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# **RECOVERING NUTRIENTS FROM COMPOSTING PLANT WASTEWATER**

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# ABSTRACT

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## **Recovering Nutrients from composting plant wastewater**

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Applying the membrane separation technologies has drawn significant attentions specifically in recent decades. Their high effectiveness along with the cost-effectiveness of the entire processes make them amongst the favorable processes in industries. Composting process is permanently associated with generating significant amount of wastewater. The produced wastewater is rich in nutrients. In order to lead the leachate to the wastewater treatment plant, the level of organic compounds and especially nutrients in the wastewater should be reduced. This study has been conducted with the purpose of reusing these nutrients specifically phosphorous and take advantages of them as valuable substances. Recovery of phosphorous, nitrogen and carbon which could negatively affect the water quality are mainly studied. Turning these nutrients into environmentally-friendly products such as fertilizers and soil amendments could enhance the biophysical characteristics of the soil.

Literature part of this work deals with the diverse methods of treating composting and landfill leachate. Predominately, appropriate approaches of recovering nutrients were assessed by focusing on the phosphorous recovery as a valuable compound for agricultural usage.

In the experimental part different types of commercial membranes were tested in terms of targeting component rejection, permeate fluxes, fouling phenomena as well as operating parameters. The retention of phosphorous (P), total nitrogen (TN), total organic carbon (TOC), and chemical oxygen demand (COD) were analyzed. Ultrafiltration with RC70PP membranes is a promising option for recovering phosphorous from composting leachate due to the high permeability as well as high retention for phosphorous. UF retained about (40-64)% of the total

phosphorous. NF270 in its spiral-wound module showed satisfactory results in terms of rejection of targeting component compared to flat-sheet NF270. Reverse osmosis filtration with SW30 membranes, which was placed after nanofiltration proceeded effectively in terms of rejection of components and permeability. NF step plays an important role in the effectiveness of RO experiment. In other words, eliminating the NF step hindered the productivity of reverse osmosis step.

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## TABLE OF CONTENT

1	INTRODUCTION.....	4
1.1.	Goal and objectives .....	4
2	LITERATURE REVIEW.....	7
2.1	Treatment processes for biodegradable wastes.....	7
2.1.1	Anaerobic digestion method.....	7
2.1.2	landfill leachate.....	7
2.1.3	Composting.....	8
2.2	Composting leachate treatment methods.....	9
2.2.1	Biological treatment processes .....	9
2.2.2	Physio-chemical treatment methods .....	10
2.2.3	Advanced oxidation processes (AOPs).....	14
2.3	Recovering nutrients from wastewaters .....	14
2.3.1	Nitrogen recovery methods .....	15
2.3.2	Approaches of phosphorous recovery .....	20
2.4	Chemical Precipitation .....	23
2.5	Struvite recovery .....	23
3	METHODOLOGY.....	29
3.1	Materials and methods .....	29
3.1.1	Composting leachate.....	29
3.1.1	Washing chemical .....	30
3.1.2	Membranes .....	30
3.1.3	Filtration equipment.....	31

3.1.4	Analyzing equipment .....	34
3.2	Methods .....	35
3.2.1	First batch experiment .....	36
3.2.2	Second batch experiment.....	38
3.2.3	Third batch experiment .....	40
3.3	Analyzing methods.....	41
3.3.1	Phosphorous.....	41
3.3.2	COD measurement.....	42
3.3.3	Total suspended solids analysis (TSS).....	42
3.3.4	Dry matter.....	43
3.3.5	Organic matter .....	43
3.3.6	Total carbon and total nitrogen measurement .....	43
3.3.7	Dissolved carbon dioxide (CO <sub>2</sub> ) .....	43
3.4	Calculation.....	44
4	RESULTS AND DISCUSSION.....	46
4.1	First batch experiment.....	46
4.1.1	Pure water fluxes before and after filtration experiment in the first batch experiment .....	47
4.1.2	Permeability changes in the first batch experiment over time.....	49
4.1.3	Permeability changes vs. VRF in the first batch experiment .....	54
4.1.4	Retention values of targeting components in the first batch experiment .....	55
4.2	Second batch experiment.....	58
4.2.1	Pure water fluxes measurement in the Second batch experiment.....	59
4.2.2	Permeability changes in the second batch experiment over time .....	60
4.2.3	Retention values of the targeting component in the second batch experiment....	63

4.3	Third batch experiments .....	65
4.4	Pure water fluxes measurement in the third batch experiment .....	66
4.4.1	Permeability changes in the third batch experiment over time.....	67
4.4.2	Retention values of the targeting component in the third batch experiment .....	69
4.5	The main reasons of RO fouling .....	70
4.6	Solution for scaling prevention.....	74
4.7	RO Experiment with new system.....	77
4.7.1	Permeate fluxes changes over time in the RO experiment.....	79
4.7.2	Pure water fluxes measurement in the RO experiment .....	80
4.7.3	Retention values of the targeting component in the RO experiment .....	81
4.8	Characterization of matter in the influent and effluent of RC70PP membranes .....	82
4.8.1	Total Suspended solids and phosphorous measurement .....	83
4.8.2	FT-IR spectroscopy of RC70PP (third batch experiment) .....	85
5	CONCLUSION.....	87
6	REFERENCES.....	89

## LIST OF FIGURES

<b>Figure 1.1.</b> Representative scheme of the composting leachate pollutants origin (Roy et al, 2018).....	5
<b>Figure 2.1.</b> Schematic scheme of experimental pilot plant technology with two-stage arrangement of RO membrane (Sir et al., 2012).....	13
<b>Figure 2.2.</b> Schematic representation of the continuous stripping bench plant .....	18
<b>Figure 2.3.</b> Chemical of chemical precipitation of struvite (Morse et al, 1998).....	25
<b>Figure 2.4.</b> The Configuration of the air-cathode single-chamber MFC (from Ichihashi and Hirooka 2012, Elsevier).....	26
<b>Figure 2.5.</b> Condition of a solution during the crystallization (from Mullin, 1992 P).....	27
<b>Figure 3.1.</b> DSS Labstack M20 filter used in the nanofiltration and reverse osmosis filtration experiments .....	32
<b>Figure 3.2.</b> a) Permeation plate b) Filtration plate. ....	32
<b>Figure 3.3.</b> CR-250 filter used in ultrafiltration experiments. ....	33
<b>Figure 3.4.</b> Diagram of the first batch experiment. ....	37
<b>Figure 3.5.</b> Diagram of the second batch experiment.....	39
<b>Figure 3.6.</b> Diagram of the third batch experiment. ....	40
<b>Figure 3.7.</b> COD reactor used in the COD and phosphorous analysis. ....	42
<b>Figure 4.1.</b> Color rejection in the first batch experiment from right to left. ....	46
<b>Figure 4.2.</b> Permeate flux reduction over time in the membranes, applied pressure for RC70PP was (2.4-3) bar, (19-30) bar for NF270, (22-40) bar for SW30-1 <sup>st</sup> , (20-36) bar for SW30-2 <sup>nd</sup> and (20-27) bar for SW30-3 <sup>rd</sup> . ....	50
<b>Figure 4.3.</b> Irreversible fouling of the RO membranes (SW30-1 <sup>st</sup> = first step of RO filtration, SW30-2 <sup>nd</sup> = second step of RO filtration, SW30-3 <sup>rd</sup> = third step of RO filtration) .....	52
<b>Figure 4.4.</b> The permeability of RC70PP, NF270, SWRO (three steps) vs. VRF in the first batch experiment. ....	54
<b>Figure 4.5.</b> Color rejection in the second batch experiment from right to left, permeate of RC20PP, NF270, SW30 membranes.....	58
<b>Figure 4.6.</b> The permeability of RC70PP, NF270 (Spiral wound module), SW30 vs. VRF in the second batch experiment.....	61
<b>Figure 4.7.</b> Color retention in the third batch experiment .....	65

<b>Figure 4.8.</b> The permeability of RC70PP and SW30 vs. VRF in the second batch experiment. ....	67
<b>Figure 4.9.</b> SEM images of fouled RO membranes in the third batch experiment. ....	72
<b>Figure 4.10.</b> Membrane filtration apparatus applied in RO experiment.....	77
<b>Figure 4.11.</b> Rectangular filter used in RO experiment.....	77
<b>Figure 4.12.</b> Pemeation fluxes (kg/m <sup>2</sup> .h) and conductivity retention of SW30 membrane in different pressures. ....	79
<b>Figure 4.13.</b> The permeation fluxes of SW30 vs. time in the new system, pressure 30±3 bar.	80
<b>Figure 4.14.</b> FT-IR spectroscopy of virgin RC70PP in the third batch experiment as well as virgin RC70PP membrane. ....	85

## LIST OF TABLES

<b>Table 2.1.</b> Phosphorous removal and recovery technologies (Morse et al, 1998). .....	22
<b>Table 2.2.</b> An overview of nutrients recovery from nutrient-rich wastewaters. ....	28
<b>Table 3.1.</b> Characteristic of the composting plant leachate used in the experiments. ....	29
<b>Table 3.2.</b> Characteristic of the used membranes. ....	30
<b>Table 3.3.</b> Operating limits of the membranes. ....	31
<b>Table 3.4.</b> Equipment used for analysis. ....	35
<b>Table 4.1 .</b> Pure water values before, after filtration, and after washing in the first batch experiments. ....	47
<b>Table 4.2.</b> Retention of the target components for membranes in the first batch experiment. .	56
<b>Table 4.3.</b> Pure water values before filtration, after filtration, and after washing in the second batch experiments. ....	59
<b>Table 4.4.</b> Retention of the target components for membranes in the second batch experiment. ....	63
<b>Table 4.5.</b> Water fluxes measurement before, after water cleaning and after chemical cleaning in the third batch filtration experiment including ultrafiltration and reverse osmosis (UF <sub>RC70PP-RO<sub>SW30</sub></sub> ). ....	66
<b>Table 4.6.</b> Retention of targeting component in the third batch experiment. ....	69
<b>Table 4.7.</b> EDS analysis results in SW30 membrane in third batch experiment. ....	71
<b>Table 4.8.</b> Water fluxes measurement before filtration, after water cleaning and after chemical cleaning in the RO experiment. ....	80
<b>Table 4.9.</b> Retention of targeting components in the RO experiment. ....	81
<b>Table 4.10.</b> Organic and mineral content of the influent and effluent of RC70PP membranes. ....	83
<b>Table 4.11.</b> Total suspended solids, total and dissolved phosphorous of influent and effluent of RC70PP in three batches of experiment. ....	84

## LIST OF ABBREVIATIONS

<i>A-CSTR</i>	Anaerobic continuous stirred tank reactor
<i>AD</i>	Anaerobic digestion
<i>Al</i>	Aluminum
<i>AOP</i>	Advanced oxidation process
<i>ASBR</i>	Anaerobic sequencing batch reactor
<i>BES</i>	Bio electrochemical system
<i>BOD</i>	Biological oxygen demand
$Ca^{2+}$	Calcium ions
$CaCO_3$	Calcium carbonate
$CaSO_4$	Calcium sulfate
$CO_2$	Carbon dioxide
<i>COD</i>	Chemical oxygen demand
<i>CP</i>	Concentration polarization
<i>DM</i>	Dry matter
<i>EDS</i>	Energy-dispersive X-ray spectroscopy
<i>EGSB</i>	Expanded granular sludge bed bioreactor
<i>Fe</i>	Iron
<i>FR</i>	Flux reduction
<i>FTIR</i>	Fourier transform infrared spectroscopy
<i>HRT</i>	Hydraulic retention time
<i>LOI</i>	Loss of ignition
<i>MBR</i>	Membrane bioreactor
<i>MF</i>	Microfiltration
<i>MFC</i>	Microbial fuel cell
$Mg(OH)_2$	Magnesium hydroxide
$MgCl_2$	Magnesium chloride
$MgNH_4PO_4 \cdot 6H_2O$	Struvite
<i>MgO</i>	Magnesium oxide

<i>MgSO<sub>4</sub></i>	Magnesium sulfate
<i>Mn</i>	Magnesium
<i>MSW</i>	Municipal solid waste
<i>MWCO</i>	Molecular weight cut off
<i>NaCl</i>	Sodium chloride
<i>NF</i>	Nanofiltration
<i>NH<sub>3</sub></i>	Ammonia
<i>NH<sub>4</sub><sup>+</sup></i>	Ammonium cation
<i>NH<sub>4</sub><sup>+</sup>-N</i>	Ammonium-Nitrogen
<i>NOM</i>	Natural organic carbon
<i>OM</i>	Organic matter
<i>P</i>	Phosphorous
<i>PO<sub>4</sub><sup>3-</sup></i>	Phosphate
<i>PWF</i>	Pure water fluxes
<i>R</i>	Retention
<i>RO</i>	Reverse osmosis
<i>S</i>	Sulfur
<i>SEM</i>	Scanning Electron Microscopy
<i>TC</i>	Total carbon
<i>IC</i>	Inorganic carbon
<i>SI</i>	Saturation index
<i>TEP</i>	Transparent exopolymer particles
<i>TN</i>	Total nitrogen
<i>TOC</i>	Total organic carbon
<i>TSS</i>	Total suspended solid
<i>UF</i>	Ultrafiltration
<i>VRF</i>	Volume reduction factor

## LIST OF SYMBOLS

$m_f$	Mass of feed solution
$P$	Pressure, bar
$P_m$	Permeability, Kg/m <sup>2</sup> .h.bar
$PWF_a$	Pure water flux after filtration, kg/(m <sup>2</sup> .h)
$PWF_b$	Pure water flux before filtration, kg/(m <sup>2</sup> .h)
$T$	Time, min
$V_0$	Volume of initial feed, L
$V_P$	Volume of permeate, L

# 1 INTRODUCTION

## 1.1. Goal and objectives

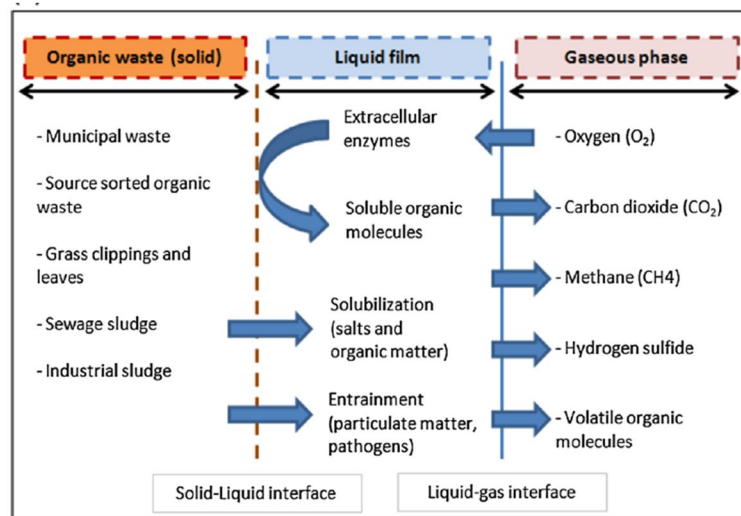
In this research, the main purpose is recovering valuable nutrients from nutrient-rich streams by management of composting plant leachate including two main phases:

- 1) Developing a membrane based separation method during which, the leachate is treated to meet the standards for discharging into the wastewater treatment plant by applying the combination of UF, NF and RO. In this stage, the efficiency of the membranes for reduction of total carbon (TC) either organic (TOC) or inorganic (IC), total nitrogen (TN) and phosphorus (P) was studied. In order to reduce the total suspended solids (TSS) and colloids an ultrafiltration membrane was applied before nanofiltration as a pre-treatment stage.
- 2) Concentrates management by recovering phosphorous and nitrogen, which is the most important part of this project. Testing the membranes efficiency in concentrating carbon, nitrogen and phosphorous as well as studying other important parameters in membrane-based technology such as permeability and fouling of the membranes.

Biodegradable wastes such as, municipal solid waste (MSW), forestry waste, agricultural waste, food waste, residual waste, etc. can go through several treatment process such as Landfill, thermal treatments, mechanical treatments, composting process as well as anaerobic digestion and fermentation. Amongst the diverse methods, which have been applied for treating bio-waste and biodegradable waste, digestion and composting have been demonstrated as the most favorable means for decreasing the waste formation rate and generating energy (Ediviani et al, 2018 ; Sayven et al, 2014). While, these processes end up with a hazardous wastewater called leachate. Due to the huge amount of waste production especially in the last few decades, treatment of waste leachates has been identified as one of the most significant challenging topics.

Composting is one of the most economical methods for waste management and the last stage of industrial and agricultural waste disposal, while huge amount of leachate produced during the

composting process is one of the main concerns of today's world. Nonetheless, Composting technologies are capable of reducing the volume of the initial waste by around 50% (Roy et al., 2018), and its final product can be used for soil amendment. Composting leachates contain diverse forms of hazardous contaminants, which could negatively influence the water bodies, and nearby environment. Therefore, developing sustainable and operative technologies with potential of sufficient treatment of leachates is of great importance (Mokhtariani et al, 2015). Predominantly, composting leachates contain high content of nutrients such as phosphorous, nitrogen, toxic compounds (heavy metals) and plasticizers, biodegradable and non-biodegradable organic matter (Figure 1.1) which arisen from the percolation of water through organic waste in composting process. The characterization of compost leachate and its composition greatly depend upon the type of waste, the composting procedure and the climatic circumstances (Hashemi et al, 2016).



**Figure 1.1.** Representative scheme of the composting leachate pollutants origin (Roy et al, 2018).

Although, numerous researches and studies have been advocated to the technologies of leachates treatment, a few of them are related to the composting leachates and most of them have investigated the landfill leachates.

Moreover, the world is facing the lack of effective solutions of removing almost all contaminants presence in the leachate. Different types of treatment methods have been applied to treat the composting leachate including, biological treatment (Biofilters, MBR and anaerobic bioreactors), physiochemical methods (membrane-based methods, coagulation-flocculation) as well as advanced oxidation technologies.

Biological methods and membrane-based processes are the most affordable processes including MBR with the lowest operating process cost (0.21-0.75 USD/m<sup>3</sup>) and the combination of NF and RO (0.80-1.05 USD/m<sup>3</sup>) (Roy et al, 2018). However, concentrate management would be another imperative part of leachates management that should be taken into consideration. Advanced oxidation processes, which are applied mainly as a post-treatment method for wastewaters treatment, are amongst the most expensive technologies, which can be applied with combination of biological treatment methods in order to achieve a complete economical method.

While none of these technologies resulted in an effluent, which could meet the National water quality standards, membrane and MBRs have been known as the most promising technologies.

One of the most significant advantageous of membrane is their commercial availability in a wide range of molecular weight cut off (MWCO), and production of a constant quality of water in spite of variation of contaminants in the feed, however, membrane fouling, concentration polarization and operating cost are the main drawbacks of membrane separation technologies. Regarding to the point that RO and NF has shown promises in leachates treatment, there are just a few studies related to the composting leachate management by them, in this research the combination of NF, and RO have applied in order to evaluate their efficiency in composting plant leachate treatment and recovering nutrients such as phosphorous and nitrogen which have negative consequences on the environment such as eutrophication and soil acidification. Adding economization to the processes and transforming nutrients into the more effective and sustainable sources are the main objectives of this research work.

## **2 LITERATURE REVIEW**

### **2.1 Treatment processes for biodegradable wastes**

#### **2.1.1 Anaerobic digestion method**

Anaerobic digestion (AD) process is a method for producing the energy from waste sources, such as biowaste, residual waste and mixed waste. This process end up with an effluent called digestate, which contains solids and liquid. Digestate is a stabilized product of biological treatment processes that can be formed as liquid and semi-solid. In anaerobic digestion process, the breakdown of biodegradable compounds take place under managed conditions, for instance, anaerobic conditions or temperature is kept in a range which is appropriate for bacteria. Owing to its high content of nutrients, it should be treated before discharging into the environment. Digestate is widely used as a fertilizer due to its high content of some elements such as nitrogen, phosphorous and potassium to enhance the soil properties. The whole fraction of digestate is often applied directly in agriculture or it can be separated into solid and liquid fraction. The solid fraction could go through further post treatment called composting and the liquor fraction may be used as a fertilizer or undergo several treatment processes to get more purified water (Aziz et al, 2010).

#### **2.1.2 landfill leachate**

One of the most preferred methods for disposal of municipal solid waste (MSW) is sanitary landfill. There are lots of advantages for this method, such as its simplicity and cost-effectiveness although it produce high amount of leachate, which is hazardous to the environment (Aziz et al, 2010). Leachates are rich in several chemical impurities including refractory organic compounds such as ammonium, phosphate, heavy metals, sulfide, chloride as well as inorganic compounds (Erkan & Apaydin, 2015). Landfill leachate treatments differs from chemical to physical and biological methods. Based on the landfill leachate characteristics and the targeted contaminants, the most appropriate treatment method should be opted. In order to achieve the standard value of discharge, methods are often used together. Biological and

physicochemical methods are the most common methods for treating this wastewater (Anglada et al, 2011 & Bashir et al, 2009) despite many disadvantages associated with them such as formation of sludge at the end of the process, low efficiency of biodegrading the refractory compounds and removing color, high retention time in addition to the difficulty of controlling the flow rate and organic load.

Biological processes are highly effective for leachate landfill treatment with great amount of biological oxygen demand (BOD), although, its usage is hindered by the existence of recalcitrant compounds in the wastewater, therefore physical-chemical processes have been gained interests in recent decades (Lei et al, 2007).

Except Fenton method that is effective in treating landfill leachate, advanced oxidation procedures (AOPs), are not very successful in treating these effluent due to the high alkalinity of leachate and the acidic condition that is needed for these treatment methods (Sabour & Amiri, 2017; Zhao et al, 2010).

### **2.1.3 Composting**

Composting process is a waste management method during which organic wastes are transformed into compost products that are biologically stable. Although, this process has known as one of the efficient methods for wastes management, it ends up with an aqueous hazardous effluent containing various unwanted substances that can have adverse effects for the environment; consequently, treating it before discharging into the environment is of great importance in wastewater treatment (Roy et al, 2018). Generally, great amount of organic matter (biodegradable and non-biodegradable), such as humic-based substances, nutrients, heavy metals as well as other contaminants including ammonia-nitrogen and pesticides can be found in composting leachates. Organic matter removal from composting leachate is the primarily essential stage prior to dispose it to the waterbodies (Renou et al, 2008). Diverse methods have been developed for the composting leachate treatment, which are generally categorized into three main groups; 1) Biological treatment processes 2) physico-chemical technologies 3) advanced oxidation methods.

