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**Recycling of Deep Eutectic Solvents with a Membrane-Based Process**

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## **ABSTRACT**

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Deep eutectic solvents (DES) are non-flammable, non-toxic, biodegradable solvents which recycling opportunities are still poorly studied. One of the possible applications of DES includes lignin extraction from lignocellulosic materials. The aim of this work was in examining of feasibility of DES (choline chloride and lactic acid in molar ratio of 1:10) recycling with ultrafiltration process. The difficulty with high viscosity of DES was tackled with addition of 99% ethanol to spent DES. The influence on stability and flux of ultrafiltration was examined analyzing such factors as concentration of ethanol, temperature of filtration, and presence of suspended solids during filtration. Resultingly, most effective concentration was proved to be 60 vol% DES in ethanol. A conclusion has been made that a higher DES concentration should be filtered at higher temperature. Presence of suspended solids during filtration was proved to significantly decrease flux. In addition, membrane resistance to DES and 60% DES in ethanol solution was examined. FTIR analyses did not reveal any signs of membrane degradation. Ultrafiltration process showed the feasibility of the tested membrane for DES recycling.

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I always thought that the result determines the work. It is still true for me. However, it is the process that evokes the wider range of emotions. Life should not be divided into checkpoints. It is an endless process with quite unexpected outcomes. I really enjoyed the process while making this thesis.

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## LITERATURE REVIEW

### 1 INTRODUCTION

Since Abbott et al. first thoroughly described deep eutectic solvents (DES) phenomenon in 2003, these solvents were studied for various applications such as organic synthesis, chromatography, electrochemistry, biocatalysis, aromatic removal (Fisher, 2015, Li and Row, 2016). The most important of them, though, is an application as a replacement of organic solvents due to unique DES characteristics such as thermal stability, nonvolatility, nontoxicity, safety and biodegradability (J.G.P. van Osch et al., 2017).

As “green solvents” DES substituted ionic liquids (ILs) which are inferior to DES in terms of environmental friendliness (L. Benvenuti et al., 2019; K.M. Jeong et al., 2015). At the same time, many properties of ILs are very similar to DES properties which means that DES implementation into industries can be far more rapid and wide. The greatest limitation that hinders IL-based processes introduction to many industries is their considerably high cost which is related to expensive preparation, expensive operation and expensive recycling (Jeong et al., 2015). Even though DES preparation is easier and cheaper, the problem of their recycling is limiting also their wider use in industry. Concerns related to gradual loss of DES extraction efficiency after each cycle of regeneration is the main challenges in the recycling of these novel solvents (X. Liang et al., 2019). Thus, this work focuses on increasing the understanding on the possibility to recycle DES used in the recovery of lignin from biomass with a process based on membrane technology. Among great variety of possible recycling process, membrane filtration was chosen because it consumes relatively low amount of energy (for example, comparing to evaporation or distillation). Low energy requirement stems from the fact that in membrane separation no phase change occurs. In addition, membrane processes generally demonstrate compact footprint which means more efficient space use (Lau & Perez de los Rios 2018). The aim of the research was examining the feasibility of recycling spent deep eutectic solvents obtained after DES used as solvent for woody biomass treatment by membrane filtration process. The correlation between concentration of spent DES in 99% ethanol and efficiency of ultrafiltration of spent DES solutions was investigated. Further, the effect of DES on the membrane performance was evaluated by the exposure of the membrane to pure DES and 99% ethanol diluted DES over different time periods. The effect of temperature and presence of suspended solids on the efficiency and duration of filtration of spent DES solutions were also studied.

## 2 LIGNOCELLULOSIC MATERIALS

All lignocellulosic materials mainly consist of three big parts: cellulose, hemicellulose and lignin. First two polymers are carbohydrates. Cellulose has a linear structure while lignin and hemicellulose demonstrate non-linear structure. This notice is important for further understanding of chemical and physical properties of lignocellulosic materials. Aside from the mentioned three main parts of lignocellulosic materials, extractives materials, which are the group of materials that can be extracted by solvents, are also present. (K. Karimi et al., 2013) Depending on the source, some amount of pectin can be present at lignocellulosic biomass (Gulichsen, 2000). Because of the combination of linear and non-linear polymers lignocellulose is quite dense and resistant to biodegradation. Reasonably, a particular kind of wood has its own characteristics which can differ from other kinds. However, considering the proportions of the main parts in average, the following values can be used: 25 – 40 w% hemicellulose, 40 – 50 w% cellulose, 7 – 30 w% lignin. (Biermann, 1996)

### 2.1 Cellulose

This material is considered as one of the most common polymers in the world since it is one of the main products of photosynthesis. Because of its chemical properties, cellulose cannot be used as a food source, but it is the main component that holds the structure of plants. It is synthesized by wood, hemp, different plants and by algae and some fungi. (Reeve, 1996)

Cellulose takes up to 40 – 50 % of the dry weight of the wood. Cellulose's net formula is  $(C_6H_{10}O_5)_n$ , and its structure is presented in Figure 2.1.

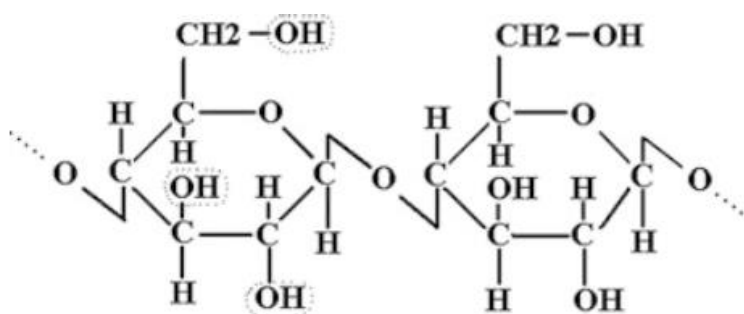


Figure 2.1 Structure formula of a one cellulose unit (Lee et al., 1994)

Cellulose is a polysaccharide that consists of D-glucose units, which are bonded to each other with glycosidic bonds. It is made of microfibrils, the presence of which leads to high crystallinity (up to 95%). A scheme of microfibrils structure is presented in Figure 2.2.

