with the used membrane was measured in order to estimate the loss of permeability after urine filtration. After this, the membrane was cleaned and water flux across the cleaned membrane was measured in order to estimate the permeability recovered with the cleaning method employed.

Membrane cleaning was performed based on the manufacturer instructions and other researchers such as Waeger et al. (2010) and Legierse (2013) . Membranes were cleaned by soaking in a 0.1M NaOH solution for at least 30 minutes, followed by soaking in acid for another 30 minutes and finally rinsing thoroughly with distilled water.

The graphs of water flux vs TMP were plotted and the slope represented the permeability of the membrane. Membrane resistances were determined using the values of permeability. Refer to section 2.2.3 for the description of the method employed here to calculate the resistances.

Modified fouling index (MFI) and specific cake resistance were also measured through the method described with details in section 2.2.4. MFI was determined by measuring the volume of the permeate at different TMPs i.e., 10, 30 and 50 kPa. Then, the filtration time divided by the permeate volume (t/v) was plotted against volume and the slope of the linear section gives the MFI. Using the MFI, specific cake resistance was calculated according to Equation 2-11.

The rejection of the organic and ionic species was determined using Equation 3-1

$$R = 1 - {}^{c_p}/_{c_f} \qquad \textit{Equation 3-1}$$

Where:

R Rejection

c_p Concentration of permeate (mg.L^{-1})

c_f Concentration of feedstock (mg.L^{-1})

3.5. Chemical /physical analyses on the feedstock and permeate

The concentrations of ionic species, organic matter, solids and particles were measured in the feed and permeate samples. The solution properties, such as the electrical conductivity and pH, and the suspension characteristics, such as particle size distribution, were also analyzed. All the tests were done according to standard operating procedures based on those from water and wastewater analysis (Federation and Association, 2005).The physic-chemical analyses and their significance are shown in Table 3-1. Refer to Appendix H for detailed procedures.

Chemical Oxygen Demand (COD) is an indicator of the organic matter content in the sample. It was measured using a closed reflux titrimetric method. In this method, the sample is digested in a microwave digester at 120 ℃for 2 hours in a strong dichromate acid in stoichiometric excess, using silver sulphate as a catalyst and mercuric sulphate as a masking agent to prevent chloride interference. The dichromate is partially reduced by the oxidizable organic material present in the sample. The excess dichromate is titrated with ammonium iron (II) sulphate and the COD value deduced from the amount of dichromate previously consumed. This procedure is only applicable to samples with COD values between 40-400 mg.L^{-1} otherwise dilution is required. Thus, the urine sample was diluted by a factor of 10 prior to COD measurements.

For total solid (TS) analysis, a known volume of sample (30 mL) was evaporated to dryness in a porcelain crucible placed in an oven at 105ºC for 24 h. The residual material in the crucible is classified as total solids, and consists of organic and inorganic matter from the sample. For the total suspended solids (TSS) analysis, a measured volume of the urine sample was firstly filtered through a vacuum system, across a 110 mm diameter glass fibre filter of 0.45 µm pore size which was dried and weighed prior to the experiments. Afterwards, the filter with the residue on its surface was dried at 103-105ºC for 2 h. The increase in weight of the filter corresponds to the total suspended solids, which represents the fraction of the solid that cannot pass through the filter. The total dissolved solids (TDS), which represents the fraction of the solid able to pass through the filter, was calculated by subtracting the TSS from the TS.

Electrical conductivity and pH (Hach MM150) were measured using a conductivity and pH meter respectively. For this, the electrodes were immersed in the urine sample and the reading was displayed on the meter.

Chloride concentration was measured using the chloride analyzer M926, which gives a direct reading on a digital chloride meter. This method is based on the coulometric titration of the reagent, silver ions which combine with chloride to form silver chloride. This reagent is quantitatively generated during analysis by passing a constant current between donor electrodes. When excess silver ions are present in the solution, a sensing electrode is used to measure the change in the solution. The sample volume used during experiments is 0.5 mL. The measurement range has to be comprised between 10-999 $mg.L^{-1}$ chlorides, otherwise dilution is necessary. For the samples from the present work, a dilution factor of 20 was required.

Total phosphate concentration was determined using spectroquant test kits and a spectrophotometer Merc KGaA, 64293. The procedure was conducted according to the Merck operational manual. The measurement of the concentration has to be ranged between 0.11 – 11.46 $mg.L^{-1}$. A dilution factor of 100 was then applied for the samples from this work. The sample was firstly digested using a microwave digester at 120 ℃ for 30 min. The spectroquant chemicals were added in order to give coloration to the sample after which the phosphate concentration was measured in the spectrophotometer.

Particle size distribution was analyzed using the Malvern Mastersizer 3000, which can detect particles in the range of 0.01 to 3 500 µm. This apparatus measures the size of particles contained within a sample by transmitting red laser light and blue light through a sample. It then uses its detectors to generate data about light scattering pattern caused by particles in the sample. This data is then interpreted by the Mastersizer software to provide accurate particle information. Large volume of samples were needed for the analysis in the present work. PSD also measures the amount of particles at each size measured. The main constraint of using this technique is that the sample must be homogenous otherwise the results will be incorrect.

Some parameters (COD, PO_4^-, Cl^-) were not measured for the diluted urine and were considered to be 5 times lower according to the dilution factor. This was based on the assumption that dilution does not alter the amount of these compounds. As a confirmation of this, on a study about the recovery of plant nutrients from diluted solutions of human urine, Kocatürk and Baykal (2012) reported a COD value of 3 350 $mg.L^{-1}$ and 6 950 $mg.L^{-1}$ for 50% and 100% urine concentration respectively, which was almost equivalent to the applied dilution factor of 2. In all the cases, dilution is required for the measurement of these parameters in order to be in the measurement range of the instrument.

Table 3-1: Physico-chemical analyses on the urine and permeate samples

Parameter	Purpose for measuring
Chemical Oxygen Demand (COD)	To determine the rejection of organic matter
Total solids(TS)	To determine the rejection of solids
Total suspended solids (TSS)	To determine the rejection of large size particles that cannot pass through a filter
Electrical conductivity	Indicator of changes in the electrolyte composition after filtration
pH	Indicator of changes in the chemical equilibrium of the solution and also to monitor the pH of solution so as not to damage the membranes
Phosphates	Indicator of rejection of polyvalent ions
Chloride	Indicator of rejection of monovalent ions
Particle size analysis	Indicator of the particle sizes rejected by the membrane

3.6. Statistical analysis

The uncertainty bars were determined using a t-student distribution at 95% confident interval. The error analysis was undertaken for each of the experimental and sampling procedures. Each data point represents the average of the replicate tests (6 replicates for cases 1 and 3; 4 replicates for case 2).3 significant figures was considered suitable based on the uncertainties of the measurements.

4. RESULTS AND DISCUSSION

This section is divided into three parts. The first part presents the permeate flux during the filtration of stored urine and diluted urine. The second part presents the study of fouling (membrane permeability, hydraulic resistance, MFI and specific cake resistance). Finally, the third part shows the physico-chemical changes undergone by the urine stream during filtration and the membrane rejections.

4.1. Permeate flux during filtration of stored urine and diluted urine for the 3 cases

Figure 4-1 presents the permeate flux of stored urine and diluted urine for the 3 cases. Case 1 and 2 deal with stored urine, and case 3 with diluted urine. The pressure is set in an ascending order, from 10 to 60 kPa, for Case 1 and 3, and in descending order, from 60 to 10 kPa, for Case 2. Each point represents the average flux for each TMP step. The repetitions of these tests are presented in 0. There was no significant difference between the repetitions i.e. the error was less than 5% at 95% confidence interval, which indicates good reproducibility of the results.

These flux rates present a water recovery of 23% for case 1, 26% for case 2 and 45% for case 3 after 1 h of filtration experiment. The volume flowrate of permeate passing through the membrane was determined and used to calculate the mass of cake build up per unit surface area of the membrane. The results are presented in Table 4-1.

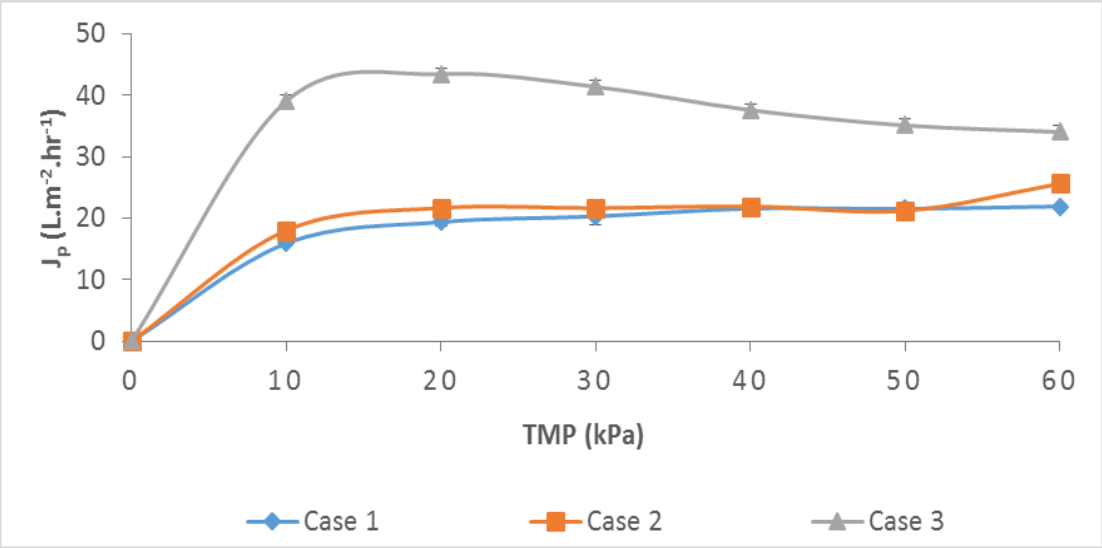


Figure 4-1: Permeate flux at 20℃ against transmembrane pressure for case 1 (urine flux 10-60 kPa), case 2 (urine flux 60-10 kPa) and case 3 (diluted urine flux)

Table 4-1: Summary of the mass of cake build up and water recovery during filtration of the 3 cases

Experimental Case	Volume flowrate ($m^{-3}.h$)	Water recovery (%)	Mass of cake ($kg.m^{-2}$)
Case 1	8.08×10^{-5}	23	4.99×10^{-6}
Case 2	8.97×10^{-5}	26	5.54×10^{-6}
Case 3	1.57×10^{-4}	45	1.88×10^{-6}

4.1.1 Case 1: stored urine filtration in ascending TMP (10 – 60 kPa)

During urine filtration from 0 to 40 kPa, the flux increased up to 21 $L.m^2.h^{-1}$, then remained constant at higher pressures. From 40 kPa, fouling could counterbalance the increase of flux by increasing the TMP, leading to a constant flux which becomes independent of the applied pressure. A similar flux behaviour was observed by Defrance and Jaffrin (1999) during the filtration at fixed TMP in a membrane bio-reactor (MBR) for wastewater treatment.

Cake formation (fouling layer) was not significant as the pressures was increased from 10 to 20 kPa. This can be observed from the flux behaviour which increases linearly between these pressures (see Figure 4-1.). As the pressure is increased from 20 to 40 kPa, the permeate flux increases but very slowly probably due to the increased concentration of particle on the surface of the membrane. At higher pressure from 50 to 60 kPa, the flux becomes independent of the pressure because of the consolidation of the particles resulting to cake formation. The mass of the cake deposited on the membrane surface was calculated according to Equation 2-13 and was found to be 4.99×10^{-6} $kg.m^{-2}$ after an hour of filtration experiment. Note that from Equation 2-13, the values of Cs represent the concentration of suspended solids in the feed as presented in section 4.3.2.

4.1.2 Case 2: stored urine filtration at descending TMP (60 – 10 kPa)

In case 2, the TMP was set in descending order so as to verify if the filtration occurs in the same way or differently if starting at high pressure, compared to case 1 which initiates at low pressure. It was hypothesised that starting from high to low pressure would result to high permeate flux compared to the previous case but could increase the fouling potential. It was noted that the flux was the highest at the highest pressure, 60 kPa, with a value of 26 $L.m^{-2}.h^{-1}$. It then dropped to 21 $L.m^{-2}.h^{-1}$ at 50 kPa and remained relatively constant up to 20 kPa. At 10 kPa, the flux slightly decreased to 18 $Lm^{-2}.h^{-1}$.

The highest flux at 60 kPa could be due to the fact that membrane was virgin at the beginning of the experiment. From 50 to 20 kPa, the flux is independent on TMP, probably due to the fouling layer formed at 60 kPa. The flux may decrease further at 10 kPa because of the low TMP. The mass of cake build up after 1 hour was 5.54×10^{-6} $kg.m^{-2}$ which is higher compared to case 1 indicating more fouling by cake formation.

4.1.3 Case 3: diluted urine filtration at ascending TMP (10 – 60 kPa)

In this case, the flux increased with increasing TMP up to 20 kPa with a flux value of approximately 43 $L.m^{-2}.h^{-1}$. It then further declined by increasing the TMP until a value of around 34 $L.m^{-2}.h^{-1}$ at 60 kPa.

From 0 to 20 kPa, flux increased linearly maybe because the fouling layer was not enough influencing, in contrary to the filtration from 30 to 60 kPa where flux decreased. The flux decrease at higher TMP could be as a result of the compression of the cake layer formed on the membrane surface (cake compressibility test is presented in section 4.2.3.1). The mass of cake build up after an hour was 1.88×10^{-6} $kg.m^{-2}$ which is less than the value reported for the previous cases indicating less fouling by cake formation.

4.1.4 Flux comparison of the 3 cases

The general flux behaviour for all the 3 cases as observed in Figure 4-1 shows that there is no considerable gain in flux after 10 kPa for all the three case. Similar fluxes were observed for case 1 and case 2 except at 60 kPa where the flux was slightly higher for case 2. In contrast, significantly higher fluxes were observed during diluted urine filtration

The cake formed per unit surface area of membrane had different mass build up for all the 3 cases. Case 3 had the least amount of cake build up followed by case 1 and finally case 2 which had the most cake build up. The mass of cake build up is directly proportional to the degree of fouling by cake formation i.e. cake resistance (see section 4.2.2 for the detailed study on membrane resistance). This implies that case 2 (pressure down experiment) has the most fouling by cake formation.

4.2. Study of fouling

This section presents the study on fouling based on membrane permeability and hydraulic resistance.

4.2.1 Study of membrane permeability

This section presents the analysis on clean water flux (CWF) tests done on the membranes for the 3 cases presented above. These tests were performed on: first, the virgin membrane; second, the membrane after filtration; and third, after cleaning the membrane.

Figure 4-2 illustrates the type of graphs that have been used to determine permeabilities. It presents the permeate flux of clean water versus TMP for case 1. Graphs for case 2 and case 3 including repetitions of the tests are presented in Appendix D. There was no significant difference between the repetitions, indicating good reproducibility. Values of permeability are here reported as an average of the total number of tests. As it could be expected, the flux increased with the increase of the TMP for the virgin membrane, the membrane after use and the membrane after cleaning for all the cases. The summary of the permeabilities are presented Table 4-2.

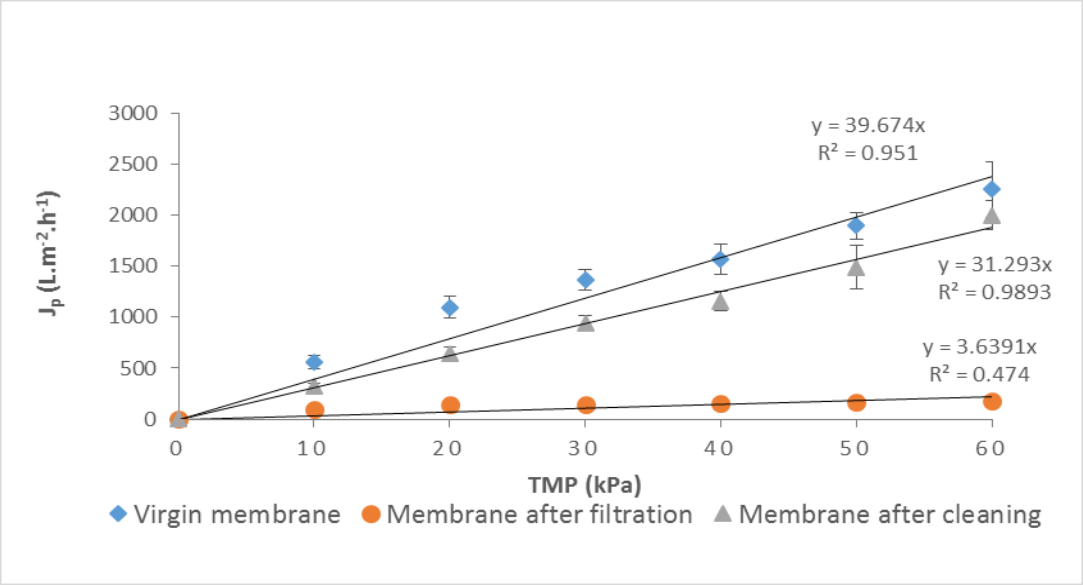


Figure 4-2 Permeate flux as a function of the transmembrane pressure for the virgin membrane, membrane after filtration and after cleaning during the clean water flux tests for case 1

Table 4-2: Summary of the permeabilities of the virgin membrane, after urine filtration and after cleaning

	Permeability ($L.m^{-2}.h^{-1}.kPa^{-1}$)			Loss of permeability after filtration	Recovered permeability after cleaning
	Virgin membrane	After filtration	After cleaning	%	%
Case 1	39.8	3.6	32.1	91	80
Case 2	39.3	2.1	14.4	95	37
Case 3	39.6	3.9	33	90	84

Figure 4-3 presents the permeabilities measured from the slope of flux vs TMP, as previously described in section 3.4. For the three cases, the permeability of the virgin membrane was relatively similar with about 40 $L.m^{-2}.\ h^{-1}\ .kPa^{-1}$. This could be expected as all the membranes had the same specifications. After urine filtration, the permeability of the membrane was drastically diminished to values lower than 4 $L.m^{-2}.h^{-1}.kPa^{-1}$, surely due to high fouling formed during urine filtration. After membrane cleaning, permeability recovery was almost the same for case 1 and case 3, i.e., approximately 80% of the initial permeability (~ 32 $L.m^{-2}.h^{-1}.kPa^{-1}$) for case 1 and 3 (~ 33 $L.m^{-2}.h^{-1}.kPa^{-1}$). However, only approximately 37% permeability recovery (~ 15 $L.m^{-2}.\ h^{-1}.kPa^{-1}$) was achieved for case 2. These results show that an important part of the fouling on the membrane is removed after cleaning. The irreversible fouling, which cannot be removed by cleaning, depends on how the filtration has proceeded. Operating from high to low pressures leads to higher irreversible fouling than operating from low to high pressures.

In summary, urine filtration leads to considerable fouling. Operating at high pressures seems to lead to a much higher irreversible fouling, compared to filtration at low pressures.