## **2.2 Composting leachate treatment methods**

### **2.2.1 Biological treatment processes**

Biological treatment processes is a treatment method in which microorganisms such as algae, fungi and bacteria are used to oxidize organic matter and convert them into cells and biodegradable substances, which can be eliminated from the wastewater. Biological treatment can be progressed under aerobic or anaerobic condition. (Samer, 2015).

Biological methods has been directed considerable attention for composting and landfill leachate treatment due to their cost-effectiveness and easiness of the process compared to physico-chemical and advanced methods, however their drawbacks including high amount of sludge production and large value of hydraulic retention time ( $HRT > 48h$ ) make their application limited (Roy et al, 2018). The basic means of selecting the suitable biological method is based on the  $BOD_5/N/P$  ratio according which for a 100/5/1 ratio, aerobic treatment processes is recommended (Lafrance et al, 1996) while, anaerobic methods could be applied for the ration of 250 to 500/5/1 (Mokhtarani et al, 20012).

Based on the studies within past years focused on the bio-treatment technologies such as, biofilters, membrane bio reactors (MBR) and anaerobic bioreactors, Only a limited studies have been allocated to the composting leachate treatment by biofilters which are not effectively applicable for COD removal. However, their efficiency in  $NH_3$  removal was quite promising. (Tyrrel et al, 2008; Savage and Tyrrel, 2005).

Anaerobic reactors operate more efficiently with regard to high COD degradation and produce less sludge (Elyasi and Amani, 2015). This biotreatment method that could be end up to usable biogas, have been greatly studied by simple and complexes systems such as anaerobic continuous stirred tank reactor (A-CSTR) (Romero et al, 2013), anaerobic sequencing batch reactor (ASBR) (Amani et al, 2014) as well as anaerobic migrating blanket reactor (AMBR) (Hashemi et al, 2016a) and expanded granular sludge bed bioreactor (EGSB) (Liu et al, 2010).

Membrane bioreactors (MBR) with the utmost efficiency for treating wastewater would be a favorable alternative to other bio-treatment methods despite of its drawback of membrane fouling (Hashemi et al, 2016a).

Granular activated carbon usage with a MBR aiming the reduction of membrane fouling has been studied, demonstrated the improvement of the process by reducing fouling phenomena without any negative effects on the refractory compounds removal in composting leachates (Hashemi and Khodabakhshi, 2016). The reports focused on the different configuration of MBRs resulted from the diverse combination of membrane and bioreactors have been presented by researches. The highest COD and nitrogen removal that was 99.7% and 99.95 respectively gained by submerged membrane installed in an aerobic tank, although the operation conditions were unrealistic such as the high HRT (95 days) which can be considered as impractical (Brown et al., 2013).

Biological processes are simple and cost effective procedures predominantly for leachate treatment with high concentration of BOD. Biological treatment methods are highly effective for removing organic matter and nitrogen from immature leachates in which BOD/COD ratio is higher than 0.5; however, their existence of refractory compounds such as fulvic and humic acid contribute to limit the effectiveness of the process (Renou et al, 2008).

### **2.2.2 Physio-chemical treatment methods**

Several studies focused on the physio- chemical treatment technologies, which mainly divided into two groups of coagulation/ flocculation and membrane-based separation technologies.

Main drawbacks of the coagulation/flocculation are the cost of chemicals and the sludge production through the process. Although the amount of sludge production and cost of the process have not been studied so far, it has been well discussed as a standalone method for composting leachate treatment in terms of COD, TSS and heavy metals removal efficiency (Roy et al, 2018).

### **Coagulation- flocculation**

Coagulation/ flocculation is a very imperative stage in the water and wastewater treatment plants. In this physico-chemical process, fine particles are brought together and form a larger particle, which is separable from water. Coagulant, which are chemicals with the charge opposite of the particles presence in the water are applied for neutralization of non-settable solids charge through rapid mixing, and eventually the suspended particles stick together and form flocs, which can be easily eliminated from water (Bui et al, 2019). Several studies have been conducted on the landfill leachate treatment by coagulant and flocculants with the aim of recognizing the most effective coagulants and determining the optimum experimental conditions (e.g. appropriate pH range, flocculants dosage, etc.). This method is a quite simple process for treating landfill leachate. Aluminum sulfate, ferrous sulfate and ferric chloride are the most widely used coagulants (Maleki et al, 2009). It has been reported that the iron salts are one of the most effective coagulants due to their contribution to COD reduction (above 56%), for alum and lime this values hardly reaches 39% (Tatsi et al, 2003).

### **Membrane-based processes and filtration methods**

Membrane processes are separation technologies, according which a permeable membrane is used to separate compounds from water. The stream, which pass through the membrane is called permeate side and the molecules and compounds and molecules that cannot penetrate from the membrane called retentate (Biu et al,2019). Membrane-based processes have been widely used in different varieties of industrial applications such as composting leachate, landfill leachate, etc. The capacity of filtration in membranes are highly dependent upon the molecular weight cut off (MWCO) as well as their manufacturing materials (Simonic et al, 2017).

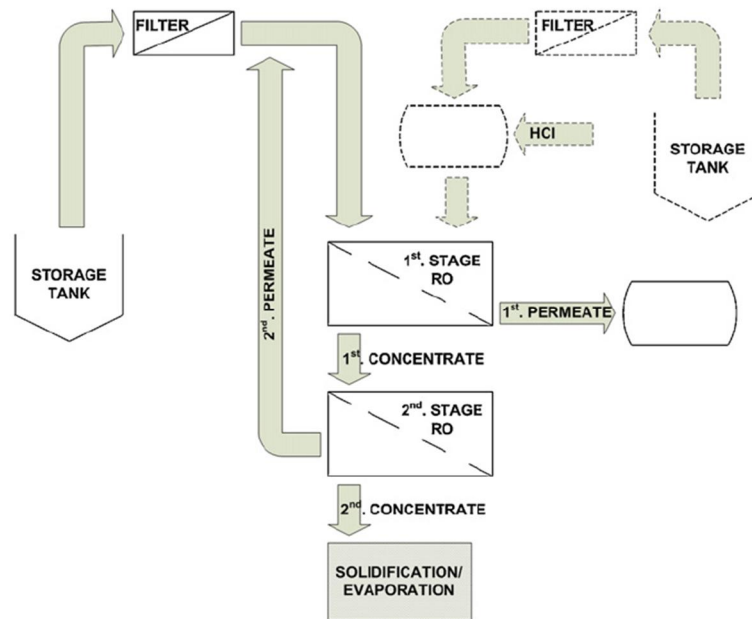
Microfiltration (MF) is a suitable method for removing colloidal and suspended particles which, could be used as a pre-treatment stage in a process contains other membranes applications (UF, NF and RO) or a chemical treatment process. Ultrafiltration (UF), is applied to remove particles and macromolecules depending on the manufacturing materials of membrane. UF as a pretreatment method could greatly enhance the process efficiency specifically prior to RO

membranes. It is highly applied for removing large molecular weight substances and reducing the fouling phenomena in RO membranes.

Cakmackci and Ozyaka have studied the application of four membranes including NP030, NP010, NF270 and NF90 for removing COD, TOC,  $\text{Cl}^-$  and  $\text{NH}_4^+$  from composting leachate. The results was in the favor of NF90, which had the maximum elimination efficiency (Cakmackci and Ozyaka, 2013). An experiment were conducted based on the combination of chemical processes and NF membranes for treating compost leachate. Polyaluminum chloride was used as coagulant, which resulted in 75% of COD and colloid reduction followed by applying two types of nanofiltration membrane including DL and NF270. The final COD removal efficiency of (98.7 and 99.6 % respectively) were achieved. UC030 which is a type of ultrafiltration membrane was used as pre-treatment stage. According to the results, COD reduction was around 17% and not considerable removal for  $\text{NH}_4^+$  were reported (Simonic et al, 2017). Gagnaire at al. (2012) applied lime as a precipitate in a process followed by a UF process and reported the optimum lime dosage in which the maximum COD and N-NH<sub>4</sub> removal were obtains 48 and 45-77%, respectively. Then using a RO membrane (BW30) process the removal of COD and ammoniacal nitrogen contaminants increased to 95 and 93%, respectively and complete removal of TSS. Using RO membrane without any pre-treatment method could lead to the fouling at the beginning of filtration in raw composting leachate and a drastic reduction in permeate flow (80%) (Gagnaire et al, 2012). While, the combination of NF and RO is an effective method in elimination of COD,  $\text{NH}_4$  and TSS from composting leachate.

It has been reported that hydrophobic natural organic matter (NOM), are the main foulant compounds that reduce the flux by forming a cake layer on the membranes surface and consequently increase the concentration polarization (Simonic et al, 2017). Sir et al. (2012), tested a type of RO membrane (SW30-4040) in a pilot plant for treatment of landfill leachate, which was mainly rich in heavy metals, arsenic, ammonia, nitrogen and chlorinated compounds. All the experiments conducted in a batch mode in two stages. Figure 2.1 demonstrates the scheme of experimental pilot plant. The dashed lines in the figures displays the supplement of acidified leachate for experiment. They reported 94% of ammonia nitrogen removal, 99% and

99.3% of two-valent ions and TDS removal respectively and 94% of feed flow recovery (Sir et al, 2012).



**Figure 2.1.** Schematic scheme of experimental pilot plant technology with two-stage arrangement of RO membrane (Sir et al, 2012).

Membrane separation methods as an emerging technology have been demonstrated promising results in landfill and composting leachate treatment in recent years. It has been proved that RO and NF with the potential of achieving more than 98% contamination removal are amongst the best solution of landfill and composting leachate purification while, membrane fouling and high operational cost are the main drawbacks of membrane-based technologies. Therefore, the management of concentrate purification and choosing an effective pre-treatment method needs to be further improved for reducing fouling and increasing the cost-effectiveness of the processes (Roy et al, 2018).

### 2.2.3 Advanced oxidation processes (AOPs)

Due to the existence of refractory compounds in the leachates, often a post-treatment method can be applied to degrade the hardly biodegradable organic matter. AOPs produce hydroxyl radical ( $\cdot\text{OH}$ ), which is a strong oxidant. This oxidant are capable of degradating organic compounds and converting them into small inorganic molecules. Fenton and photo Fenton,  $\text{O}_3$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ , UV/ $\text{TiO}_2$  and  $\text{O}_3$ /persulfate, etc., are applied to generate hydroxyl radicals. Advanced oxidation processes (AOPs) have been developed in order to achieve a sufficient treatment processes specifically for COD and color removal in composting leachates, however their high cost of operation hinder their usage in industrial scales. Advanced oxidation technologies have been investigated in previous studies (Roy et al, 2018). Mokhtariani et al, studied the post-treatment of a composting leachate by oxidation with  $\text{O}_3$  in a type of leachate with low concentration of COD, which resulted in complete removal of color and 51% removal of COD. Two years after, Soubh and Mokhtariani, conducted the post-treatment experiment with the same reactor by adding persulfate as oxidants, which lead to increasing the COD removal to 87%. (Mokhtariani et al, 2014; Soubh and Mokhtariani, 2016). Combination of hydrogen peroxide and ozone enhance the efficiency of leachate treatment (Tizaoui et al, 2007).

## 2.3 Recovering nutrients from wastewaters

Nutrient recovery from the nutrient-rich streams such as, digestate, composting and landfill leachates in the form of marketable products are becoming more and more vital in today's world, which is not only due to the providing the market demands, but also for meeting the Environmental legislation. The aim of this chapter is presenting a comprehensive summary of available technologies for nutrient recovery from waste streams with high contents of nutrients as well as their economic considerations and final products. Nutrients rich streams and wastewaters are amongst the main sources of nutrients that have attracted considerable attention in recent years since their high value of nutrients, as well as large amount of wastewaters production in the world. Nutrients recovery from wastewaters highly improves the

environmental and economic aspects of the life by reusing of the materials, which could negatively affect the water quality and converting them into environmentally- friendly products such as fertilizers (Yan et al, 2018).

Phosphorous and nitrogen, which are the main nutrients in wastewaters, could lead to the eutrophication and cause harmful effects on the aquatic life and the quality of water (Yan et al, 2018). Phosphorous in wastewaters exist in two forms of dissolved phosphorous and solid phosphorous (Sengupta et al, 2015). In wastewaters, P and N mainly present as phosphate ions and ammonium respectively (Yan et al, 2018). Various methods are applied to recover N and P from wastewaters including ion exchange, adsorption methods as well as biological procedures and membrane filtration. Bio-electrochemical systems have identified as an effective method for recovering nitrogen as  $\text{NH}_3$  (g) or  $(\text{NH}_4)_2\text{SO}_4$  (Sengupta et al, 2015).

### **2.3.1 Nitrogen recovery methods**

Nitrogen is one of the main imperative nutrients, which is found in waste streams. Despite the high amount of non-reactive and stable form of nitrogen existing in atmosphere in the form of nitrogen gas (78%), its content in soils is inadequate. Consequently, in order to increase its values in the soils, it should be fixed in the form of a usable and reactive compound including, nitrate, amino acids and ammonia. The possible methods for recovering nitrogen is discussed below and the important results is presented for recovering this nutrient from nutrient-rich wastewaters (Sengupta et al, 2015).

#### **Ion exchange and adsorption approaches**

$\text{NH}_4^+$  is the dominant form of nitrogen in wastewaters along with one of the main contaminants existing in polluted waters and urine. Ion exchange which is an adsorption methods are highly effective due to the matter that  $\text{NH}_4^+$  is a cation, which is better selected and adsorbed by ion exchange media and adsorbents (Sprynsky et al, 2005). Moreover, their high removal efficiency, and readily regeneration methods as well as fast adsorption kinetics and simplicity of the process, make them a promising method for recovering nitrogen from wastewaters. Zeolite is the most widespread adsorbent/ion exchange for nitrogen recovery from aqueous

solution. Zeolite as a naturally occurring and non-expensive adsorbent enable to release non-toxic types of cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$ , etc. More than 50 different form of zeolite has been identified with diverse characteristic originated from regional geological creation variations. Accordingly, in order to specify the optimum performance of each zeolite, it has to be studied in terms of pH, the initial concentration of  $\text{NH}_4^+$ , size of grain, temperature, hydraulic retention time, adsorbent dosage, etc. modification of zeolite enhances the adsorption capacity and zeolites purity, which can carried out mainly by acids, alkali, alkaline metal salts, calcinations and microwave modification methods. Zeolite products can be used directly for agricultural purposes or it can be regenerated for reuse. Regeneration with  $\text{NaCl}$  is a common way of obtaining a more concentrated  $\text{NH}_4^+$  stream. Other regeneration methods include acid regeneration, heating regeneration and biological means (Alshameri et al, 2014; Li et al, 2011).

Liberti et al, resulted that applying both anions and cations, which were concentrated and the simultaneous precipitation of ammonium and phosphate ions lead to the formation of a valuable slow-release fertilizer called struvite (Liberti et al, 2001).

In a research, clinoptilolite, wollastonite and naturally occurring zeolite used for recovering nutrients as struvite by adding tiny amount of  $\text{MgO}$  resulting 65-80 % recovery of crystalline structure of struvite (Lind et al, 2000). Lin et al, applied a method during which, the adsorption of  $\text{NH}_4^+$  on the zeolite resulted in releasing  $\text{Ca}^{2+}$  in the solution and formation of a type of zeolite, which could be applied as a fertilizer (Li et al, 2014). Huang et al, modified zeolite by means of  $\text{MgCl}_2$ , in order to produce struvite from nitrogen and phosphorous which, was recovered from swine wastewater in addition of a source of magnesium that was loaded into the zeolite during the adsorption process (Huang et al, 20014). Recently, several studies have been conducted on the removal of ammonium from wastewaters, reported diverse adsorbent with different adsorption capacity including natural adsorbents, and synthesized substances such as carbon nanotubes, wheat straw, modified chitosan, hydrogels, sawdust, etc. (Sengupta et al, 2015).

### **Bio-electrochemical Systems (BES)**

These systems operate based on the bio-oxidation of organic matters by microorganisms and conversion of the organic substances to the electrical energy in a microbial cell, which is classified, into two types of galvanic and electrolytic. Microbial fuel cells (MFCs), has shown promise in recent years for hydrogen production. In MECs, microorganisms at the anode, transform the organic matters into electron, proton and CO<sub>2</sub>. Generated electrons are directed to the cathode over an electrical circuit followed by reduction reactions in cathode and the formation of hydrogen. In order to prevent from the reactions between oxidation and reduction products, two ion selective membranes are applied in the cell between the anode and cathode chambers. Microbial fuel cells (MFCs) are highly similar to MECs with difference that in MFCs, an external voltage is applied for carrying out the electrons and hydrogen reduction (Yu et al, 2018).

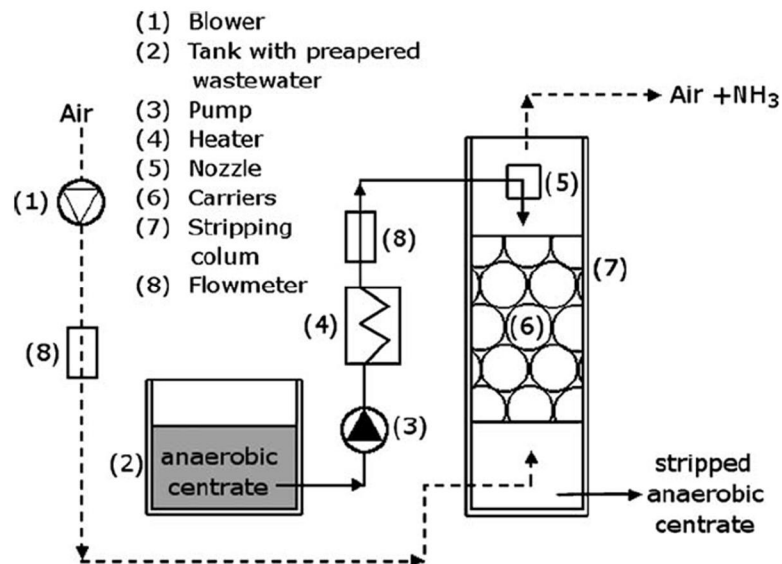
Bio-electrochemical systems are identified as a sustainable methods of wastewater treatment due to the electricity production. These systems are capable of recovering ammonia by taking advantageous of low-quality substances that are rich in carbon , which consequently leads to the reduction of carbon usage. Although, the low amount of recovered energy is considered as the main challenge associated with this process (Sengupta et al, 2015). Subject to the recovery of ammonium, the oxidation of organic compounds in wastewaters takes place at the anode by microorganisms, and then through a selective cation exchange membrane, ammonium ions are transferred at cathode where the ammonium is recovered at high pH (Kuntke et al, 2011). Kuntke et al, developed a MFC for recovering ammonium from urine along with producing energy. They used a gas diffusion cathode at high pH, in which volatile ammonium is produced from ionic ammonium. Recovery of ammonia was carried out by the volatilization and subsequent absorption into an acid solution. (Kuntke et al, 2012).

In BES systems, ammonia recovery significantly affected by current density, it is reported that higher current density could greatly improve the ammonia recovery in an MFC (Haddadi et al, 2013). BES systems are emerging and novel technologies, which should be developed in order to optimize the parameters and applied in full scales. Low recovered energy and ammonia

besides the high cost of operations and optimization of various parameters such as, pH, concentration of ammonium ions and current density are the most challenges associated with this technology (Sengupta et al, 2015).

### Air stripping of ammonia

This process is used for turning ammonium nitrogen into ammonia gas at pH about 9.3. Applying lime or caustic soda during the process keep the pH at alkaline range around 10.8-11.5, which transforms ammonium ions to ammonia and consequently by supplying air, it is converted into ammonia gas. The efficiency of the process greatly depends upon various parameters including, concentration of ammonium, hydraulic loading, flow rate of air and mainly pH and temperature. Gustin et al, investigated the effect of these parameters in a bench plant (Figure 2.2) for recovering ammonia from anaerobic digestion plant. A rise in the pH from 8 to 11 increase the ammonia recovery efficiency from 27.4% to 92% (Gustin et al, 2011).



**Figure 2.2.** Schematic representation of the continuous stripping bench plant (Gustin et al, 2011).

Guo et al, concluded that the efficiency of ammonium recovery increases from 80% to 92% by increasing the pH from 8 to 11 in the process of landfill leachate treatment (Geo et al, 2010). Ledda et al, proposed a scheme for recovering ammonium sulphate from anaerobically digested dairy manure resulted in the 90% ammonia recovery, electricity and biogas also produced as products (Ledda et al, 2014).

### **Membrane-based recovery methods**

Membrane filtration processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been used in treating diverse types of wastewaters and recovering their nutrients. Membrane-based methods are simple and physical separation techniques, which can be applied without any chemicals and energy, therefore, their lower cost of operation and maintenance make them amongst the promising technologies in water and wastewater treatment plants.

Combination of membrane with other separation techniques such as, precipitation and biological methods have been demonstrated promising outcomes for nutrient recovery from wastewaters (Yan et al, 2018) (Gerardo et al, 2013) (Zhang et al, 2013) (Qiu et al, 2014) (Gong et al, 2017) (Xie et al, 2014).

In Table 2.1, a summary of nutrient recovery in different types of membrane are presented.

**Table 2.1.** Summary of nutrient recovery by membrane process technologies.

<b>Type of wastewater</b>	<b>Type of membrane</b>	<b>Nutrients rejection</b>	<b>Operating pressure</b>	<b>Fouling</b>	<b>Reference</b>
Synthetic urine	NF (NF270)	ammonium: 55% phosphate: 94%	20 bar	Not applicable	(Pronk et al, 2006)
Digested sludge	NF	phosphate: 50%	25 bar	Not applicable	(Blöcher et al, 2012)
Urine	RO	Ammonium: 70%; phosphate: 73%; potassium: 71%	50 bar	Membrane scaling	(Maurer et al, 2006)
Activated sludge	FO-NF	Ammonium >97% phosphate >99%	operating pressure of NF: 80 psi	Cake formation	(Hau et al, 2014)
Activated sludge	FO-RO	Ammonium >92.1% phosphate >99.8%	-	Pore blocking surface fouling	(Holloway et al, 2007)
Municipal wastewater	UF & NF	Total phosphorous rejection by UF% 26%. NF: 97%	-	-	(Marzena Smol, 2018)

### 2.3.2 Approaches of phosphorous recovery

Phosphate has known as one of the world imperative non-renewable fossil resources, which is listed amongst first 20 critical raw material for European Union that is published in 2014. Despite the fact, that this element makes a significant contribution to the development of industries and agriculture, its discharge to the surface waters in wastewaters has resulted in

irreparable effect on the environment, consequently, the development of phosphorous recycling technologies in parallel with its removal from wastewaters has been increasingly considered in recent decades (Morse et al, 1998; Naji et al, 2016).