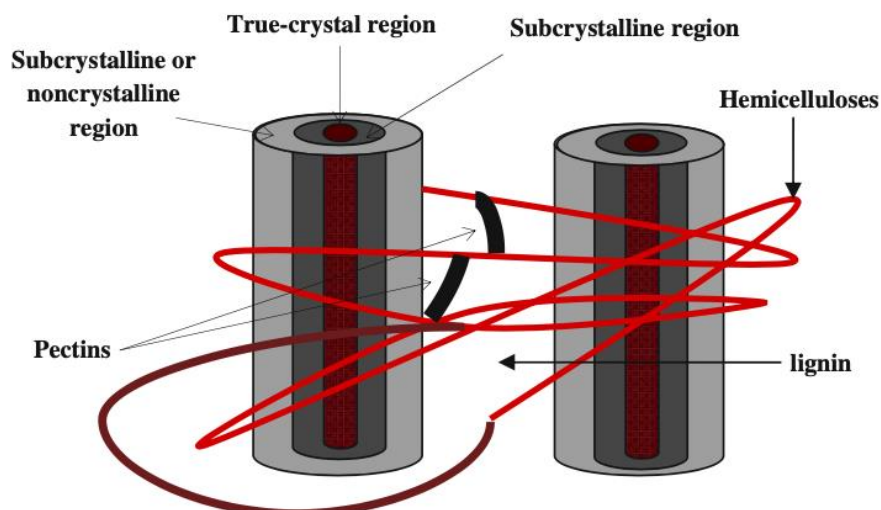


Figure 2.2 Structure of cellulose microfibrils (K. Karimi et al., 2013)

It is noticeable that microfibrils consist of three layers: noncrystalline region is an external layer, subcrystalline region is a middle layer and a true-crystal region is a core of a microfibril. The core region is the hardest to get dissolved during biofractionations. (K. Karimi et al., 2013) In addition, due to the big impact of hydrogen bonds, which occur both inside molecules and between molecules, cellulose is quite stable (Chang et al., 1981). A great tendency to form H-bonds can be easily explained by the presence of three non-hindered hydroxyl groups, which can easily form bonds with other free OH groups. Except for stabilizing effect, it also leads to swelling of cellulose in water. (Fengel and Wegener, 1984)

## 2.2 Hemicellulose

Hemicellulose (or polyoses) accompanies cellulose in the vast majority of lignocellulosic materials. Hence, it is on the second place after cellulose by abundance in plants and trees. Unlike cellulose, hemicellulose is not a pure polysaccharide, but a combination of polysaccharide and polyuronide. Polyuronide part ensures differences in properties between cellulose and hemicellulose. Polyuronides are less robust chemically and biologically, thus, hemicelluloses are more prone to hydrolysis by acids and hemicellulose enzymes. Because of the low polymerization degree of hemicelluloses – 90 – 200 which is in 70 – 90 times lower than the polymerization degree of cellulose – hemicellulose demonstrates weak, amorphous structure. Hemicelluloses are heteropolymers with different units and there are many variations of them. (K. Karimi et al., 2013)

The main monomers are depicted in Figure 2.3.

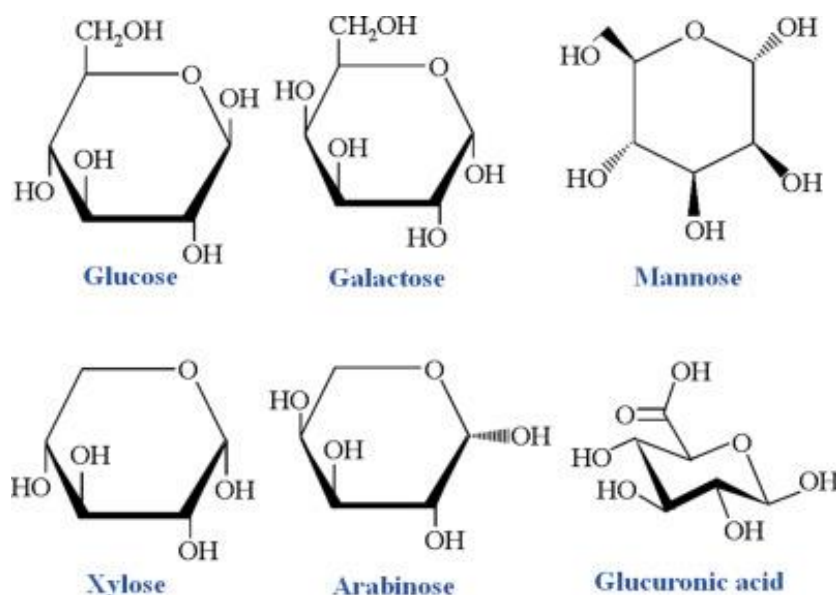


Figure 2.3 Main monomers of hemicellulose (K. Karimi et al., 2013)

In softwood mannose prevails while xylose prevails in hardwood. It means that the content of hemicellulose differs, depending on the type of biomass (Girio et al., 2010).

## 2.3 Lignin

Lignin is a non-carbohydrate component of lignocellulosic materials. It is strong, rigid, robust and due to its properties, it plays two major roles – it cements cells, forming a firm structure and it protects plants from destruction (either chemical or biological). Therefore, higher lignin concentrations lead to higher plant resistance to degradation. (Chernysh et al., 1992)

Lignin content differs from the source of plant. The greatest amount of lignin is contained in softwoods (30 – 40 %). Less amount is contained in hardwoods (15 – 25 %). The least amount is contained in agriculture residuals (10 – 15 %) (K. Karimi et al., 2013). This difference in lignin content among different types of plants leads to significant differences in bio-fractionation treatment. Less proportion of lignin in hardwoods leads to a greater number of vessels. Vessels are good heat providers. In other words, treatment of hardwood and agricultural residues is less energy demanding as a softwood treatment. (Cochard and Tyree, 1990; Hepworth et al., 2002; Kim et al., 2011)

Unique properties of lignin are caused by its genuinely complex chemical structure. It consists of units such as guaiacyl, syringyl and hydroxybenzaldehyde. The proportions of these monomers are related to the type of plant sources and its age. One of the variants of lignin structure is depicted in Figure 2.4.

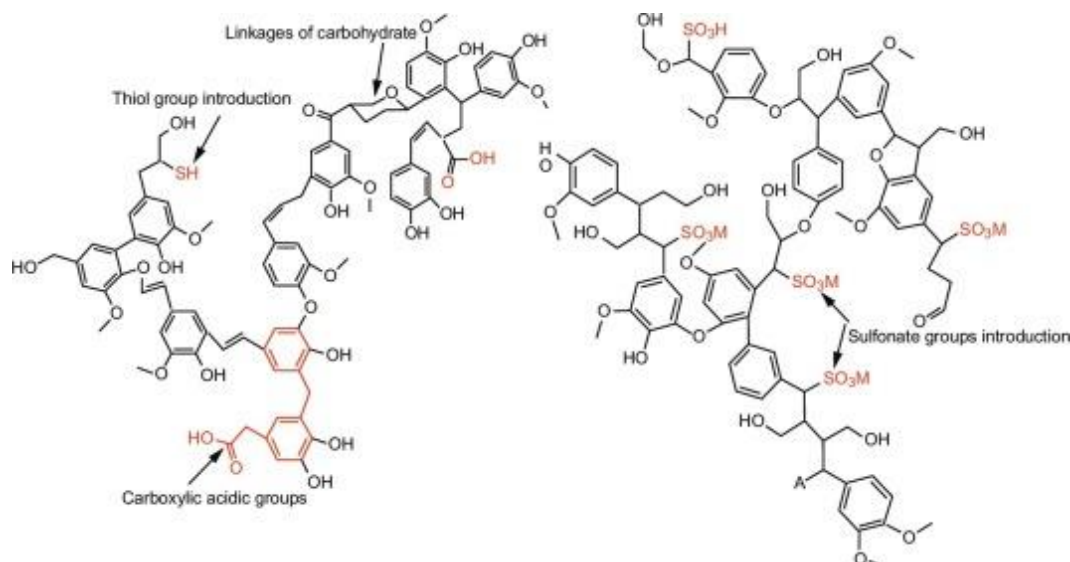


Figure 2.4 Possible lignin structure (A. Nasrullah, 2017)