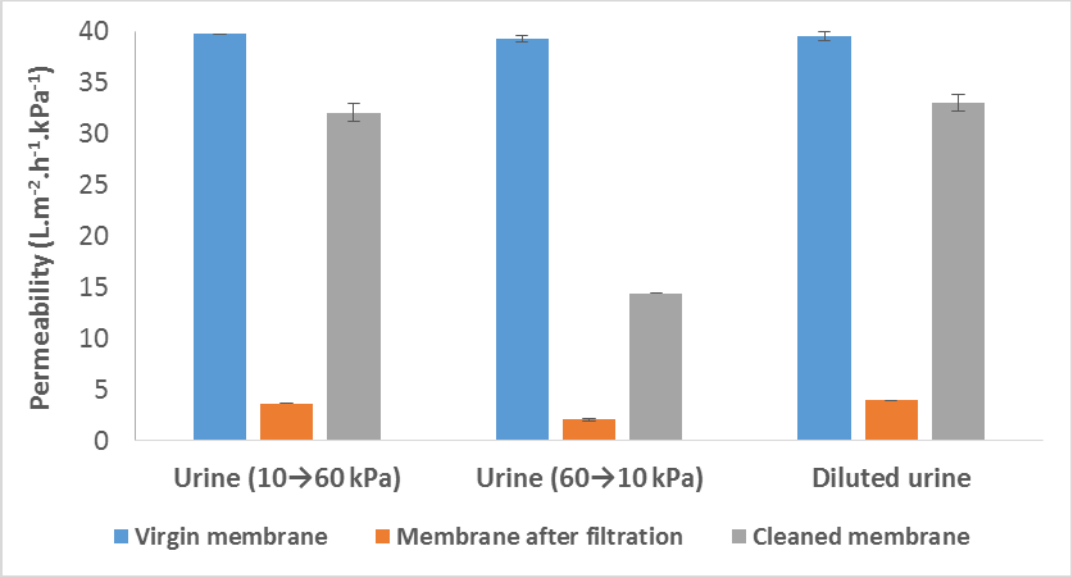


Figure 4-3: Permeability of the membrane before filtration, after filtration, and after cleaning

4.2.2 Study on the hydraulic membrane resistances

The hydraulic resistances of the membranes were determines from the permeabilities presented in the previous section. Three types of resistances were calculated: the intrinsic membrane resistance (R_m), the resistance due to irreversible fouling (R_f) and the resistance due to cake layer (R_c). The procedure for the calculation of these resistances is detailed in section 2.2.3. The results are presented in Table 4-3 and is further depicted in Figure 4-4.

For each case, the cake resistance was the most influencing with a contribution to total resistance of over 85%, while the contribution of intrinsic membrane resistance remained below 10%. Irreversible fouling had the minimum contribution to the total resistance with a value lower than 2% for case 1 and case 3. Nonetheless, its contribution was higher for case 2 with 9%. Therefore, irreversible fouling was low if formed at lower pressures, but can increase at higher operating pressures.

In conclusion, there was high fouling for all the cases. Much higher values for cake resistance indicates that cake is the dominant fouling mechanism during urine filtration. The influence of irreversible fouling is considerably lower on membrane fouling than cake. Higher fouling seems to be favoured at higher pressure as seen from the mass of cake build up presented in section 4.1.

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Table 4-3: Hydraulic membrane resistances during the filtration of stored urine and diluted stored urine

	Hydraulic Resistance (m^{-1})		Contribution to total resistance, R_t
Case 1	R_m	9.04E+10	9%
	R_f	2.17E+10	2%
	R_c	8.79E+11	89%
	R_t	9.91E+11	-
Case 2	R_m	9.15E+10	5%
	R_f	1.58E+11	9%
	R_c	1.49E+12	86%
	R_t	1.74E+12	-
Case 3	R_m	9.09E+10	10%
	R_f	1.17E+10	1%
	R_c	8.04E+11	89%
	R_t	9.07E+11	-

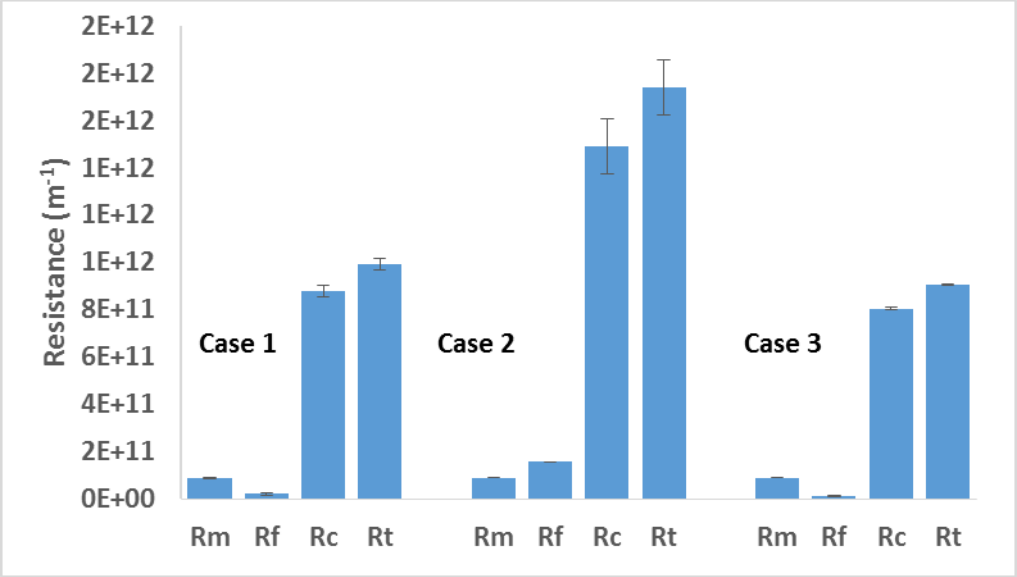


Figure 4-4: Membrane hydraulic resistances during filtration for the 3 experimental cases

4.2.3 Membrane fouling index and specific cake resistance

This section presents the data from the calculation of the MFI and specific cake resistance for the 3 experimental cases. MFI indicates the fouling potential of a membrane with respect to a particular feed stream (Le-Clech et al., 2003, Listiarini et al., 2009), while α is an indicator of cake characteristics, such as porosity and foulants particle size (Boerlage, 2001, Chang and Kim, 2005).

Figure 4-5a presents the data for the calculation of the product of αC_s during filtration of stored urine starting from 10-60 kPa at a reference pressure of 50 kPa this reference pressure has been selected for demonstration purposes due to a larger variation of the curve tangent slope at this pressure as reported by researchers such as Hwang et al. (2007) and (Pillay, 2011) and . Despite using 50 kPa as the reference pressure, MFI has been determined at other pressures as presented in section 4.2.3.1. A linear extrapolation was constructed from the last six data points corresponding to the approximate location of cake filtration (region II). This linear extrapolation plot is presented in Figure 4-5b. From the slope, the fouling propensity was 2×10^{11} $s.m^{-6}$. Knowing the amount of TSS in stored urine, specific cake resistance was then calculated using Equation 2-11 and was 1.35×10^{15} $m.kg^{-1}$. MFI for case 2 and case 3 were determined in a similar manner and their graphs are presented in Appendix E.

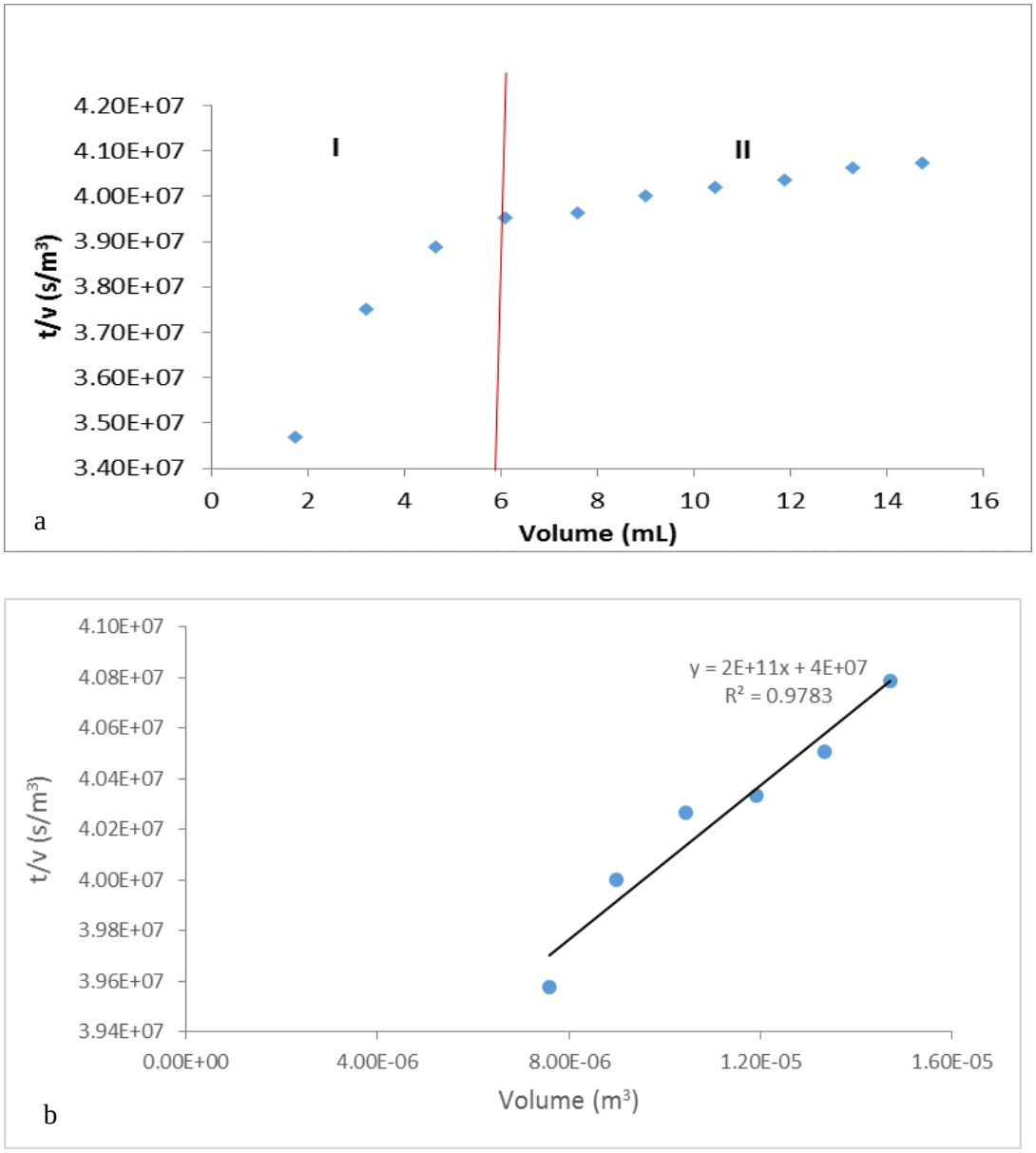


Figure 4-5: Plots of t/V versus volume at 50 kPa of stored urine 10-60 kPa for a) the entire curve and b) Linear regression.

4.2.3.1 Cake compressibility test

Prior to analysis of the specific cake resistance it is important to know the characteristics of the cake formed. The cake formed on the surface of the membrane can be characterised as either compressible or incompressible. As presented in section 4.2.3, specific cake resistance calculation in this study was demonstrated at a reference pressure of 50 kPa. However, this method does not give the cake characteristics at other pressures but at 50 kPa. Therefore, it is necessary to determine whether the specific cake resistance is a function of the applied pressure or not by determining the specific cake resistance at all the applied pressures. If it is independent of pressure then it indicates an incompressible cake and vice versa. A similar procedure as the one in the previous section (4.2.3) was used to determine the specific cake resistance at different pressures.

Figure 4-6 presents the linear section of the graph of t/v vs V for case 1. The slopes represent the MFI at different pressure. It can be seen that the MFI is constant for the sampled pressure points which is an indication of a constant specific resistance and hence an incompressible cake for this particular case. A similar trend was observed for case 2. For case 3 however, the MFI increased with increasing pressure as shown in Figure 4-7 . This implies that the specific cake resistance is a function of the applied pressure for this particular case hence a compressible cake.

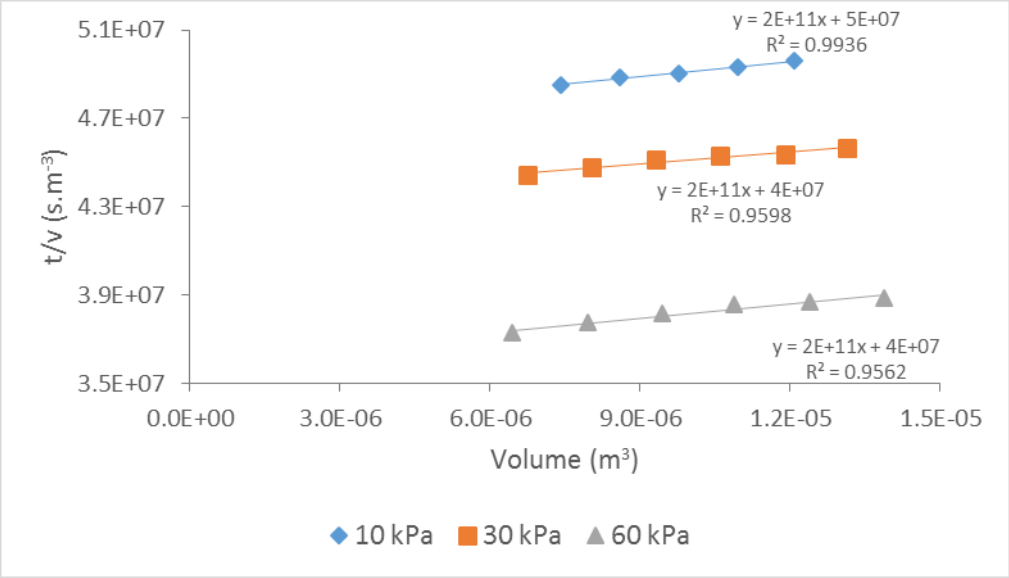


Figure 4-6: Summary of plots of t/v vs. V at different pressures for case 1

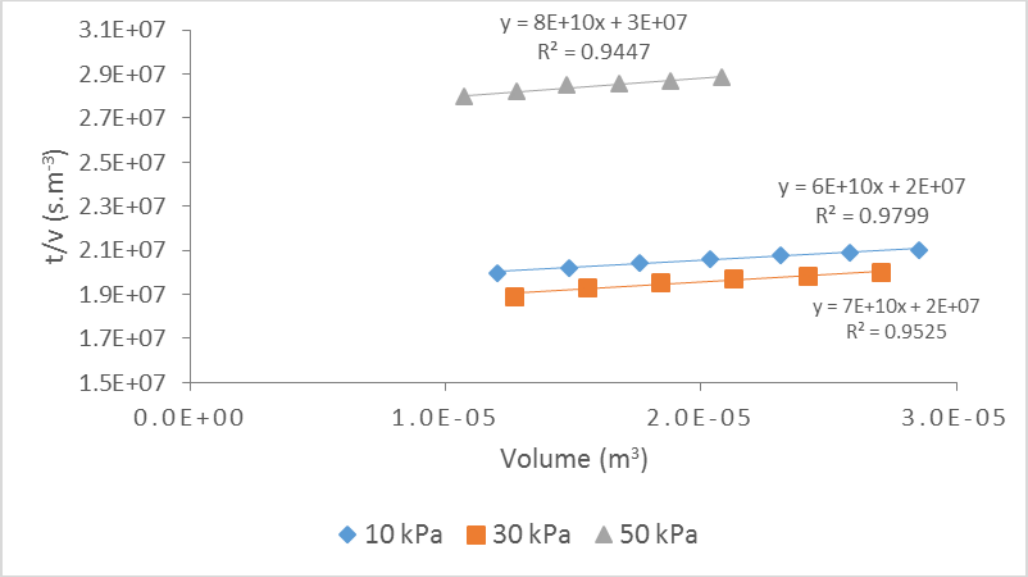


Figure 4-7: Summary of plots of t/v vs. V at different pressures for case 3

Using the values of MFI, the specific cake resistance values were calculated. Table 4-4 and Table 4-5 presents the summary of the MFI and specific cake resistance values for the undiluted urine filtration (case 1 and case 2) and diluted urine filtration (case 3) respectively. Since the MFI is similar for case 1 and 2, so is their specific cake resistance.

As seen in Table 4-5 the higher the TMP applied, the higher the slope (MFI) during diluted urine filtration. This can further explain the permeate decreases with increasing pressure for this particular case (Figure 4-1). If the MFI was to decrease with increasing pressure as observed by Shan (2004) during filtration of primary and secondary effluent of waste water, it would be an indication that the flux increases with increasing pressure. Knowing that the cake formed during diluted urine filtration is compressible, it is thus important to determine the degree of compressibility by determining its compressibility index, n.

Table 4-4: Modified fouling index and specific cake resistance for case 1 and case 2

	MFI ($s.m^{-6}$)	α ($m.kg^{-1}$)
Case 1	2×10^{11}	1.4×10^{15}
Case 2	2×10^{11}	1.4×10^{15}

Table 4-5: Modified fouling index and specific cake resistance for case 3

Pressure (kPa)	MFI ($s.m^{-6}$)	α ($m.kg^{-1}$)
10	6×10^{10}	2.0×10^{15}
30	7×10^{10}	2.3×10^{15}
50	8×10^{10}	2.7×10^{15}

Figure 4-8 presents the plot of the graph used to determine the compressibility index, n, of the particles forming the cake during diluted urine filtration. The compressibility index was determined according to the procedure described in section 2.2.4.2. The slope of this graph represents the compressibility index. The compressibility index, n, was found to be 0.18, indicating that the cake is slightly compressible; since a compressibility index of 0 represents an incompressible cake and 1 represents a compressible cake. It can be concluded that the particles forming the cake during undiluted urine filtration are incompressible while those of diluted urine filtration are slightly compressible.

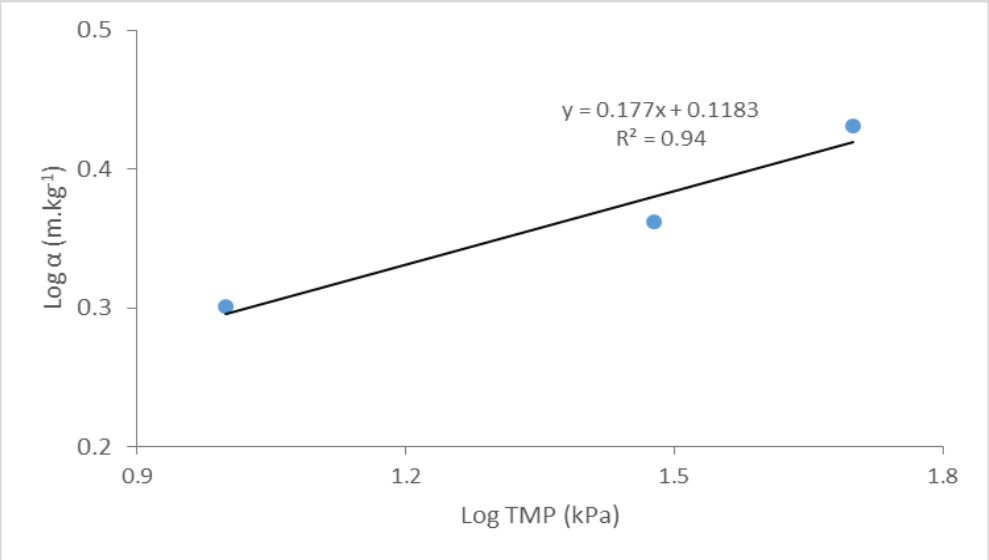


Figure 4-8: Plot of log α vs. log TMP to get the compressibility index of the cake formed during diluted urine filtration

4.2.3.2 Comparison of the cake behavior for the 3 cases

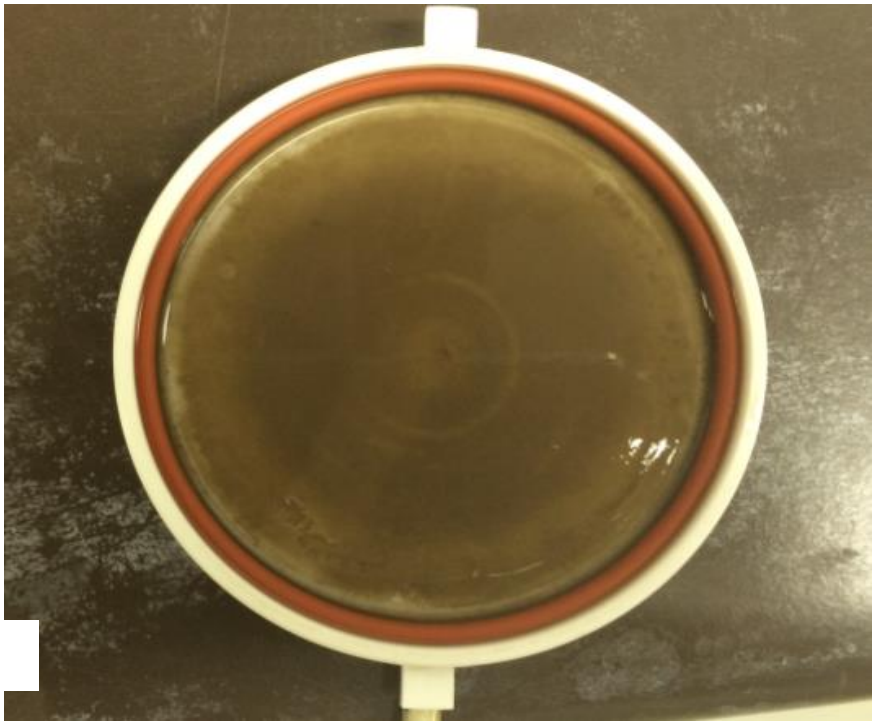
The MFI was independent of pressure (i.e. constant) and the same for the cases dealing with undiluted urine filtration (case 1 and case 2). For diluted urine filtration (case 3), the MFI was dependent on the applied pressure, increased linearly and had a lower value compared to undiluted urine. This explain the permeate flux behaviour observed in Figure 4-1: at a given TMP, the flux for case 1 and 2 were relatively similar, while it was considerably higher for case 3. In general, higher MFI corresponds to a higher fouling propensity. This implies that dilution reduces the tendency of membrane fouling as expected.