There are numerous approaches developed for recovering phosphorous from wastewaters including industrial and municipal wastewaters and sewage sludge ashes in order to reclaim it as a fertilizer or white phosphorous (Naji et al, 2016). Chemical precipitation processes are capable of removing 80-99 % of phosphorous in wastewaters followed by recovering it as a fertilizer (Struvite). Recovered phosphorous can be converted into phosphate fertilizer and applicable phosphoric acid using acid hydrolysis. Physico-chemical adsorbents and ion exchangers have high potential of reclaiming P with trace amount of waste production. Combination of biological methods and constructed wetlands can remove 70-85 % of the P from wastewaters (Sengupta et al, 2015).

The removal and recovery of the phosphorus from wastewaters is highly affected by its chemical form. For capturing P from wastewaters, it should convert into the recoverable or inorganic form. Organic phosphorous has been known as “non-reactive” components due to its specific structure in which P is fixed into the cellular materials (Rittman et al, 2011). A summary of phosphorous recovery technologies are demonstrated in Table 2.2 (Morse et al, 1998).

**Table 2.2.** Phosphorous removal and recovery technologies (Morse et al, 1998).

<b>Technology</b>	<b>Objective</b>	<b>Process Summary</b>	<b>Main input</b>	<b>Main output</b>
Chemical Precipitation	P removal	Addition of metal salt to precipitate metal P removed in sludge	Wastewater	Chemical Sludge
Advanced chemical Precipitation	P and N removal	Crystallization of calcium phosphate using sand as a seed material	Wastewater(primary influent)	Chemical sludge
Biological Precipitation	P removal (may also include N removal)	Uptake of P by bacteria in aerobic stage following anaerobic stage	Wastewater (primary effluent)	Biological sludge
Crystallization	P removal and recovery	Crystallization of calcium phosphate using sand as a seed material	Wastewater (secondary effluent)	Calcium phosphate (40-50%)
Magnetic	P removal	Precipitation, magnetic attachment, separation and recovery	Wastewater (secondary effluent)	Primarily calcium phosphate
P adsorbents	P removal	Adsorption and precipitation	Wastewater	No information
Tertiary filtration	Effluent polishing	Filtration	Secondary effluent	Tertiary sludge
Sludge treatment	Sludge disposal	E.g. sludge drying, reaction with cement dust	Sludge	Soil conditioner

## 2.4 Chemical Precipitation

Chemical precipitation method, which is first started in 1950 for removing phosphorous from wastewater in Switzerland, is a physio-chemical process, which ends up with an insoluble metal phosphate by addition of a multivalent metal salt to the wastewater. The most commonly used metals are iron and aluminum (Morse et al, 1998). This method has been identified as one the most promising procedure for removing phosphorous from wastewaters. Iron, lime and alum are widely used for precipitating an insoluble salt.

## 2.5 Struvite recovery

Magnesium ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), identified, as struvite is a valuable compound that can be recovered from wastewaters. Struvite is a marketable slow-release fertilizer, which is mainly obtained via precipitation of magnesium ammonium phosphate as following reaction (Kim et al, 2018).



Precipitation of struvite in wastewater takes place at alkaline environment (pH above 7.5) and low concentration of suspended solids. The required concentration of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$  in the wastewater should be in the molecular ratio of 1:1:1. Therefore, in some cases with different molar ratio of components, supplement of specific ions is required in order to precipitate struvite. For instance, in wastewaters that are rich in ammonium such as, municipal wastewaters, addition of magnesium is essential in order to reach the appropriate molar ratio (De- Bashan et al, 2004).

The most common technique for struvite precipitation in wastewater is magnesium salts addition while pH adjustment or stripping  $\text{CO}_2$ .  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  and  $\text{MgO}$  are the most favorable salt source of Mg whereas,  $\text{Mg}(\text{OH})_2$  and  $\text{MgCO}_3$  are of less importance in practice (Zeng and Li, 2006). Leachates are considered as one of the ideal sources of struvite extraction by magnesium dosing. Leachates, which contain high amount of  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ -N and salts cause serious

pollution difficulties. Due to the toxicity of  $\text{NH}_4^+\text{-N}$  to the microorganisms, biological treatment methods are not efficient for leachate treatment. Moreover, over time the leachate compounds changes since the variation of leachate compounds over time during which the organic compound concentration decreases and inorganic matter and refractory parts of leachate become more stable (Kumar et al, 2015).

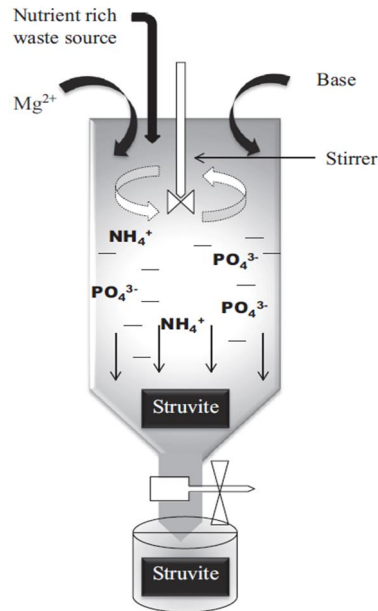
Struvite as a source of scaling compound is mostly identified as a problematic phenomenon in wastewater treatment plants, since it can be formed spontaneously when the magnesium, phosphate and ammonium reach an equal molar ratio of 1:1:1. The observation of struvite as a crust of crystalline material dates back to 80 years ago when it was firstly introduced by Rawn et al, in 1937 in digestion systems (Rawn et al, 1937).

#### **Methods of recovering struvite from wastewaters**

- Precipitation
- Microbial fuel cells (MFCs)
- Crystallization
- Membrane integrated hybrid treatment (MIHT)

#### **Chemical precipitation**

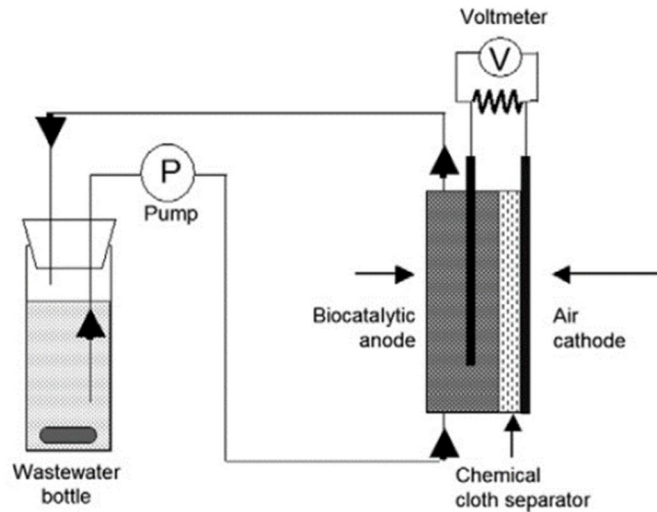
Chemical precipitation of phosphorous is carried out by adding a metal ions (e.g.  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , etc) to the wastewater, which often ends up with sludge formation (Figure 2.3) . Due to the binding of P to metals, its recycling associated with difficulties, which make its industrial recovery value very low (Morse et al, 1998).



**Figure 2.3.** chemical precipitation of struvite (Morse et al, 1998).

### Microbial fuel cells (MFCs)

MFC is an apparatus for converting microbial metabolic into electricity using an electrogenic microorganism which enable to treat the wastewater while recovering the organic matter as electricity as displayed in Figure 2.4. Fischer et al. (2011), concluded, that MFC technology could be applied for recovering phosphorous from digested sewage sludge. During the process, magnesium and ammonium is added subsequently to the system beside adjustment of pH. During the swine wastewater treatment, phosphorous accumulate on the liquid side surface of the air cathode. The higher pH near the cathode than somewhere else result in the struvite precipitation. Struvite crystal precipitates when the concentration of ions including  $Mg^{2+}$ ,  $NH_4^+$ , and  $PO_4^{3-}$  surpass the solubility boundaries of struvite formation. Solubility of struvite decrease at higher pH and at the same time is influenced by the activity of ion in the solution. Near the cathode, generation of hydroxide occur as by product, where water is being consumed. (Ichihashi and Hirooka, 2012).



**Figure 2.4.** The Configuration of the air-cathode single-chamber MFC (from Ichihashi and Hirooka 2012, Elsevier)

## Crystallization

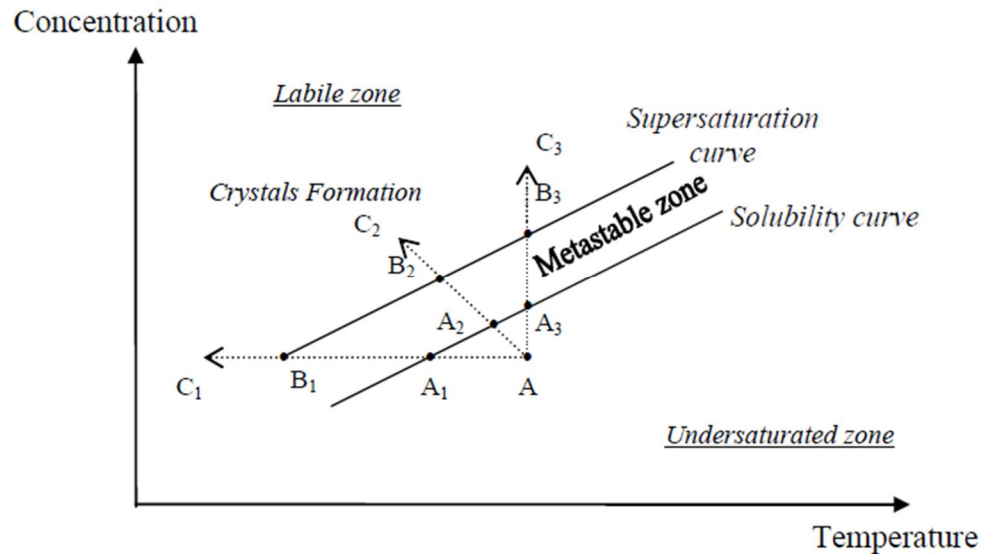
The formation of primary particles during the crystallization occurs in nucleation (crystal birth) stage and crystal growth stage, which is continued until the equilibrium. Both stages are highly affected by supersaturating. Controlling the crystallization mechanism is quite complicated due to the contribution of diverse parameters such as, thermodynamic of the equilibrium, kinetics of reactions, transfer of material between solid and liquid phase as well as other physicochemical factors including, pH of the solution, supersaturating, temperature, contribution of foreign ions and mixing energy (Le Corre et al, 2009).

## Saturation

Saturation is an important parameter, which could well describe the possibility of crystal development in a solution. As an illustration, three zones are characterized in order to specify the state of crystals in a solution (Figure 2.5).

- Undersaturated zone, in this zone crystallization does not occur and adding solids and crystals result in dissolving them in solution.

- Metastable zone, the solution is saturated meaning that the spontaneous nucleation is not possible but seed addition can enable the growth.
- Oversaturated zone, where the high free energy induce the nucleation and rapid crystallization take place without seeding.



**Figure 2.5.** Condition of a solution during the crystallization (from Mullin, 1992).

Nucleation process are divided into two groups, primary and secondary. Primary nucleation process can take place either heterogeneous or homogenous, homogenous nucleation process occurs in highly purifies solution without any impurities, whereas the heterogeneous process occurrence is integrated with the presence of foreign impurities in the solution (Mullin., 1992).

Some of the nutrient recovery processes with high efficiency are summarized in Table 2.3.

**Table 2.3.** An overview of nutrients recovery from nutrient-rich wastewaters.

Source of Wastewater	Process summary	Objective	Efficiency (%removal)	Conditions	References
Anaerobic digestion, Animal slurries	Membrane-RO and Ultrafiltration following by air stripping	NH <sub>4</sub> removal	90		(Ledda et al, 2013)
Anaerobic digestion	Air stripping of ammonia	NH <sub>4</sub>	92.8		(Guštin et al, 2011)
Coke wastewater	Chemical precipitation via a membrane-integrated approach	Struvite precipitation	95	Optimum pH: 9.5  Auxiliary input: MgCl <sub>2</sub> , Na <sub>2</sub> HPO <sub>4</sub>	(Kumar et al, 2013)
Landfill leachate	Chemical precipitation in a stirred batch reactor	NH <sub>4</sub> <sup>+</sup> -N recovery via struvite precipitation	92 % via MgCl <sub>2</sub> , 36% via MgO & 70% via MgSO <sub>4</sub>	Optimum pH: 9 Molar ratio Mg:N:P=1:1:1	(Li et al, 2003)
Landfill leachate	Chemical precipitation via stirred jar test apparatus	NH <sub>4</sub> -N recovery via struvite precipitation	99 % P recovery & 87% NH <sub>4</sub> <sup>+</sup> recovery	Addition of struvite seed (increase struvite formation), MgCl <sub>2</sub> , KH <sub>2</sub> PO <sub>4</sub>	(Kim et al, 2009)
Landfill leachate	Chemical precipitation	NH <sub>4</sub> -N recovery via struvite precipitation	≤95 NH <sub>4</sub> <sup>+</sup> recovery	Optimum molar ratio: 2:1:1 Optimum pH: 9 auxiliary input: MgO, H <sub>3</sub> PO <sub>4</sub>	(Iaconi et al, 2010)

### 3 METHODOLOGY

#### 3.1 Materials and methods

##### 3.1.1 Composting leachate

Composting plant wastewater samples were collected from Kekkilä composting plant, located in Lappeenranta, which is the place of municipal wastes collection of Lappeenranta city. The samples were taken from the same place in different months and atmospheric conditions, which highly influence the wastewater properties. The samples, which were collected three times during the experiments, transferred to the LUT laboratory and stored in the freezer at temperature of  $-20^{\circ}$  C. Table 3.1. Summarized the characteristics of the three wastewater samples.

**Table 3.1.** Characteristic of the composting plant leachate used in the experiments.

Parameters	First wastewater sample	Second wastewater sample	Third wastewater sample
Conductivity (mS/Cm)	63	67	42
Ph	7.5	8.3	7.6
Dissolved TOC (mg/L)	12000	5900	22800
Dissolved TN (mg/L)	11650	3600	9500
UV analysis (210nm)	210	130	480
Phosphorous (mg/L)	40	11	79
COD (mg/L)	30000	10400	51000
Total suspended solids	2810	1825	3790
Dry matter (%)	4.77	5.02	3.52
Chloride (Cl <sup>-</sup> ) (mg/L)	-	-	2271
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	-	-	5445

### 3.1.1 Washing chemical

After each experiment, membranes were washed using a chemical washing liquid called P3-Ultrasil 110 from Oy Ecolab Ab. This washing reagent is an alkaline and corrosive liquid which contains organic complex formers as well as anionic tensides and NaOH.

### 3.1.2 Membranes

Different types of commercial membranes including, ultrafiltration membrane (RC70PP), nanofiltration membrane (NF270) and reverse osmosis membrane (SW30) were applied in the experiments. Membrane characteristics and their operational limits are summarized in Table 3.2 and Table 3.3., respectively.

Table 3.2. Characteristic of the used membranes.

<b>Membranes used in the experiments</b>	<b>Types of membranes</b>	<b>Module</b>	<b>Molecular weight cut off (Da)</b>	<b>Material</b>	<b>Company</b>
RC70PP	Ultrafiltration	Flat-sheet	10000	Regenerated cellulose acetate	Alfa Laval
NF270	Nanofiltration	Flat-sheet	200-400	Polyamide thin-film composite	Dow Filmtec
NF270-2540	Nanofiltration	Spiral-Wound	200-400	Polyamide thin-film composite	Dow Filmtec
SW30	Reverse Osmosis	Flat-sheet	100	Polyamide thin-film composite	Dow Filmtec
SW30	Reverse Osmosis	Spiral-Wound	100	Polyamide thin-film composite	Dow Filmtec

Table 3.3. Operating limits of the membranes.

Membranes used in the experiments	Module	pH ranges	Operating pressure (bar)	Temperature (°C)
RC70PP	Flat-sheet	1-10	1-10	5-60
NF270	Flat-sheet	2-12	1-41	1-45
NF270-2540	Spiral-Wound	2-11	1-41	1-45
SW30HR	Flat-sheet	2-11	1-69	1-45
SW30	Spiral-Wound	2-11	1-69	1-45

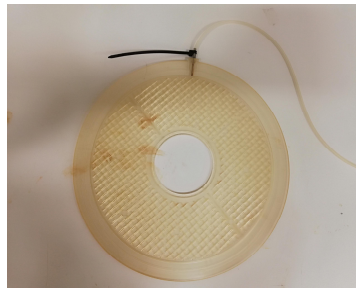
### 3.1.3 Filtration equipment

#### DSS Labstack M20

DSS Labstack M20 allows the use of multiple membranes, which are placed in parallel. Membranes are placed on the both side of a permeation plate, which is surrounded with two filtration plates. Four reverse osmosis SW30 membranes were used in the experiments with the total area of 0.72 m<sup>2</sup>. In addition, of the advantage of simultaneous use of several membranes, DSS Labstak M20 is capable of operating at high pressures, which is necessary for reverse osmosis membranes. The filtration equipment are presented in Figure 3.1. The temperature and cross-flow velocity were kept constant during the experiment. The temperature was kept constant by a cooling system, which circulated cold water throughout the feeding tank. The flow velocity was kept at 0.7 m/s during the filtration. The permeate flow was collected in a separate container while, the retentate was returned back to the feeding tank. The pressure adjusted during the filtration in order to get higher permeate flux. The maximum pressure tolerance for DSS is 40 bar.



**Figure 3.1.** DSS Labstack M20 filter used in the nanofiltration and reverse osmosis filtration experiments.



(a)



(b)

**Figure 3.2.** a) Permeation plate b) Filtration plate.

### **CR250-filter**

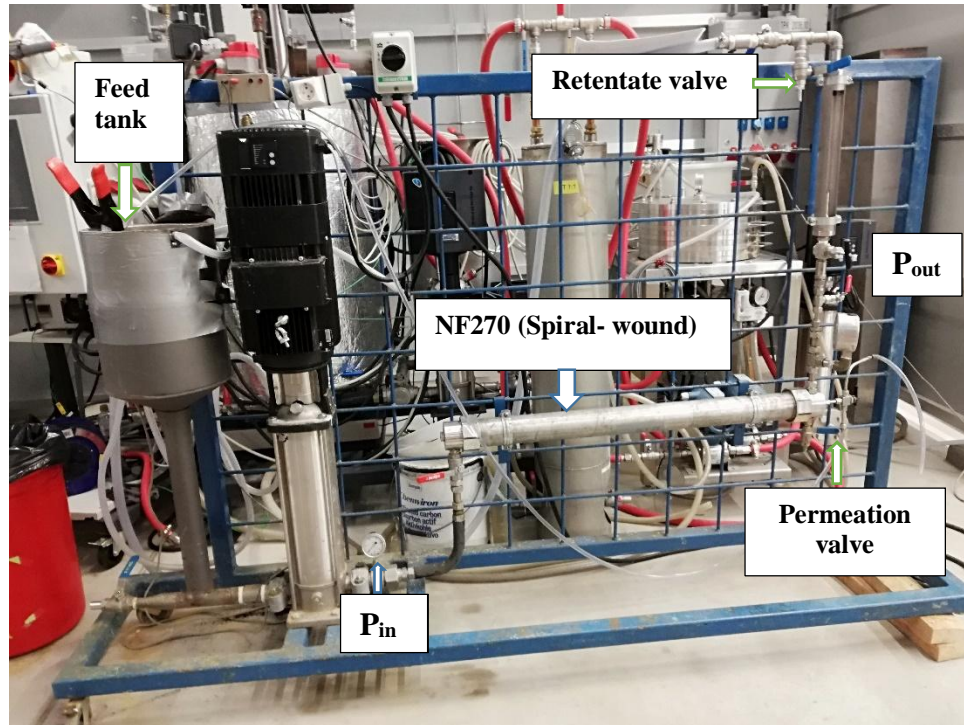
CR250-filter was used in ultrafiltration as a pretreatment step for removing high molecular weight components as well as suspended solids and fine particles in the composting leachate. CR filter is a high shear-rate cross-rotational filter in which the rotor is used to intensify the turbulence. Two RC70PP membranes were cut and soaked in water and then placed in the CR250 in parallel. The combined area of membranes equals to  $2 \times 0.045 \text{ m}^2$  (Figure 3.3).



**Figure 3.3.** CR-250 filter used in ultrafiltration experiments.

### **Spiral wound system**

Figure 3.4, shows the equipment used in the nanofiltration in the second batch experiment. It is a cross-flow membrane filtration unit for  $2.6 \text{ m}^2$  spiral wound element. It was operated at constant flow rate of  $0.8 \text{ L/h}$ .



**Figure 3.4.** Spiral-wound equipment used in nanofiltration experiment in the second batch.

### 3.1.4 Analyzing equipment

TOC, COD, TN, pH, conductivity, phosphorous were measured in all the feed, permeate and concentrate samples. The amount of organic compounds were evaluated with UV absorbance measurement at 210 nm. All the equipment, which were used in analyzing the samples, are presented in Table 3.4.