## 2.4 Extractives

Extractives are a relatively small part of lignocellulosic materials content. They take from 2 to 10 wt% in dry wood. (B. Pecha and M. Garcia-Perez, 2015) Extractives took their name from the fact that they can be extracted by solvents such as benzene, toluene, acetone, ethanol, water. Among variety of extractives some can be mentioned - fats, phenolics, waxes, pectin, proteins, sterols and flavonoid. (A. Pattiya, 2018)

## 3 PURPOSE OF DELIGNIFICATION PROCESS

Delignification process is generally aimed at lignin isolation. There are two main reasons for delignification: 1) it hinders further processing of cellulose; 2) lignin as raw material in variety of applications (Glasser, 2019). The first group of processes, where cellulose is the main product, is related mainly to paper production (Q. Tarres et al., 2017) or bioethanol production (Baig et al., 2018). The second group of processes, where lignin is the main product, is related to different lignin applications such as thermosetting materials (Hemingway & Conner, 1989); resistant to fire foams (Glasser & Leitheiser, 1984); tensile-strong materials (Wei et al., 2006); thermoplastic blends (Ito et al., 1998) and carbon fiber source (Dave et al., 1993).

#### 4 SUMMARY OF CONVENTIONAL DELIGNIFICATION PROCESSES

Prior to delignification process, wood is usually milled because small pieces tend to be soaked and penetrated much better than big and thick pieces. Effective hydrolysis can be provided only to particles with size around 1 – 2 mm. (Kratky & Jirout, 2011)

At the same time, there is always a tradeoff between particle size and economical sustainability as long as smaller fractions require significant amount of energy of milling. Nevertheless, the best particle size is usually defined based on the type of wood and operational parameters for hydrolysis. Hence, milling is an important pre-treatment process. (Baig et al., 2018)

Organic solvents demonstrate a range of drawbacks such as compelling cost of operation, toxicity, inflammability and non-biodegradable. Nevertheless, organic solvents are able to extract hemicellulose and lignin of high purity which is the main reason for their wide exploitation. (Karimi et al., 2013)

The following range of organic solvents is typically used: alcohols, ketones and halogenated hydrocarbons (Baig et al., 2018).

Table 4.1 Lignin removal efficiencies of some organic solvents (Baig et al., 2018)

Substrate	Lignin removed (%)	Organic solvent
Sugarcane bagasse	80	Aqueous formic acid
Eucalyptus	14,1	Dioxane
Eucalyptus	3	Methanol
Wheat straw	75	85% ethanol solvent
Eucalyptus globulus	16	50% ethanol solvent
Yellow poplar	90,4	Peracetic acid and H <sub>2</sub> SO <sub>4</sub>
Flex fiber	14,88	Acetic acid and H <sub>2</sub> O <sub>2</sub> fractionation

Recycling of organic solvents makes the process more cost efficient. Recycling of these solvents is conducted either by distillation or extraction. However, both processes increase operational costs. (Bensah & Mensah, 2013)

Besides using organic solvents, some processes use inorganic solvents. One of the industrially wide-spread processes of delignification with inorganic solvents is a Kraft process. According

to the review of Huber et al. (2014) Kraft process consists of delignification with a mix of sodium sulfide and sodium hydroxide (also known as “white liquor”) under high temperature (145-170 °C). Around 90% of lignin can be removed from biomass with Kraft process. Solvent after delignification is called “black liquor. It is concentrated up to 65% of solids and then burnt to produce heat. (J. Fernandez-Rodriguez et al., 2019)

Steam explosion consists of two stages – hydrolysis and explosion. The explosion is followed by penetration of steam through the plant walls. Hydrolysis has an aim to dissolve hemicellulose and solubilize or alter lignin structure in the way that it is no longer able to support and protect cellulose. Explosion leads to small plant fragments formation. This process is operated at a range of temperatures from 160 °C to 260 °C. Depending on temperature, pressure can be from 0.69 to 4.83 MPa. Residence time varies from a fraction of a minute to a few minutes. (Baig et al., 2018)

Ozonation is conducted by ozone addition. Due to high instability of ozone, it is produced immediately prior to its usage. Unfortunately, a number of research claim the impracticality of ozone treatment due to different reasons: unreasonably big contact time (Binder et al., 1980), material loss (Vidal & Molinier, 1988) and inability of ozone to perform the reaction (Silverstein & Chen, 2007). Residence time, temperature, ozone concentration and flow rate depend on the type of biomass and desired lignin removal. The least severe conditions with the greatest possible delignification degree (43%) were proposed by Garcia-Cubero et al. (2009). The contact time was 150 minutes, ozone flow rate was 60 L/hour with concentration 2.7% w/w.

Enzymatic delignification differs from the listed above methods vastly due to its eco-friendliness, safety and substrate specific delignification mechanism. The most wide-used enzymes in delignification are: lignin peroxidase, aryl-alcohol oxidase, manganese peroxidase (Ergun & Urek, 2017). Enzymatic processes are quite convenient for a wide pH range (4 – 8) and of temperatures (20 °C to 80 °C) are suitable (Kuila et al., 2011). Enzymatic process demonstrates the highest lignin removal rates among the rest of delignification process. In addition, the lignin removal can be increased by combining enzymatic delignification with other processes. For instance, with microbial delignification. (Yang et al., 2011)

## **5 DEEP EUTECTIC SOLVENTS**

### **5.1 Properties and kinds**

The term of deep eutectic solvents (DES) was coined in 2003 during the research conducted by Abbott et al. The term itself is genuinely comprehensive if each word is considered

separately. “Eutectic” comes from the Greek word εὐτηκτός which stands for “easy melting”. “Deep” means that the mixture, which makes a DES, undergoes deep temperature depression compared to the temperatures of the pure compounds of the mixtures. “Solvent” identify the main way of utilization of mixtures of this type – they are used as green-solvents instead of ionic liquids (ILs) and volatile organic compounds (VOCs). E.L. Smith et al. (2014) defined DES as “systems formed from a eutectic mixture of Lewis or Brønsted acids and bases which can contain a variety of anionic and/or cationic species”. DES is a mixture which consists of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). In Figure 5.1 some possible HBDs and HBAs that can form DESs are presented (Francisco et al., 2013). It is apparent that the great number of hydrogen bonds is a central part of the system and it fully contributes to low lattice energy which makes the temperature depression possible.