In contrast, the specific cake resistance from diluted urine filtration was higher and increased with increasing pressure. There was no difference of specific cake resistance when operating from low to high pressure or vice versa for undiluted urine as observed in the previous section because in both instances, the cake was incompressible. As known, the specific cake resistance depends on cake porosity and particle size. If the particle size of the foulants is lower, the formed cake will be more dense, so with lower porosity. In fact, the space between the particles is reduced in the cake as particles have a smaller size. The lower specific cake resistance of diluted urine could be due to the smaller particle sizes in this sample, as indicated by the particle size distribution analysis (discussed in detail in the next section): undiluted urine presents particle sizes ranging from 0.4 to 280 µm, approximately 55% in the range of 50 to 280 µm, while diluted urine has particles with sizes in the range of 0.2 to 150 µm, approximately 92%in the range of 0.2 to 100 µm. Based on this explanation, the flux decline by increasing the TMP from 20 kPa during diluted urine filtration could be then due to the densification of the compressible cake. The incompressible cake formed during undiluted urine filtration could explain the independent pressure plateau achieved with increasing TMP.

In the context of wastewater treatment, the specific cake resistance in an activated sludge was reported by Sørensen and Sorensen (1997) as 10^{12} $m.kg^{-1}$ while that of primary and secondary effluents from a wastewater treatment plant was reported by Shan (2004) as 10^{15} $m.kg^{-1}$. According to Sürücü and Çetin (1989), the typical value of α during filtration of a solution with suspended solids is 10^{15} $m.kg^{-1}$.These values are in the same order of magnitude as those reported in this study (10^{15} $m.kg^{-1}$).

It can be concluded that undiluted urine has greater fouling which results in low permeate flux. This can be seen directly on the surface of the membrane after the experiment i.e., a thicker and darker cake layer is observed (Figure 4-9a). On the other hand, diluted urine has lower fouling and lower cake formation (see Figure 4-9b). However, the cake is denser and so its resistance is similar to case 1 (according to previous section).

a



b

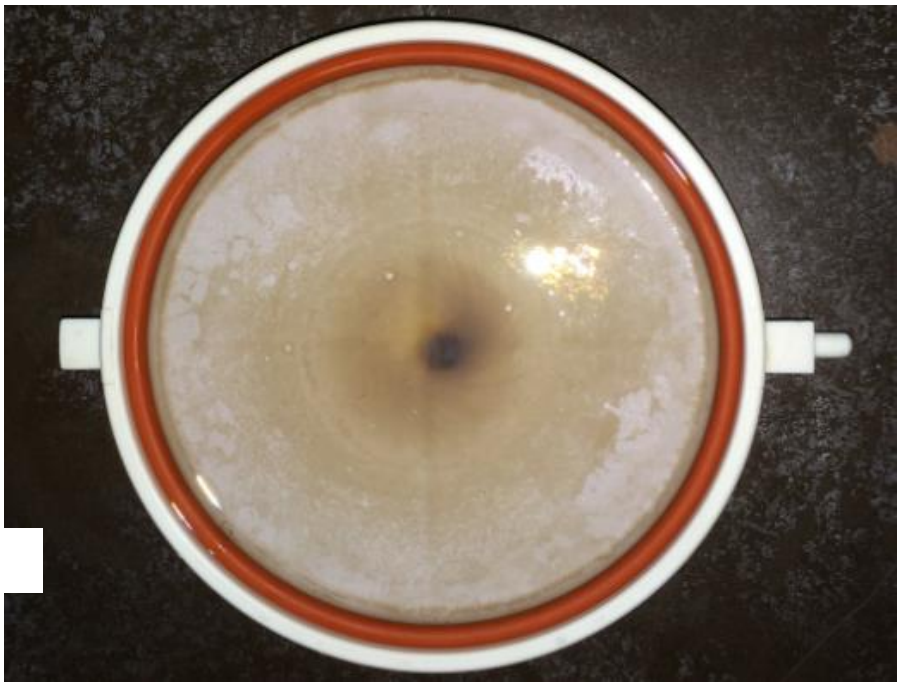


Figure 4-9: Photograph of the membrane after urine filtration - a) Undiluted urine filtration; b) Diluted urine filtration

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4.3. Physico-chemical results for stored urine before and after filtration

Physico-chemical analyses done on the feedstock and the permeate for stored urine and diluted urine included: COD measurement; TSS and TS analysis; particle size distribution (PSD); PO_4- and Cl^- concentration measurements; electrical conductivity and pH measurements. Figure 4-10 presents the rejections achieved, while Table 4-6 and Table 4-7 summarize the overall results from the physico-chemical analyses for urine (case 1) and diluted urine (case 3) respectively.

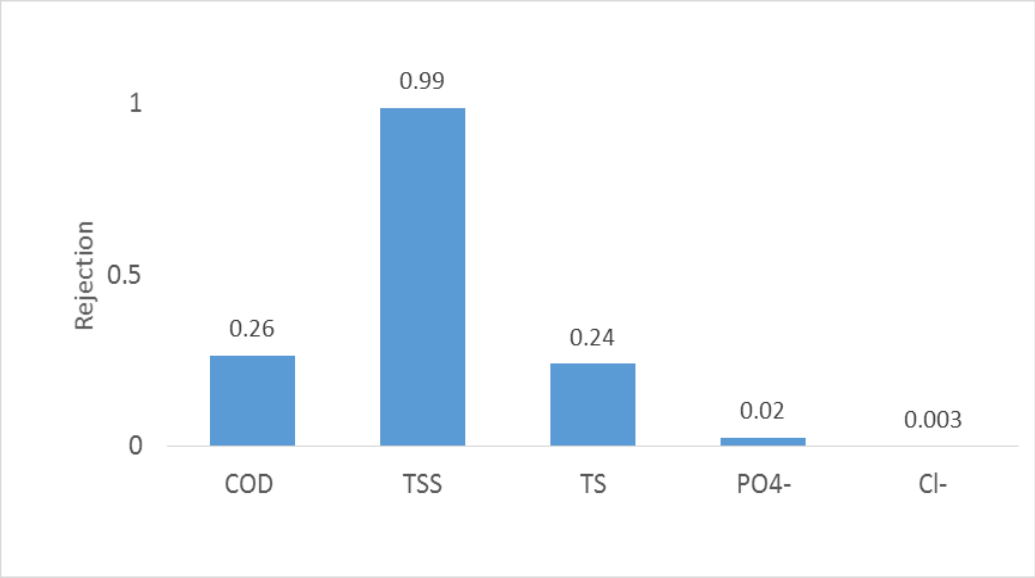

Figure 4-10: Rejections during urine filtration

Table 4-6: Physico-chemical analysis on the feedstock and the permeate after urine filtration (N = number of tests done)

	Feedstock						Permeate				
Parameter	**Unit**	**Min**	**Max**	**Average**	**±**	**N**	**min**	**max**	**Average**	**±**	**N**
COD	mg.L-1	1 591	2 776	2 176	501	8	1 206	1 982	1 599	322	8
TSS	mg.L-1	240	270	258	10	6	0	5	1	2	9
TS	mg.L-1	10 013	12 620	11 369	533	8	8 013	9 613	8 635	681	4
Particle size	µm	41.2	45.3	43.1	2.1	3	0.01	0.1	0.1	0.03	3
PO_4	mg.L-1	242	256	245	4	6	216	252	240	13	6
Cl^-	mg.L-1	3 980	4 020	4 000	16	4	3 960	4 000	3 980	16	4
EC	$mS.cm^{-1}$	20.1	32.9	26.5	4.0	15	20.8	32.6	26.5	3.7	15
pH	-	8.7	8.9			12	8.7	8.9			12

Table 4-7: Physico-chemical analysis on the feedstock and the permeate after diluted urine filtration (ND= Not Detected)

	Feedstock						Permeate				
parameter	**Unit**	**Min**	**Max**	**Average**	**±**	**N**	**min**	**max**	**Average**	**±**	**N**
COD	mg.L-1	319	555	435	100	8	241	396	320	65	8
TSS	mg.L-1	110	135	123	10	6	0	0	0	0	6
TS	mg.L-1	2 013	2 090	2 051	33	6	1 770	1 793	1 772	20	3
Particle size	µm	34.4	49.9	40.8	6.6	3	ND	ND	ND	ND	ND
PO_4	mg.L-1	48.9	49.2	49.1	0.2	6	47.1	48.7	47.9	1.1	6
Cl^-	mg.L-1	796	804	800	3.3	4	792	800	796	3.27	4
EC	$mS.cm^{-1}$	6.7	7.2	7.0	0.2	12	6.7	7.2	7.0	0.2	12
pH		8.8	8.9			12	8.9	8.9			12

4.3.1 Chemical Oxygen Demand

Organic matter content in the urine feedstock and the permeate was determined by the COD measured through the method described in section 3.5. The average COD value for the stored urine was 2 176 ± 501 mg.L^{-1} which is in the range of values reported by researchers such as Udert et al. (2003), Pronk et al. (2007b) and Hug and Udert (2013) who reported 1 650 mg.l^{-1}, 4 500 mg.l^{-1} and 3 600 mg.L^{-1} respectively . Much higher values were reported by Ronteltap (2006) and Von Münch (2009): 6 900 mg.L^{-1} and 10 000 mg.L^{-1} respectively. This is an indication that the organic content in stored urine varies greatly. The COD in the diluted urine was considered five times lower than that of undiluted (435 ± 100 mg.L^{-1}), according to the dilution factor as explained in section 3.5.

The average COD from the permeate was 1 599 ± 323 mg.L^{-1}. From this measurement, the COD rejection after urine filtration was estimated to 26%. After NF of stored urine, Pronk et al. (2006) reported a COD removal of 30-40 %. These authors concluded that a high fraction of low molecular weight organics, which can go through NF membranes (so also MF/UF membranes), are present in urine.

Removal of organic molecules is considerable i.e. ~ 25% but most of these molecules can pass through the membrane. This reduction of COD may have resulted in the decrease of the odour in the permeate since it was not as strong as that of the feed.

4.3.2 Total solids and total suspended solids

The average TS content of urine was 11 369 ± 533 mg.L-1. This value is slightly higher compared to the values reported by Vinnerås et al. (2000),ranging from 4 000 to 8 500 mg.L^{-1}. Diluted urine present an average TS content of 2051 ± 33.3 mg.L^{-1}. After filtration, the TS contents of the permeate were 8 635 ± 681 mg.L^{-1}, and 1 772 ± 20 mg.$L^{-1}$for urine and diluted urine respectively. Rejections of 24% and 14% were then respectively achieved.

The average of the TSS content of the undiluted urine was 258.28 ± 10 mg.L^{-1}. The permeate shows a TSS content almost null, which indicates a nearly complete TSS rejection as expected. On the other hand, diluted urine presents an average value of 121.61 ± 9.8 mg.L^{-1}. After filtration, no TSS were measured, implying 100 % of rejection. Note that dilution reduced the content of TSS in urine to only 2 times lower instead of 5 times according to the dilution factor. This could be probably because of the increase of solubility of the suspended solids.

After filtration, it was noted that urine was less turbid (see Figure 4-11)below.The decrease of the coloration after filtration is as a result of the decrease of TSS.

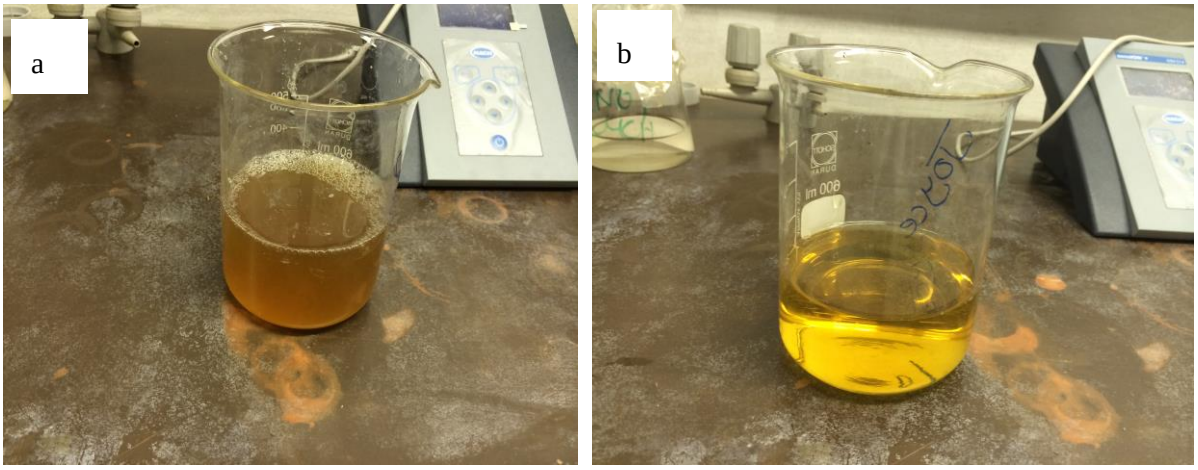

Figure 4-11: Photograph of stored urine - (a) before filtration (feedstock) (b) after filtration (permeate)

From the TS and TSS content, the total dissolved solids (TDS) content in urine was calculated: it was 11 111 mg.L^{-1}in the feedstock while 8 634 mg.L^{-1}in the permeate indicating a rejection of 22%. Note that the TDS represents most of the TS in urine with a fraction of 98%. The TSS only represents 3% of the TS. The results obtained are as expected for MF/UF membranes because the TDS are small compared to the membrane pores.

4.3.3 Total phosphates and chloride concentrations

The phosphates concentration in the urine was 245 ± 4 mg.L^{-1}. On studies about struvite precipitations from source separated urine in Nepal, Etter et al. (2011) and Hug and Udert (2013) reported a similar phosphorous concentration of 195 mg.L^{-1}, as the same as Ronteltap et al. (2010) with a concentration of approximately 240 mg.L^{-1}. Much higher concentrations were found by Von Münch (2009) with 540 mg.L^{-1} during her study on urine composition, while Ronteltap (2006) reported a value of 940 mg.L^{-1}. After filtration, the phosphate concentration was 240 ± 13 mg.L^{-1}. Phosphate rejection was thus insignificant. The diluted urine had a phosphate concentration of 49 mg.L^{-1} according to the dilution factor and this value remains almost unchanged for the permeate, i.e. 48 mg.L^{-1}.

The chloride concentration in urine, 4 000 ± 16 mg.L^{-1}, was similar to the values reported by Ronteltap (2006) and Hug and Udert (2013) with 3 060 mg.L^{-1} with 3 800 mg.L^{-1}. Similar to phosphate, chloride concentration did not vary significantly before and after filtration, so chloride rejection was null. Diluted urine has a chloride concentration of 800 and 796 mg.L^{-1} before and after filtration respectively indicating also nil rejection.

In summary, there was no significant difference in the phosphate and chloride concentration in the feed stream and the permeate. This result was expected as MF/UF membranes usually do not remove monovalent and divalent ions.

4.3.4 Electrical conductivity and pH

Electrical conductivity was 27± 4 $mS.cm^{-1}$ for the urine and the permeate. No variation of electrical conductivity occurs after filtration., Etter et al. (2011), Kocatürk and Baykal (2012) and Teshale et al. (2014) reported close values in the range 26 – 34 $mS.cm^{-1}$. Diluted urine had an electrical conductivity of 7.0 ± 0.2 $mS.cm^{-1}$. Again there was no difference of electrical conductivity before and after filtration. Dilution reduced the EC in stored urine to 3.8 times instead to 5 times, which corresponds to the dilution factor. According to Ronteltap et al. (2010), conductivity is reduced upon dilution but due to many different interactions between ions, the reduction is not necessarily linear.

The pH of stored urine was 8.8 ± 0.1. After filtration, the pH remained relatively the same with an average value of 8.9 ± 0.1. These values correspond to those reported by most of researchers who reported a value around 9. Contrary to EC, dilution did not change the pH of urine because of the buffer effect of urine at pH 9, in fact, the pKa of ammonia/ammonium is 9.3 (Siegrist et al., 2013).

4.3.5 Particle size distribution analysis

The particle size distribution of urine and diluted before and after filtration is presented in Figure 4-12. The replicates from this analysis are presented in Appendix E. The method used to determine the particle size distribution in this assumes that the particles are spherical in shape and that these particles will scatter the laser beam light at an angle that is directly related to their size (Brittain, 2001). The volume distribution was used as opposed to the diameter or surface area distribution because the laser diffraction measurement is fundamentally a measurement of volume distribution and reports particles as a volume equivalent sphere diameter.

Stored undiluted urine had particles with sizes ranging from 0.4 -280 µm. The ratio of the smaller particles (<1-100 µm) to the larger particles (100-280 µm) was 85:15. The weighted mean particle size was 43 ± 2 µm (3 replicates). This result is to be expected because the mean particle size obtained is in the range from those reported by other authors, such as Morales et al. (2013) with values ranging from 42.5 to 79.5 µm .

Stored diluted urine contained particles with size ranging from 0.2 – 150 µm. The ratio of the smaller particles (<1-100 µm) to the larger particles (100 -150 µm) was 92:8. The weighted mean particle size in diluted urine was 41 ± 6.6 µm (3 replicates). Dilution changes the PSD because the solubility of the particles should be increased. It decreases the maximum particle size (from 270 before dilution to 160 µm after) and increases the proportion of small particles inferior to 20 µm. However, the weighted mean particle size is unchanged. Dilution was carried by adding known volume of distilled water to a known volume of urine and performing the analysis immediately. It can be speculated that if more time was allowed after dilution, more particles would dissolve and the ratio of smaller particles would be more.

The particle sizes in the permeate were in the range of 0.01 -2.13 µm. The ratio of the smaller (0.01-1 µm) to the larger particles (1- 2.13 µm) was 86:14. The average particle size was 0.10 ± 0.03 µm (3 replicates). Therefore, 99% of the particles with size greater than 0.1 µm was retained on the membrane during filtration. On a study about ultrafiltration of stored urine for its safe reuse, Triger et al. (2012) reported that particles responsible for fouling, with a size in the range of 0.1 – 100 µm, could be completely removed by the ultrafiltration membranes, as seen in the present work.