**Table 3.4.** Equipment used for analysis.

<b>Parameter</b>	<b>Analysis equipment Method</b>
TOC-TN	TOC-5050 analyzer. Estimation of TC, IC, TOC, and TN content in the wastewater.
COD	Hach DR2010 spectrometer, 620 nm, ISO method
pH	Metrohm 744 pH meter
Conductivity	Knick Konduktometer 703
Phosphorous	phosphate cell test
UV at 210 nm	UV-Vis spectrometer at wavelength 210 nm
Scanning Electron Microscopy (SEM)	Hitachi SU3500 Scanning Electron Microscope
Energy dispersive X-ray spectroscopy (EDS)	Thermo Scientific UltraDry SDD EDS, dual detector. Software Pathfinder

### 3.2 Methods

Three pilot-scale batch experiments were conducted for concentrating the nutrients in the concentrate stream as well as decreasing the total organic carbon (TOC), total nitrogen (TN) and phosphorous concentration in the permeate stream via membrane filtration. In all the experiments ultrafiltration used as a pretreatment stage before nanofiltration and reverse osmosis. The function of each step has been studied in terms of permeate fluxes, fouling phenomena as well as the degree of retention for all targeting components in permeate and concentrate side. The flux of pure water were measured before and after all filtration experiments in order to determine the membranes fouling during the experiments. After filtration, the membranes were washed three times using water in order to remove reversible

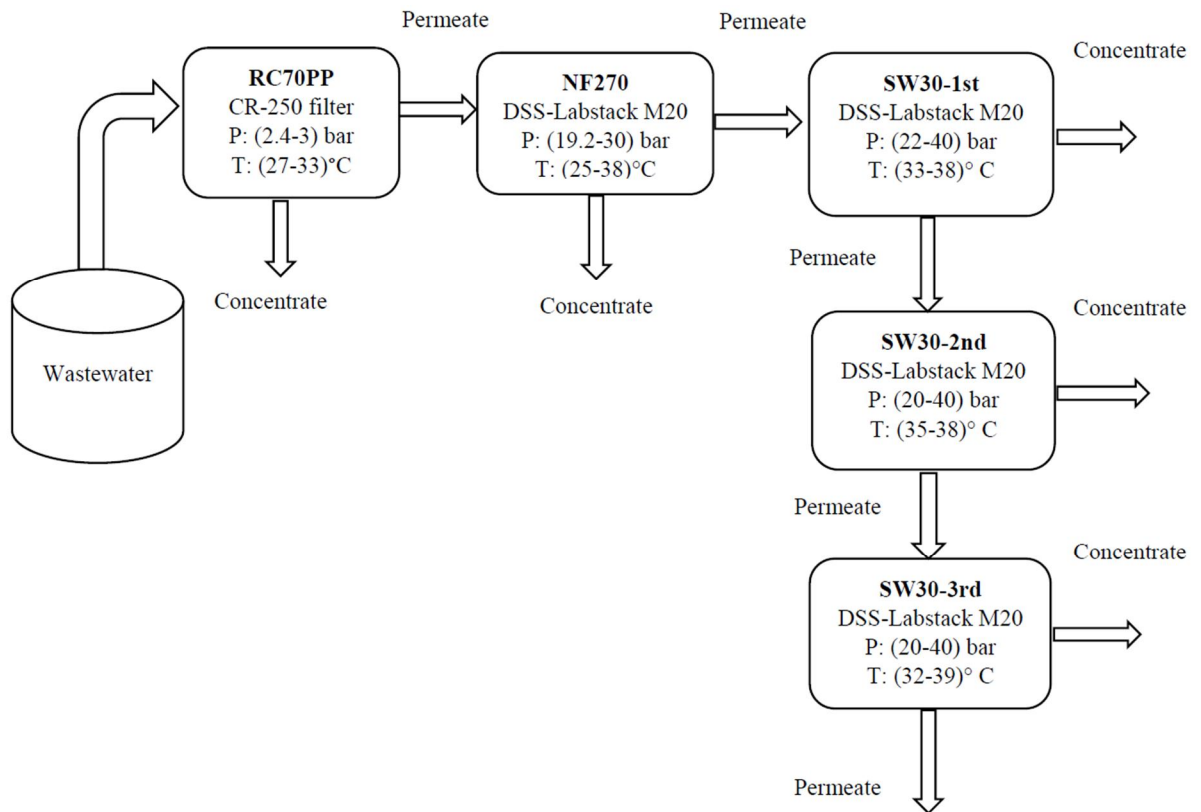
fouling, which is followed by measuring pure water fluxes. Finally, chemical cleaning would be required to remove the foulants from membranes and reclaim the membranes permeability. The chemical cleaning was performed using alkaline agent (Ultrasil 110 solution 0.05% for 15 min) and the pure water fluxes (PWFs) were measured again after cleaning. Comparison of initial PWFs and PWFs after each washing step provides the possibility of determining the fouling. . Fouling could be divided into reversible and irreversible fouling. Reversible fouling can be removed after washing the membrane with water. Irreversible fouling, which is generated from adsorption of solute or deposition of mineral on the membrane surface could be eliminated using a chemical reagent (Kanani et al, 2008). In all batches of experiments, new brand of membranes were used to assure similar condition except NF270 spiral-wound that was applied in the second batch. In continue all the experiments are explained in details.

Pressurizing of the membranes were carried out before filtration. The pressure that is applied for pressurizing was higher than the pressure, which is applied during the experiment. Therefore, after ensuring of the cleanliness of the system, membranes were pressurized for 15 min. RC70PP, NF270 and SW30 were pressurized at 3, 40 and 40 bar respectively. The reason for pressurizing of the membranes before the experiments is preventing the negative effects arising from compaction phenomena during the experiment.

### **3.2.1 First batch experiment**

Based on the first batch experiments, as shown in Figure 3.5, composting wastewater has undergone a series of ultrafiltration, nanofiltration and reverse osmosis filtration in order. All the membranes module were flat-sheet. CR250 filter was used in ultrafiltration and DSS Labstack M20 filter for nanofiltration and reverse osmosis filtration. The pressure and temperature was adjusted during the experiments in order to take an acceptable value of permeate flux. Composting plant leachate was fed into the tank of CR-250 followed by filtration via RC70PP membranes in ultrafiltration step. The VRF value that was 1 at the beginning of experiment, reached 5.2 after 315 min, in which the filtration stopped and 19.3 Kg of permeate

was collected. The filtration carried out at rotor velocity of 500 rpm, Pressure of 3 bar and temperature of  $30 \pm 3^\circ\text{C}$ . The permeate of UF is fed into the tank of DSS where it is filtered with NF270 in cross flow mode, proceeded by the next three stages of reverse osmosis filtration via SW30 membranes with DSS Labstack M20 filter. After each filtration experiment, the membranes were washed with water three times and after measuring the PWFs, they were washed again with cleaning agent for 15 min. The water fluxes were measured after washing to check the effectiveness of washing based on which, the water fluxes should be more than 85 % of the initial water fluxes measurement. Therefore, in some cases with lower water fluxes, more washing were conducted. Operational conditions of all stages are represented in Figure 3.5.

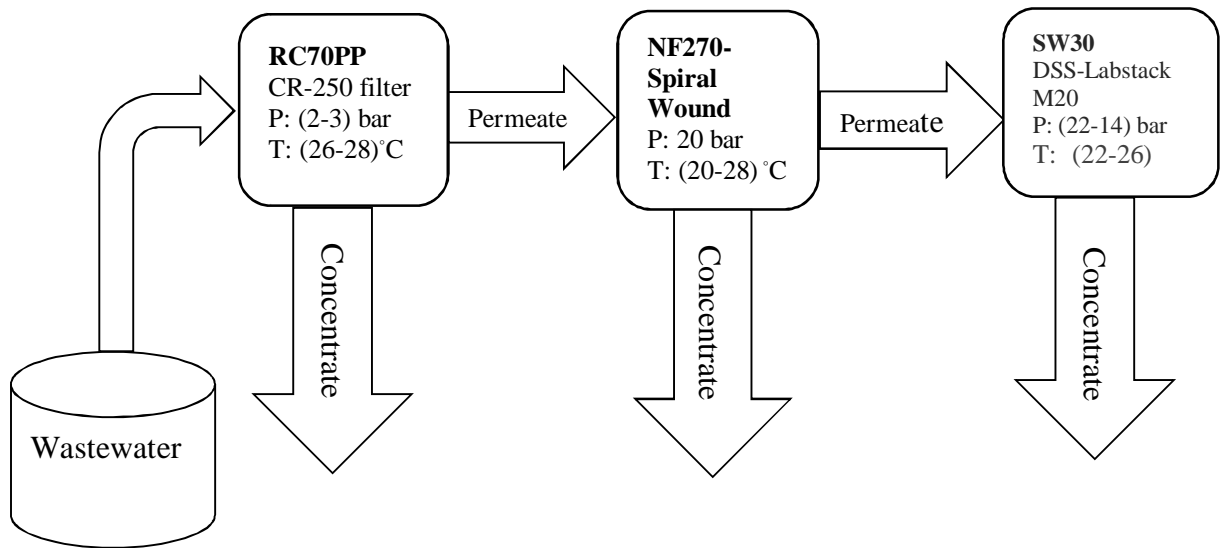


**Figure 3.5.** Diagram of the first batch experiment.

The permeate is collected into a separate container and the concentrate were turned back to the feed tank in both filtration system. Samples were taken from permeate line frequently in order to check the flux and adjust the pressure and temperature accordingly. Temperature was measured with a thermometer placed in the feed tank.

### **3.2.2 Second batch experiment**

In the second batch experiment, the second sample of wastewater was used. Analytical results has demonstrated remarkable variation in the concentration of target components in the wastewater compared to the first wastewater sample, which could be due to the seasonal changes and the number of wastewater circulation in the plant. The more leachate was circulated in the plant, the higher amount of nutrients were accumulated into it. In the second batch filtration experiment, RC70PP membranes were applied in the first step similar to the first batch experiment and ultrafiltration experiment was carried out using CR250-filter, while the second step which was filtration with flat-sheet NF270 in the first batch experiment with DSS was replaced with a spiral-wound NF270 module for evaluating the differences of these two modules and comparing their functionality. NF was carried out in the pressure of 20 bar and flow rate of 0.4 m/s. The main reason of replacing flat-sheet NF270 with its spiral-wound module was the low permeability of wastewater and low values of permeate fluxes as well as low values of retention in flat-sheet NF270 membrane in the first batch experiment. The experiment was continued with RO filtration using SW30 membranes. The SW30 membranes used in this step, were spiral-wound new brand, which were cut in flat-sheet form in order to be placed in DSS Labstack M20 Filter. Figure 3.6, displays the operation diagram of the second batch experiment including UF, NF and RO filtration steps in order.

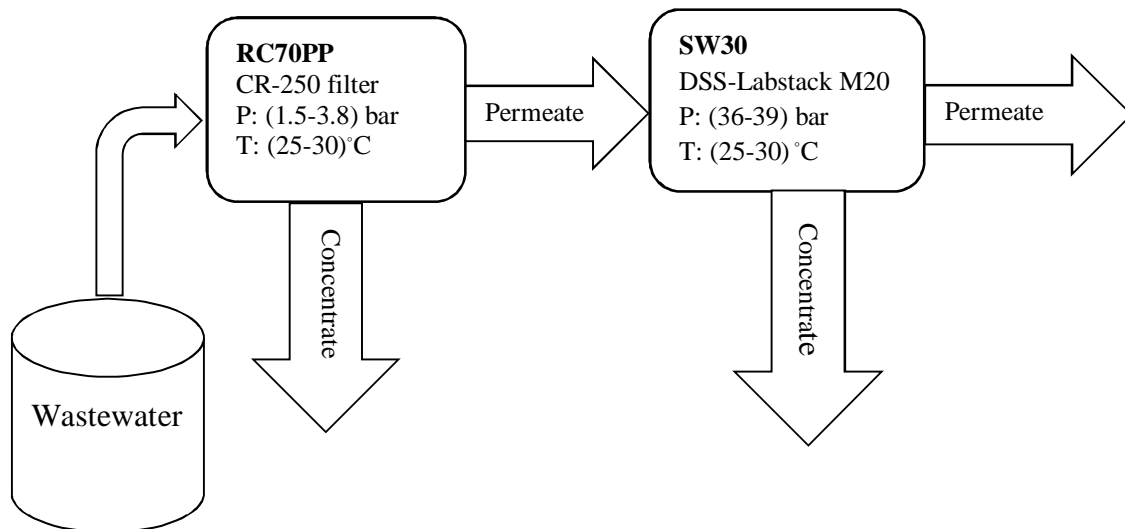


**Figure 3.6.** Diagram of the second batch experiment.

Similar to the first batch of experiment CR250 filter was used in ultrafiltration. RC70PP membranes were pressurized at temperature of 40°C, pressure of 3 bar for 15 min. After stabilizing the system, pressure was adjusted as 1 bar and water permeate fluxes were measured (Table 4.1). In this batch experiment 170 Kg of wastewater was filtered during which the pressure was increased slowly in order to get the ample amount of permeate. The temperature was kept at 40°C during the experiment. The filtration experiment stopped after 38 h and reaching the VRF of 6. In the next, the permeate of RC70PP was used as feed of nanofiltration with NF270 spiral wound membranes. The filtration was carried out at temperature of 40°C, pressure of 20 bar and flow rate of 0.4 m/s but due to the high considerable flux reduction it stopped after 286 min at VRF of 1.6. Eventually, the wastewater was filtered by SW30 membranes, which were pressurized at 34°C and pressure of 38 bar with DSS Labstack M20. Temperature of wastewater during the filtration was 26°C and the initial pressure of 20 bar increased to 37 at the end of filtration when the VRF was 5.2.

### 3.2.3 Third batch experiment

In the third batch experiment, the nanofiltration step has been eliminated for evaluating its performance as well as testing UF and RO membranes in terms of fouling, permeation fluxes and retention values. The wastewater used in this batch of experiment was the third composting leachate sample (Table 3.1). Similar to the first and second batch experiment, ultrafiltration was carried out with RC70PP, the effluent of UF was fed to the DSS and filtered with SW30 membranes. The membranes were cut and soaked in the water one night before filtration. RC70PP membranes were pressurized at 3 bar and 40°C. Ultrafiltration started at the pressure of 1.5 bar and rotor velocity of 500 rpm which were increased until 3.8 and 1000 respectively (Figure 3.7). Duration of ultrafiltration was 560 min and it stopped at VRF of 6 with 83% water recovery. The process was progressed with reverse osmosis filtration in DSS-Labstack M20 filter. The spiral wound SW30 membranes were cut, soaked in water overnight and eventually placed in the DSS system and pressurized at pressure of 38 bar and temperature of 40°C for 15 min. Due to the significant flux reduction over time, the filtration was stopped after 570 min at VRF of 1.6. Figure 3.7 demonstrates the diagram of this batch of experiment.

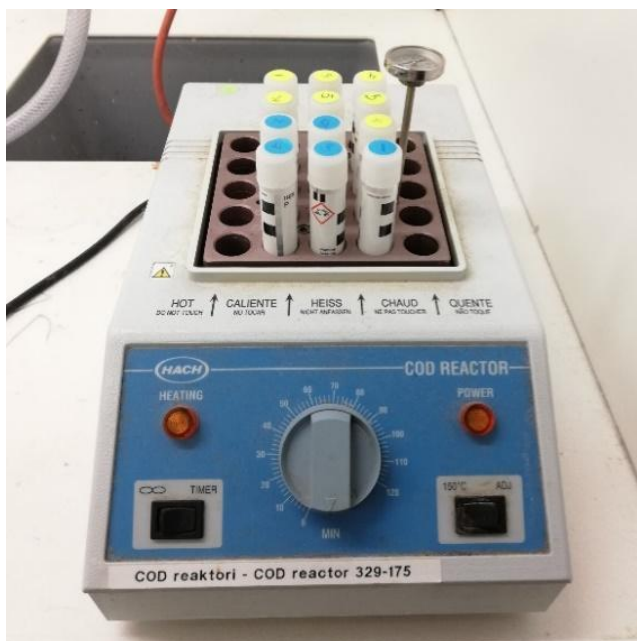


**Figure 3.7.** Diagram of the third batch experiment.

### **3.3 Analyzing methods**

#### **3.3.1 Phosphorous**

In order to specify the phosphorous quantity in a sample, phosphorous should be converted into the dissolved orthophosphate, which is measurable photometrically. The phosphorous presence in the water can be found in different forms including, organic phosphorous, orthophosphate (dominant inorganic form of phosphorous) and condensed phosphate (solid form). One of the most commonly used procedure for analyzing phosphorous is the method of ascorbic acid, which is capable of determining the orthophosphate in wasters and wastewaters (Towns et al, 1986). Measurement of the phosphorous concentration in the samples was carried out using the phosphate cell test. The first step is preparation of the samples based on which each sample was diluted and filtered with a PHENEX RC 0.45- $\mu$ m syringe filter and was pipetted into the phosphate tubes and then it was heated in a reactor for 30 min (Figure 3.8), later it kept in a rack until reaching the room temperature. Once the temperature reached the room temperature, reagent 2 and 3 were added to the tubes followed by mixing and finally the test tube was left in a stand for 5 min and the phosphorous content of the samples was measured in a photometer. The P value obtained from this stage is the dissolved phosphorous of samples. In order to measure the amount of total phosphorous of the samples, after dilution the samples, measurement should be conducted and the filtration stage with PHENEX filters were eliminated. total phosphorous concentration of the samples, the filtering stage was removed from the instruction.



**Figure 3.8.** COD reactor used in the COD and phosphorous analysis.

### 3.3.2 COD measurement

Chemical oxygen demand (COD) content measurement of samples was carried out using Hach spectrometer at 620 nm. The measuring range of used COD Cell tests was between 0-1500 mg/l COD. In this method, 2 ml of water sample was pipetted into a tube containing sulfuric solution of potassium dichromate and silver sulfate (catalyst) proceeded with heating in the COD reactor at 148°C for 2 hours. Dichromate oxidized the organic and inorganic components and the green  $\text{Cr}^{3+}$  was measured in a photometer. Samples were diluted based on their TOC concentration and filtered using 0.45 $\mu\text{m}$  filter before analysis.

### 3.3.3 Total suspended solids analysis (TSS)

Total suspended solids determine the amount of solids in the solution, which is removable with filtration in specified condition. Suspended solids value was measured using standard method (EN 872:2005). According to the method, the samples are filtered (vacuum or pressure filtration) by means of a glass fiber filter followed by drying at 105°C in an oven. The mass of residues on the filters determine the total suspended solids.

### **3.3.4 Dry matter**

The content of total solids in the wastewater, which can be measured by drying a specific amount of solution at 105°C. In this method the water evaporates and the left after drying is called dry matter (DM) (Andersen et al, 2005). materials

### **3.3.5 Organic matter**

Organic matter content measurement was carried out using loss of ignition (LOI) based on which organic matter ignited at 550°C (Santisteban et al, 2004). According to this method, samples are heated in a furnace at the temperature of 550°C and the organic matter converted into carbon dioxide, (Rowell et al, 2003). %OM can be determined by comparing the weight of initial samples and their weight after they have been ignited in a muffle furnace. The remained portion of samples after ignition is the mineral content (ash content).

### **3.3.6 Total carbon and total nitrogen measurement**

Total carbon including total organic carbon and total inorganic carbon as well as total nitrogen were measured with Shimadzu TOC-5050 analyze. Samples were prepared by filtering the wastewater and diluting them. Therefore, the amount of TN and TC is the dissolved amount of total nitrogen and total carbon since all the filterable solid particles were removed from the samples before analysis.

### **3.3.7 Dissolved carbon dioxide (CO<sub>2</sub>)**

Dissolved carbon dioxide presence in the wastewater solution was determined using coulometric method. Based on this method, a sample solution is injected into a chamber, in which a carrier gas continuously removes dissolved carbon dioxide from the wastewater solution. then, the degassed CO<sub>2</sub>, is transported and collected into coulometer, which can be measured (Chang & Lee, 2002).

### 3.4 Calculation

Mass flux (J), is the permeate mass flow rate flowing through a membrane surface area, which is calculated based on the equation in this study.

$$J = \frac{M_p}{A_m} \quad (1)$$

where, J is the mass flux (Kg/m<sup>2</sup>.h), A<sub>m</sub> is the surface area of the membrane and M<sub>p</sub> is the permeate mass flow rate (Kg/h).

Permeability (Kg/m<sup>2</sup>.h.bar), in all the samples were calculated using equation (2).

$$\text{Permeability (P}_m) = \frac{J}{P} \quad (2)$$

Where, J is the mass flux (Kg/m<sup>2</sup>.h), and P is the applied pressure (bar).

Retention is a key parameter for evaluating a membrane performance in retaining a specific compound. Retention (R) can be calculated with equation (3).

$$R = \frac{C_f - C_p}{C_f} \quad (3)$$

where C<sub>f</sub> is the solute concentration in the feed, C<sub>p</sub> is the solute concentration in the permeate (Mudler, 1992).

Volume reduction factor (VRF), determines the amount of feed that is concentrated during the filtration process which can be calculated with equation (4).

$$\text{VRF} = \frac{V_0}{V_0 - V_p(t)} \quad (4)$$

Where, V<sub>0</sub> is the volume of initial feed and V<sub>p</sub>(t) is the permeate volume at time of t (min) (Balannec et al, 2005).

The membranes fouling evaluation was carried out based on the flux reduction of pure water fluxes (PWFs) and calculated according to equation (5).

$$FR = \frac{(PWF_b - PWF_a)}{PWF_b} * 100 \quad (5)$$

Where,  $PWF_b$  is the pure water fluxes before filtration and  $PWF_a$  is the pure water fluxes after filtration and cleaning the system with water.

Total suspended solids were calculated with equation (6).

$$TSS \text{ (mg/L)} = \frac{(M_2 - M_1)}{V} \quad (6)$$

Where  $M_2$  is the mass of dry residues and filter (mg),  $M_1$  is the tare weight of filter (mg) and  $V$ , is the volume of filtered sample (L).

Dry matter was calculated using equation (7)

$$DM = \frac{M_2}{M_1} * 100 \quad (7)$$

Where,  $M_1$  is the initial weight of sample (wet),  $M_2$  is the weight of samples after drying it at 105°C.

LOI (loss of ignition) was calculated using equation (8).

$$LOI = \frac{M_2}{M_1} * 100 \quad (8)$$

Where,  $M_1$  is the initial weight of sample and  $M_2$  is the final weight of sample after heating it at temperature of 550°C.

## 4 RESULTS AND DISSCUTION

Studying the performance of the membranes in water and wastewater treatment and recovering the valuable materials is not just limited to the retention values of targeting components, but it also includes investigating the operational parameters such as permeate fluxes and fouling phenomena throughout the filtration experiment. In this chapter, the retention values of target components in different types of used membrane are presented as well as other important parameters such as fouling amount, flux reduction and the permeability variations of wastewater during each filtration. COD, phosphorous, TOC, TN, conductivity, pH and UV retention were measured for all the samples determining the effectiveness of each membrane for nutrients rejection in diverse types of components.

VRF values are determined using equation 4 (chapter 3), permeability and permeation fluxes are calculated according equation 1 & equation 2 (chapter 3) respectively.

### 4.1 First batch experiment

As it was mentioned in the third chapter in detail, the first batch experiment includes, UF, NF and tree stage of SWRO filtration. Figure 4.1, shows the color retention in the first batch experiment. The changes in color of permeate can be observed from right to the left during the filtration. It can be observed that color retention is moderate for all the membranes.



**Figure 4.1.** Color rejection in the first batch experiment from right to left.

#### 4.1.1 Pure water fluxes before and after filtration experiment in the first batch experiment

The strategy of cleaning membranes in periodic cycles is an effective method for removing the reverse fouling. Cleaning are carried out either physically or chemically. Chemical cleaning are commonly applied when the physical methods are not effective as a standalone cleaning stage. Selecting the chemical agent used in cleaning as well as optimizing the process is of great importance since it needs profound understanding of the fouling mechanism and the complex interactions taking place between membrane and foulants (Malczewska et al, 2019). Table 4.1 summerized the values obtained for permeat fluxes before the experiment and after water and chemical cleaning.