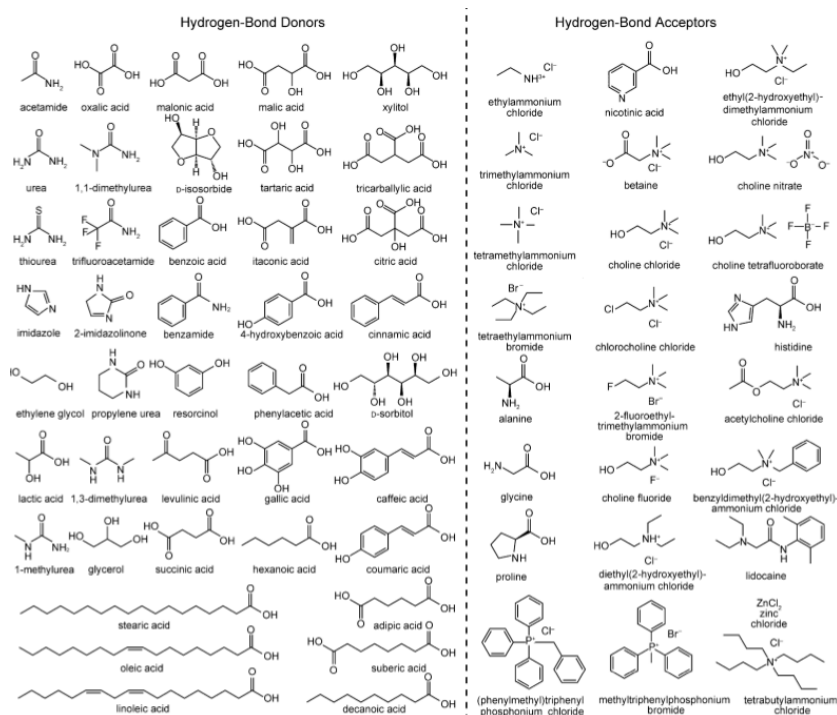


Figure 5.1 Possible HBDs and HBAs that can form DESs (Francisco et al., 2013)

The general formula of DES is presented below (Smith et al., 2014):



Where  $Cat^+$  – mostly ammonium cation,  $X^-$  – Lewis base (in most cases halide ion),  $Y$  – Lewis or Brønsted acid,  $z$  – a number of active molecules that perform interaction with the anion.

Due to convenience in dealing with choline cation in practice the most popular hydrogen bond acceptor is choline chloride (Martins et al., 2018).



DESs can be easily classified in accordance to the nature of its consisting parts. All types of DESs are presented in Table 5.1.

Table 5.1 Types of DES (Smith et al., 2014)

Type	General formula	Terms
Type 1	$Cat^+X^-zMCl_x$	$M = Zn, Sn, Al, Ga, In$
Type 2	$Cat^+X^-zMCl_x \cdot yH_2O$	$M = Cr, Co, Cu, Ni, Fe$
Type 3	$Cat^+X^-zRZ$	$Z = CONH_2, COOH, OH$
Type 4	$MCl_x + RZ = MCl_{x-1}^+ \cdot RZ + MCl_{x+1}$	$M = Al, Zn$ and $Z = CONH_2, OH$

When discussing properties of DESs it is frequently mentioned that DESs are non-volatile, non-flammable, non-(low-)toxicity, with negligible vapor pressure. But at the same time one of the main properties which hinders DES recycling is viscosity. It is 20-1000 times higher than viscosity of water under the same conditions (Francisco et al., 2013). There is an inverse dependence between viscosity and temperature. Majority of deep eutectic solvents demonstrate melting temperature around 50 °C.

DESs based on choline salts demonstrate high conductivity, hence less viscosity, with the anionic species in them able to move freely. Composition is related to the nature of HBA, it influences the charge shield and thus the strength of the hydrogen bonds. When it comes to density, the higher the relative ratio of anionic part to hydrogen bond donor part, the higher the structuring effect on the liquid and the lower the free volume. Lower free volumes mean less molecular motion, which inevitably leads to higher viscosity. (Paiva et al., 2018)

Viscosity along with density, conductivity and surface tension depends on the temperature. Since higher temperature means higher rate of molecular motion, the molar volume of DES becomes greater under greater temperatures. All reported DESs are detected to have a linear correlation between density and temperature (Francisco et al., 2013). Following this line, Kareem et al. showed a linear dependency of refractive index and pH value on temperature for DESs based on phosphonium salts. Changes in viscosity and conductivity lie in the Arrhenius model.

Water has a lower viscosity and density than the majority of DESs, resulting in a decrease of the values of both properties upon increasing the water content. (E.L. Smith et al., 2014)

Basically, two systems of DES and water mixtures exist – “water-in-DES” and “DES-in-water”. M.J. Roldan-Ruiz et al. (2019) studied by Brillouin and  $^1\text{H}$  NMR spectroscopy solutions of DES in water from the range of 100 to 40 wt%. DES was prepared with malic acid (MA) and choline chloride (ChCl). The result showed that a 70 wt% of DES is a threshold concentration. If the concentration is higher the system is “water-in-DES”. Otherwise, the system is “DES-in-water”.

## 5.2 Comparison of DESs with ILs

The main concept of DESs lies in the fact that these solvents share the main beneficial properties of ionic liquids but at the same time they are less expensive and less toxic. The greatest advantage that DESs have in common with ILs is the fact that they are able of being customized in terms of their physical properties and phase behavior by selecting suitable constituents, relative compositions and water content. (Dai et al., 2013)

It is well-known that ILs preparation goes with a chemical reaction. DESs preparation goes physically and the result fully depends on the ratio of the initial constituents. This makes DESs much more attractive in terms of flexibility and convenience of operation than ILs. (Jeong et al., 2015)

Ionic liquids also differ from DES from the point of intermolecular forces. In ILs these forces are represented by ionic bonds while in DES by hydrogen bonds. Hydrogen bonds are not as strong and stable as ionic bonds which lead to major differences. For example, differences in melting points. Lower melting points of DES mixtures makes the preparation process much easier than preparation of ILs. (Jeong et al., 2015)

## 5.3 DES Preparation

The topic of deep eutectic solvents is genuinely innovative so there are no standardized methods for DES preparation. According to Dai et al. (2013) two methods can be named. The first one involves reagents mixing, heating (either in a water bath or a heat plate) and the subsequent cooling. Heating is conducted at such temperature that ensures fast dissolution of one constituent in another. In case of the eutectic mixture of choline chloride in lactic acid temperature is maintained around 60 °C with a stir bar till the components transform into transparent liquid. DESs are usually cooled to the room temperature. The second path involves evaporating. Two parts of the DES must be diluted in water, and this mixture is then evaporated at around 50 °C. Another procedure for the manufacturing via heating was discussed by Abbott

et al. (2003) The required weights of the components are heated at rather high temperatures around 100 °C with permanent stirring until the moment when the “homogeneous colorless liquid” is obtained. However, prior to heating, the components are dried under vacuum. According to Nam et al. (2015), DES can be also prepared via freeze-drying. In this method the required ratio of components is weighed and then the components are dissolved with small amount of distilled water. Then the mixture is centrifuged for approximately 10 minutes. Subsequently, the mixture must be cooled to -80 °C for 90 minutes so that lyophilization could take place. The duration of lyophilization can be 18 hours or even more (till the weight of the mixture remains stable). Lyophilization is a very good alternative to evaporation because with the help of this method it is possible to remove up to 99% of water from the mixtures (Nail et al., 2002). The principle of the process lies in sublimation of ice crystals. This process is always conducted under vacuum and due to gradual raise of temperature.