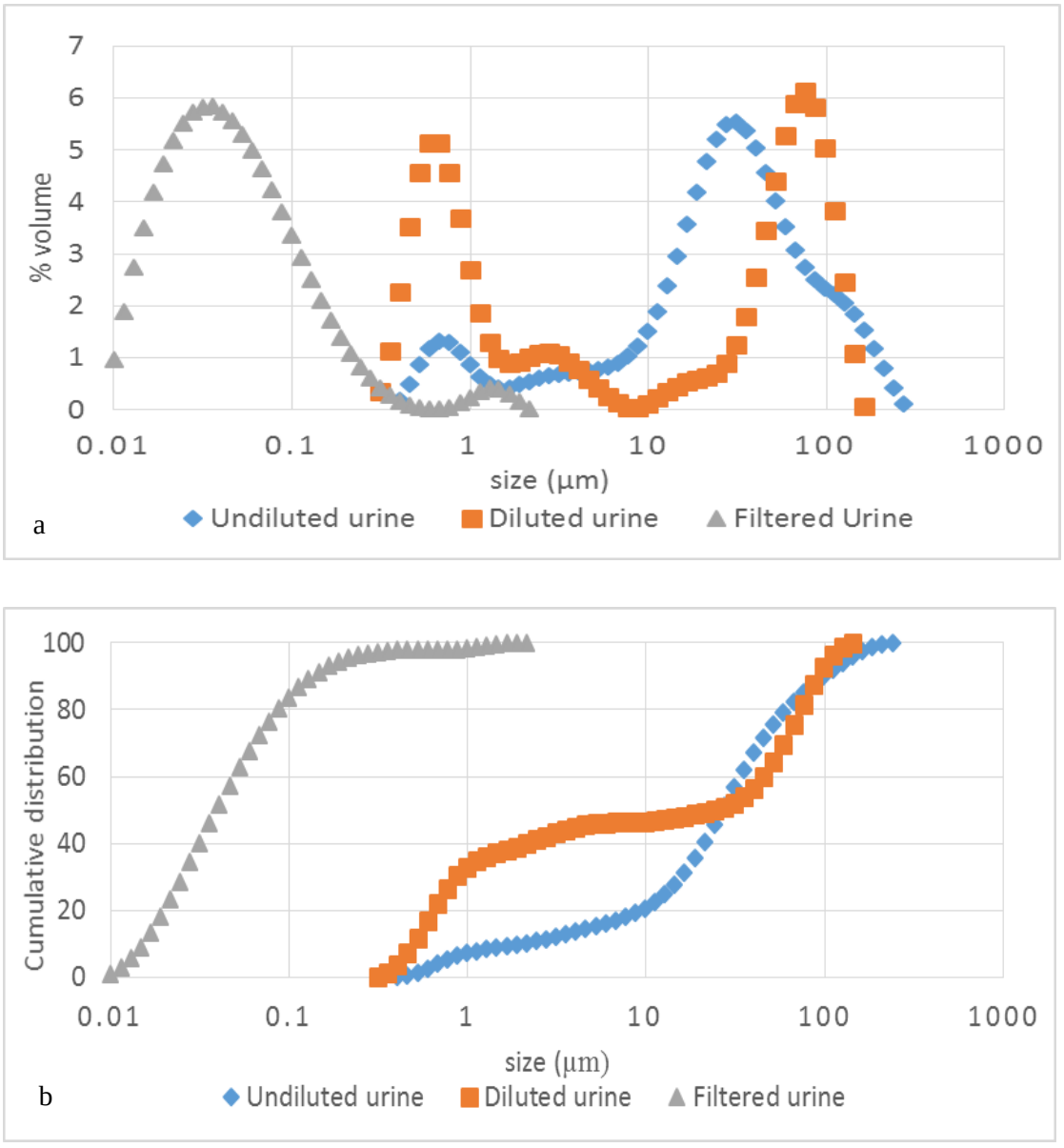

Figure 4-12: Particle size distribution in the stored undiluted and diluted urine, and in the permeate - (a) volume distribution; (b) cumulative volume distribution

5. CONCLUSIONS

This study investigates the use of pressure driven MF/UF membranes for urine and diluted urine filtration in a laboratory scale device. The rotational speed of the magnetic stirrer (fluid shear on the membrane surface) was similar throughout the experiments. However, the fluid shear was not studied in detail in this study. An amicon® stirred cell (model 8400) in the dead-end filtration mode and. polyethersulphone (PES) disc membranes 76 mm diameter (PBVK07610) from Millipore were used. The disc membranes had a molecular weight cut-off (MWCO) of 500 kDa and an effective area of 0.00418 m^2. The filtration process was characterized through the permeate flux, membrane permeability, fouling parameters (hydraulic resistances, MFI) and rejections. All the permeate flux values were normalised to 20 ℃. Three filtration experimental cases were studied in a pressure range of 10 to 60 kPa. Stored urine was used as feedstock for case 1 and 2, and urine diluted with deionized water for case 3. In case 1 and 3, the pressure was applied from low to high values whereas for case 2 the imposed pressure order was the inverse. The duration of the experiment at each pressure step was 10 min.

From the results of the experiments in this study, the following conclusions can be drawn:

- From 0 to 20 - 30 kPa, the flux increases as the TMP is increased. However, there is no considerable gain in permeate flux if pressure is increased over 10. For undiluted urine filtered from low to high pressure, a flux plateau independent of pressure was achieved after 40 kPa while for undiluted urine, the flux declines with increasing pressure after 20 kPa. During filtration from high to low pressure, the highest flux was achieved at the highest pressure and thereafter the flux remained relatively constant as the pressure was lowered.
- The membrane permeability decreased after urine filtration: approximately 90-95% of the initial permeability was lost for the different experimental cases due to membrane fouling. After cleaning the membranes by chemical and physical means, part of the membrane permeability was recovered. Recoveries were around 80% for case 1 and 3, and 37% for case 2. Since a permeability recovery of 100% could not be achieved for any of the cases, irreversible fouling occurs after urine filtration. In conclusion, fouling is very high during urine filtration for all the 3 cases.

- Cake resistance represents 85% of the total hydraulic membrane resistance, approximately 1-9% is due to irreversible fouling, and 5-10% is due to the intrinsic hydraulic resistance of the membrane. A major part of the fouling during urine filtration can be attributed to cake formation, and in much lower extent to irreversible fouling. In general, fouling (cake formation and irreversible fouling) produced at higher TMP seems be more important than that from lower TMP. Also, minimizing cake formation would improve filtration a lot since resistance due to fouling is almost negligible when operating from low to high pressure.
- With a higher MFI, undiluted urine has a higher fouling propensity than diluted urine which explains higher permeate flux for diluted urine.
- The higher specific cake resistance obtained from diluted urine filtration reflects a more dense cake compared to that from undiluted urine. As possible reason to this, it was observed that dilution reduced the diameter of the particles in urine possibly due to the increase of the solubility of the particles with dilution, so the smaller particles could cause the formation of a less porous cake. Based on this assumption, the densification of the cake while increasing the TMP could explain the flux decline observed during diluted urine filtration. Even if a lower amount of cake is observed for case 3, it has similar cake resistance to undiluted urine, probably due to its higher density (lower porosity).
- Cake compressibility study showed that undiluted urine forms an incompressible cake while diluted urine forms a compressible cake with a compressibility index of 0.18. This value presents a cake that is slightly compressible since the compressibility index of incompressible cakes is 0 while that of compressible cakes is 1.
- Almost complete rejection of suspended solids and particles greater than 0.1 µm in size (> 99%), and considerable rejections of COD and TS (~ 25%) were observed. Note that the TSS could be related to the particles higher than 0.1 µm in size, explaining their similar rejection. There was no rejection of ions, as indicated by the concentration of PO_4^-, Cl^- and electrical conductivity. Therefore, the permeate obtained after urine MF /UF filtration is much less loaded in solids and organic compounds compared to the feedstock, but the concentration of the ionic species remains similar.

- MF/UF can be used as a pre-treatment step in urine processing for nutrient and water recovery. The pre-treatment would help reduce the TSS and particle size so as to minimize fouling in other membrane processes with smaller pore size such as nanofiltration and reverse osmosis. Micro-pollutants and viruses can be present in the permeate (as indicated by the COD) Furthermore, valuable salts to agriculture (N, P, K), are also in the permeate as well also harmful salts (Na, Cl) Based on these reasons, it is recommended to further treat the urine instead of directly reusing of the permeate

6. PERSPECTIVES

From the conclusions of this study, the following perspectives in the field of MF/UF of stored urine are proposed:

- Fouling is one of the main critical parameter limiting the performance of the membranes. It would be interesting to test different pretreatment methods in order to reduce the fouling, such as coagulation and centrifugation. Precipitation/ coagulation combined with MF/UF could be an interesting axis of research for the recovery of nutrients such as struvite, hydroxyapatite and calcite. Otherwise, the foulants characterization could be an interesting research axis. This could be helpful to find methods to prevent fouling and improve membrane cleaning. For this, the acid/base solution used to clean the membrane, as well as the fouled membrane, can undergone chemical and physical analysis (SEM coupled to XRD, COD, elemental analysis and PSD). Another important parameter of fouling is fluid shear on the membrane surface. It would be interesting to research on this so as to determine how different shear rates influence cake formation on the membrane surface. Characteristics of MF/UF fouling based on adsorption kinetics and mechanics of cake formation would be another interesting area of study.
- The experiments in this study were performed under constant transmembrane pressure. Therefore, it would be interesting to the perform experiments at constant flux instead of constant transmembrane pressure and compare the performances.
- It was noted the formation of a dark layer on the top surface of the urine samples after a determined time of storage as detailed described in Appendix G. It could be then interesting to perform a study in order to better understand urine changes during its storage, such as the dark layer formation, and determine if these changes affect the membrane filtration process.

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Appendix A Filtration procedure

1. Take urine sample (approximately 1 liter) from the storage urine tank (JOJO) which is located next to PRG laboratory. Use immediately or keep in the cold room at 4 ℃.
2. Soak virgin membrane in the milli Q/distilled water for at least 1 hour with the shiny side up, changing the water for at least 3 times.
3. Place the membrane on the membrane holder (shiny side up) and an O-ring in the perimeter with the O-ring.
4. Fit the membrane holder into the cell body (cylindrical vessel) and screw the base firmly at the bottom.
5. Place the permeate outflow tube onto the exit spout of the membrane holder and the stirrer assembly into the cell body.
6. Fill the filtration cell with deionized water to 350 ml mark and cover with the cap assembly.
7. Connect the pressure reservoir to the cap assembly and ensure that the gas inlet is oriented opposite the filtrate exit port on the holder.
8. Set the pressure relief valve knob on the cap assembly in the horizontal (open position) so as not to pressurize the cell yet.
9. Slide the cell into the support stand and place on the magnetic stirrer.
10. Turn the pressure relieve valve knob on the vertical (closed) position.
11. Adjust the pressure using the regulator to 10 kPa.
12. Turn on the magnetic stirrer and adjust the stirring rate until the vortex created is approximately one-third the depth of the liquid volume.
13. Place a thermometer in the beaker which is placed on the mass balance.
14. Launch LabVIEW software on the PC.
15. Run LabVIEW program and tare the balance simultaneously.
16. Let the experiment run for 10 minutes while the mass is continuously logged by LabVIEW as you measure the temperature of the permeate each minute. (NB: water flux on clean membranes did not last for more than 10 minutes except at 10 kPa).
17. Increase the pressure in steps of 10 kPa and repeat steps 14-16 until arriving to a TMP of 60 kPa (for the determination of the initial permeability of the membrane).

18. Fill the cell with the undiluted or diluted urine and repeat steps 7 to16 (for the determination of urine/diluted urine flux).
19. Fill the cell again with deionized water without removing the membrane. Tilt the cell while filling it so as not to disturb the fouling layer that has been formed during urine filtration, then repeat steps 7 to 16 (for the determination of the resistance due to the cake layer).
20. Remove the membrane from the cell, soak it in a solution of 0.1 M NaOH for 30 minutes, followed by a solution of HCl of pH 4, and finally rinse with distilled water.
21. Use the cleaned membrane to repeat steps 3-16 (for the determination of permeability/flux recovery and the resistance due to irreversible fouling).

Appendix B Plots of flux vs time

The curves of flux versus TMP were derived from the curves of flux versus time at different TMP steps, which are presented in Figure B-1 for urine filtration and Figure B-2 for clean water flux tests.

At each TMP, the flux declines with time and then stabilises, except during filtration with deionised water. In this case, the permeate flows out the cell so fast that the latter is emptied before flux stabilisation. However, for fouled membranes (before cleaning), a stabilised plateau was achieved during filtration using deionised water.

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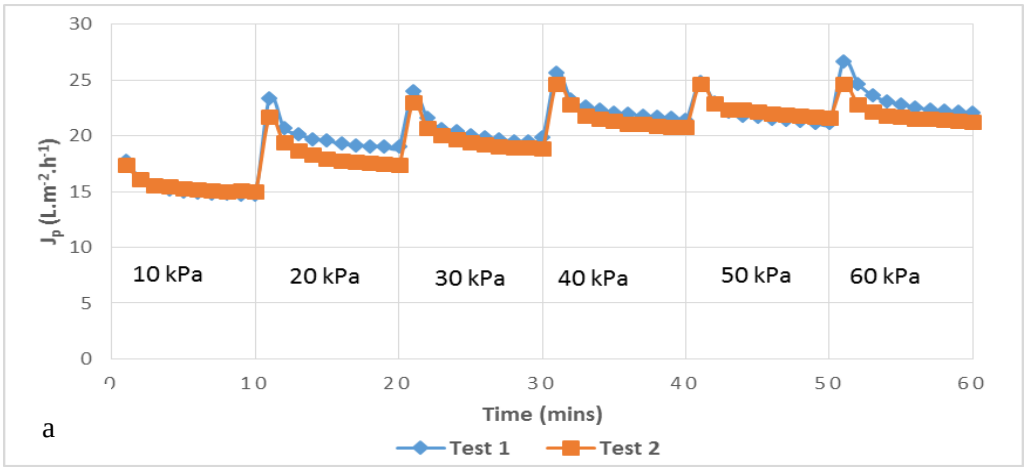

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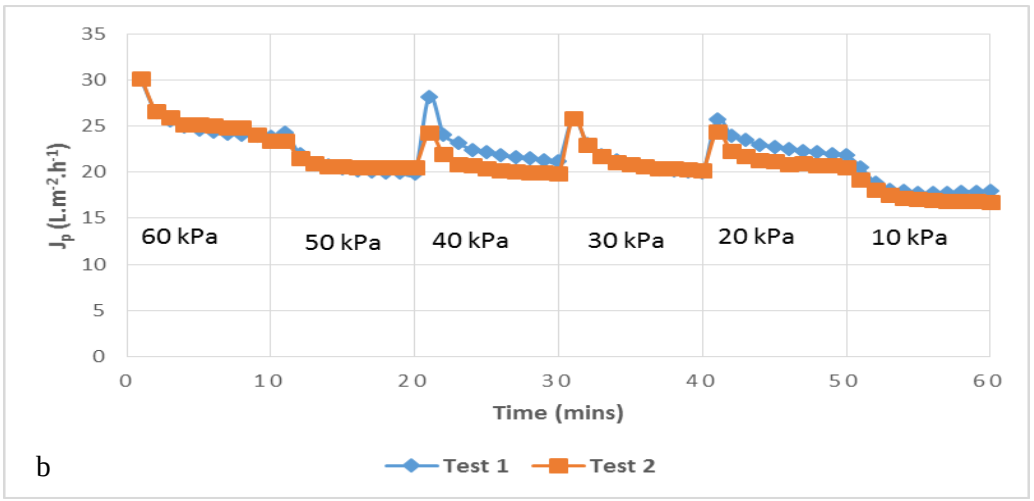

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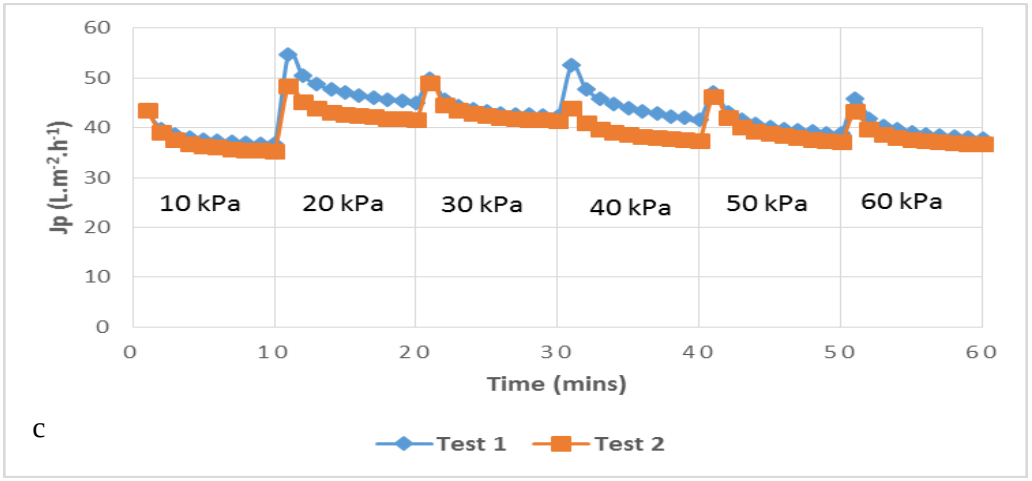


c

Figure B 1: Flux vs time during at different TMP steps during stored urine filtration for: a) case 1, b) case 2 and c) case 3

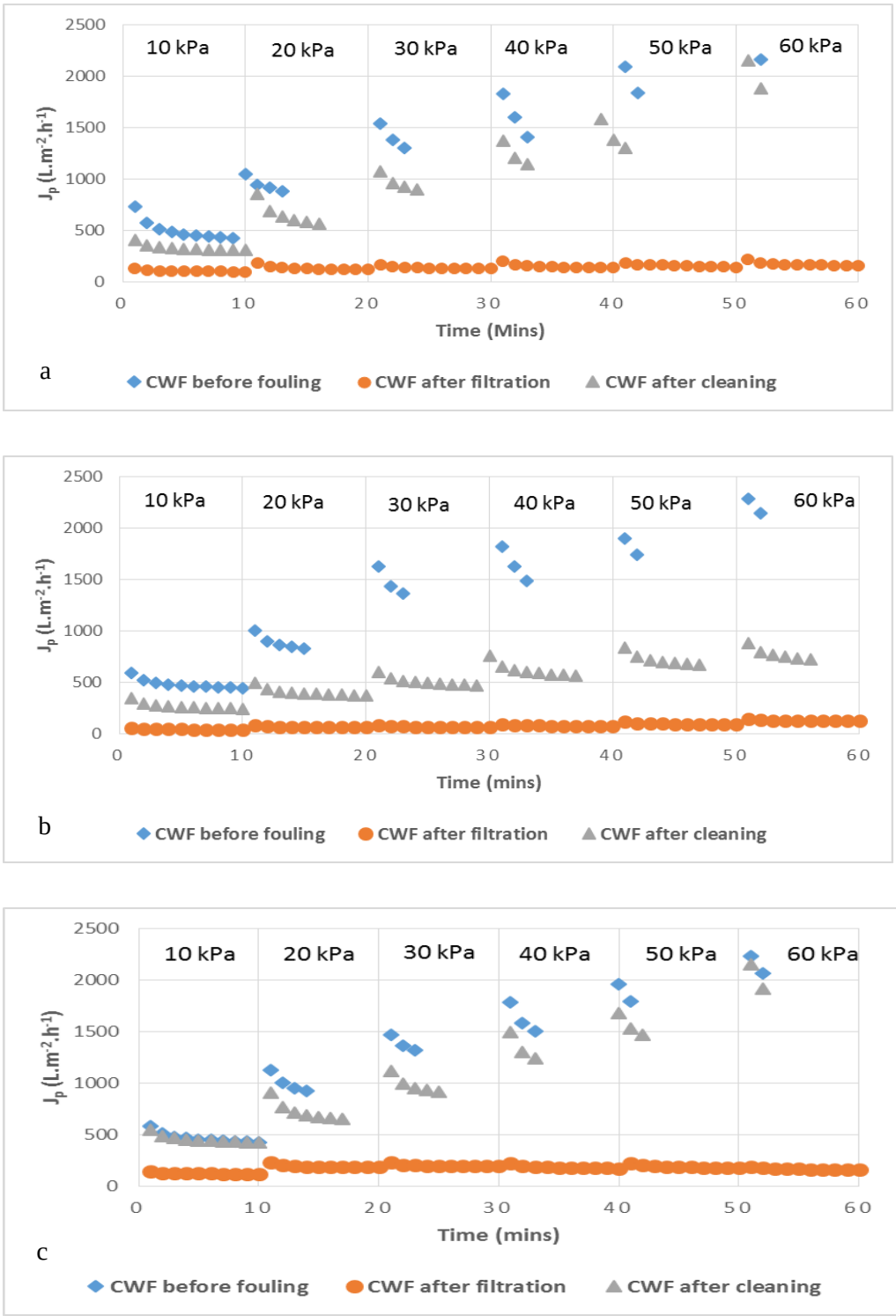


Figure B 2: Figure B 1: Flux vs time at different TMP during clean water fluxes (filtration of deionised water) for: a) case 1, b) case 2 and c) case 3

Appendix C Replicates of flux measurements during urine filtration

For case 1, the tests were performed on 3 membranes: membrane 1, 2 and 3 (Figure C-1). On membrane 1 (Figure C-1a) the flux increased with increasing TMP up to 40 kPa with a value of 22 $L.m^{-2}.h^{-1}$ and thereafter remained relatively constant. A similar trend was observed on the repeated tests indicating good reproducibility of results.