**Table 4.1 .** Pure water values before, after filtration, and after washing in the first batch experiments.

Membrane used in the experiments	MWCO (Da)	PWFs Before filtration (Kg/m <sup>2</sup> .h)	PWFs after water cleaning (Kg/m <sup>2</sup> .h)	Flux reduction (%)	PWFs after chemical cleaning	T (°C)	P (bar)
RC70PP (UF)	10000	75	101	-34	114	40	1
NF270 (NF)	200-400	70	49	30	64.5	40	3
SW30 (RO-1 <sup>st</sup> )	100	53	37	32	40	40	10
SW30 (RO-2 <sup>nd</sup> )	100	57	38	33	50	40	10
SW30 (RO-3 <sup>rd</sup> )	100	51	33	35	45	40	10

(PWFs= pure water fluxes)

In RC70PP membranes, PWFs after filtration is considerably higher than PWFs before filtration. It can be justified in light of several reasons such as, partial deterioration of membrane surface during the experiment, modification of membrane surface or membrane pores size expansion

during the filtration. Since the filtration were carried out in the defined operational range (temperature  $< 60^{\circ}\text{C}$  , pressure  $<10$  and pH  $<10$ ) the membranes surface were unlikely to be damaged or the change in their surfaces is very small since it could not be observed after filtration.

The characteristic of membrane including porosity, hydrophilicity and roughness could affect the pure water filtration. Membranes with higher hydrophilicity often demonstrates higher water permeability (Macedo et al, 2015). Roughness of the membranes is another important parameter related to the membrane surface properties, which may have impact on the water permeability. Nabe et al, deduced that roughness is very imperative in order to measure the maximum pure water fluxes during the filtration according which, higher pure water fluxes in the membranes with smoother surface were observed. (Nabe et al, 1997).

Woo et al .(2015), studied the relationship between membrane surface roughness and permeate fluxes. They compared two similar membrane with similar characteristic, which were different surface roughness and applied for humic acid filtration. The result demonstrated that, membrane with smoother surface, showed higher permeate flux compared to another membrane with rough surface.

Therefore, the reason of improving water fluxes after filtration in RC70PP membranes could be due to the membrane surface alterations including the changes in its roughness as well as the improvement of hydrophilicity of the membrane.

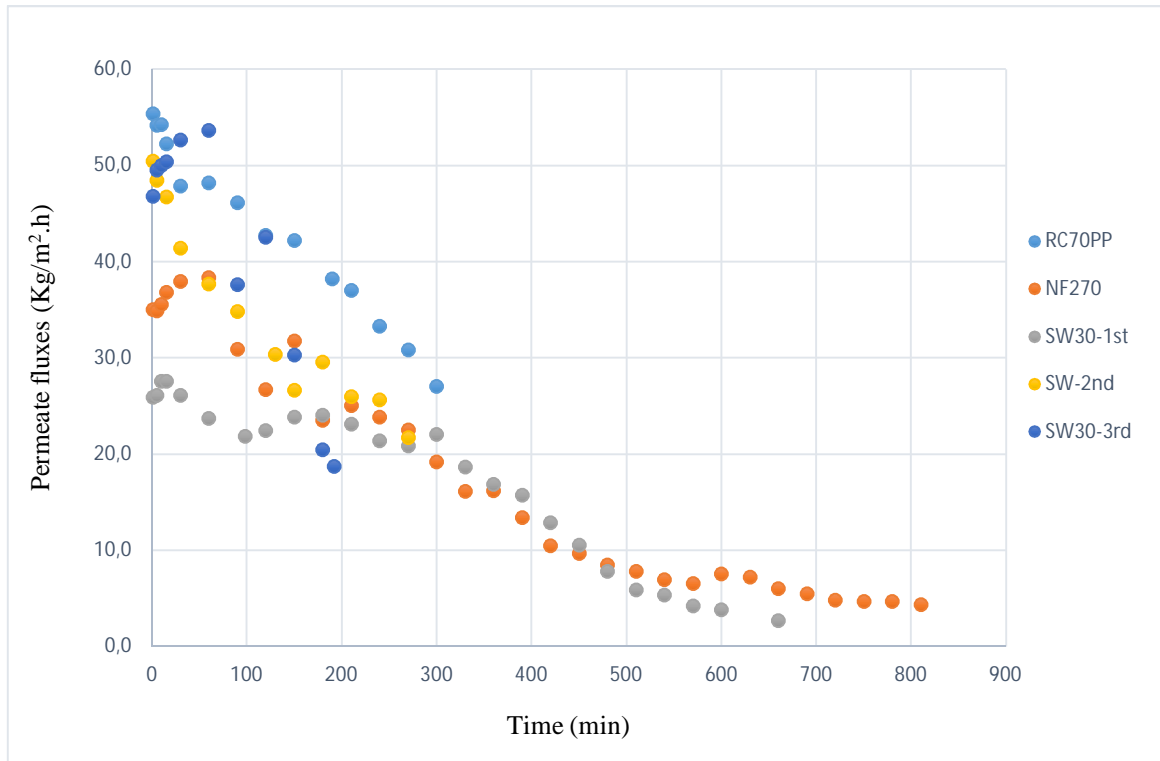
It is evident that the chemical cleaning of the membranes could cause the partial deterioration of the membranes surface. Malczewasla et al, investigated the changes in the structure of polyethersulfone ultrafiltration membranes subjected to the chemical cleaning. They ended up with the conclusion based on which, the exposure of the membranes to chemical cleaning cause PES degradation and consequently reduction of the membranes productivity. Although chemical cleaning often is capable of removing the foulants and retrieve the membrane performance, it could lead to the membrane degradation over time and affects its performance adversely and shorten the membrane lifespan (Malczewasla et al, 2019).

Based on the results, the fouling in NF270 membrane was 30%, which was highly retrieved by chemical cleaning (23%). Therefore the irreversible amount of fouling for NF270 membrane was 7%, which displays that chemical cleaning was quite effective for this membrane.

RO membranes demonstrated similar flux reduction through the filtration (32-35)%. Irreversible fouling of RO membranes are presented in Figure 3.4. The efficiency of chemical cleaning of the membrane increased from the first RO stage to the third one. In the first stage, chemical cleaning retrieved 8% of the permeation fluxes and in the second and third stage, the permeate flux recovered around 20 and 24% respectively. Therefore, since the duration of filtration experiment, the amount of feed and the concentration of organic matter in the feed solutions were different, presenting an exact comparison would be challengeable, but the results displays that, the irreversible fouling of first stage RO membranes are higher and eventually the efficiency of its chemical cleaning is lower.

#### **4.1.2 Permeability changes in the first batch experiment over time**

Permeate fluxes of all membranes reduced considerably with the passage of time, implying the fouling phenomena of the membranes as it could had been expected before the filtration experiments (Figure 4.2).



**Figure 4.2.** Permeate flux reduction over time in the membranes, applied pressure for RC70PP was (2.4-3) bar, (19-30) bar for NF270, (22-40) bar for SW30-1<sup>st</sup>, (20-36) bar for SW30-2<sup>nd</sup> and (20-27) bar for SW30-3<sup>rd</sup>.

During wastewater filtration with all pressure-driven membranes, flux reduction occurred which could have two main reasons: 1) the concentration polarization and 2) fouling of the membranes. Concentration polarization occurs when the rejected solutes and particulates accumulate in the boundary layer close to the membrane surface and form a concentration gradient above the surface of the membrane (Field, 2010). The solution, which is directed to the membrane surface by means of permeation flow, divided into two part, the solvent molecules passing through the membranes and solutes which are rejected and remained on the membrane surface. Concentration polarization is the consequence of accumulation of these molecules that are not capable of diffusing back to the solution (Baker, 2012) Over time, this considerable amount of substances accumulation above the membrane hinder the passage of solvent through the membrane and flux decline occurs. Concentration polarization declines the permeate flux since it increases the resistance of component transportation through the membrane, increased

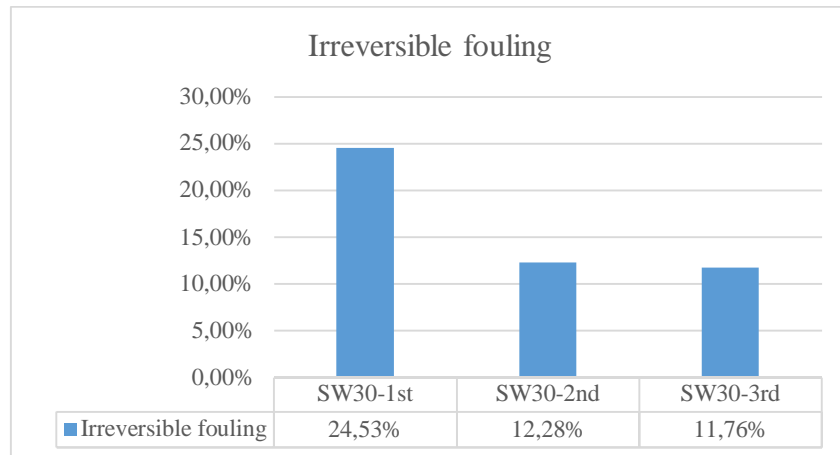
osmotic pressure which can be the result of high concentration of molecules on the membrane surface, could increase the residence of transport and disrupts the influence of trans-membrane pressure. (Field, 2010). In ultrafiltration, concentration polarization is the main issue of the macromolecules (Hughes & Taha, 2006). Fouling of the membranes is another reason of flux reduction during the filtration referring to the phenomena during which the material presence in the bulk solution deposit on the membrane surface or trapped into the porous structure of the membranes. Concentration polarization have a reversible nature in contrast to the fouling, which could occur as reversible or irreversible. Reversibility of fouling could consider as a fouling characteristic and according to some research studies, reversibility and irreversibility of the fouling is defined based on the fouling resistance to cleaning process. Although reversible fouling can be removed with chemical, physical or hydraulic cleaning, irreversible fouling is strongly resistance to the cleaning (Shi et al, 2014). These phenomenon lead to a driving force reduction in the filtration or increasing the resistance of permeate passage during the filtration which end up reducing the permeate flux. The flux reduction is influenced by numerous variables related to the solution characteristic, equipment and the operational parameters. The higher permeate fluxes in RC70PP membrane is due to its molecular cut-off value (10 kDa) which is remarkably higher in comparison with NF and RO membranes. UF fouling is the consequence of adsorption, pores blocking as well as cake or gel formation during the filtration (Shi et al, 2014). The increase of permeation fluxes in some points is due to applying more pressure in that specific time in order to get higher fluxes since the pressure is not constant during the experiments and it was increased frequently. Based on the water fluxes values presented in Table 4.1, the higher water fluxes after filtration compared to the initial ones demonstrates that, the fouling removed totally after cleaning with water, which makes this type of membrane a promising UF membrane option in treatment of composting plant wastewater. One of the reasons of high permeate fluxes of RC70PP membrane is its high hydrophilicity. Hydrophilic membranes could lessen the adsorption phenomena that is an irreversible process and consequently decrease the irreversible fouling (Marshall & Daufin, 1995).

NF experiment, which was carried out using NF270 flat-sheet membranes started at the approximate pressure of 20 bar and temperature of 25°C. The initial permeate flux that was equal

to 35 (Kg/m<sup>2</sup>.h) swiftly dropped and after 1 hour, the permeate fluxes reduction remarkably increased. NF membranes lost considerable value of initial permeate flux (87%) during the filtration, implying high amount of fouling. Filtration was stopped at VRF of 5.5 after 810 min when the flux reached 4.3 (Kg/m<sup>2</sup>.h) and pressure was 30 bar. High value of flux reduction could be due to the high amount of fouling (32 %) caused by type of used wastewater rich in organic matter content and high applied osmotic pressure.

Shu et al, reported significant amount of fouling in NF membrane used for composting leachate treatment (Shu et al, 2016).

Experiment continued with three stages of separate reverse osmosis filtration with SW30 membrane. As it was shown in Figure 4.3, The wastewater permeation fluxes and permeability increased from the first step to the third ( $P_{SW30-1st} < P_{SW30-2nd} < P_{SW30-3rd}$ ). The reason for this, is the variations of NOM and target components in the feed of these RO filtrations. In the first step the feed was the permeate of NF270 which contained more contaminants in comparison with the second and third stage that used the permeate of first RO and second RO as a feed respectively.



**Figure 4.3.** Irreversible fouling of the RO membranes (SW30-1<sup>st</sup>= first step of RO filtration, SW30-2<sup>nd</sup>= second step of RO filtration, SW30-3<sup>rd</sup> = third step of RO filtration).

Irreversible fouling of the RO membranes were measured after washing system with pure water, which proceeded by chemical cleaning for 15 min. In all the RO filtration experiments new brand of membranes were applied. Figure 4.3, represents the fouling of SWRO membranes in three stages of RO filtration. Based on the results, the highest fouling is related to RO membranes of the first step during which the permeate of NF270 was filtered which was due to the higher concentration of organic matter. The fouling in the second and third step is approximately at the same range although the feed of second step is more polluted which could be likely due to the presence of some refractory components that cause fouling and were not rejected effectively by RO membranes.

Özyaka et al. (2015), reported low permeate fluxes for SW30 membrane in landfill leachate treatment based on which the filtration of landfill leachate with MF, UF and two different types of RO membranes including SW30 and BW30 were assessed in terms of flux values, COD and chloride retention. Sharp flux reduction was observed in the membranes. This might be due to the rapid formation of a cake layer on the membrane surface because of the coarse particles in the composting leachate and the existence of fine particles, which result in cake formation on the membrane surface. They concluded that BW30 could be effectively combined with MP005 and ZW-UF membranes. The chloride removal efficiency of BW30 was 95-97%, while in SW30 it was 98% at pressure of 35 bar. COD efficiency removal of BW30 and SW30 were 98.45% and 98.32% respectively.

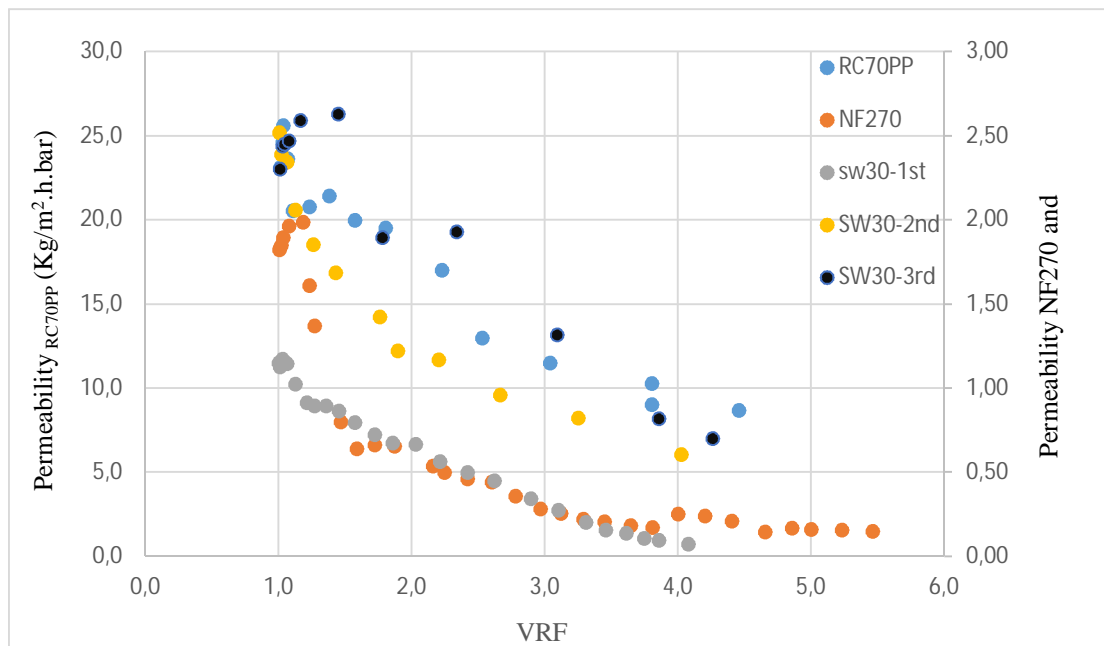
Lee et al, investigated the effects of NF and RO membranes fouling on the boron rejection and reported that decline in salt retention in NF membranes is more than RO membranes due to the charge exclusion reduction which is more effective in NF membranes (Lee et al, 2004). SWRO membranes are a widely used type of reverse osmosis membrane in desalination seawater plants. The fouling of SWRO membranes could be originated from the presence of either organic or inorganic substrates in the feed solution. Membrane fouling management for diverse types of foulants includes various strategies. Fouling triggered by inorganic matter is easier to manage with applying proper operational condition (e.g. pH adjustment, antiscalants addition) however, there are challenges associated with fouling caused by organic components since comprehensive

information on the organic matter characteristics are required (Khan et al, 2013 ; Ning et al, 1999).

Miyoshi et al, reported that transparent exopolymer particles (TEP) and protein-like organic substances could make a significant contribution in SW30 membranes fouling. Based on their research the organic fraction that were measured using liquid chromatography cannot be assessed via water quality indices such as TOC and dissolved COD (Miyoshi et al, 2016).

#### 4.1.3 Permeability changes vs. VRF in the first batch experiment

The permeability of all UF, NF and RO membranes reduced significantly over time with increasing volume reduction factors (Figure 4.4) and it was very low at the end of filtration experiments. Left horizontal axis demonstrates the permeability of RC70PP (10 kDa permeates) and the right horizontal axis is related to NF270 and SW30 permeability in different volume reduction factor (VRF) values.



**Figure 4.4.** The permeability of RC70PP, NF270, SWRO (three steps) vs. VRF in the first batch experiment.

For instance at VRF of 1.9 which approximately 47% of the feed was recovered as permeate, the permeability of RC70PP was equal to 18.5 ( $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ), the permeability of NF270 was 0.65 ( $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) and the SW30 permeability in first, second and third step were 0.67 ( $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ), 1.22 ( $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) and 1.89 ( $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) respectively. These permeability values demonstrate that RC70PP has the highest permeability and NF270 permeability has the lowest value. The permeability of SW30 membranes increased from the first stage to the end due to the cleaner feed. With progressing the filtration and increasing the VRF, the concentration difference between feed and permeate stream increased as the feed became more concentrated, therefore, the osmotic pressure increased as a result permeability decreases.

The maximum pressure applied during filtration experiment in RO steps were 40 bar which was the maximum tolerable pressure limit for DSS-Labstack M20 filter. The higher flux likely to be achieved in different operational condition such as higher flow rates and pressures.

Peter et al, which applied RO membranes in combination with NF membranes for landfill leachate treatment, reported high effectiveness of the reverse osmosis experiment in pressure higher than 120 bar in which the permeate recovery rates increase to 95% (Peter et al. 1998).

#### **4.1.4 Retention values of targeting components in the first batch experiment**

In order to better understand the membranes behavior in terms of rejection values for different components, comprehensive information of membrane properties containing hydrophobicity of membranes, pore sizes and surface charge would be required. Essential factor of predicting the component rejection and solute separation of membranes is MWCO, which is provided for all membranes from the manufactures. Hydrophilicity of the membrane could be deduced from either material or contact angle values. Membrane hydrophilicity is considered as a crucial parameter of membrane performance specifically for organic molecules separation from aqueous solution. The most common means of characterizing the hydrophilicity is the contact angle measurement.

Surface charge of the membrane is another important factor affecting the rejection of solutes and components during the filtration. When the membranes are in contact with an aqueous solution, its surface becomes charged. The membrane charging which is a key parameter in filtration properties could be due to the various reasons including, effects of the functional groups, adsorption of ions, charged molecules and polyelectrolytes on the surface of the membranes or even into the pores of membranes. Zeta potential characterization is a common way of estimating the surface charge of membranes, which is carried out using streaming potential. (Cho et al, 1999 ; Wiley, 2011). The degree of rejection for all targeting components for UF, NF and RO membranes are summarized in Table 4.2.

**Table 4.2.** Retention of the target components for membranes in the first batch experiment.

Membranes	P retention (%)	TOC retention (%)	TC retention (%)	IC retention (%)	TN retention (%)	COD retention (%)	UV retention at 210 nm	Conductivity retention (%)
RC70PP	40	31.7	31	4	2.5	23	38	13.3
NF270	33	10	11.5	40	30	11.3	42	22
SW30-1 <sup>st</sup>	50	47	46	36.7	50	50	37	34.5
SW30-2 <sup>nd</sup>	51	61	60	21	52	50.2	55	32.2
SW30-3 <sup>rd</sup>	71	71	70	8	67.5	71	67	65.5

The accuracy of the results were tested using mass balance equations and in order to obtain reasonable data which fits into the mass balance equations, several repetition for analysis were carried out. RC70PP membrane has shown promises for rejection of total organic carbon and phosphorous, while its total nitrogen retention is very low and it is not surprising since UF membranes are not effective for nitrogen removal. The dominate form of nitrogen in composting leachate is ammonium and the nitrite and nitrate content of the wastewater is negligible. Molecular weight cut-off value (MWCO) is the most imperative parameter corresponding to the potential of solute retention level in UF membranes. Furthermore, the retention could be

influenced by the component adsorbed on the surface of the membrane or even the effects of polarized solutes on the membrane surface. Generally, membranes retention is defined based on their intrinsic passage, while the real passage differentiates highly according to the polarization. At low fluxes, the intrinsic and real passage are the same, although at higher fluxes, the polarization increase leading to the increase of membrane selectivity for some components (Drioli, 2010).

The retention of TOC (10 %) and phosphorous (33%) in NF was unexpectedly lower than TOC and P retention in UF which was 30% & 40 % respectively. TN and conductivity retention in NF was higher than UF, however, the retention of target components in NF270 membrane is relatively low especially for TOC component, which could arise from the low permeate fluxes during the experiment. The retention of molecules in NF membranes is according to their charge, which is identified as ionic NF separation as well as the sieving mechanism referring to the separation mechanism of unchanged molecules based on their molecular weight (Mona et al, 2018). Both electrostatic interactions and size exclusion contribute to the separation mechanism of charged components (Mänttari et al, 2000). In case of organic components, hydrophobicity might also affect on the retention of target (Braeken et al, 2005b). NF270 is a hydrophilic membrane, which is prone to fouling by NOM. The behavior of NF membrane are pretty complex rather than UF, since the retention values could decrease or increase depending on the nature of organic matter (molecular size, chemical characteristics as well as their shape) while, it is evident that in UF, fouling could result in enhancement in retention of organic matter (Schäfer et al, 2000). The results demonstrated that in the composting plant leachate the rejection of components decreased significantly, which could be due to the organic fouling.