#### **5.4 Applications of DESs**

During the last 20 years DES found applications and implementations in many processes such as chromatography (T. Cai, H. Qiu, 2019), rust removal (Omar and Sadeghi, 2020), liquid-liquid microextraction (A. Jouyban, et al., 2020), electrocatalysts production (V.S. Protsenko et al., 2019), biomass pretreatment and conversion (Chen & Mu, 2019), analytical chemistry (A. Shishov et al., 2017), aromatic nitrogen compound removal (Li & Row, 2016) and biocatalysis (Fisher, 2015).

### **6 DES AND IL RECYCLING**

Recycling is one the keystone methods of circular economy and sustainability. Multiple reuse of materials lowers carbon and water footprints and preserves natural resources from an early depletion. Due to this fact, the latest breakthroughs in DES and ILs recycling should be observed.

#### **6.1 Recycling of DES and ILs**

Being effective and benign solvents, DES and ILs are frequently used in biomass treatment. During biomass treatment water is added either for dilution, lowering viscosity or as anti-solvent for the extracted material precipitation. Thus, a mixture of DES/ILs with water eventually occurs at the final stage of biomass treatment. In order to be able to reuse, recycle DES or ILs, water should be removed. In addition, properties of solvents from the ionic liquid family depend on the ratio of their constituents, regeneration methods should also make sure that the recycled solvents have the same ratios than the initial solvents. According to the retrieved data, the majority of previous research focused on water or anti-solvents removal

from DES solutions. Retaining of the ratio of DES components has not yet been thoroughly discussed.. Hence, a big part of the methods listed below concentrate only on water separation. Recovery and recycling are significant issues for all DES-based/IL-based biorefineries. It keeps DES and ILs usage in their infancy (Liang et al., 2019, J. Yin et al., 2019, Brandt et al., 2013).

## **6.2 Summary of the methods reported for DES and IL recycling**

DES recycling still is not deeply investigated. According to the best of retrieval from scientific papers, only 3 scientific articles touch upon DES recycling – Liang et al., 2019, Chen & Mu, 2019, Jeong et al., 2015. Based on the mentioned three articles, the methods, which were proved to be feasible with DES, are observed. Subsequently, ionic liquid recycling methods are discussed because of the mentioned similarities in DES and IL properties. The similarities in properties lead to conclusion that feasible methods of IL recycling can be to a certain extent feasible for DES recycling.

### **6.2.1 DES Recycling**

#### **6.2.1.1 Combination of ultrafiltration and electrodialysis**

In the experiments, conducted by Liang et al. (2019) ultrafiltration (UF) process was exploited in order to separate lignin and the products of depolymerization. DES was prepared by mixing ethylene glycol and choline chloride in the mole ratio of 2:1. Minimate OAPMP-220 (UF) membrane modules with MWCO 0,65 kDa proved to provide finer separation of lignin and some impurities related to by-products formation. Electrodialysis (ED) was implemented since, one of the constituents is electrolyte (choline chloride) while the other one demonstrates non-electrolyte behavior (ethylene glycol). Hence, electrolyte would transfer through an ion-exchange membrane while a non-electrolyte would remain motionless. Thus, electrodialysis was exploited in order to separate DES constituents. After the electrodialysis separation of DES constituents, DES was re-prepared, and was reported to be reused again in the same process of lignin extraction.

Results of the experiments show that not only was a 0,65 kDa UF membrane able to retain a significant amount of lignin. Degradation substances tend to foul an ion-exchange membrane during electrodialysis, but the most prominent drawback of depolymerization products is that they remained in DES after recovery. Their presence leads to deterioration of DES efficiency during further usages. The efficiency of lignin removal was measured by the lignin separation degree parameter  $K$ . Greater values of the  $K$  parameter indicates greater lignin removal by DES. The changes in DES efficiency expressed through the  $K$  parameter and depending on the treatment of DES are presented in Table 6.1

Table 6.1 Lignin removal results by DES after different treatments

Source of DES		parameter $K$
Original DES		8,03
Reuse without ED	After 1 kDa UF	5,51
	After 0,65 kDa UF	4,98
Reuse with ED	After 0,65 kDa UF and ED	7,33

It should be kept in mind that despite the close values of the lignin removal of the reconstituted DES to the original DES, the impurities in the reconstituted DES will continue to accumulate. The  $K$  parameter will be decreasing after each reuse. Nevertheless, membrane separation strategy of DES recovery by Liang et al. is still a state-of-the-art model. Alternative DES recovery methods based on membrane separation have not been observed yet.

#### 6.2.1.2 Lyophilization

Lyophilization is a dehydration process. Among different variations of dehydration processes lyophilization (or freeze drying) is considered the most energy demanding and thus, the most expensive. It is applied in industries where the eventual product is so valuable that its value justifies high operational expenses (Ratti, 2001). Lyophilization starts with water molecules freezing. Then the ice evaporates without melting under vacuum (Berk, 2018). Ideal conditions for sublimation can be observed through a phase diagram. A phase diagram of pure water is depicted in Figure 6.1.

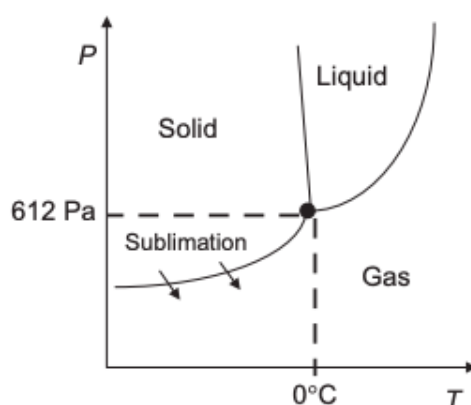


Figure 6.1 Phase diagram of pure water (Berk, 2018)

According to Figure 6.1, sublimation occurs when water is below its triple point. In other words, sublimation of pure water requires the pressure below 611,73 Pa and the temperature

below 0,01 °C. However, a common pressure of lyophilization in practice is around 50 Pa. Freeze drying is usually conducted in two stages. The first is sublimation when ice is sublimated and then frozen again by condenser. The second step is desorption of initially adsorbed water and its further removal. In the end, the moisture content of the treated substance should be around 2%. (Oetjen & Haseley, 2004) According to Jeong et al., lyophilization is a feasible method for DES recycling. DES was used as a solvent in the treatment aimed at ginsenosides extraction. After separation and washing, DES contained water which was removed by lyophilization. Recovered DES was reused as an extraction medium three times. Each time an extraction efficiency of DES was deteriorating – 91.1%, 85.4% and 82.6% respectively for the first, second and third reuses. Decreasing efficiency values were caused by the degradation products accumulation which cannot be solved by simple water removal (Jeong et al., 2015).