For case 2, the tests were performed on another 2 identical membranes: membrane 4 and 5 (Figure C-2). On membrane 4 (Figure C-2a) it was noted that the flux was significantly higher at 60 kPa with 26 $L.m^{-2}.h^{-1}$. It then dropped to 21 $L.m^{-2}.h^{-1}$ at 50 kPa and remained relatively constant up to 20 kPa. At 10 kPa however, the flux was 18 $L.m^{-2}.h^{-1}$. A similar trend was observed when the test was repeated on membrane 5, Figure C-2b, indicating good reproducibility of results

For case 3, the tests were performed on another 3 identical membranes (membrane 6, 7 and 8).on membrane 6, Figure C-3a, the flux increased with increasing TMP to 20 kPa to a value of approximately 47 $L.m^{-2}.h^{-1}$. It then declined to 43 $L.m^{-2}.h^{-1}$ at 30 kPa. The flux declined but very slightly above 30 kPa. Finally at 60 kPa, flux values of approximately 40 $L.m^{-2}.h^{-1}$. On another membrane, however, (membrane 7) Figure C-3b, the flux increased with increasing TMP up to 30 kPa with a flux value of approximately 45 $L.m^{-2}.h^{-1}$. It then declined sharply to a flux value of 34 $L.m^{-2}.h^{-1}$ at 40 kPa. The flux values continued to decline further as the pressure was increased and at 60 kPa, a value of 31 $L.m^{-2}.h^{-1}$ was recorded. A similar trend was observed for the when the test was repeated on another membrane, 8. The tests were reproducible on two membranes (membrane 7 and 8) except for one (membrane 6) at which it was slightly different.

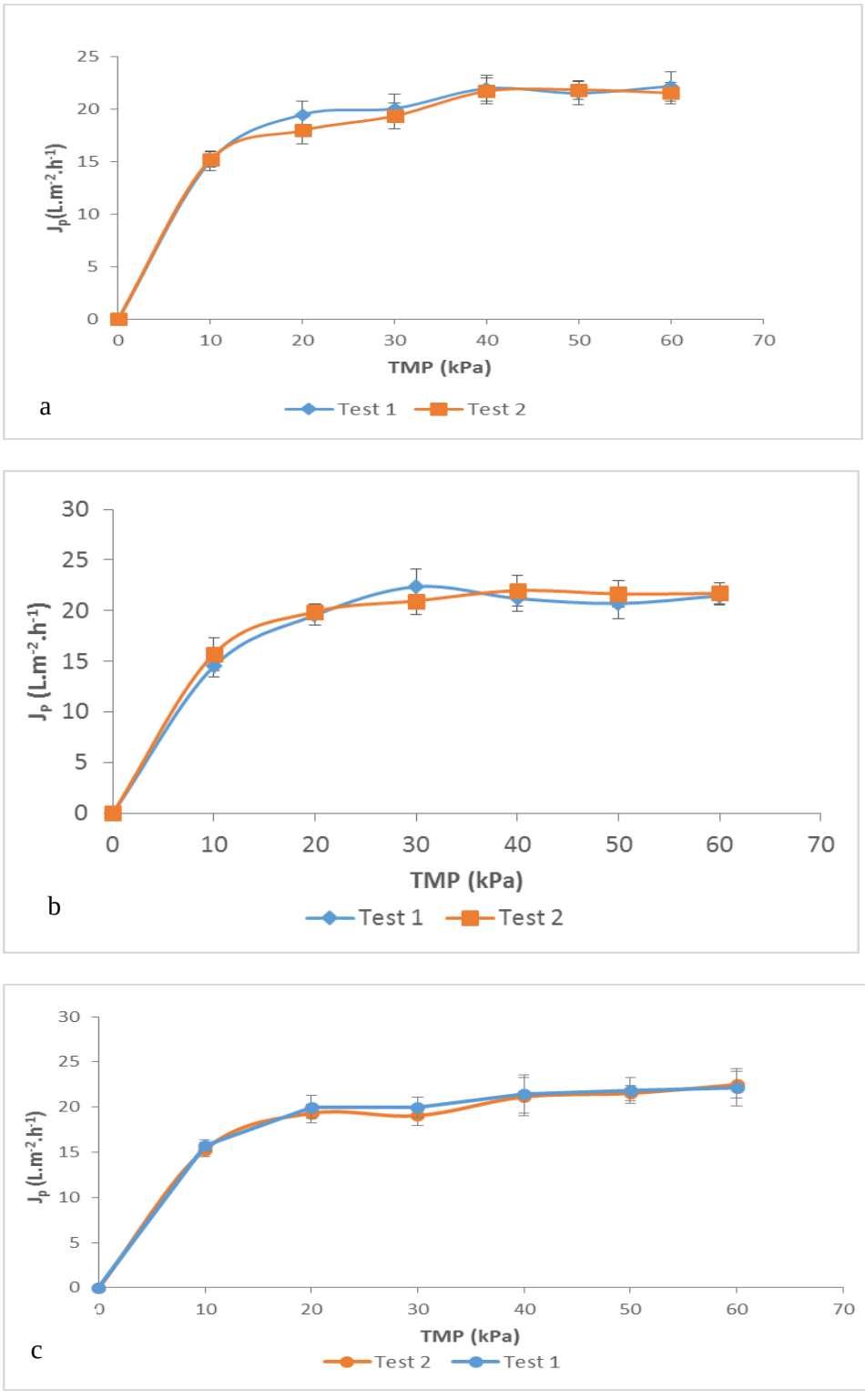


Figure C 1: Permeate flux at 20℃ obtained during urine filtration for case 1 - a) membrane 1 ; b) membrane 2; c) membrane 3

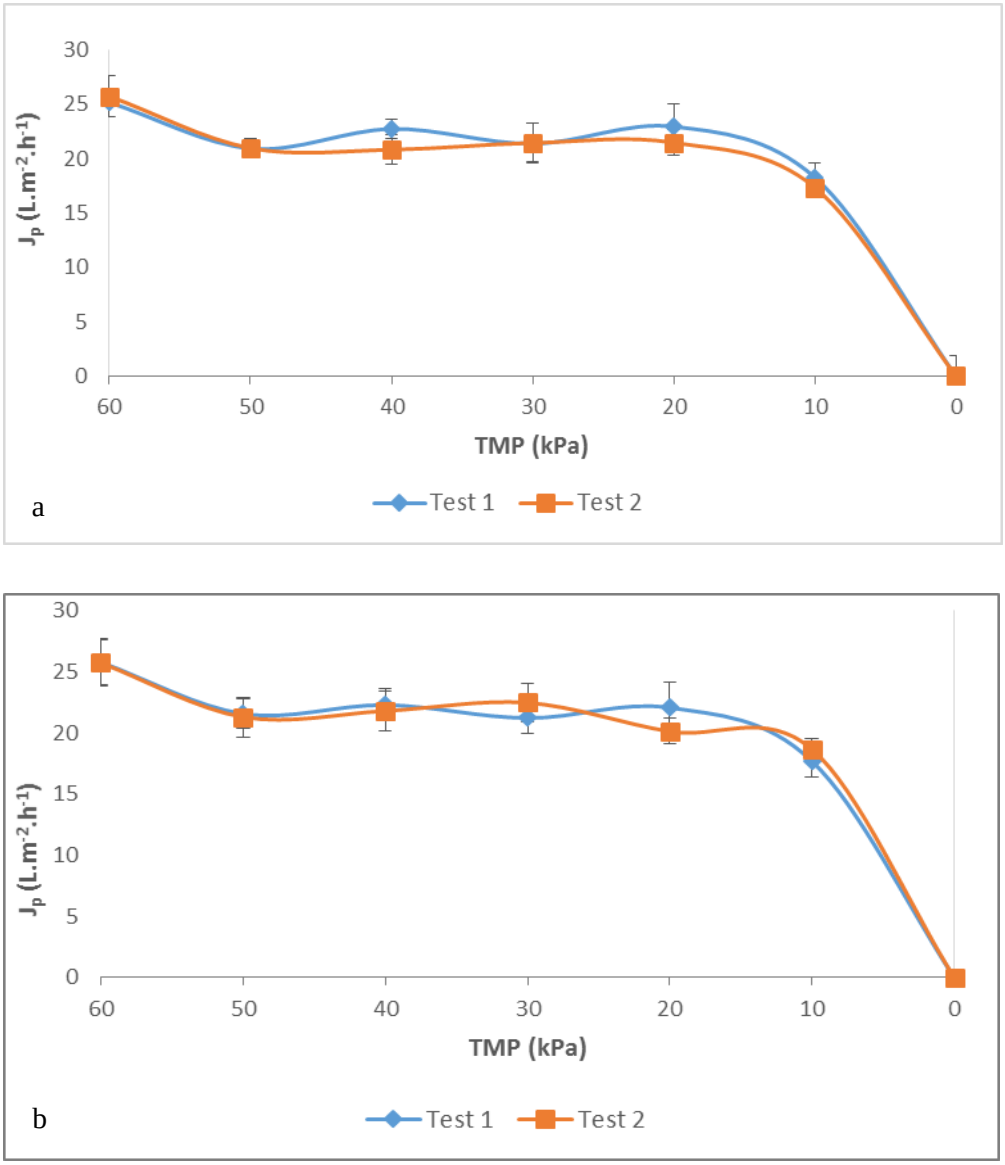
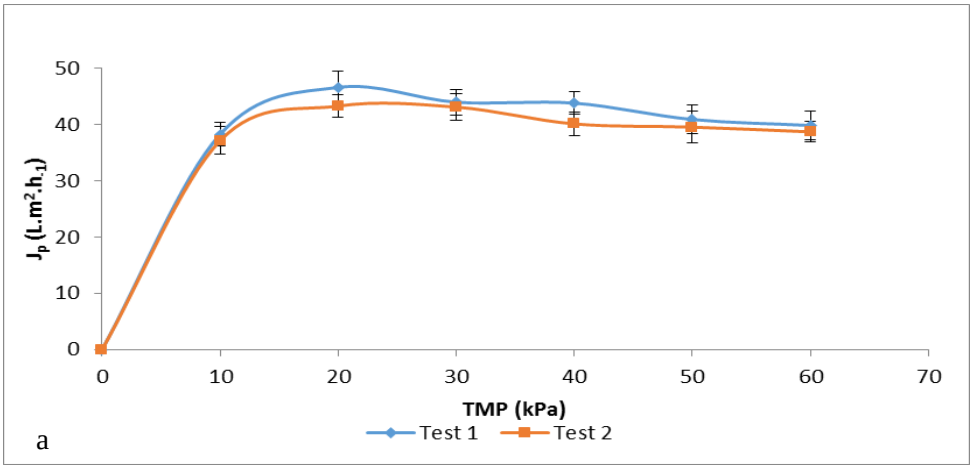
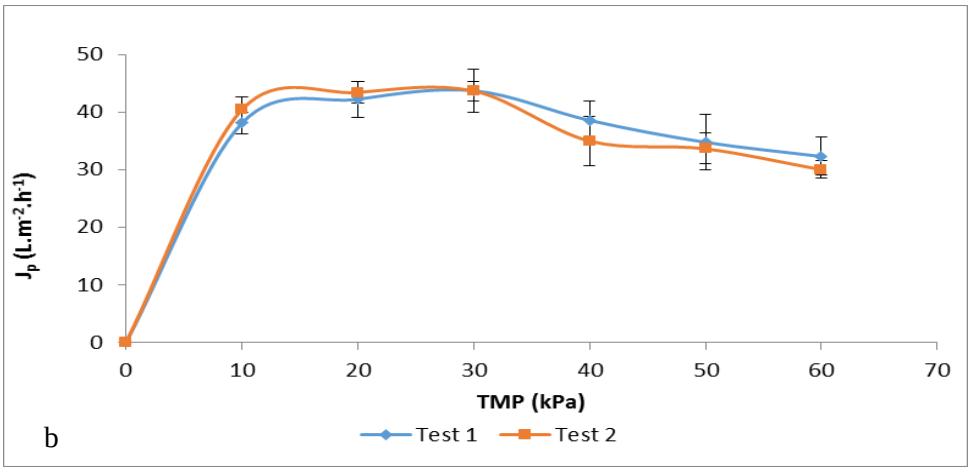


Figure C 2: Permeate flux at 20°C obtained during urine filtration for case 2 - a) membrane 4 ; b) membrane 5





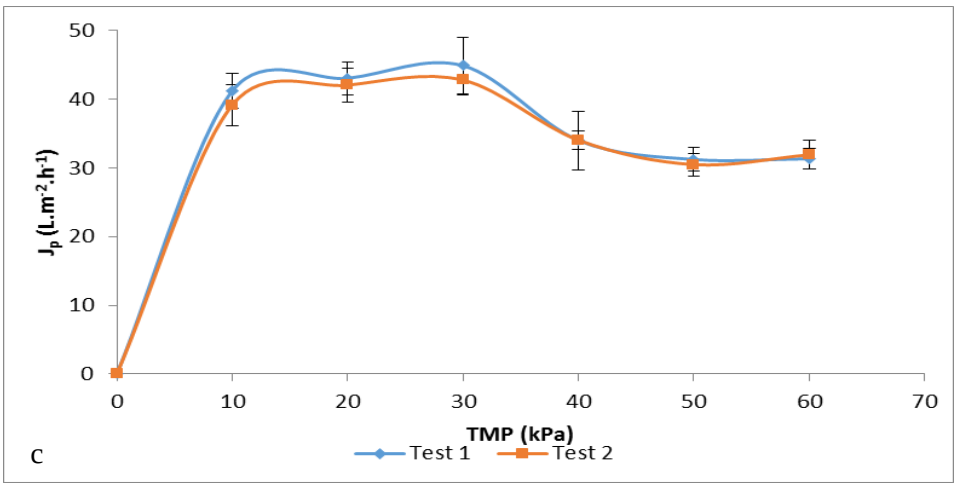
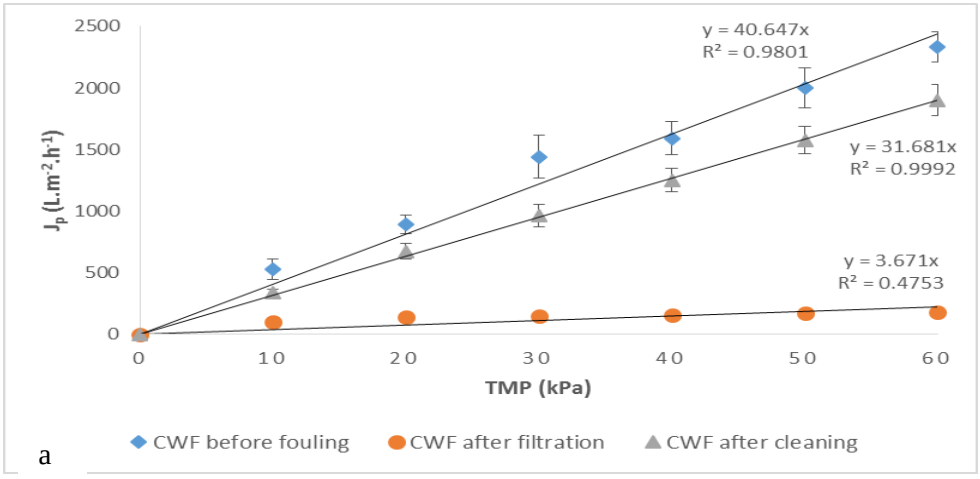


Figure C 3: Permeate flux at 20℃ obtained during urine filtration for case 3 - a) membrane 6 ; b) membrane 7; c) membrane 8

Appendix D Replicates of clean water flux tests



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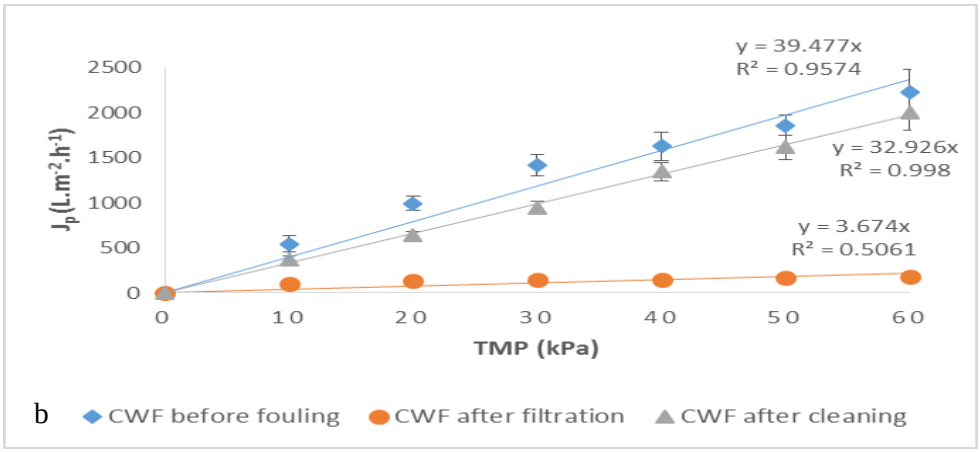