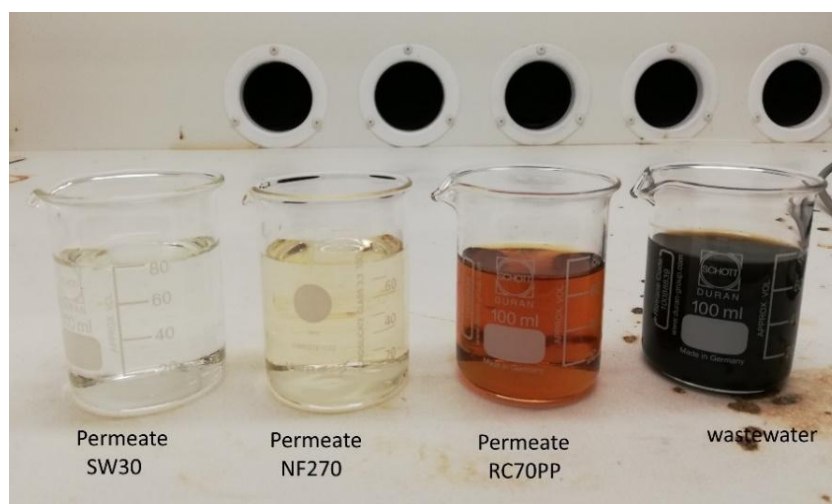
The retention values for all targeting components in filtration with SW30 membranes increased from the first step to the last one. The higher retention values for targeting components were obtained at the third RO experiment, in which the fouling was less than first and second RO experiment. As the filtration progressed, the concentration polarization increase, which leads to the increase of concentration of organic matter on the membrane surface as well as deposition of salts on it. Therefore, the concentration of components on the membrane surface become

higher than the original feed. This concentration difference make the diffusion of components possible through the membrane and decrease the retention values. (Vrijenhoek et al, 2001).

## 4.2 Second batch experiment

The pilot-scale experiments were conducted in the second batch experiment with second wastewater sample, that differentiate considerably from the first sample in terms of the amount of components, although the target components exist in both samples. This sample was taken on November while the first sample was collected in the summer when it was warmer and the microorganism activity were considerably higher. The wastewater then filtered using RC70PP, NF270 and SW30. The SW30 used in this batch of experiment were new brand of SW30HR spiral wound module which were cut in flat-sheet form to fit into DSS Labstack M20. Nanofiltration were carried out using NF270 Spiral-Wound module.

Figure 4.5, demonstrates the photo of color rejection in wastewater during the above-mentioned stages. As it can be observed the permeates color of NF step was much clearer than the first batch as it had been expected before the experiment due to the high active area per unit volume of spiral wound module of the NF membrane ( $2.6 \text{ m}^2$ ) although the unexpected high flux reduction hinder the progress of filtration and it was stopped at VRF of 1.8.



**Figure 4.5.** Color rejection in the second batch experiment from right to left, permeate of RC70PP, NF270, SW30 membranes.

#### 4.2.1 Pure water fluxes measurement in the Second batch experiment

Similar to the first batch experiment, pure water fluxes were measured after cleaning the system with water and chemical cleaning. The average value of the water fluxes after water permeation stabilization are presented in Table 4.3.

**Table 4.3.** Pure water values before filtration, after filtration, and after washing in the second batch experiments.

Membrane used in the experiments	MWCO (Da)	PWF Before filtration (Kg/m <sup>2</sup> .h)	PWFs after filtration (Kg/m <sup>2</sup> .h)	Flux reduction during filtration (%)	PWFs after washing (Kg/m <sup>2</sup> .h)	T (°C)	P (bar)
RC70PP (UF)	10000	78.5	68.7	12.5	116.9	40	1
NF270 (NF-Spiral Wound)	200-400	71	60.2	13.7	72.5	40	5
SW30 (RO)	100	45.9	41.9	8.7	43.4	40	10

Based on the data summarized in Table 4.3, unlike the first batch experiment, pure water fluxes after ultrafiltration decreased and 12.5% flux reduction was observed which could rationally be reasoned due to the long term of ultrafiltration (38 h) and great amount of filtered wastewater (170 Kg) in the second batch experiment (around seven times higher than the first one). The filtration stopped several times at nights and the permeation valve was returned to the feed tank while the pump was working and pumped the wastewater on the membranes surface, which could be the reason of UF membranes fouling in this batch of experiment.

The high value of water fluxes after chemical cleaning that is 48% more than PWFs before filtration, demonstrates that the fouling could be reversed with washing via alkaline reagent although the high amount of water fluxes improvement was most probably due to the membrane deterioration during washing with chemical reagent. The flux of RC70PP at the beginning of

experiment was relatively high 53 ( $\text{kg}/\text{m}^2\cdot\text{h}$ ) which decreased until 28 ( $\text{Kg}/\text{m}^2\cdot\text{h}$ ) at the end of filtration when the VRF reached 6 at the pressure of 3 bar, implying 47% flux decline throughout ultrafiltration.

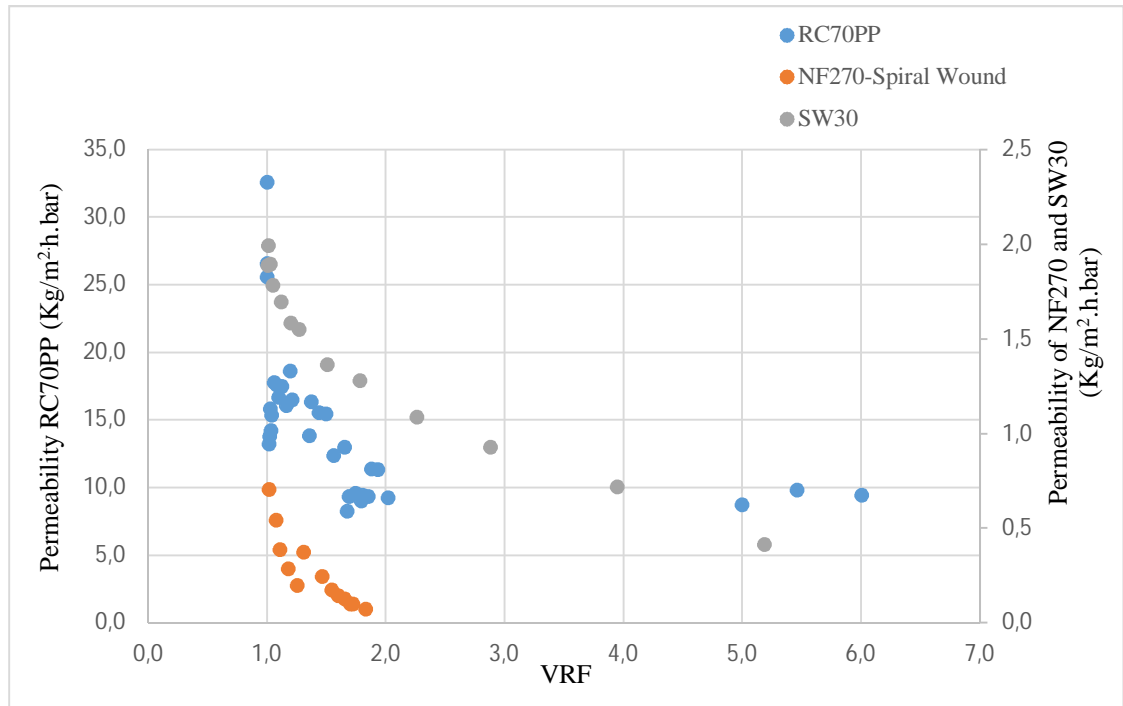
In the NF270 spiral wound, the water fluxes values after cleaning with water indicated 13.8% reversible fouling which was completely removed by chemical cleaning.

Reversible and irreversible fouling of SW30 membranes were 8.8% and 5.3 % respectively. The lower fouling either reversible and irreversible obtained after RO filtration in the second batch experiment is due to the cleaner wastewater obtained after NF stage with considerably less amount of inorganic salts and organic matter that was applied as feed of RO.

#### **4.2.2 Permeability changes in the second batch experiment over time**

The permeability variation of the membranes used in the second batch over time is shown in Figure 4.6. Left horizontal axis demonstrated the permeability of RC70PP and the right horizontal axis demonstrates NF270 and SW30 permeability in different VRF values.

In all types of membranes, considerable permeability decline observed during the filtration. The UF started with relatively high initial permeability 26.5 ( $\text{Kg}/\text{m}^2\cdot\text{h}\cdot\text{bar}$ ) which lost 64% of its initial permeability during the filtration and reached 9.4 ( $\text{Kg}/\text{m}^2\cdot\text{h}\cdot\text{bar}$ ) at the end of filtration. At VRF of 1.9, permeability of RC70PP was 9.3 ( $\text{Kg}/\text{m}^2\cdot\text{h}\cdot\text{bar}$ ) that was obtained after 18.5 h filtration. In the first batch experiment permeability value at the same VRF was 18.5 which was obtained after 2.5 h. The reason of this huge alteration is due to the difference in the amount of feed and the composition of the nutrients in the wastewater. Therefore, it is quite clear that, as the amount of feed is more; filtration experiment would take more time, consequently, the fouling would be higher leading to less permeability at the same VRF.



**Figure 4.6.** The permeability of RC70PP, NF270 (Spiral wound module), SW30 vs. VRF in the second batch experiment.

Permeability of NF270 is quite low and it reduced considerably during the filtration. NF reached the maximum VRF of 1.8 after 286 min in a condition, that the pressure and flow rate was kept constant (20.5 bar and 0.4 Lit/h respectively). Permeation fluxes reduced at the beginning of filtration demonstrates that the fouling started to proceed quickly after starting filtration. The initial permeation flux of NF270 was 14.4 (Kg/m<sup>2</sup>.h) at the pressure of 20 bar, which dropped below 10 (Kg/m<sup>2</sup>.h) after 30 min and eventually at VRF of 1.8 it reached 1.4 (Kg/m<sup>2</sup>.h). Therefore, in the NF stage of second batch experiment 90 % flux reduction occurred. The flux decline could be due to either membrane compaction or concentration polarization of the membranes. Conducting NF at high pressure (20 bar), increase the concentration polarization and consequently, decrease the permeation fluxes considerably. Membrane compaction is a common phenomenon observed specially in pressure driving membrane filtration. Membrane compaction could have several reversible and irreversible impacts on the structure of the membrane, for instance, it may contribute to mechanical destruction of the surface membrane

by affecting its porous structure, which is arisen from the applied pressure (Volkov, 2015). Different parameters are associated with the severe fouling of NF270 membrane, which worsen the performance of the membrane such as solution chemistry (composition of the wastewater and pH).

Existence of dissolved organic materials could be an acceptable explanation for NF membranes fouling. Humic substances, which are the major fraction of NOM, are refractory substances anion macromolecules consisting of aliphatic and aromatic components with mainly phenolic and carboxylic functional groups. NOM substances are capable of reacting with multivalent cations leading to the formation of fouling layer and drastic flux reduction during the filtration (Seidel et al, 2002; Hong et al, 1997). The pH is a critical factor affecting the humic material fouling behavior. The permeate of RC70PP which was highly rich in organic matter used as feed of NF. Organic fouling could lead to the reversible or irreversible flux reduction.

RO filtration proceeded until VRF of 5.2, which took 8 h and stopped when 80% of feed was recovered as permeation. The permeation fluxes monitored with increasing the pressure frequently through the filtration and permeation fluxes kept relatively high around 7 h (higher than 30 Kg/m<sup>2</sup>.h), the highest permeation fluxes decline observed at the last hour of filtration elucidating that, the main components of fouling formation were removed with NF270. The higher permeation fluxes of RO in the second batch experiment compared to the first RO stage of the first batch experiment, which was placed after NF stage, could be due to the concentration of organic components in the leachate as well as the different NF modules. The higher active area of spiral-wound module (2.6 m<sup>2</sup>) is capable of rejecting high potential of targeting component leading to much cleaner wastewater, therefore, its effluent that was applied as feed of RO membranes, facilitate the reverse osmosis filtration and lessen the fouling phenomenon in the membranes.

In RO filtration which were carried out using SW30 membranes, the initial permeate flux which was 38 (Kg/m<sup>2</sup>.h) reached 20 at the end of experiment during which the pressure was monitored and increased slowly from 20 to 37 bar.

### 4.2.3 Retention values of the targeting component in the second batch experiment

The retention values of target components in the third batch experiment are summarized in Table 4.4.

**Table 4.4.** Retention of the target components for membranes in the second batch experiment.

Membranes	P retention (%)	TOC retention (%)	TC retention (%)	IC retention (%)	TN retention (%)	COD retention (%)	UV retention at 210 nm	Conductivity retention (%)
RC70PP	57	32	29	15	3	30	40	5
NF270	71	46	46	52	75	56	74	70
SW30	87	75	75	78	56	70	76	72

The degree of rejection for organic carbon and total nitrogen (TN) as well as UV rejection is highly close to the first batch experiment in RC70PP membranes. The phosphorous rejection in the second batch experiment is higher than the first batch.

In the spiral-wound NF270 membrane, the retention values improved considerably compared to flat-sheet NF270 in the first batch experiment due to the higher membrane active area. Therefore, altering the module of NF270 membrane from flat-sheet to spiral-wound could remarkably affect the rejection although the flux decline in the NF membranes remained the main challenge of this step of experiment.

The low retention in NF is likely due to the formation of fouling layer on the membrane surface, which is rich in organic components. With increasing the accumulation of these molecules on the membrane surface, the retention values increased. As it was mentioned, the retention in the NF membranes could increase or decrease with proceeding the fouling on the membrane surface due to the complex behavior of NF membranes.

Xu et al, reported very different behavior for fouled NF membranes from one to another in retention of hydrophilic and hydrophobic components (Xu et al, 2006).

Ng et al, reported a significant decrease in the retention of organic contaminants (hormons) due to the colloidal fouling, which progressed over time and deteriorate the rejection as the adsorbed hormone on the membrane surface diffused through the membrane into the permeate stream (Ng & Elimelech, 2004).

The retention of organic matter also depends on operational conditions including, temperature, and pressure and flow rate. Increasing the temperature leads to the decrease in viscosity and consequently increase the fluxes. Sierka et al, reported that increasing the temperature increased the fluxes of wastewater in UF membrane (NTR-7410) and the rejection amount of TOC and color decreased, the reason for this, is the diffusion of organic matter at higher temperature. Moreover, the dissolved salt retention was not influenced by temperature (Sierka et al, 1995).

Mänttari et al, reported decrease in the retention of TC with increasing the temperature, while conductivity was not affected. Generally, conductivity is defined as a measurement method of dissolved salt, which is mostly associated with solution-diffusion model and affected by the concentration variance in the membranes (Mänttari, et al, 2004).

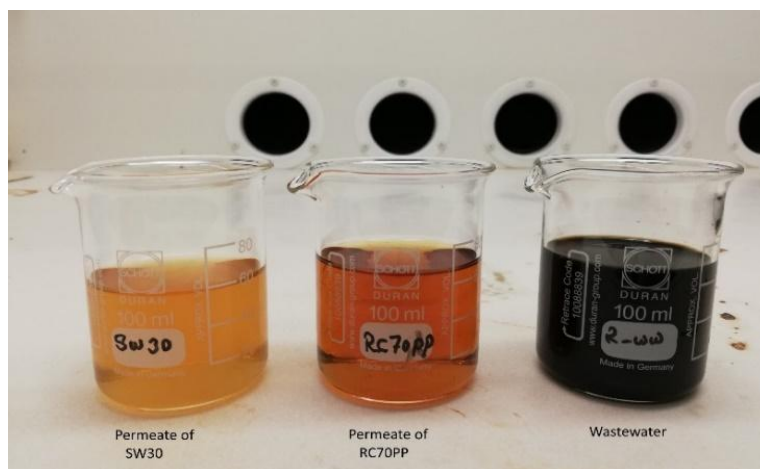
The retention of all components in SW30 membranes increased significantly compared to the first batch experiment. It could be due to the type of SW30 membrane which differentiated from the SW30 used in the first batch experiment.

### 4.3 Third batch experiments

The third sample of composting plant leachate, which was used in this batch, was remarkably rich in TOC and phosphorous compared to the first and second wastewater samples. This wastewater was returned to the plant and circulated several times, although the nutrients and components presented in it is similar to all leachate samples.

NF step was eliminated in the third batch and effluent of RC70PP were used as feed of RO filtration, which was conducted with SW30 membranes. A surprising flux reduction were observed in RO filtration and the permeability decreased swiftly during the filtration, therefore the RO filtration did not proceeded effectively and it was stopped after 9.5 h at VRF of 1.6. However, the rejection values obtained for different components were promising.

Figure 4.7, displays the color rejection of UF and RO filtration. It can be observed that the permeate of RO filtration is darker compared to the first and second SWRO effluent (Figs 4.5 and 4.1).



**Figure 4.7.** Color retention in the third batch experiment.

#### 4.4 Pure water fluxes measurement in the third batch experiment

Pure water fluxes for third batch experiment were summarized in Table 4.5.

**Table 4.5.** Water fluxes measurement before, after water cleaning and after chemical cleaning in the third batch filtration experiment including ultrafiltration and reverse osmosis (UF<sub>RC70PP</sub>-RO<sub>SW30</sub>).

Membrane used in the experiments	MWCO (Da)	PWF Before filtration (Kg/m <sup>2</sup> .h)	PWF after filtration (Kg/m <sup>2</sup> .h)	Flux reduction during filtration (%)	PWF after washing (Kg/m <sup>2</sup> .h)	T (°C)	P (bar)
RC70PP (UF)	10000	60.7	96.5	-37	104.4	40	1
SW30 (RO)	100	45.5	35.8	21	40.9	40	10

Pure water fluxes in UF increased 37% after filtration and cleaning with water, similar to the first batch experiment. Cleaning the membranes with Utrasil 0.5%, again 7.5% increased the water fluxes (further explained in the first batch experiment).

21% flux reduction or fouling occurred in the SWRO, which is relatively higher than the fouling of SW30 at the first and second batch experiments due to the thicker feed, which contains higher amount of nutrients and inorganic salt. Chemical cleaning used in this RO experiment could reverse almost 10% of this fouling amount.

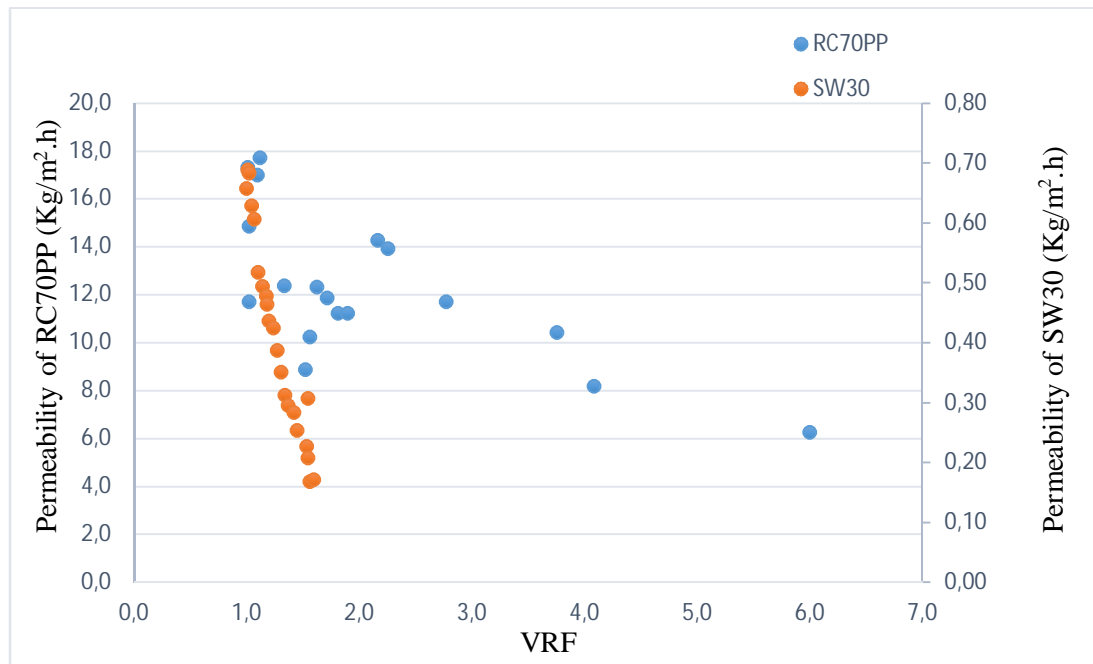
According to the obtained results, NF stage prior to RO filtration played a significant role in proceeding the RO step with improving the fluxes as well as reducing the fouling of the membranes. NF which is capable of eliminating majority of humic substances and di/multivalent ions (Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>) facilitate the process for RO step and generally increase the effectiveness of the entire wastewater treatment process. NF has great potential of ammonia rejection that is considered one of the main nutrients in composting plant and landfill leachates.

Ramaswami et al, studied the ammonia recovery from landfill using nanofiltration. Based on their research, the retentate of RO provided using a landfill site was filtered with NF270. In the

landfill site the leachate was processed using two stage of RO filtration. The retentate of RO plants was reinjected to the landfill. Therefore, in order to prevent the circulation concentrate of RO in the plant, NF along with chemical dosage (Mg & P) were applied to precipitate phosphorous as struvite and enhance the economy of the process by removing ammonia from landfill leachate and turning it into a marketable product. Permeate of NF was devoid of hazardous heavy metals and multivalent cations such as,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , etc., as a result permeate the permeate of NF could be used as clean struvite and sold as a fertilizer. (Ramaswami et al, 2016).

#### 4.4.1 Permeability changes in the third batch experiment over time

The permeability variation of the membranes used in the second batch over time is demonstrated in Figure 4.8. Left horizontal axis illustrates the permeability of RC70PP and the right horizontal axis demonstrates SW30 permeability over time.



**Figure 4.8.** The permeability of RC70PP and SW30 vs. VRF in the second batch experiment.

The initial permeability of RC70PP was 17.3 ( $\text{Kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) which reduced quickly after 30 min. applying higher pressure (maximum 3.8 bar) and increasing rotor velocity after VRF of 1.5 from 500 to around 1000 rpm helped to keep the flux higher than 30 ( $\text{Kg/m}^2\cdot\text{h}$ ). UF proceeded until VRF of 6 in which the permeability was 6.3 ( $\text{Kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) implying 64% of permeability lost during the filtration. This value of permeability decline is the same as UF in the second and first batch of experiment, however, the initial permeability are different in different batches due to the diverse types of used wastewater. The initial permeability of third batch is lower compared to the UF of the first and second batch experiment as the filtered wastewater was highly rich in nutrients, and the concentration of organic matter was considerably higher.