#### 6.2.1.3 Aprotic solvent addition

Chen & Mu (2019) claim that DES can be regenerated from water without any difficulties by addition of an aprotic solvent. Aprotic solvents are organic substances in which hydrogen is not bonded with oxygen and nitrogen. Thus, there is no protons and this substance is called aprotic (McMurry, 2011). Aprotic addition technique is proved by V. Majova et al., 2017 and M. Francisco et al., 2012. For example, Francisco et al. (2012) used a great variety of low transition temperature mixtures (LTTMs) in lignocellulosic biomass treatment. Acetone was used in these experiments as an aprotic solvent to phase separate hydrogen bond solvents.

Chen & Mu (2019) highlight that the loss of pretreatment efficiency and the loss of conversion rate are observed when using aprotic solvents for DES recovery. However, the losses are not significant which makes this technique feasible.

#### 6.2.1.4 Evaporation

Evaporation is a quite simple mean for DES recovery from water. It is not very efficient because all products of biomass degradation remain in DES after evaporation. Nevertheless, this method is popular among researchers who investigate methods of biomass treatment with DES (Procentese et al., 2015, Kumar et al. 2016).

### **6.2.2 IL Recycling**

This chapter presents the techniques presented to be used in recycling of ionic liquids based on the literature available. Examples on the use of membrane-based separation, distillation, induced phase separation, extraction and adsorption have been found.

### 6.2.2.1 Membrane-based separation

Membrane-based separation was studied in scientific literature by means of nanofiltration (Haerens et al., 2010, Lynam et al., 2016, J. Yin et al., 2019), electrodialysis (X. Wang et al., 2012), pervaporation (Haerens et al., 2010, Shafer et al., 2001) and reverse osmosis (Haerens et al., 2010).

Nanofiltration membranes demonstrate pore size in the range around 0,001  $\mu\text{m}$  which is too small for bulky ionic liquid molecules to pass, but at the same time big enough to pass water. Several studies were devoted to nanofiltration based on polymeric membranes (Haerens et al., 2010, Lynam et al., 2016). New composite membranes such as membranes with two- and three-dimensional materials have been recently developed (H. Jia et al., 2018). Two-dimensional materials in the composite membranes proved to provide high permeability and selectivity in many separation processes. If earlier a graphene oxide was in the center of scientific research, currently new two-dimensional materials become popular among scientific community. One of the cutting-edge materials for two-dimensional membranes are transition metal dichalcogenides (TMDs). (Grayfer et al., 2017) Yin et al. (2019) studied two-dimensional membranes based on Molybdenum disulfide ( $\text{MoS}_2$ ) to investigate its efficiency in IL separation from water. Aqueous  $\text{BmimBF}_4$  and  $\text{HmimCl}$  solutions were exploited in the experiments. As a result, it was established that rejection rate for  $\text{BmimBF}_4$  and  $\text{HmimCl}$  was 40.8% and 86.2%, respectively. The fact that  $[\text{Hmim}]^+$  is bigger than  $[\text{Bmim}]^+$  leads to conclusion that despite the influence of the charge of the membrane, the main mechanism of separation is sieving. During the experiments conducted by Yin et al. (2019) it was also stated that greater concentration of ionic liquids lead to greater rejection rate. The flux significantly decreases, though.

The research conducted by X. Wang et al. (2012) on feasibility of electrodialysis was the first of that kind. As a result of the experiments, electrodialysis was proved to be an effective way for concentrating of ILs. The correlation between the applied voltage of ED and IL concentration was established. When increasing the voltage, the recovery grows respectively, reaching the maximum of 85,2%. After that value the growth of the applied electric force did not influence the recovery. Recovery even starts to decline. Pervaporation and reverse osmosis efficiency in ILs recovery were thoroughly studied by Haerens et al. (2010). Pervaporation happened to be much less efficient than reverse osmosis. The membrane area of pervaporation membrane for proper removal of water should be much bigger than the area of the existing pervaporation membranes (such as PERVAP 2201). In order to make pervaporation method feasible, water flux should be improved. Reverse osmosis, though, did not revealed promising

results as well. The efficiency of reverse osmosis was restricted by the osmotic pressure of ions. The highest concentration of ionic liquids that was achieved during the experiments was 30 vol%.

Membrane-based separation can be applied to recycling of DES, however, not in form nanofiltration. Nanofiltration separation is mainly applied to divalent ions (Mulder, 1996) while DESs usually consist of a hydrogen bond acceptor electrolyte and a hydrogen bond donor non-electrolyte (Abbott et al., 2014). At the same time sieving mechanism of ultrafiltration can be applied to DES recycling which was proved by Liang et al. (2019), whose research was briefly described in the paragraph 6.2.1.1.

#### 6.2.2.2 Distillation

Distillation has been implemented when ionic liquids have been separated either from alcohols (M.K. Wojtczuk et al., 2020) or water (Y.-P. An et al., 2020, Huang et al., 2013). In both cases distillation is viable only for those ionic liquids that are thermally stable enough and that do not tend to decompose during the process (Earle et al., 2006). Depending on the ionic liquid, nature of the mixture and energy requirements, the following methods have been used: osmotic distillation, molecular distillation and column distillation. The column distillation is operationally the least complicated process among them. It is used only for separation of methanol and ethanol due to their lower boiling points than water. Due to high energy requirements of either heating or vacuum or both (molecular distillation), distillation is often used as a post-treatment process, usually eliminating small residues of water. (Reinert et al., 2012) It was mentioned previously that aprotic ionic liquids are more stable than protic under low pressures. Nevertheless, Kirchner explored ionic liquids with strong hydrogen bonds such as methylpyrrolidinium acetate or dialkylammonium carbamate salts. In other words, all aprotic ILs can be distilled and some protic ILs which obtain strong hydrogen bonding. (Kirchner, 2013)

Two most recent researches on ionic liquids recycling by distillation present an interest. The first study is devoted to methanol and ethanol separation from [C<sub>2</sub>mim][OAc] and [C<sub>2</sub>mim][SCN]. It was performed by M.K. Wojtczuk et al. in 2020. Results showed that the high volatility of methanol and ethanol does not provide easy achievement of ionic liquids with high purity. [C<sub>2</sub>mim][OAc] was shown to be less recyclable by distillation than [C<sub>2</sub>mim][SCN]. In addition, it was established that pre-heating of the mixtures leads to significantly lower energy requirements of distillation process. Another study was devoted to osmotic distillation of [C<sub>8</sub>mim]Cl, [C<sub>6</sub>mim]Cl and [C<sub>4</sub>mim]Cl. It was performed by Y.-P. An et al. in 2020. Vapor pressure difference was applied as a driving force to the system, which consisted of IL water



solution and an inorganic salt solution. Resultingly, more than 99,99% of IL was rejected. In spite of the promising results, membrane distillation of aqueous ionic liquid solutions is usually prone to fouling. An extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) approach was applied by H. Wu et al. to describe fouling behavior of a membrane during vacuum membrane distillation. It was found out that surface structure of a membrane does not affect the fouling behavior as much as surface chemical properties of material of the membrane. For example, for separation of water solution of [Bmim]Cl the membrane should be highly non-polar with negative zeta potential (H.Wu et al., 2018).