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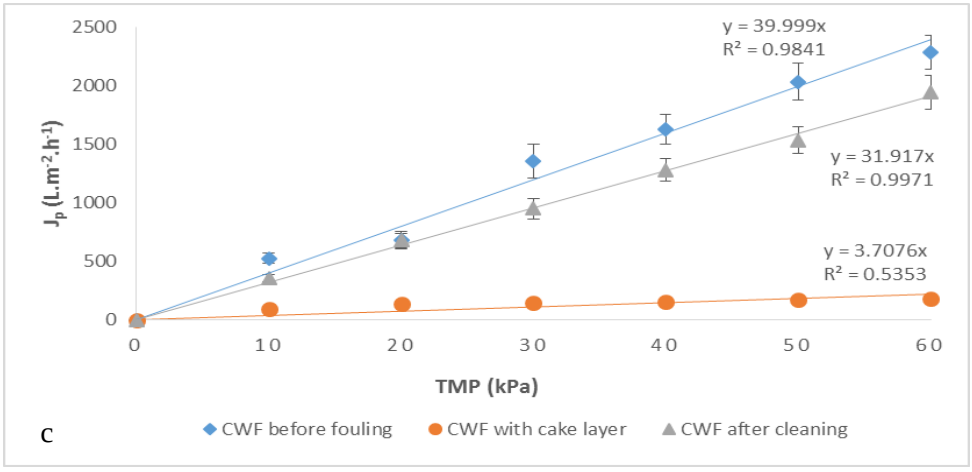
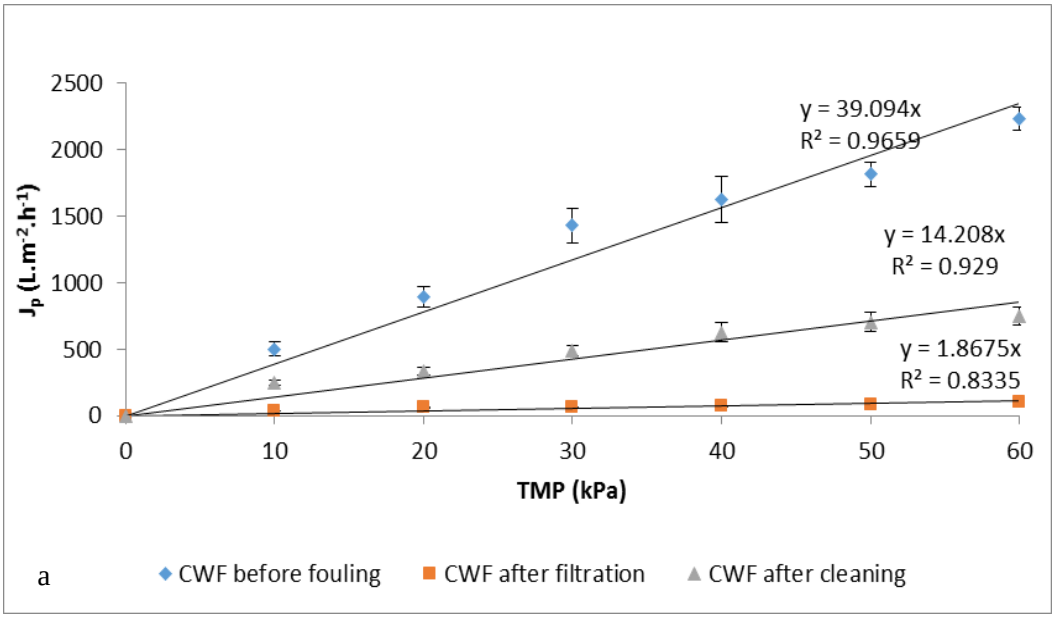


c

Figure D 1: Clean water flux tests for the membranes used in Case 1 – a) Membrane 1 ; b) Membrane 2 ; c) Membrane 3



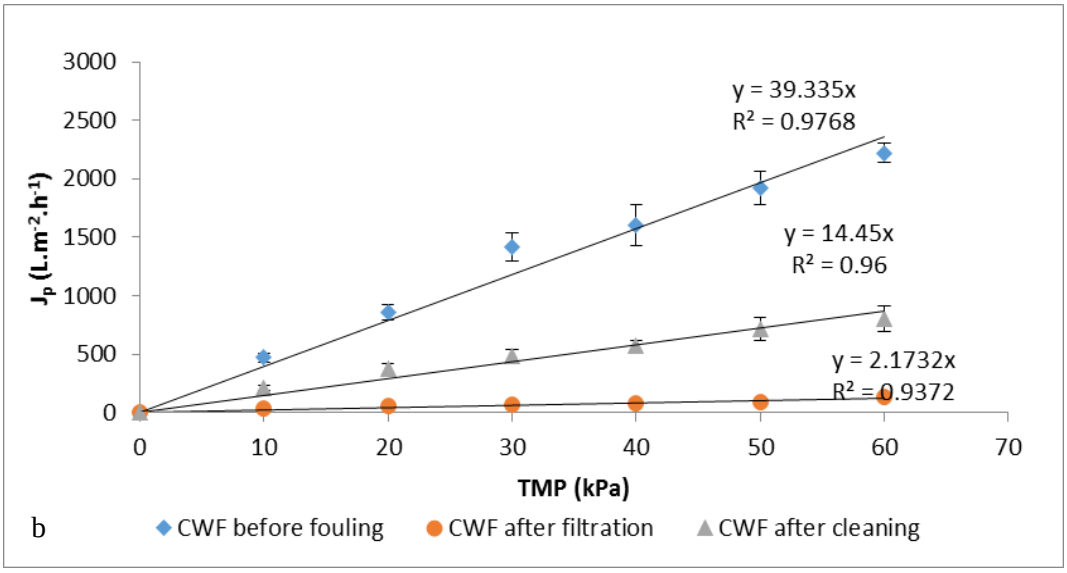
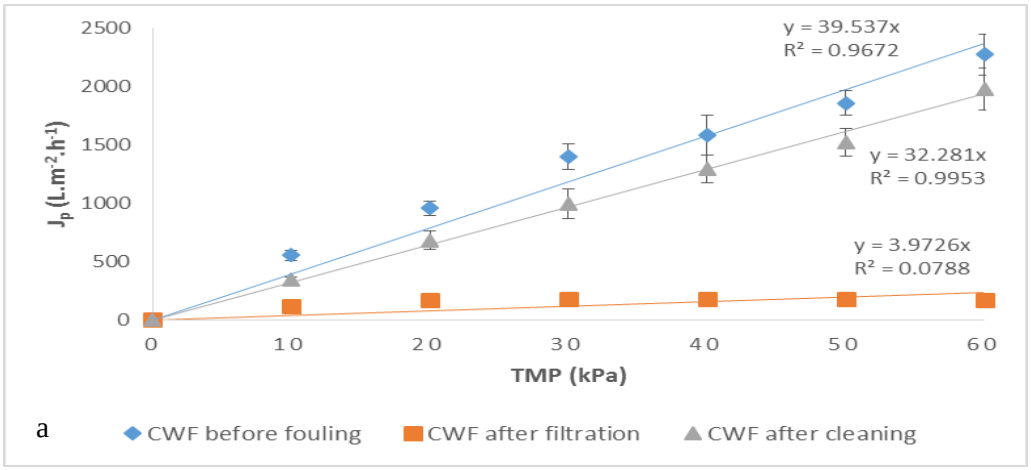
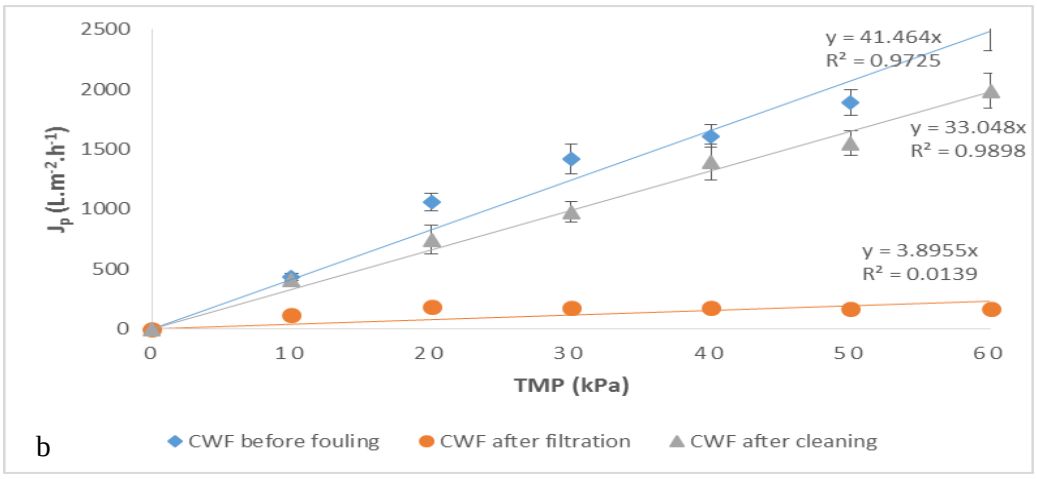


Figure D 2: Clean water flux tests for the membranes used in case 2 – a) Membrane 4 ; b) Membrane 5





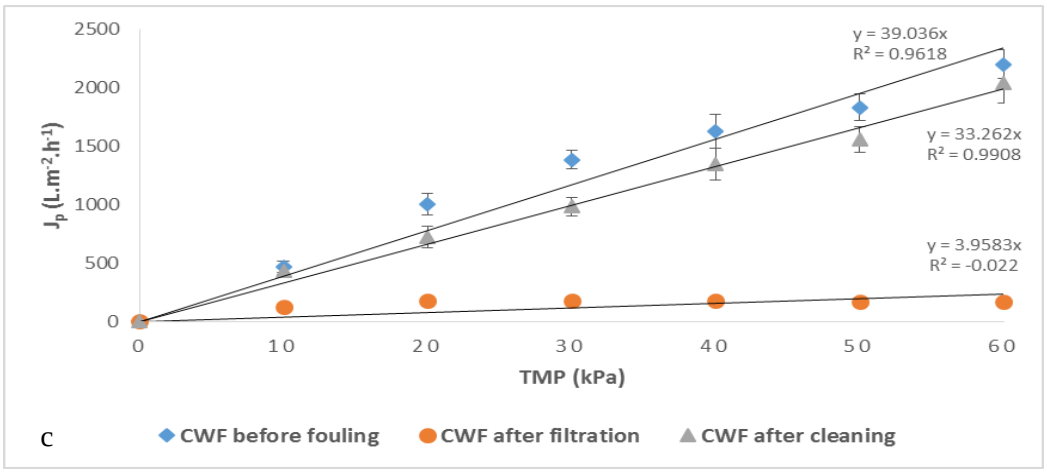
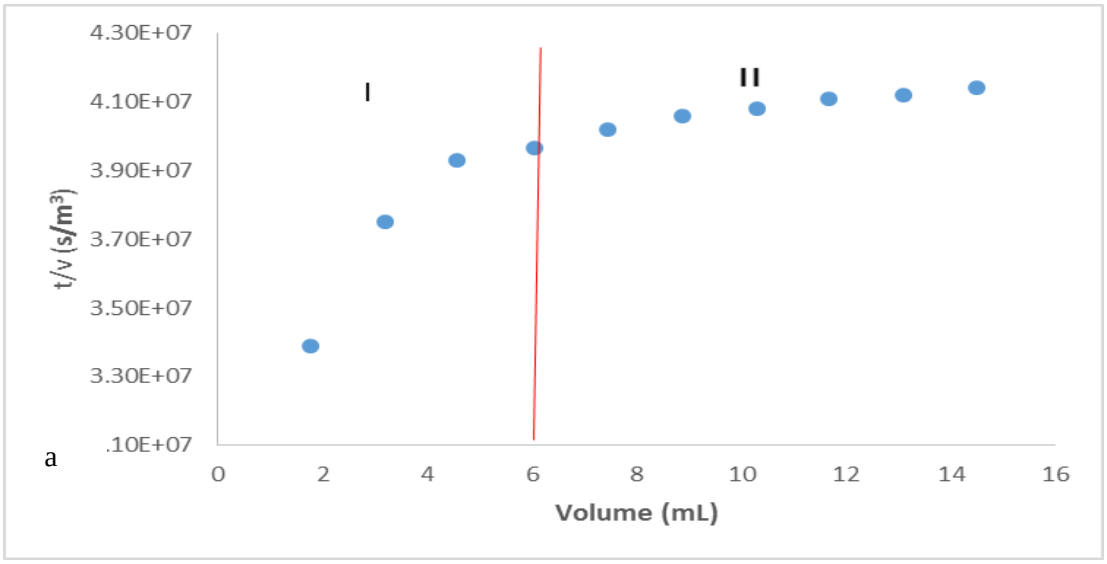


Figure D 3: Clean water flux tests for the membranes used in case 3 – a) Membrane 6 ; b) Membrane 7 ; c) Membrane 8

Appendix E Graphs for modified fouling index and specific cake resistance for case 2 and case 3



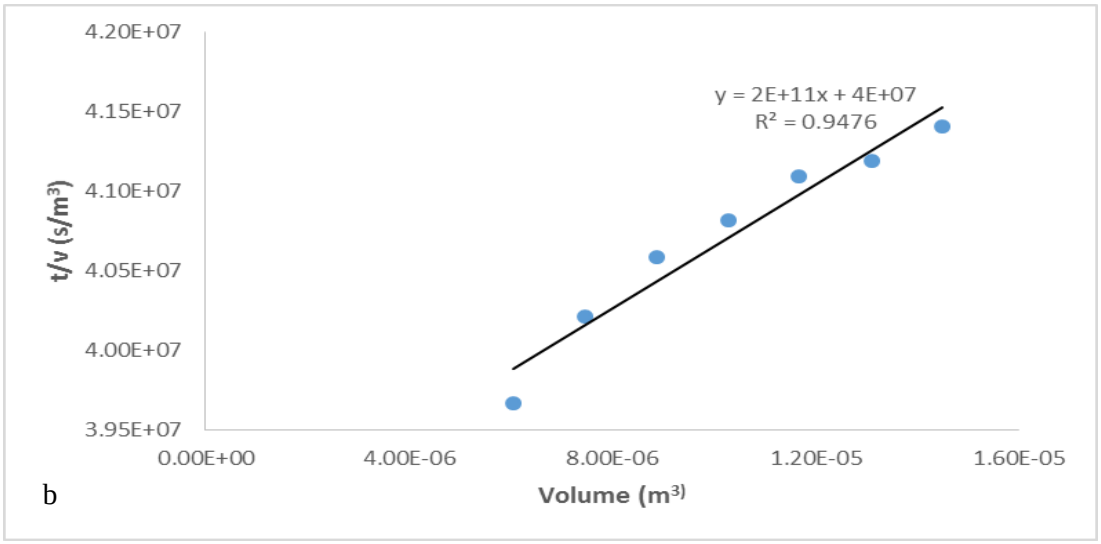
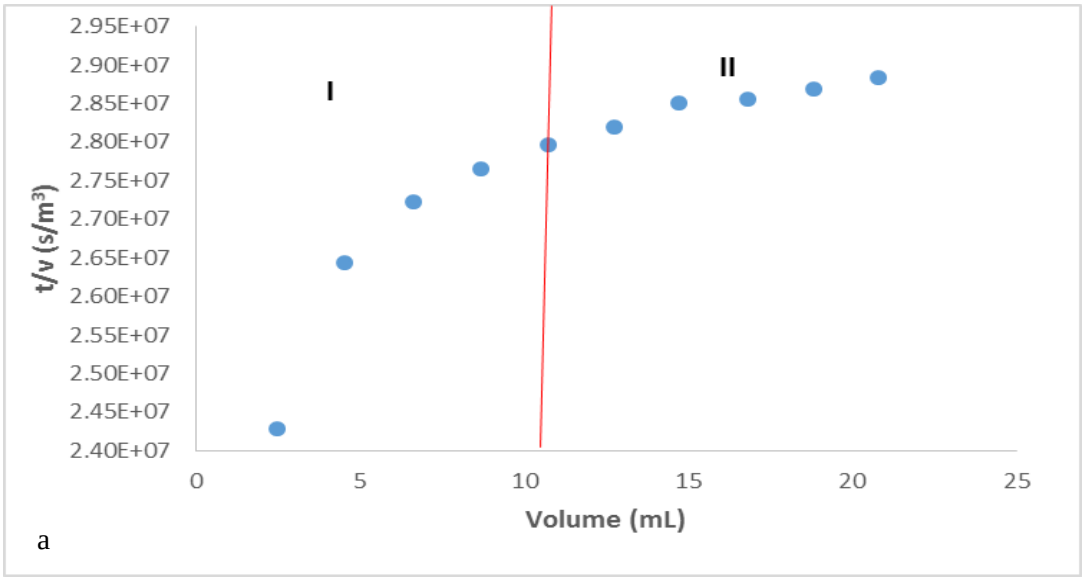
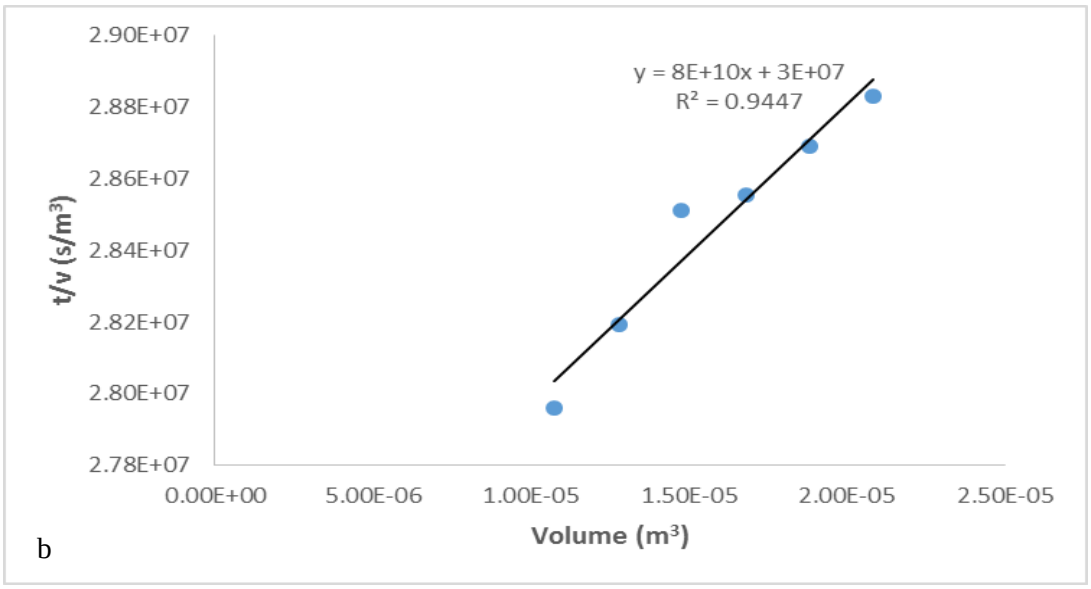


Figure E 1: Plots of time/volume versus volume at 50 kPa of stored urine 60-10 kPa for a) curve and b) Linear regression



a



b

Figure E 2: Plots of time/volume versus volume at 50 kPa of stored diluted urine 10-60 kPa for a) curve and b) Linear regression.