RC70PP membrane permeability is relatively high despite losing 64% of its permeability during the filtration. At VRF of 1.9 permeability of RC70PP was equal to 11.2 ( $\text{Kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) that was obtained after 5h filtration at the pressure of 3.6 bar. In the first batch of experiment permeability value at the same VRF was 18.5, which was obtained after 2.5 h at the pressure of 2.1 bar. In this VFR value around 50% of the feed is recovered as permeate. The feed solution of this batch of experiment was more polluted and had higher concentration of nutrients, also, the amount of feed was approximately one and a half times more than the feed of the first batch experiment, therefore, the flux decline would be higher in this UF stage and more time would be required to reach the same VRF.

SW30 filtration initiated at pressure of 36.5 bar with permeability of 0.66 ( $\text{Kg/m}^2\cdot\text{h}\cdot\text{bar}$ ) which progressed until VRF of 1.6, and due to very low permeation fluxes it was stopped at VFR of 1.6 when the permeability reached 0.17 ( $\text{Kg/m}^2\cdot\text{h}\cdot\text{bar}$ ). Based on the obtained results 74 % of permeability decline observed throughout the filtration besides the low permeation fluxes determining severe fouling occurrence during the experiment. Since the SW30 membranes of second and third batch experiments are the same, it could be more reasonable to compare them in terms of fouling and fluxes based on which the performance of RO in the second batch experiment is highly influenced by NF step placed before it.

#### 4.4.2 Retention values of the targeting component in the third batch experiment

Retention values of UF and RO membranes for targeting compounds are summarized in Table 4.6.

**Table 4.6.** Retention of targeting component in the third batch experiment.

Membranes	Total P retention (%)	Dissolved TOC retention (%)	Dissolved TC retention (%)	Dissolved IC retention (%)	Dissolved TN retention (%)	Dissolved COD retention (%)	Dissolved UV retention at 210 nm	Conductivity retention (%)
RC70PP UF	64	27	27	35	14	28	38	3
SW30 RO	87	86	86	73	84	91	88	82

The retention of all targeting components in RC70PP membranes were very close to the retention degree of components in the first and second batch, although phosphorous retention increased in the third batch experiment.

The retention of all substances in SW30 membranes of third batch experiment are remarkably higher than the SW30 membranes used in the first batch experiment. The SW30 membranes used in the second and third were from different batch (new one) than in the first experiments, which could explain the differences at least partly. In the third batch experiment, the fluxes are considerably lower generating from the type of wastewater that is the permeate of RC70PP and consequently, the higher composition of targeting component in the wastewater and higher retention values increase the accumulation of retained molecules on the membrane surface and eventually increased the concentration polarization. The high CP along with high applied osmotic pressure cause severe flux decline through the filtration. The main reasons of SW30 membranes fouling base on the literature are represented in the next chapter.

#### 4.5 The main reasons of RO fouling

- **Organic fouling:** Arises from bonding diverse type of organic macromolecules such as proteins and polysaccharide on the surface of the membrane.
- **Colloidal fouling:** the consequence of particles accumulation with the size smaller than suspended solids and bigger than dissolved solids such as, clay minerals, Al, Mn and Fe oxides, organic colloids, etc.
- **Biofouling:** which is form due to the presence of microorganisms in the solution.
- **Inorganic fouling and Scale formation:** two different crystallization routes result in scale formation, 1) bulk crystallization resulting in the salts precipitation in the solution, which are transported to the surface of the membrane 2) surface crystallization, which is generated from the crystals formation on the membrane surface. Both mechanisms are highly associated with operational conditions as well as the membrane surface characteristics (Antony et al, 2011; Lee et al, 2005).

CO<sub>2</sub> analysis demonstrated that the composting plant wastewater contained dissolved carbon dioxide. The fouled membranes both RC70PP and SW30 of third batch experiment were analyzed using Energy-dispersive X-ray spectroscopy (EDS). The results validated that calcium is the dominant element on the SW30 fouled membranes. However, the membranes were washed several times with pure water and cleaning agent after filtration, some elements still were present, for more illustration, in SW30 membrane, Ca, Si, Al, Mg, Na and S were detectable. Table 4.7, demonstrates the weight percentages of elements in four-selected point of the membrane including brighter and darker areas.

**Table 4.7.** EDS analysis results in SW30 membrane in third batch experiment.

Elements	SW30-bubble (wt.%) (1)	SW30-Darker (wt.%) zone	SW30-brightest (wt.%) (1)	SW30-bubble (wt.%) (2)
<b>C</b>	22	36	28	23
<b>O</b>	48	44	15	47
<b>Na</b>	0	0	0	1
<b>Mg</b>	1	0	0	1
<b>Al</b>	0	1	0	0
<b>Si</b>	0	10	2	3
<b>S</b>	2	8	51	4
<b>Ca</b>	27	1	4	23

Besed on EDSX spectra of polyamide membrane (AD), they have high percentages of Carbon originating from aromatic functional groups in polyamide membrane as well as considerable percentage of sulfur (usually polysulphone) caused from microporous substrate (Sachit et al, 2017).

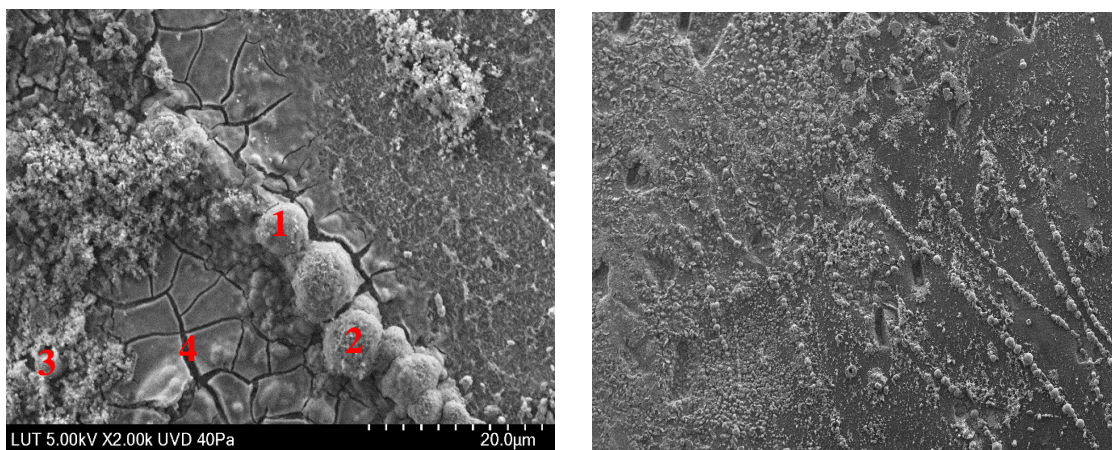
Carbonate scaling can be considered as predominant alkaline scale on the membrane surface (Figure 4.9) , which is formed because of the breakdown of bicarbonate ions according to the following reaction:



Lowering the pH of the feed water by acid dosing could be shifted the equilibrium to the left side and prevent the scale formation and deposition of  $\text{CaCO}_3$  on the membrane surface (Shahid et al, 2017).

According to the above-mentioned result, the precipitation of  $\text{CaCO}_3$  on the surface of membranes could be one of the main reasons of fouling in SW30, furthermore, composting plant

leachate includes high concentration of sulfate ( $\text{SO}_4^{2-}$ ), which can react with  $\text{Ca}^{2+}$  and lead to the formation of  $\text{Ca}(\text{SO}_4)_2$  which can precipitate on the membrane surface. In the analysis of third wastewater sample, significant amount of  $\text{SO}_4^{2-}$  were detected. It can be concluded that, this type of anion also exists remarkably in the composting leachate of the first and second wastewater sample. Figure 4.9, displays the SEM images of the fouled SW30 membranes in the third batch experiment in which the fouling of SW30 membranes were more severe.



**Figure 4.9.** SEM images of fouled RO membranes in the third batch experiment.  
1) Bubble 1. 2) bubble 2. 3) Brightest part 4) Darker parts.

In brackish water systems, formation of mineral salts including  $\text{CaCO}_3$  and  $\text{CaSO}_4$  are considered as the main sources of inorganic fouling. The precipitation of these mineral salts occurs in the membrane surface or in the solution bulk, which lead to the significant, permeate flux reduction. Therefore, in processes with high scaling potential achieving high water recovery is quite challengeable (Ochando et al, 2015).

Chan et al, who applied RO as a standalone process for landfill leachate treatment, reported very satisfactory results based on which the retention values for COD and  $\text{NH}_3\text{-N}$  were 96% and 98% respectively, with the initial COD and  $\text{NH}_3\text{-N}$  values of 8000 mg/L and 2620 mg/L. They concluded that RO could be successfully applied for stabilized leachate treatment (Chan et al, 2007).

It is reported that silica also make a significant contribution to the hard scale formation on the membranes (Matin et al, 2019).

In a similar study, Linde et al, conducted filtration experiment using RO membranes on the landfill leachate originating from biodegradable waste and contained high amount of carbonic acid. The carbonic acid was generated from the landfill bioreactors in which biogas entailing methane and carbon dioxide was produced. Based on the EDX analysis of fouled membranes, calcium, iron, chloride and sulfur, detected on the membranes surface. The presence of sulfur on the membranes corresponded to the membranes backing material. Therefore, it was concluded that the formation of  $\text{CaCO}_3$  is the main reason of the membranes fouling which could be overcome via lowering the pH from 7.1 to 6.5 using  $\text{H}_2\text{SO}_4$  (Linde et al, 1995).

The likelihood of scale formation by minerals is increased by concentration polarization. As such, the concentration polarization severity is affected by the degree of scale forming salt rejection, consequently nonporous and dense membranes including nanofiltration and reverse osmosis membranes are most involved in these phenomena (Mulder, 2012).

The probability of solute passage through the membrane and eventually into the permeate stream increases with concentration gradient growth in vicinity of the membrane surface, which could end up with several consequences including, lowering the permeate stream quality, increasing the osmotic pressure leading to permeate flux decline and increasing the risk of scaling (Wang et al, 2007).

It has been found that the increase in CP gradient close to the membrane surface encourages the scale formation phenomena. For instance, increasing concentration polarization leads to the occurrence of crystallization near the membrane surface instead of the bulk (Oh et al, 2009).

Lee et al, investigated the  $\text{CaSO}_4$  scale formation in diverse types of nanofiltration modules in order to determine the permeate fluxes variation during the nanofiltration. They conducted the tests under the condition of low supersaturation ( $< 1.1$ ) as well as low turbidity of bulk phase ( $< 1$  NTU). The results demonstrated immediate flux decline owing to the rapid crystallization

on the membrane surface. In contrary, in the turbulent conditions, scale formation mechanism behavior was totally different and revealed diverse patterns based on which, under the saturation index of  $\sim 2$ , the flux decline was insignificant, although after that point it started to be formed as well as bulk crystallization which commenced at  $SI \sim 2.7$  and lead to the permeate flux decline (Lee et al, 1999).

Abovementioned findings represents the importance of crystals morphology obtained under the various flow conditions. In lower cross-flow velocities, the possibility of cake layer formation on the membranes surface increases due to the deposition of foulants on the membrane (e.g. organic matter), and the likelihood of crystal growth on the radial direction diminish. The cake formation on the membrane surface increases the hydraulic resistance and consequently decreases the permeate fluxes.

$\text{CaF}_2$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{BaSO}_4$ ,  $\text{SrSO}_4$  are amongst the most important non-alkaline scale-forming salts, which are known as major difficulties in RO membranes due to their adherent nature as well as their low solubility. The foulants, which stick to the membrane surface, are difficult to clean and therefore, strong chemicals may be required, which could deteriorate the membrane. Hence, the use of scale inhibitors can be effectively lessen the mineral scale formation and improves the membrane performance (Boerlage et al, 2002).

Costa et al. (2019) reported that the inorganic minerals fouling result in 10-15% increase in the overall costs in RO plant.

#### **4.6 Solution for scaling prevention**

In membranes treatment processes, pre-treatment, cleaning the system, using influent acid dosage are amongst the utmost effective methods for mitigating the scale formation. The other solutions include, addition of scale inhibitors, softening and adjustment of operating variables.

Lowering the pH is an operative method to prevent the scale formation in membranes, since the kinetic of the saturation of sparingly soluble salts can be controlled and eventually, the deposition of salts could be avoided (Shahid et al, 2018).

Polymeric organic compounds such as, phosphonates and polycarboylates, are amongst the most widely used scale inhibitors. It has been proved that the zinc ions demonstrated promising function as an antiscalant in membrane processes (Lisitsin et al, 2005).

Among the non-alkaline scales,  $\text{CaSO}_4$  has been identified as one of the most common scales. Due to the difficulties, which is associated with the sulfate scale removal compared to alkaline scales in SWRO plants, the best solution for controlling  $\text{CaSO}_4$  scale is operating the membranes below the saturation level (SI) or applying an effective antiscalant.

Song et al, conducted a similar pilot-scale test with high selectivity NF membranes and SWRO. They came to the conclusion based on which applying antiscalant along with pH adjustment and recycling NF retentate results in increasing the NF permeate recovery up to 60%, while controlling the SI values of  $\text{CaSO}_4$  lower than 1 and preventing  $\text{CaSO}_4$  scale formation (Song et al, 2013).

In real life, it is not possible to inhibit scale deposition completely even via antiscalant; therefore, cleaning either chemically and mechanically is often used to remove the fouling of the membrane. For applying antiscalant influent stream is dosed with ample amount of antiscalant (Tomaszewska et al, 2018).

Silica scaling is another type of predominant scaling in membrane processes due to its low solubility in water specifically in amorphous form. Dissolution of silica in water leads to the formation of silicate according to the following reaction (Cheng et al, 2009):

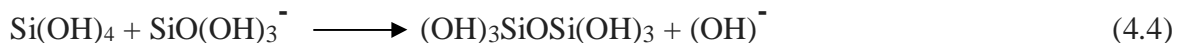


Therefore, silica presence in the water turns into silanol groups under polymerization. Eventually, the reaction of these groups results in the formation of dimers.

In acidic and neutral conditions ( $\text{pH} < 7.5$ ), silicic acid dimerizes under condensation reaction as follow:



Under alkaline conditions ( $\text{pH} > 7.5$ ), the dimerization of silica with silicate ion occurs according to the following reaction:



Silica dimers are capable of polymerizing with produced oligomers and grow to form larger particles, which could agglomerate into a gel form network, building up amorphous silica scale (Thompson et al, 2017).

Removal of silica can be carried out using precipitation with polyvalent metal hydroxide including  $\text{Fe(OH)}_3$ ,  $\text{Al(OH)}_3$  as well as  $\text{Mg(OH)}_2$ . Softening and coagulation are common methods to remove silice from water. Softening is applicable for water with high level of hardness although, coagulation is one of the most effective methods due to its cost-effectiveness. Coagulation can be applied as a pretreatment method before RO and NF processes to excel the function of membranes (Cheng et al, 2009).

Rashed et al, reported that ammonia biflouride (ABF) can be used as a promising antiscalant for water with high concentration of silica. ABF was added to the feed continuously with optimum dose of 4 mg/l using a dosing pump (Rashed et al, 2016).

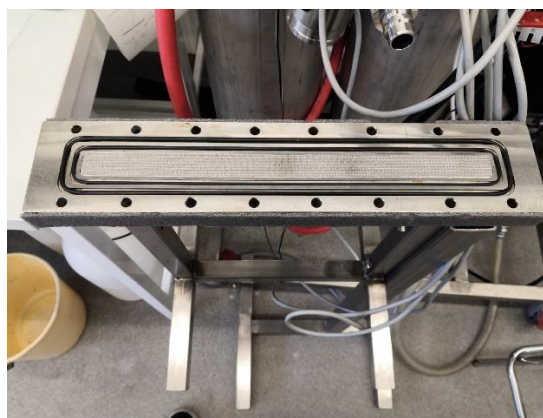
Concentrate of RO, which is obtained after using antiscalant is rich in antiscalants concentration, which have negative impact on the environment. They are toxic and cause health problems when enter into the human body. Therefore, management of RO concentrate would be required in order to eliminate the antiscalant from it. Istirokhatun et al. (2018), studied the removal of antiscalant during RO. The antiscalants include sodium hexametaphosphate (SHMP) and disodium ethylenediami-netetraacetate/ $\text{Na}_2\text{EDTA}$  which are amongst the most widely used antiscalant. Based on their results, NF has high rejection ability for antiscalant ( $> 96\%$ ), therefore, it can be used for removing antiscalant from the RO concentrate.

#### 4.7 RO Experiment with new system

According to the results of the previous experiments, which were designed and conducted in the three batches, the retention of targeting components for SW30 membrane was surprisingly lower than expected. In such a circumstances other parameters and conditions should be altered in order to better understand the processes and identify the related drawbacks. For this purpose, the RO experiment were carried out using another membrane filtration apparatus (Figure 4.10) that replaced the DSS Labstack M20 filter.



**Figure 4.10.** Membrane filtration apparatus applied in RO experiment.



**Figure 4.11.** Rectangular filter used in RO experiment.

In this experiment permeate of the NF270 membrane in the second batch of experiment which were conducted using spiral wound module were used as feed of SW30 membranes.

The mentioned experiment divided into two main phases including:

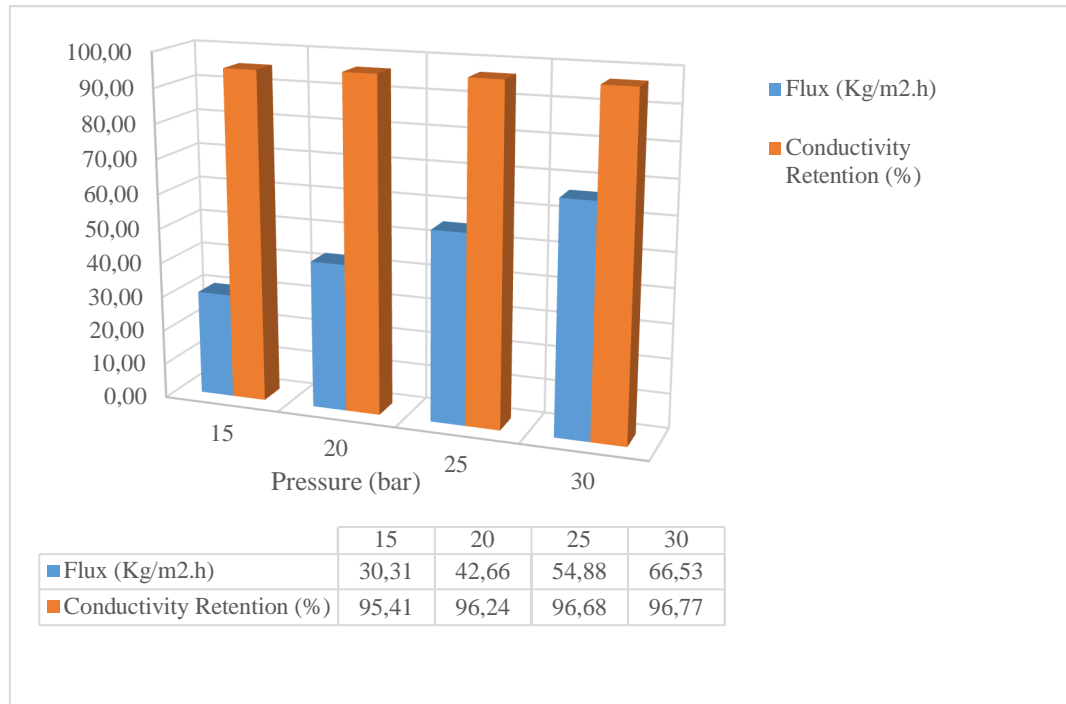
1. Filtrating the composting wastewater in different pressure in order to obtain the optimum pressure in which the retention values are higher and the flux is economically and technically feasible.
2. Conducting the filtration experiment in the optimum pressure obtained in the earlier stage followed by measuring the retention values of targeting components, permeate fluxes and the fouling of the membrane.

Temperature, flow rate and pressure kept constant during the filtration experiments. The pressure in the second experiment was slightly increased through the filtration.

All the above-mentions tests was implemented with the same membrane piece.

Analogous to the previous experiments pure water flux measurement performed before filtration, after filtration and rinsing then equipment with water in addition to chemical cleaning with Ultrasil at the end.

Figure 4.12, demonstrates the average permeate fluxes, which were measured using mass flux software in the first 20 minutes for each pressure. Based on the obtained results, at the higher pressures, the higher fluxes and conductivity rejection were achieved. Since at pressure higher than 25 bar, the conductivity retention remained constant, pressure of 25 selected as operating pressure for the main RO filtration experiment.



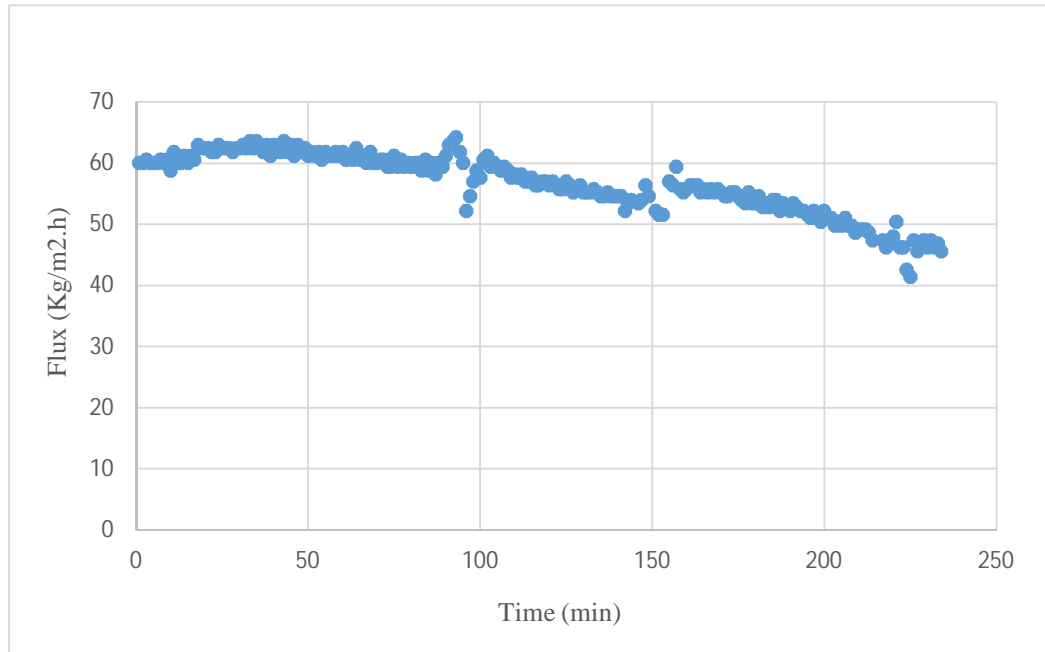
**Figure 4.12.** Pemeation fluxes (kg/m<sup>2</sup>.h) and conductivity retention of SW30 membrane at different pressures.