#### 6.2.2.3 Induced phase separation

The main principle of induced phase separation is in achieving an aqueous biphasic system (ABS). This condition can be reached by three methods: 1) addition of salt; 2) addition of carbon dioxide; 3) raising the temperature. The first two methods can be implemented to any water-ILs mixture while the third method is suitable only for a narrow class of ionic liquids which restricts its usage (N.L. Mai et al., 2014). The induced phase separation by salt addition is possible due to “salting out phenomenon”. According to Gutowski et al. (2003), the induced phase separation is possible at room temperature. The main parameter is for the IL to contact the concentrates water-structuring salt. The upper phase contains IL while water and salt are contained in the bottom layer. Salt should belong to a class of “kosmotropic” salts (N.L. Mai et al., 2014). Kosmotropic salts are remarkable for their “order-making” influence on water solutions. In other words, kosmotropic salts ensure stability of water interactions (Moelbert et al., 2004). Kosmotropic salts typically consist of the carbonates, sulphates, hydrogenphosphates anions and magnesium, lithium and aluminum cations. The effect of these salts on ionic liquid solutions can be represented by the study of Deng et al. (2009). During this study [Amim][Cl] was regenerated by  $K_3PO_4$ ,  $K_2HPO_4$  and  $K_2CO_3$ .  $K_2CO_3$  occurred to be the least efficient of IL recovery due to the fact that  $CO_3^{2-}$  is the most stabilizing anion from the Hofmeister row (Deng et al., 2009).

The induced phase separation by carbon dioxide follows the same principle of biphasic system formation. This method is eco-friendlier because it does not exploit any toxic chemicals. It also allows to obtain high recovery values – with the presence of primary or secondary amines induces phase separation by  $CO_2$  can recover up to 99% of ILs. Unfortunately, expensive equipment restricts spreading of this method. (Xiong et al., 2012; N.L. Mai et al., 2014)

The induced phase separation by temperature increase is possible only for a narrow class of ionic liquids which contain iron or derived from charge polymers or from amino acids. A

growth of temperature is enough for these solutions to form a two-phase system. (Xie & Taubert, 2010, Fukumoto & Ohno, 2007)

#### 6.2.2.4 Liquid-liquid extraction

When nonvolatile or unstable substance is separated from ILs, liquid-liquid extraction is applied. Generally, hydrophilic substances are extracted by water while for extraction of hydrophobic substances organic solvents are used (Huddleston & Rogers, 1998). Extraction demonstrates positive sides such as relative simplicity and selectivity. The process is considered to be simple because it does not require complex equipment. At the same time, cross-contamination concerns disrupt the principle of ionic liquids as environmentally friendly solvents (N.L. Mai et al., 2014). Liquid-liquid extraction was implemented to DES recycling by the use of aprotic solvents.

#### 6.2.2.5 Adsorption

Focus of many researchers has been placed on adsorption by activated carbon (AC) due to its availability and good performance in wastewater treatment (Anthony et al., 2001, Lemus et al., 2012, Palomar et al., 2009). For example, Anthony et al. (2001) obtained remarkable results for AC adsorption of ILs from wastewater. However, the recovery of ILs was hardly manageable. Lemus et al. (2012) and Palomar et al. (2009) separately draw a conclusion that hydrophobicity/hydrophilicity significantly influences adsorption efficiency. In other words, adsorption of hydrophobic ILs is feasible by itself. Hydrophilic adsorption requires modifications in order to be feasible. For example, surface of AC can be modified with hydroxyl groups which can form H-bonds with hydrophilic ILs, thus, making adsorption more efficient. Modification of adsorbent surface as well as essential desorption process are considered two major drawbacks hindering the process implementation. (N.L. Mai et al., 2014) Adsorption of DES has not been studied according to the best of scientific retrieval. The results of DES adsorption should depend on the size of DES and hydrophobic nature of HBA and HBD.

## 7 MEMBRANE TECHNOLOGY

Membrane technology is based on separation of substances due to minimal application of energy. Separation can be caused by differences in pressure, concentration, electrical potential or temperature (Baker, 2004). The main objectives of separation are concentration, purification and fractionation. Concentration involves solvent removal, while purification is removal of contaminants and impurities. Fractionation involves dividing of the treated mixture into separate fractions (Mulder, 1996). Separation in membrane technology is feasible due to a

semi-permeable membrane. A membrane can be described as a permselective barrier between phases. This barrier regulates the transport of substances from one phase into another. (Ulbricht, 2006)

## 7.1 Membrane Classification

Despite the vast variety of methods for membrane characterization, the simplest and most comprehensive one is to divide membranes in two groups: porous and nonporous membranes. Porous membranes are typical for microfiltration and ultrafiltration processes while nonporous are more widespread in pervaporation and gas separation (Prip Beier, 2007). Based on the group names, it becomes evident that porous membranes contain fixed pores and nonporous membranes does not. Therefore, in case of porous membranes retention depends on the pore size distribution meanwhile in case of nonporous the material of the membrane plays a prominent role. Material for porous membranes should withstand mainly temperature, pressure and chemical activity of the filtered solution. Material should not affect separation. However, porous membranes are more prone to fouling than nonporous. (Mulder 1996)

Schematic description of porous and nonporous membranes is presented in Figure 7.1.

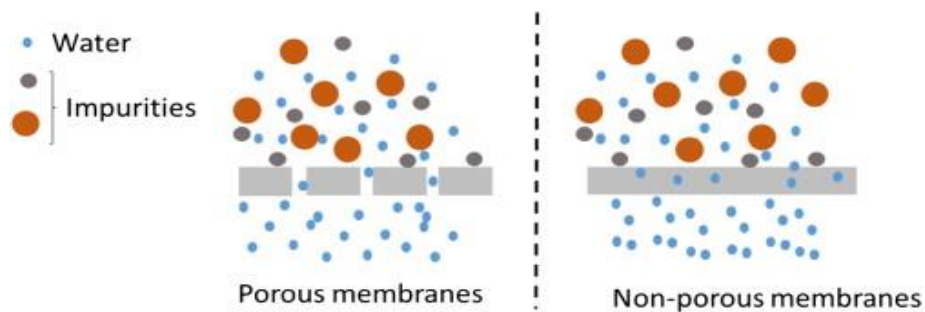


Figure 7.1 Schematic description of porous and nonporous membranes (Farah et al., 2015)

Pore size distribution is a key factor in characterization of porous membranes and thus it should be discussed more detailed. Membranes typically demonstrate heterogeneous porous structure. In other words, membranes consist of pores of different sizes. A schematic graph representing pore size distribution is depicted in Figure 7.2.