Appendix F Replicates of the particle size distribution analysis

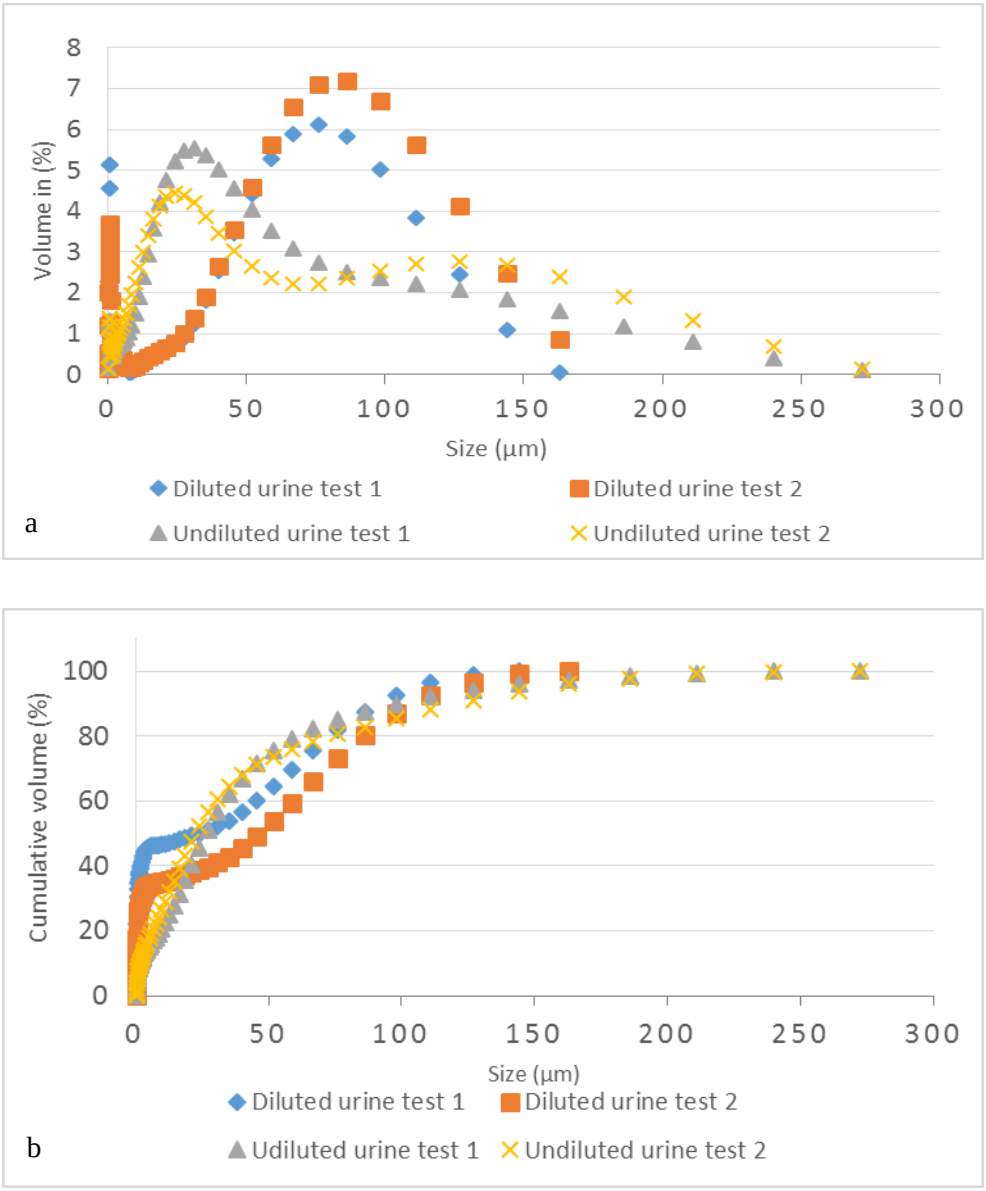
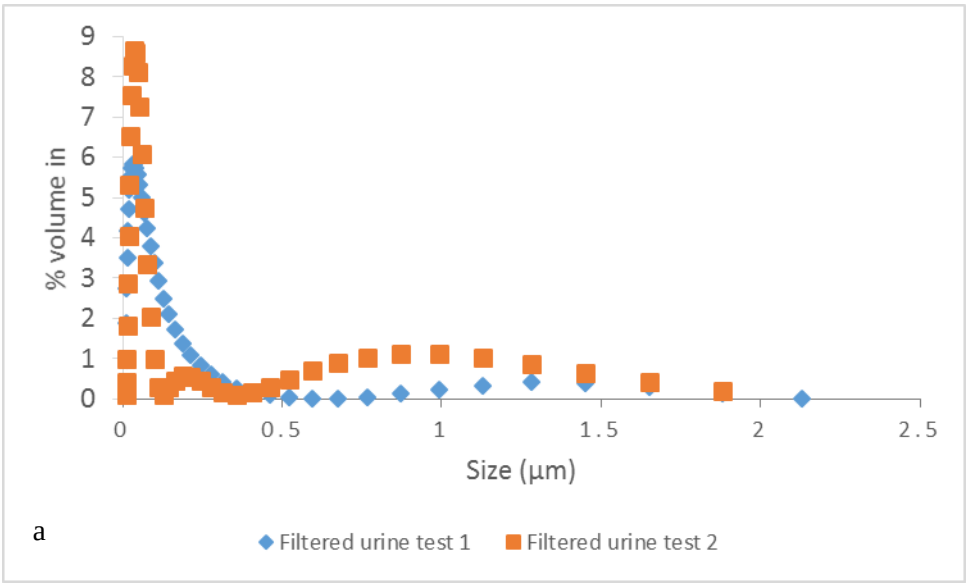


Figure F 1: Particle size distribution of stored undiluted and diluted urine before filtration - (a) Volume distribution; (b) Cumulative volume distribution



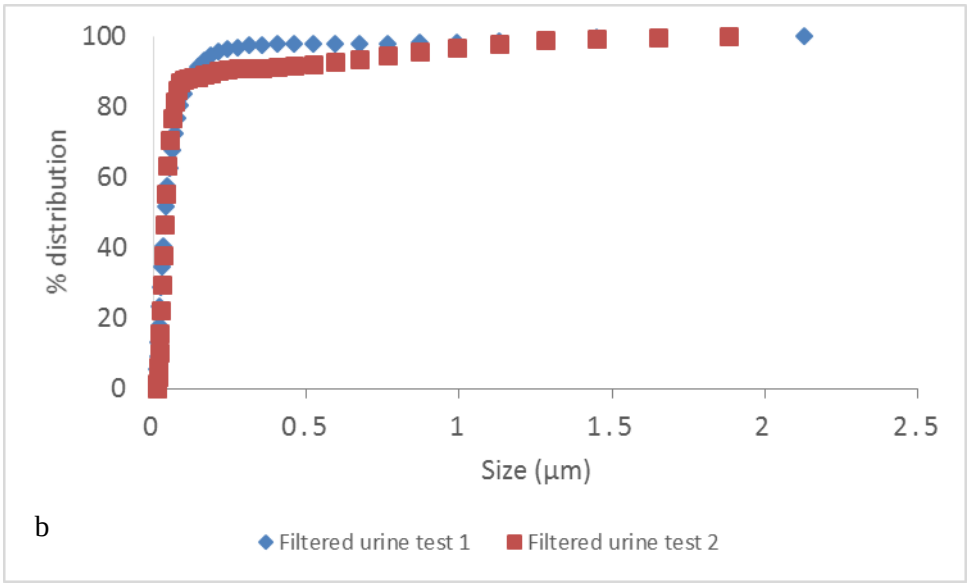


Figure F 2: Particle size distribution of stored urine after filtration - (a) Volume distribution; (b) Cumulative volume distribution

Appendix G Observation of apparition of dark layer in urine with time

It was noted the formation of dark layer on top surface of the urine with time during its storage. A hypothesis was formulated which stated that the dark layer could be due to oxidation of the organic matter in urine. This hypothesis was experimentally tested by storing equal amount of urine in 3 identical bottles under different conditions. The first bottle was purged with nitrogen to remove the oxygen from the urine then closed tightly. The second bottle was left open to air. The third bottle was closed but without nitrogen purge. The 3 bottles were monitored for 3 consecutive days. The evolution of the urine in each bottle is shown in Figure G-1. The results confirmed that the dark layer on the surface of stored urine is a result of oxidation: the urine exposed to air had the thickest layer, followed by the one in the closed bottle without purge, whereas there was almost no change in the urine from the bottle with a nitrogen atmosphere.

a

b

Figure G 1: Photographs of stored urine contained in a closed bottle previously filled with nitrogen, in a bottle open to the environment and in a closed bottle without purge of air– (a) Day 1 of storage ; (b) Day 2 of storage ; (c) Day 3 of storage

Appendix H Standard operating procedures for chemical analysis

COD

UNIVERSITY OF KWAZULU-NATAL	*Standard Operating Procedure* Pollution Research Group	Effective Date: 20 June 2013	Version.: *001*
		Reviewed by/Date:	
SOP_Chem_003 Chemical Analysis_ Chemical Oxygen Demand			Page #: *1 of 7*

Standard Operation Procedure – Chemical Oxygen Demand Closed Reflux, Titrimetric Method

1. Scope and Application

- The Chemical Oxygen Demand (C.O.D) measures the oxygen equivalent of that portion of the organic matter in a sample that is easily oxidized by a strong chemical oxidant.
- It is an important and rapidly measured parameter to measure the amount of organic compounds in stream and industrial waste studies, and in operational control of waste water treatment plants. It is also applicable for measurements on human excreta.
- This procedure described hereafter is applicable to COD values 40-400mg/L.

2. Summary

The sample is digested for 2hours in a strongly acidic dichromate solution, using silver sulphate as a catalyst and mercuric sulphate as a masking agent to prevent chloride interference. The dichromate is partially reduced by the oxidizable material present in the sample. The excess dichromate is titrated with ammonium iron (II) sulphate and the COD value calculated from the amount of dichromate.

The half reaction for the reduction of dichromate is:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

The remaining dichromate is titrated with a standard ammonium iron(II) sulphate solution:

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 7H_2O + 2Cr^{3+}$

The equivalence point is indicated by the sharp colour change from blue-green to red as the ferroin indicator undergoes reduction from iron (III) to the iron (II) complex.

3. Interferences

- Difficulties caused by the presence of chlorides in the sample are overcome by the addition of mercuric sulphate to samples before digesting. The chloride ion is then eliminated from the reaction by forming a soluble mercuric chloride complex.

- A catalyst must be used to include some organic compounds (e.g. acetic acid), while other biological compounds (eg cellulose), which are not important, are included in the determination. Pyridine is not oxidized even in the presence of the catalyst.

4. Sampling

- Preferably collect samples in glass bottles.
- Test unstable samples without delay.
- Preserve samples by acidifying with concentrated sulphuric acid to pH 2.
- Determine COD on well shaken samples. Settled samples may also be analysed if requested.
- 5ml pipette to measure out sample.

5. Safety Precautions

- Handle concentrated sulphuric acid with care.
- Always use safety goggles, gloves and laboratory coat while working in laboratory
- Wear face shield and protect hands from heat produced when contents of the vessels are mixed.
- After the analysis clean bottles and beakers with water then dry
- Dispose the used gloves after completion of analysis

- Clean the hands using antiseptic soap
- Avoid spillage and contact with skin. In the latter case use copious washings with cold water and call for medical attention.

6. Apparatus

- Carousal of 10 teflon vessels
- 100 ml Erlenmeyer flasks
- 5ml pipette
- 10ml and 5ml automatic bottle top dispensers

7. Sample Preparation –Fecal Sludge

- Weigh out between 1.8g and 2g of well mixed fecal sludge sample.
- Place the weighed out sample into a blender with 250ml of distilled water.
- Blend for 30 seconds.
- Transfer the blended mixture into a volumetric flask and top up to 1L with distilled water.
- Transfer the 1L solution to a plastic bottle and store in the cold room.

8. Reagents

Standard Potassium Dichromate $K_2Cr_6O_7$ Digestion Solution: 0.0167M

Add to about 500ml distilled water 4.913g $K_2Cr_6O_7$ previously dried at 105 °C for 2hrs.

Add 167ml concentrated Sulphuric acid H_2SO_4 and 13.3g Mercuric Sulphate $HgSO4$.

Dissolve and cool to room temperature before diluting to 1L.

Sulphuric Acid H_2SO_4 /Silver Sulphate Reagent Ag_2SO_4 (COD Reagent)

Add **26g of silver sulphate** crystals or powder to 2.5L of concentrated sulphuric acid using a magnetic stirrer. Shake well and leave for 2days for dissolution.

Ferroin Indicator 2 drops

Dissolve 1.485g 1:10 phenentroline monohydrate and 0.695g ferrous sulphate ($FeSO_4.7H_2O$) in distilled water and dilute to100ml.

Ferrous Ammonium Sulphate Fe $(NH_4)_2$ $(SO_4)_2.6H_2O$: 0.10M

Dissolve 39.2g Fe $(NH_4)_2$ $(SO_4)_2.6H_2O$ in distilled water.

Add 20ml concentrated Sulphuric acid H_2SO_4 and dilute to 1L.

Standardize daily against **Standard Potassium Dichromate $K_2Cr_8O_7$ Digestion Solution**

9. Calibration

- Prepare a standard $K_2Cr_2O_7$ solution daily to correct any variation in the concentration of the Ferrous Ammonium Sulphate.
- Prepare a blank with each set of samples consisting of 5 ml distilled water in place of sample together with all the reagents and digest together with samples.
- **Standard Preparation**
- Add 3ml of standard $K_2Cr_2O_7$ digestion solution to 5 ml of distilled water. Add 7ml COD reagent and cool it down. Titrate with FAS titrant using 2 drops of ferroin indicator.
- Quality Control: Potassium hydrogen Phthalate (KHP)
  Lightly crush and then dry out KHP to a constant weight at 120°C. Dissolve 0.0425g in distilled water and then dilute to 250ml. This solution has a theoretical COD of 200mg/L. Solution is stable if refrigerated, for a period of 3 months in the absence of biological growth.

10. Procedure

Sample Preparation

- Add 5ml sample to each teflon vessel.
- Add 5ml distilled water to another vessel (blank).
- Add 3ml potassium dichromate digestion solution into each vessel.
- Add 7ml sulphuric acid reagent (with silver sulphate) in each vessel.
- The acid must be poured down the wall of the flask while flask is tilted. If sample is too concentrated it will turn green, and a higher dilution of sample must be used.

Digestion

- Place teflon vessels into the rotor, with the temperature probe placed into the teflon vessel labeled 1.
- Switch on the microwave and select COD METHOD:
- 15min ramping time to 150 °C, 30min digestion at 150°C and 1hr cooling to 50 °C.
- Transfer contents from teflon vessels into 100ml flasks for titrating.

Titration

- Titrate the excess dichromate in the digest mixture with standard ferrous ammonium sulphate using 2 drops of ferroin indicator.
- Titrate from a sharp green/orange to red brown end point.
- Take reading.**Error! Bookmark not defined.**

Calculation

$$COD\ (mg\ O_2/L) = \frac{(Blank - Titration)\ \times molarity\ of\ FAS\ \times 8000}{Sample\ (ml)}$$

Where:
8000 = milliequivalent weight of oxygen × 1000 ml/L

$$Molarity\ of\ FAS = \frac{Volume\ 0.0167M\ K_2Cr_2O_7\ Solution\ Titrated\ (ml)}{Volume\ FAS\ used\ in\ titration\ (ml)} \times 0.10$$

$$COD\ (mg\ O_2/L) = \frac{(Blank - Titration)\ \times molarity\ of\ FAS\ \times 8000}{Sample\ (ml)} \times \frac{V}{M}$$

$$COD\ in\ Wet\ Sample\ (g\ O_2/g) = \frac{COD\ (mg\ O_2/L)}{1000}$$

$$COD\ in\ Dry\ Sample\ (g\ O_2/g) = \frac{COD\ in\ Wet\ Sample\ (g\ O_2/g)}{Total\ Solids\ (g/g)}$$

Where:

V = Total volume (L)

M = Mass of sludge used in sample preparation (g)

11. Precision and Accuracy

mg COD/L	%SD	%Error

Total Solids

Standard Operation Procedure –Solids

Introduction

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

Total Solids is the term applied to material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes total suspended solids, the potion of solids retained by a filter and total dissolved solids, the portion that passes through the filter of 2.0um or smaller. Fixed Solids, is the term applied to residue of total, suspended or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called volatile solids.

Total Solids Dried at 103-105ºC

1. Scope and Field of Application

Total Solids are determined in a wide variety of liquid and semi-liquid materials. These include portable waters, domestic and industrial waters, polluted waters and sludge produced from treatment processes. It is of particular importance for the efficient operation of a treatment plant.

2. Principle

A known volume of well-mixed sample is evaporated to dryness in a porcelain crucible in a hot air oven at 105ºC, the solids remaining are cooled and weighed. The residual material in the crucible is classified as total solids, and may consist of organic, inorganic, dissolved, suspended or volatile matter.

3. Interferences

- Highly mineralized water with a significant concentration of calcium, magnesium, chloride and sulphate may be hygroscopic and require prolonged drying, proper desiccation and rapid weighing.
- Exclude large, floating particles from the sample if it is determined that their inclusion is not desired in the final result.
- Disperse visible floating oil and grease with a blender before withdrawing sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust.

4. Sampling

- Mix the sample well to suspend solids uniformly.
- Remove the test portion rapidly before any settling of solid matter occurs.
- Use a measuring cylinder and not a pipette for sludge and wastewater samples.
- Use a crucible for feces.
- Use a volume or mass of sample to ensure a measurable residue- limit sample to no more than 200mg residue
- Suitable aliquots: Liquid samples – 100ml, Sludges -30ml, feces 10-20g.

5. Safety Precautions

- Always use safety goggles, gloves and laboratory coat while working in laboratory
- Wear gloves suitable for withstanding high temperatures when removing crucibles from the oven.
- After the analysis clean bottles and beakers with clear water keep it for drying

- Dispose the used gloves after completion of analysis
- Clean the hands using antiseptic soap
- Disinfect hands after washing with soap
- Avoid spillage and contact with skin. In the latter case use copious washings with cold water and call for medical attention.

6. Apparatus

- 50ml capacity evaporating porcelain crucibles
- Desiccator
- Drying oven
- Four – place Analytical Balance

7. Reagents

- Nil.

8. Calibration

- Check the temperature throughout the oven area by placing a calibrated thermometer on each shelf, after 30mins, check temperature at each level against oven setting.
- Adjust oven setting if necessary.
- If temperatures are uneven on the shelves, check insulation.

9. Procedure

Prepare Crucible

- If volatile solids are to be measured ignite clean crucible at 550ºC for 1hr in the furnace. If only total solids are to be measured, heat clean crucible to 103-105ºC for 1h. Store and cool dish in a desiccator until needed. Weigh immediately before use.....**W1g**

Sample Analysis

- Measure out appropriate volume (30ml) /mass (10-20g) that will yield a residue between 2.5 and 200mg of a well mixed sample using correct volume measuring cylinder or analytical balance.....**Vml**...**Wg**. Transfer quantitatively to the weighed crucible, rinsing the cylinder with small volumes of distilled water to dislodge heavy particles. Add washings to the crucible.
- Place in hot oven at 103-105°C for 24hrs
- ***Dry sample for at least 1hr in an oven 103-105°C, to dish in desiccator to balance temperature and weigh. Repeat cycle of drying, cooling, desiccating and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5mg, whichever is less.***
- Remove the next day and cool for 15 minutes and weigh.....**W2g**

10. Calculation

$$Total\ Solids\ in\ Sample\ (mg/l) = \frac{(W_2 - W_1)g \times 100\,000}{V_{sample}\ (ml)}$$

$$Total\ Solids\ in\ Wet\ Sample\ (g/g) = \frac{(W_2 - W_1)g}{W_{sample}\ (g)}$$

$$Moisture\ Content\ (g) = W_{sample}(g) - [(W_2 - W_1)]g$$

Total suspended solids

Total Suspended Solids Dried at 103-105°C

1. Scope and Field of Application

Suspended solids are useful determinants in the analysis of polluted, re-use and waste waters. It is used to evaluate the strength of domestic/industrial waste waters and to determine the efficiency of treatment units, such as settling tanks, biological filters, and the activated sludge. Use of glass fiber filter pads is preferred to crucibles because of the saving in filtration time and the only prior preparation necessary is drying in an oven for 30mins at 105°C.

2. Principle

A measured volume of well shaken is vacuum filtered through a dried pre-weighed 110mm diameter glass fiber filter. The filters and residue is dried to a constant weight at 103-105°C. The increase in weight of the filter represents the total suspended solids.

3. Interferences

- Exclude isolated large floating particles.
- Samples high in dissolved solids must be washed adequately.
- Loss in mass of the rinsed glass fiber filters must be taken into the final calculation.
- The larger the sample, the smaller the factor applied in the calculation, but avoid prolonged filtrations.

9. Sample Preparation – Fecal Sludge

- Weigh out between 1.8g and 2g of well mixed fecal sludge sample.
- Place the weighed out sample into a blender with 250ml of distilled water.
- Blend for 30 seconds.
- Transfer the blended mixture into a volumetric flask and top up to 1L with distilled water.
- Transfer the 1L solution to a plastic bottle and store in the cold room.