SW30 flat-sheet membrane was cut rectangular and placed in the system with active area of and pressurized at pressure of 40 bar and temperature of 40°C, the same as previous RO experiments. Membrane was also the same type of membrane used in the second and third batch experiments. Attempts were made to have all the conditions similar to the RO experiment in the second batch since the feed entered into the system was permeate of NF filtration of second batch experiment. Although the flow rate of new system was different (0.7 m/s).

#### 4.7.1 Permeate fluxes changes over time in the RO experiment

The permeation flux variation is presented in Figure 4.13. Based on the results permeation fluxes and permeability remained relatively high during the filtration experiment. The initial permeate flux was 60 (Kg/m<sup>2</sup>.h) at the pressure of 27 bar which declined to the 46 (Kg/m<sup>2</sup>.h) at the end of filtration when VRF was 6 and the pressure was 32.5 bar. Filtration experiment proceeded faster compared to the previous RO experiments and the flux reduction during the filtration

(24%) was significantly lower. The result illustrated that the new membrane apparatus improved the process efficiency and increased the permeation fluxes.



**Figure 4.13.** The permeation fluxes of SW30 vs. time in the new system, pressure  $30 \pm 3$  bar.

#### 4.7.2 Pure water fluxes measurement in the RO experiment

Pure water fluxes measurement of this RO filtration experiment are presented in Table 4.8.

**Table 4.8.** Water fluxes measurement before filtration, after water cleaning and after chemical cleaning in the RO experiment.

Membrane used in the experiments	MWCO (Da)	PWF Before filtration (Kg/m <sup>2</sup> .h)	PWF after filtration (Kg/m <sup>2</sup> .h)	Flux reduction during filtration (%)	PWF after washing (Kg/m <sup>2</sup> .h)	T (°C)	P (bar)
SW30 (RO)	100	52.1	51.3	1.45	51.2	40	10

The water permeation flux values indicates that the fouling of membrane is very small (1.45 %) and water cleaning after filtration could recover the permeate fluxes and chemical cleaning is not a necessary stage. In comparison with the RO experiment in the second batch experiment that membrane fouling estimated 8.7 %, the function of membrane in the new system has improved in terms of permeation flux reduction and fouling.

#### 4.7.3 Retention values of the targeting component in the RO experiment

Conductivity, phosphorous, total nitrogen and total carbon retention values either organic or inorganic were analyzed and reported in Table 4.9. The retention degree of mentioned component were higher compared to the previous RO experiments which carried out using DSS-Labstack M20 filter.

**Table 4.9.** Retention of targeting components in the RO experiment.

<b>Membranes</b>	<b>Dissolved P retention (%)</b>	<b>Dissolved TOC retention (%)</b>	<b>Dissolved TC retention (%)</b>	<b>Dissolved IC retention (%)</b>	<b>Dissolved TN retention (%)</b>	<b>Conductivity retention (%)</b>
SW30 (RO)	99	97	96	94	84.5	94

The results obtained in the last experiment of RO demonstrated the deficiencies associated with the DDS-Labstack M20 filter, which can be related to either old plates placed in the system or other parameters, which needs to be assessed future. As such, SW30 membranes satisfied the required demands in RO experiment due to the negligible amount of fouling, high degree of rejection values and low flux reduction during the filtration experiment.

#### **4.8 Characterization of matter in the influent and effluent of RC70PP membranes**

Sludge obtained from UF stage contains significant amount of organic compounds. These residues, mainly contains phosphorous, nitrogen and organic carbon concentrated in the retentate stream of RC70PP membranes, which can be utilized as fertilizer or soil amendment. The obtained sewage sludge consists of different types of materials, which are soluble or suspended. Based on the nature of these materials, they can be either organic or inorganic substances. Based on the degree of rejection of phosphorous in the RC70PP membranes in all experiment, it can be concluded that this type of UF membrane is quite efficient in retaining phosphorous for studied composting plant leachate however, it demonstrated different retention values in different batches due to the diverse types of wastewaters and different amount of feed. Therefore, due to the satisfying performance of RC70PP in P rejection, this part of study is allocated to the determination of inorganic and organic matter fraction in the influent and effluent of RC70PP membrane. Various types of methods can be used for analyzing the total inorganic and organic matter in the wastewater. For this purpose, first, dry matter was measured by oven drying, during which a specific amount of wastewater is heated at temperature of 105°C until a steady mass is obtained, the water evaporated and the remained residues are called dry matter. Total solid content or dry matter (DM) includes both suspended solids and dissolved solids in the wastewater. Then organic content of sludge was determined using loss of ignition approach (Chapter 3), (Rowell et al, 2003). Dry matter of the influent and effluent of RC70PP including retentate and permeate of RC70PP and feed were measured. In order to measure the dry matter and organic matter content of dry matter, each sample was tested two times and the average value is presented in Table 4.10.

**Table 4.10.** Organic and mineral content of the dry content of the influent and effluent of RC70PP membranes.

Sample		Residue mass (Dry matter) (%)	Ash content* (%)	Organic matter* (%)
UF <sub>1st</sub>	Wastewater	4.8	0.6	99.39
	Permeate	4.2	0.78	99.4
	Retentate	5.5	0.56	99.2
UF <sub>2nd</sub>	Wastewater	5.0	0.47	99.5
	Permeate	4.8	0.54	99.5
	Retentate	5.9	0.46	99.4
UF <sub>3rd</sub>	Wastewater	3.5	1.2	98.8
	Permeate	2.6	1	9.9
	Retentate	6.4	1.04	99

UF<sub>1st</sub> is the UF in the first batch of experiment, UF<sub>2nd</sub> is the UF in the second batch of experiment, UF<sub>3rd</sub> is the UF in the third batch of experiment.

\*Ash content and organic matter is related to the organic and inorganic content of the dry matter in the permeate, concentrate and effluent of UF membrane.

The obtained organic matter content (Table 4.10) demonstrates the high amount of OM in all samples, containing raw wastewater as well as permeate and retentate of RC70PP membranes.

#### 4.8.1 Total Suspended solids and phosphorous measurement

Total suspended solids of samples were measured using standard method (EN 872:2005). The aim of this stage of experiment is determining the phosphorous content in particulates as well as dissolved phosphorous. For this purpose, the total phosphorous of samples were measured, then the samples were filtered and after complete removal of the suspended solids phosphorous content of the filtrate samples were analyzed (dissolved phosphorous). The difference between these two values indicated the phosphorous content of particulates.

The influent and effluents of UF membranes including permeate and concentrates of three batch experiments have been used as samples for measuring total suspended solids (TSS). Standard method was used for measuring TSS based on which, each sample containing special amount of solution was filtered through a standard glass fiber filter with pore size of 0.45  $\mu\text{m}$ . Dissolved phosphorous were measure by analyzing the phosphorous content of filtrate. Each sample was tested two times and the average value was represented as a result (Table 4.11).

**Table 4.11.** Total suspended solids, total and dissolved phosphorous of influent and effluent of RC70PP in three batches of experiment.

Sample		TSS (mg/L)	Total phosphorous (mg/L)	Dissolved phosphorous (mg/L)	Solid phosphorous (mg/L)
UF <sub>1st</sub>	Wastewater	2810	40	16	24
	Permeate	900	24	10	14
	Retentate	7300	110	35	75
UF <sub>2nd</sub>	Wastewater	1825	12	7	5
	Permeate	746	4,5	3	0.8
	Retentate	6860	64	30	34
UF <sub>3rd</sub>	Wastewater	3790	62	23	39
	Permeate	533	19.3	8.1	11.2
	Retentate	20900	290	99	191

TSS=Total suspended solids

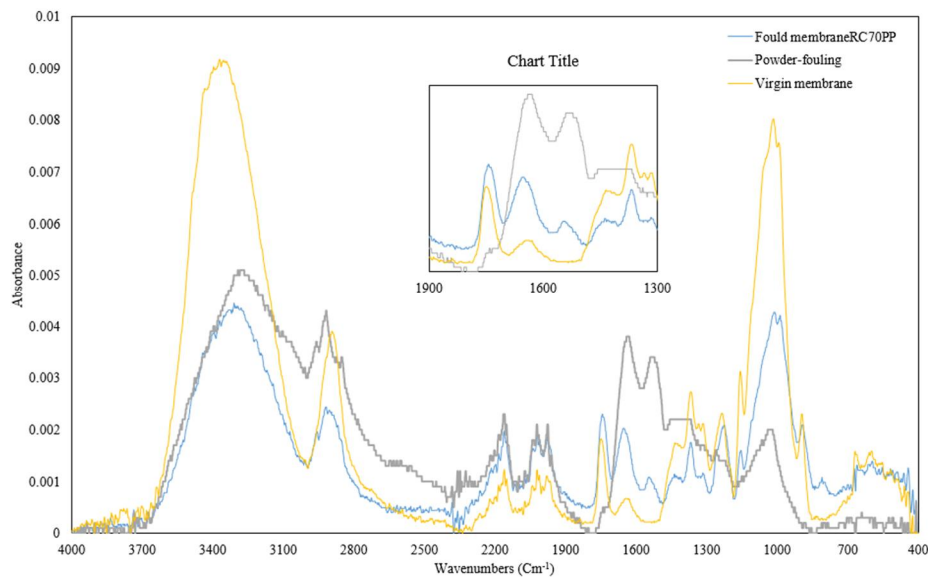
Based on the Table 4.11, almost the higher amount of the phosphorous is related to the particulates (58-68%), the high amount of P concentrated in the retentate of UF, make RC70PP a promising option for recovering P from composting plant leachate as well as nutrient-rich wastewaters, although UF is not effectively capable of TN removal. Considerable amount of P an N along with other components such as calcium, magnesium which were accumulated in the retentate of RC70PP membranes makes the retentate stream of this type of UF membrane a promising fertilizer for agricultural applications.

Rationally the permeate stream of RC70PP should be free of suspended solids, however the obtained values for TSS represents the crystallization phenomena in the solution since the samples stored in the fridge for a long term and precipitation may be happened.

#### 4.8.2 FT-IR spectroscopy of RC70PP (third batch experiment)

Fourier transform infrared spectroscopy (FTIR) is a widely used approach for the qualitative analysis of chemical nature of a component including, chemical bonds and molecular interactions along with the energy levels of molecules using the adsorption peaks related to a specific functional groups (Vinodhini et al, 2017). The FTIR spectra of fouled RC70PP membrane and RC70PP virgin membrane represented in Figure 4.14. The grey line is related to the fouling material which were separated from the membrane surface and dried and analyzed.

Based on Fig 4.14, the FTIR peaks of the virgin membrane changed in adsorbance intensity owing to membranes surface coverage with functional group of foulants.



**Figure 4.14.** FT-IR spectroscopy of virgin RC70PP in the third batch experiment as well as virgin RC70PP membrane.

The fouled membrane exhibited new FTIR peaks at 1540-1570 and 870  $\text{cm}^{-1}$ , demonstrating the probability of proteins, polysaccharide, and amino sugars existence as the main foulants. The presence of a peak at 870  $\text{cm}^{-1}$  indicates the possible presence of aliphatic components in the foulants.

## 5 CONCLUSION

Composting plant leachate is considered as one of the most hazardous wastewaters containing high concentration of organic matter and nutrients, which are required to be managed in an appropriate way. The objective of this study was recovering these nutrient using membrane separation technologies. For this purpose, three batches of pilot-scale experiments were carried out with commercial membranes including ultrafiltration (RC70PP), nanofiltration (NF270) and reverse osmosis membranes (SW30). The retention of TOC, COD, TN, P and UV were studied along with the performance of each membrane in terms of permeability and fouling. The composting plant wastewater was used in all the batches, but since the samples were collected in different months of the year, the concentrations of the components in different leachate were different.

From all the above-mentioned experiments, the following results were obtained which should be considered in recovering nutrients from wastewater rich in nutrients with membrane technologies:

- RC70PP ultrafiltration membrane retained 40-64% of total phosphorous. Therefore, applying this type of membrane for composting plant leachate prior to its entrance to the wastewater treatment plant is an effective way to recover high amount of phosphorous, which can be applied as fertilizer. Also, providing a type of wastewater devoid of particulates and less amount of organic carbon, which can be led to the wastewater treatment plant.
- For designing a series of membranes applied for composting plant leachate as well as any types of wastewater rich in nutrients, RC70PP can be considered as an effective type of UF membrane which could be used as a pretreatment stage prior to NF and RO stages. The possibility of reaching high VRF in which the maximum permeate could be obtained and the low volume of obtained retentate make this process attractive, furthermore, the high phosphorous and carbon rejection ( $\geq 40\%$  &  $30\%$  respectively), make the retentate side a valuable source of nutrients with high degree of organic matter that can be used as fertilizers.

- The severe fouling which is caused due to the organic matter presence in the wastewater, makes the NF270 usage very challenging in all batches of experiment since the efficiency of NF membranes is highly affected with the presence of NOM, therefore due to its low permeability as well as the low degree of rejection for almost all targeting components (TOC, P and TN), further studies are required to enhance the NF effectiveness in the streams rich in organic matters.
- NF stage prior to RO filtration could play a significant role in proceeding the RO step with improving the fluxes and reducing the fouling of the membranes. NF which is capable of eliminating majority of humic substances and di/multivalent ions ( $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ) facilitate the RO experiment step and generally increase the effectiveness of the entire wastewater treatment process. Therefore, the fouling and scaling of reverse osmosis membranes could be highly reduced.
- Presence of dissolved  $\text{CO}_2$  in this type of wastewater is another important challenge, which influence the NF and RO membranes function, since it reacts with  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  presence in the composting plant wastewater and results in severe scaling, which could greatly decrease the permeation fluxes and retention of targeting components.
- SW30 commercial membranes have great potential of recovering nutrients from composting plant wastewater as an RO membrane. The high degree of retention for targeting components (99% of P, 97% of TOC & 85% TN retention), low amount of fouling and high permeation fluxes make them a promising option for streams rich in nutrients.

And finally, to sum up all the findings and based on the results obtained from diverse batches of experiments, using RC70PP, a type of UF membrane to filter composting plant leachate could simultaneously recover the phosphorous as a valuable compound to high extent as well as bringing the water to the acceptable level of standards which can be directed to the wastewater treatment plant. In order to reach the higher qualified water, NF270 and SW30 membranes are suggested as effective filtration membrane for NF and RO stages.

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**Table 1.** Phosphorous concentration of samples in the first batch experiment (RC70PP, NF270, SW30-1<sup>st</sup>, SW30-2<sup>nd</sup> – SW30-3<sup>rd</sup>)

Sample		Dissolved Phosphorous (mg/L)		
		Measurement 1	Measurement 2	Average
RC70PP	CPWW	38	40	39
	Permeate	22	23.5	22.7
	Concentrate	95	110	102.5
NF270 (Flate-sheet)	Feed	24	23	23.5
	Permeate	14.7	16.1	15.4
	Concentrate	65	63.2	64.1
SW30- 1 <sup>st</sup>	Feed	14.1	15.4	14.7
	Permeate	7.1	7.6	7.3
	Concentrate	28	25.5	26.7
SW30-2 <sup>nd</sup>	Feed	6.4	6.8	6.6
	Permeate	3.45	3.2	3.3
	Concentrate	14	18	16
SW30-3 <sup>rd</sup>	Feed	4.1	3.5	3.8
	Permeate	1.2	0.9	1
	Concentrate	17.6	17.1	17.3

CPWW: composting plant wastewater, SW30-1<sup>st</sup>= first step of RO filtration with SW30 membrane, SW30-2<sup>nd</sup> = second step of RO filtration with SW30 membranes, SW30-3<sup>rd</sup> = second step of RO filtration with SW30 membranes.

**Table 2.** Concentration of total organic carbon, total carbon and inorganic carbon of the samples in the first batch experiment.

Sample		Dissolved carbon measurement (mg/L)					
		TOC (mg/L)		TC (mg/L)		IC (mg/L)	
		Measurement 1	Measurement 2	Measurement 1	Measurement 2	Measurement 1	Measurement 2
RC70PP	CPWW	11400	12433	11820	12816	420	383
	Perm	8133	8490	8503	8857	370	367
	Con	19134	15083	19788	16183	654	1100
NF270	Feed	9300	8474	9657	8857	357	382
	Perm	7550	7617	7782	7846	232	229
	Con	10027	8369	10130	8475	103	105
SW30-1 <sup>st</sup>	Feed	7891	7961	8104	8172	213	211
	Perm	4177	4213	4311	4347	134	133
	Con	19120	19367	19176	19456	56	89
SW30-2 <sup>nd</sup>	Feed	3956	4063	4080	4230	124	211
	Perm	1599	1627	1630	1732	31	105
	Con	11812	11308	11893	11424	47	116
SW30-3 <sup>rd</sup>	Feed	1497	1621	1540	1669	43	48
	Perm	427	462	466	506	40	44
	Con	9000	8032	9052	8139	52	107

CPWW= Composting plant wastewater, Perm= Permeate, Con= Concentrate.

**Table 3.** Conductivity and pH of the samples in the first batch experiment.

Sample		Conductivity (mS/Cm)	pH
RC70PP	CPWW	63	7.5
	Permeate	55	7.8
	Concentrate	54	7.8
NF270 (Flate-sheet)	Feed	53.2	7.7
	Permeate	42	7.8
	Concentrate	123	7.6
SW30- 1 <sup>st</sup>	Feed	38.5	8.1
	Permeate	25.2	7.9
	Concentrate	82	7.6
SW30-2 <sup>nd</sup>	Feed	22.3	8.4
	Permeate	15.1	8.6
	Concentrate	67.7	8
SW30-3 <sup>rd</sup>	Feed	13.1	8.4
	Permeate	4.5	8.7
	Concentrate	47.1	7.5

**Table 4.** Concentration of chemical oxygen demand (COD) of the samples in the first batch experiment.

Sample		Dissolved COD (mg/L)		
		Measurement 1	Measurement 2	Average
RC70PP	CPWW	29500	30500	30000
	Permeate	22700	23500	23100
	Concentrate	50500	52500	51500
NF270 (Flat-sheet)	Feed	-	-	-
	Permeate	20700	20300	20500
	Concentrate	28500	29500	2900
SW30- 1 <sup>st</sup>	Feed	-	-	-
	Permeate	10260	11400	10830
	Concentrate	53800	56300	55050
SW30-2 <sup>nd</sup>	Feed	-	-	-
	Permeate	5100	4500	4800
	Concentrate	36000		31000
SW30-3 <sup>rd</sup>	Feed	-	-	-
	Permeate	-	1450	1450
	Concentrate	-	20400	20400

**Table 5.** Total nitrogen concentration of the samples in the first batch experiment

Sample		Dissolved TN (mg/L)
RC70PP	CPWW	11644
	Permeate	11352
	Concentrate	13820
NF270 (Flate-sheet)	Feed	11180
	Permeate	7852
	Concentrate	27820
SW30- 1 <sup>st</sup>	Feed	7590
	Permeate	3793
	Concentrate	17355
SW30-2 <sup>nd</sup>	Feed	3445
	Permeate	1648
	Concentrate	9996
SW30-3 <sup>rd</sup>	Feed	2326
	Permeate	757
	Concentrate	7582

**Table 6.** Concentration of total organic carbon, total carbon and inorganic carbon of the samples in the second batch experiment.

Sample		Dissolved TOC (mg/L)	Dissolved TC (mg/L)	Dissolved IC (mg/L)	Dissolved COD (mg/L)
RC70PP	CPWW	3586	4376	790	5860
	Permeate	2450	3120	670	4120
	Concentrate	11776	13200	1424	17200
NF270 (Spiral wound)	Feed	1976	2580	604	4100
	Permeate	1073	1400	290	2300
	Concentrate	2235	3120	885	6200
SW30	Feed	880	1695	917	2300
	Permeate	217	416	199	650
	Concentrate	4750	7450	2700	12160

CPWW= Composting plat wastewater, TOC = Total organic carbon, TC = Total carbon, IC = Inorganic carbon, COD = Chemical oxygen demands)

**Table 7.** Concentration of total organic carbon, total carbon and inorganic carbon of the samples in the second batch experiment.

Sample		Conductivity (mS/Cm)	pH
UF RC70PP	CPWW	70	8.3
	Permeate	66.4	8.2
	Concentrate	66.5	8.1
NF NF270 (Spiral wound)	Feed	57.8	8.2
	Permeate	17.3	8.9
	Concentrate	91.5	8.3
RO SW30	Feed	15.8	8.8
	Permeate	4.4	9.4
	Concentrate	65.3	8.7

UF=Ultrafiltration, NF= Nanofiltration, RO= Reverse osmosis

**Table 8.** Concentration of total organic carbon, total carbon and inorganic carbon of the samples in the second batch experiment.

Sample		Dissolved TN (mg/L)	Dissolved P (mg/L)	UV at 210 nm
UF RC70PP	CPWW	10850	8.1	130
	Permeate	10515	4.2	78.6
	Concentrate	16700	33	483
NF NF270 (Spiral wound)	Feed	9550	3.9	73
	Permeate	2340	1.12	19
	Concentrate	17030	6.7	113
RO SW30	Feed	2212	0.9	14
	Permeate	965	0.1	3.4
	Concentrate	10420	4.5	76.4

**Table 9.** Concentration of total nitrogen, phosphorous and UV at 210 nm in the third batch experiment.

Sample		Dissolved TN (mg/L)	Dissolved P (mg/L)	Dissolved UV at 210 nm
RC70PP	CPWW	9480	23	480
	Permeate	8126	8.1	298
	Concentrate	16800	99	1300
SW30	Feed	7850	18.9	278
	Permeate	3150	2.4	32.5
	Concentrate	58000	26	483

**Table 10.** Concentration of total organic carbon, total carbon and inorganic carbon of the samples in the third batch experiment.

Sample		Dissolved TOC (mg/L)	Dissolved TC (mg/L)	Dissolved IC (mg/L)	Dissolved COD (mg/L)
RC70PP	CPWW	22840	23391	548	51000
	Permeate	16610	17156	546	36700
	Concentrate	50363	51434	1071	114000
SW30	Feed	13835	14352	517	34100
	Permeate	1910	2050	140	3150
	Concentrate	21814	22390	576	58000

**Table 11.** Conductivity and pH of the samples in the third batch experiment.

Sample		Conductivity (mS/Cm)	pH
RC70PP	CPWW	42.4	7.6
	Permeate	41.2	7.6
	Concentrate	42.6	7.5
SW30	Feed	40	7.7
	Permeate	7.2	7.2
	Concentrate	58.5	8