10. Procedure

Dry Filter Paper

- Use 110mm glass fiber filter paper Whatman No 4(20-25um)
- Mark the filter paper with a pen
- Place papers on the stainless steel mess of appropriate size
- Position on top shelf in oven at 105ºC for 30min
- If volatile solids are to be measured ignite at 550 ºC for 15min in a furnace.
- Transfer to desiccator
- Cool for 20 minutes before weighing

Weigh Filter Paper

- Transfer filter paper rapidly to balance
- Note mass**(W1)**grams, to fourth decimal place

Prepare for Analysis

- Place filter pare into a 110mm diameter funnel, with the marking on the lower side
- Measure out appropriate volume to yield between 2.5 and 200mg dried residue of well mixed sample

- Place funnel into flask with side arm attached to a vacuum pump.
- Apply pump
- Wet paper with distilled water to seal edges of the paper to surface of the funnel
- Pour sample onto the filter paper, keeping sample in the middle of the paper.
- When filtration is complete. Remove paper by placing the end of a small thin spatula along the edge of the filter paper and lift slowly.
- Remove the paper with a pair of tweezers, taking care not to tear the paper.
- Fold paper twice to form a triangle enclosing sample residue. This seals the residue in the filter paper and protects it from contact with air.

Dry and Weigh

- Place triangles on a stainless steel mess
- Place in oven at 105ºC for 2hrs
- Remove from oven and place in desiccator
- Cool to room temperature
- Weigh after 20 mins, as rapidly as possible
- Note mass **(W2)**grams

11. Calculation

$$Total\ Suspended\ Solids\ (g/ml) = \frac{(W_2 - W_1)}{V_{sample}(ml)}$$

$$Total\ Suspended\ Solids\ in\ Wet\ Sample\ (g/g) = TSS\ (g/ml) \times DF$$

$$Total\ Suspended\ Solids\ in\ Dry\ Sample\ (g/g) = \frac{TSS_{wet\ sample}}{Total\ Solids\ (g/g)}$$

Total phosphates

Standard Operation Procedure – Phosphate and total P Analysis (Cat. No. 1.14848); (Cat. No. 1.14543)

1. Scope and Field of Application

The measurement of total phosphorus and phosphate is essential for performance studies on the struvite reactor. The phosphate concentration in influent and effluent gives indication on the performance of the reactor operation whereas the total P values (influent and effluent) demonstrate the effectiveness of the filtration material used. The recovery can be calculated based on these measurements.

(Phosphate) Measuring range 0.02 – 11.46 mg/L P_2O_5

(Total Phosphate) Measuring range 0.11 – 11.46 mg/L P_2O_5

2. Principle

In sulfuric solution orthophosphate ions react with molybdate ions to form molybdophosphoric acid. Ascorbic acid reduces this to phosphomolybdenum blue (PMB) that is determined photometrically.

3. Interferences

- Sample for phosphate analysis must be pretreated by filtration (0.45µm) to remove most of turbidity (interferes with photometric measurement)

- In case of total P sample mustn´t be filtrated! The filtration step would remove already precipitated struvite during urine storage and thus false the analysis
- In any case urine should be diluted at least 1:100 to avoid matrix effects
- (Other interferences are mentioned in operational manual of test kits)

4. Sampling

- Preferably collect samples in glass bottles.

5. Safety Precautions

- Handle concentrated acid with cares
- Always use safety goggles, gloves and laboratory coat while working in laboratory
- After the analysis clean bottles and beakers with clear water keep it for drying
- Dispose the used gloves after completion of analysis
- Clean the hands using antiseptic soap
- Disinfect hands after washing with soap
- Avoid spillage and contact with skin. In the latter case use copious washings with cold water and call for medical attention.

6. Apparatus

- Heating Block for Total P measurement
- Spectrophotometer

Total P measurement:

- Digestion for the determination of total phosphorus (Wear eye protection!):
  - Pipette 5.0 mL pretreated sample into a reaction cell.
  - Add 1 dose Reagent P-1K, close cell tightly, and mix.
  - Heat the cell at 120°C in the preheated thermoreactor for 30 min.
  - Allow the closed cell to cool to room temperature in a test-tube rack.
  - Do not cool with cold water!

- Shake the tightly closed cell vigorously after cooling.
- Add 1 dose Reagent P-2K, close the cell tightly, and mix.
- Add 1 dose Reagent P-3K, close the cell tightly, and shake vigorously until the reagent is completely dissolved.
- Leave to stand for 5 min (reaction time), then measure the sample in the photometer.

Procedure (Using Standard Solution - Reagent R-1)

Note: The error caused by the photometric measurement system and the mode of operation can be determined by means of the standard solution. This is used **without dilution** in place of the sample solution.

Basic Procedure: Proceed according to the instructions given in the package insert of the respective test kit and in the manual of the photometer used (as described in the total P measurement procedure using UD samples). In this case, however, use **undiluted reagent R-1** in place of the sample without adjusting the pH!

Detailed Procedure:

Total P measurement using a standard solution (reagent R-1):

- Digestion for the determination of total phosphorus (Wear eye protection!):
  - Pipette 5.0 mL **undiluted reagent R-1** into a reaction cell.
  - Add 1 dose Reagent P-1K, close cell tightly, and mix.
  - Heat the cell at 120°C in the preheated thermoreactor for 30 min.
  - Allow the closed cell to cool to room temperature in a test-tube rack.
  - Do not cool with cold water!

- Shake the tightly closed cell vigorously after cooling.
- Add 1 dose Reagent P-2K, close the cell tightly, and mix.
- Add 1 dose Reagent P-3K, close the cell tightly, and shake vigorously until the reagent is completely dissolved.
- Leave to stand for 5 min (reaction time), then measure the **standard sample** in the photometer.

11. Disposal of Waste Chemicals

- Dilute 10 ml into 1000ml.
- Slowly add NaCO3 until ph 6-8 is reached.
- Flush down the sink with excess water.

12. Calculations

$$Wet\ Sample\ Concentration\ (g/g) = \frac{A}{1000} \times \frac{V}{M}$$

$$Dry\ Sample\ Concentration\ (g/g) = \frac{Wet\ Sample\ Conc.\ (g/g)}{Total\ Solids\ (g/g)}$$

Where:

$A - Spectroquant\ Reading\ Concentration$
$V - Volume\ of\ Dilution\ (L)$
$M - Mass\ of\ Sludge\ used\ in\ sample\ preperation\ (g)$

Chloride

Standard Operation Procedure – Chloride Analysis

1. Scope and Application

- The M926 Chloride analyzer is used for the determination of chloride ions. It is an instrumental analogue of 'Argentimetry', the titrimetric methods using Silver Nitrate reagent. Like these classical methods it relies on the chemical formation of the very insoluble salt, silver chloride. The importance of chloride determination has been realized for well over a centuary, with many variations and changes being made to the techniques in order to improve the detectability and selectivity.
- The M926 Chloride analyzer is a direct reading, digital chloride meter. It is designed for fast and accurate determinations of chloride levels in industrial samples.
- Sample volume is 0.5ml and results are displayed on a digital readout in mg/L(milligrams per liter chloride) or mg%(milligram percent)salt as sodium choride

2. Summary

- An accurately measured volume of sample(0.5ml is added to an acid buffer. The analyser automatically titrates chloride ions by passing a known constant current between two silver electrodes which provides a constant generation of silver ions.
- These silver ions combine with the chloride in the sample to form silver chloride, which is held in suspension by the colloid stabilizer.
- During the titration period the digital readout is updated every 0.3seconds. During these periods the number of silver ions introduced into the sample combine with one unit measurement of chloride.
- When all the chloride has been precipitated as silver chloride, free silver ions begin to appear and the solution conductivity changes.
- This change is detected by the detector electrodes and the readout is stopped, displaying the results directly readout in mg/L(milligrams per liter chloride) or mg%(milligram percent)salt as sodium chloride.

- Another sample may now be added to the same buffer and the cycle repeated.
- The digital display is held until starting another cycle, when it is automatically reset to zero.
- **Sample range: 10-999mg/l chloride or 2-165mg%salt.**

3. Interferences

- Never leave bottles of Standard solution uncapped, as prolonged exposure to the atmosphere will affect the solution's concentration.

4. Sampling

- Most reliable results are obtained on fresh samples

5. Safety Precautions

- Always use safety goggles, gloves and laboratory coat while working in laboratory
- Use eye and hand protection when preparing acid or handling color reagent
- Prepare and keep color reagent in fume hood

6. Apparatus

- Sherwood Chloride Analyser Model 926

7. Reagents

8. Sample Preparation – Fecal Sludge

- The mg% salt value is ontainedfrom the mg/l chloride result by a fixed calculation. This calculation is only correct for sample /diluent ratios equivalent to 1gm.sample per 100ml.diluent used to 'dissolve/diluent'the sample.
-
- Weigh out between 1.8g and 2g of well mixed fecal sludge sample.
- Place the weighed out sample into a blender with 250ml of distilled water.
- Blend for 30 seconds.
- Transfer the blended mixture into a volumetric flask and top up to 1L with distilled water.
- Transfer the 1L solution to a plastic bottle and store in the cold room.

9. Procedure

1. Connect power, switch on and allow 5 minutes for the machine to warm up.
2. Fill the plastic beaker, supplied, to the mark with the combined acid buffer, place the beaker on the platform and raise the platform until it locates in the up position.
3. Pipette 0.5ml of 200mg/l standard solution into the beaker.
4. Press the 'condition' button and wait for the condition cycle to complete.
5. Pipette 0.5ml of sample into beaker and press titrate button.
6. When the stirrer stops, note the reading on the display. If the results are required in mg% salt depress the select button to mg% salt.
7. Repeat 4 and 5 for further samples.
8. At the end of the 5th titration, the message 'condition in 2' will appear on the screen. If only two further samples are to be run, return to number 4. If more than two samples are to be run, continue with number 9. 'Condition 1' will be shown after the 6th titration.

   IMPORTANT

When the 7th titration is complete any further sample added will be lost. "change buffer and condition / condition required" will be displayed on the screen and the titrate button will have no effect. Go to number 9.

9. If " change buffer and condition / condition required" is displayed, continue with number 9.
10. Lower beaker and empty out contents. Rinse with deionized water and dry with clean tissue.
11. If necessary, adjust the vertical position of the anode, Item 2, so that it is the same length as the other electrodes.
12. If more samples are to be titrated return to number 2.
13. When determinations are complete, remove the beaker and dry the electrodes and stirrer by blotting with a clean tissue.

10. Operating Precautions and hazards

- The electrodes may go black during use; clean electrodes only if there are measurement errors.
- The analyser requires a warm up period of 5 minutes to meet the stated specification.
- Reproducibly accurate results are dependent on the reproducible pipetting from sample and from aqueous standard to sample. If the calibration is checked with an aqueous standard and reproducibly low results are obtained, hold up in the pipette should be suspected and a rinse out technique employed.
- **Samples should have low ionic strength, neutral ph and free of sulphide, sulphydryl silver halides, silver reactive substances(other than chloride), solid matter and high levels of dissolved solids.**

pH

Standard Operation Procedure – pH of Faecal Sludge

1. Scope and Field of Application

This method is an electrometric procedure for measuring pH in soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20% of the total volume of the sample.

2. Interferences

Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1, may give incorrectly high pH measurements.

Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water, or (3) be cleaned per the manufacturer's instructions.

3. Safety Precautions

- Always use safety goggles, gloves and laboratory coat while working in laboratory
- After the analysis clean bottles and beakers with clear water keep it for drying
- Dispose the used gloves after completion of analysis
- Clean the hands using antiseptic soap
- Disinfect hands after washing with soap

- Avoid spillage and contact with skin. In the latter case use copious washings with cold water and call for medical attention.

4. Apparatus

- pH meter with means for temperature compensation.
- Glass electrode.
- Reference electrode -- A silver-silver chloride or other reference electrode of constant potential may be used.
- 50 ml beaker
- Thermometer and/or temperature sensor for automatic compensation.
- Analytical balance -- capable of weighing 0.1 g.

5. Procedure

Sample Preparation

- To 20 g of waste sample in a 50 ml beaker, add 20 ml of distilled water, cover, and continuously stir the suspension for 5 min. Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices.
- Let the waste suspension stand for about 15 min to allow most of the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 ml of reagent water.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned if it becomes coated with an oily material.

Measurement of pH

Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish good electrical contact through the ground glass joint or the fiber-capillary hole.

Insert the electrode into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

If the sample temperature differs by more than 2 °C from the buffer solution, the measured pH values must be corrected.

6. Results

Report the results as "waste pH measured in water at __°C" where "__°C" is the temperature at which the test was conducted.

7. References

http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9045d.pdf

Particle size analysis

Standard Operation Procedure – Mastersizer 3000_Particle size analyzer

1. Scope and Application

The Malvern Mastersizer 3000 measures the size of particles contained within a sample, and presents the data according to the user's needs.

2. Summary

The purpose of the unit is to transmit red laser light and blue light through a sample and then use its detectors to generate data about the light scattering pattern caused by particles in the sample, which can be interpreted by the Mastersizer software to provide accurate particle size information.

Dispersion unit-Hydro EV is a wet dispersion unit designed to circulate a liquid sample held within a standard sized lab beaker through the measurement cell.

Measurement cell - the sample is routed between measurement windows in the cell so that the laser can pass through it in order to make a measurement

The size range is 0.01-3500microns.

3. Interferences

4. Sampling

Correct preparation of the sample before it is added to the system is very important. Over half the problems encountered when measuring a sample are caused by poor sample preparation. If the sample is sticking together, dissolving or floating on the surface, or if it is not a representative sample, the result will be incorrect.

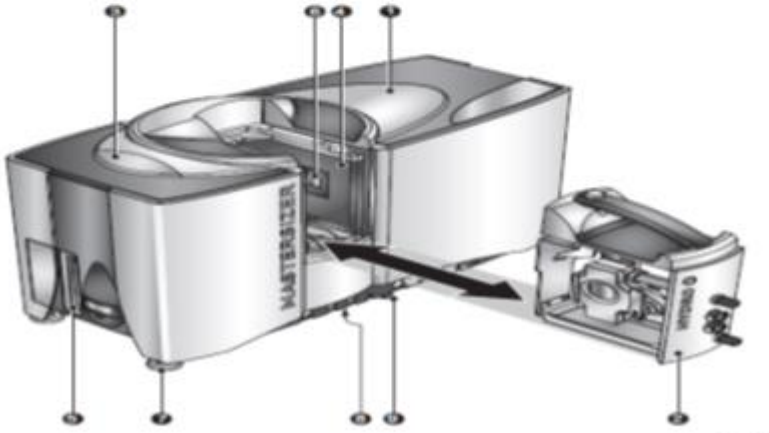
- Mix a quarter spatula of feacal sludge into slurry and add directly to the 600ml mastersizer beaker.

5. Safety Precautions

- Always use safety goggles, gloves and laboratory coat while working in laboratory
- After the analysis clean bottles and beakers with water then dry
- Dispose the contaminated gloves after completion of analysis
- Clean the hands using antiseptic soap
- Avoid spillage of sample and contact with skin. In the latter case use copious washings with cold water and soap.

6. Apparatus

- Mastersizer 3000 (Mastersizer optcal unit) Model:MAZ3000
- Hydro EV (Extended volume(EV) user-interactive wet dispersion unit Model:MAZ3400

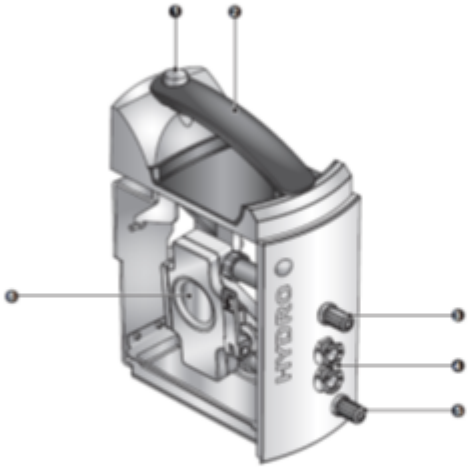


1. **Optical unit**
2. **Wet cell**
3. **Instrument status LED**-Standby-powered on but not making a measurement: pulsating dim; Active making a measurement-constant bright; Error-flashing bright.
4. **Cell bay**-holds the cell securely in the instrument so that sample passing between the cell windows can be analyzed by the optical unit's laser beam.
5. **End panel**-provides the communication connectors for the optical unit as well as the power connection and switch.
6. **Protection window**-stops dust/dirt entering the system.
7. **Adjustable feet**-it is important to ensure that the instrument is leveled on the bench.
8. **Drain**-allows any spillages in the cell area to exit onto the laboratory bench.
9. **Tube**-neatly routes all connection pipes and cables underneath the instrument.

8. Reagents

600ml of tap Water

9. Procedure



1. **Cell inject button** –ejects the cell from the cell bay locking mechanism so that it can be withdrawn from the cell bay.
2. **Cell handle**-only lift the cell by its handle.
3. **Sample output (blue)**-connected to the sample in (blue) on the dispersion unit.
4. **Temperature regulator throughput**-provide throughput connections to a water jacket within the cell.
5. **Sample input(yellow)**-connected to the sampleout(yellowon the dipersion unit.
6. **Cell windws**-sample passes through the window and is measured by the system.

Inserting the cell

1. Lift the cell by its handle.
2. Insert cell into the instrument.
3. Do not force the cell into the instrument-only slide it into the cell holder until it stops.
4. The cell now automatically locks into place within the cell bay.

Removing the cell

1. Press the cell eject button to eject the cell from the bay.
2. Withdraw the cell from the instrument using its handle and pull towards you.

NOTE

If the cell is raised and lowered too many times in a short period, the firmware will lock the cell in place for a period of time before it can be ejected again; this is to prevent damage to the locking mechanism.

- Power up the computer and printer.
- Connect the optical unit's power supply to the mains power supply
- Press the on/off switch on the instrument's side panel once to power on.
- The blue indicator on the top of the instrument illuminates, together with the blue indicator on the front of the dispersion unit, which pulsates to indicate that the standby mode is active.
- Log in to the computer and start the mastersizer software by double clicking on the mastersizer 3000 icon.
- **Wait for 30minutes for the laser to stabilize before using the instrument to measure a sample.**
- Ensure that the status bar indicates that the instrument is connected correctly. This is indicated by the green bar as shown below.

Creating or editing an SOP and a making measurement

- Select **Run SOP** from the **Measurement** section of the ribbon.
- The **SOP Selector** window lists all available SOPs.
- Create a new or if SOP already exists, choose an appropriate SOP for the measurement to be undertaken e.g. SOP_VIP
- The progress bar at the top of the window reports both the current status and what to do next. The first status reported is the **initialize instrument**.
- Note from **Initialize instrument** display, the laser must read 100% before addition of the sample (green bar on left)
- Click the start button to **initialize the instrument**, the system prompts the user to enter/confirm sample documentation details. Following this stage, the system automatically moves to **Measure Background** stage to measure both the blue and the red light scattering.
- Note also the light scattering: it should be set according to SOP blue and red light, and should be well spread across the x-axes of the graph.
- When the laser has reached 100%, fill the beaker with 600ml of water.
- Add about ¼ full spatula of the sample in slurry form.
- The sample is added until **obscuration** is within the range: this may be monitored from the bar on the left, which should be between 10-20% for a **wet dispersion unit**. (This is a rough guide only as this setting is highly sample-dependent-refer to the Help system for more information).
- Click on **Measure sample**. The SOP may make a number of measurements before completion depending on the **Number of Measurements** specified in the SOP settings.
- Complete the measurement by closing the **SOP Measurement** window and the results are present in the **Record view**.
- After measurement is completed, clean the system by following the prompts on the user interface.