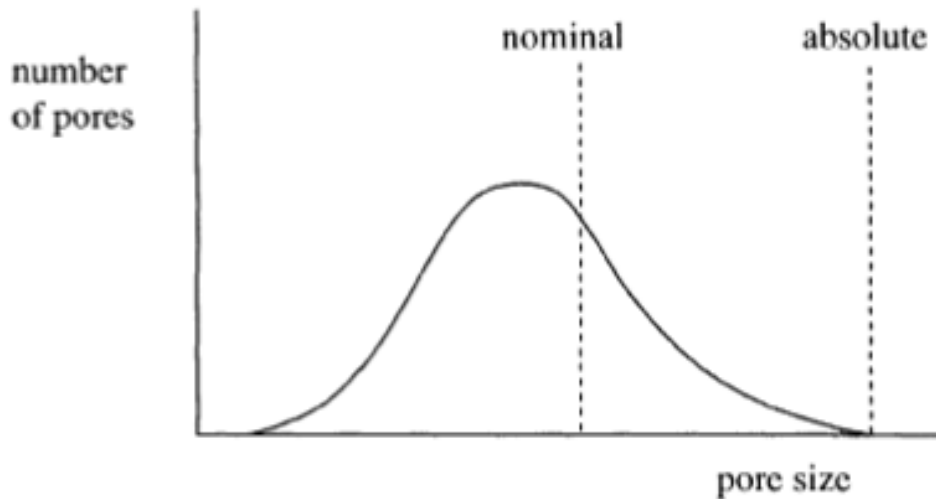


Figure 7.2 Schematic representation of pore size distribution (Mulder, 1996)

According to Figure 7.2, pore size can be classified as nominal or absolute. At nominal pore size 95-98% of molecules of that size or bigger are retained. At absolute pore size 100% of molecules of that pore size or bigger are retained. These values should not be confused with another important characteristic of membrane – Molecular Weight Cut-Off (MWCO). MWCO indicates the molecule weight of the molecules which are 90% retained by the membrane (Prip Beier, 2007).

## 7.2 Essential Principles of Membrane Separation

Schematically, membrane process is represented in Figure 7.3.

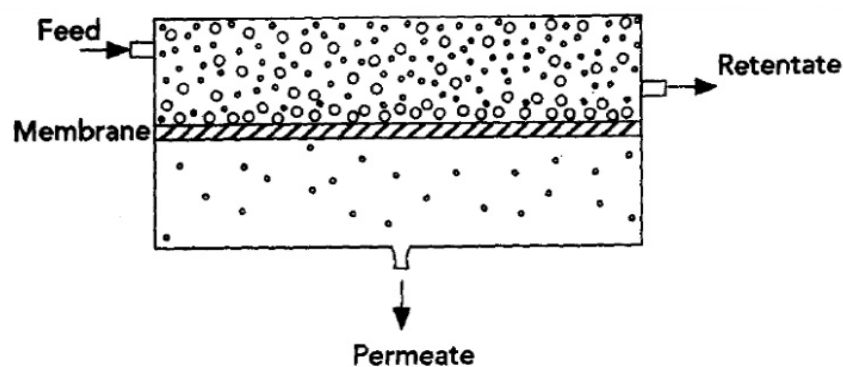


Figure 7.3 General scheme of a membrane process (Lau & Perez de los Rios 2018)

Feed is an initial solution that is loaded into a filter. A stream that has passed through the membrane is called permeate. Liquid that was retained by the membrane is called retentate. (Baker, 2004)

When evaluating the membrane's efficiency, the main parameters to be taken into consideration are flux and retention (Saleh & Gupta, 2016). Flux through the membrane is caused by driving force. In addition, flux is directly dependent on the applied driving force. This nature of flux can be illustrated by Eq 2.

$$J = -K \frac{dX}{dx} \quad \text{Eq (2)}$$

Where,  $J$  – flux (kg/m<sup>2</sup>·h);  
 $K$  – phenomenological coefficient;  
 $X$  – gradient of a driving force (temperature, concentration, pressure);  
 $x$  – coordinate perpendicular to the transport barrier.

“Minus” means that flux is always looking forward to the decrease of the driving force. The greater the decrease of the driving force, the bigger the flux. (Mulder, 1996)

The phenomenological coefficient depends on the nature of a driving force. This work primarily discusses pressure driven processes with volume flux. In that case, Eq 2 becomes the Darcy's law and the coefficient becomes permeability  $A$  (kg/m<sup>2</sup>·bar·h). Permeability can be found as a slope coefficient of a line which represents correlation between flux and pressure (Baker, 2004).

Retention is a very important characteristic of a membrane because it shows how well the membrane is dealing with retaining one species and letting through the other species. Retention is illustrated by Eq 3.

$$R = \left( 1 - \frac{c_p}{c_f} \right) \quad \text{Eq (3)}$$

Where,  $R$  – retention;  
 $c_p$  – solute concentration in permeate;  
 $c_f$  – solute concentration in feed.

The most essential benefits and drawbacks of membrane separation are presented in Table 7.1.

Table 7.1 Benefits and drawbacks of membrane separation (Mulder 1996, Saleh & Gupta 2016)

Benefits	Continuous separation
	Compatibility with another processes
	Mild conditions of separation
	Easy up-scale
	Adjustable properties of membranes
	Absence of necessary additives
Drawbacks	Linear up-scaling
	Membrane fouling

Membrane technology combines chemical and physical processes. The variety of processes is presented in Table 7.2.

Table 7.2 Classification of membrane separation processes (Saleh & Gupta 2016)

Physical processes	Pressure-driven processes	Microfiltration
		Ultrafiltration
		Nanofiltration
		Reverse Osmosis
	Diffusional processes	Pervaporation
		Perstraction
		Dialysis
		Extraction
	Heat processes	Distillation
		Vacuum distillation
Chemical processes	Electric processes	Electrodialysis
	Supported membranes	
	Liquid membranes	
	Active transport	
	Hemodialysis	

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis are briefly discussed further.

### 7.3 Microfiltration

Microfiltration (MF) is the coarsest process among membrane processes. It is often exploited as pre-treatment before finer separation processes. The reason why it is considered coarse is in the relatively big pore size – 0.1-10  $\mu\text{m}$ . MWCO for MF is higher than 10000 Da. Due to big pores and high MWCO, high pressure is not required for filtration which makes the process the least energy-consumptive among all the membrane processes. The operational pressure is usually 1-2 bars because pores are quite big, and particles can pass through relatively easily. Microfiltration is widely used in clarification of suspensions and emulsions due to the big size of particles in these colloidal systems. In addition, microfiltration is widely used in sterilization because it retains protozoa, microorganisms and big bacteria. However, viruses are not efficiently retained during the process. Viruses are small which let them go through a MF membrane. Partial rejection is possible due to adsorption of viruses to the membrane's material. This phenomenon is encountered also in the case of fine particles filtration (Baker, 2004). Microfiltration application is combined with other membrane or disinfection processes because it is not very efficient alone. The most common applications of microfiltration are as follows: sterilization of beverages and pharmaceuticals; clarification of juices, beer and wine; wastewater treatment (Mulder, 1996). A brief summary of microfiltration is presented in Table 7.3.

Table 7.3 Summary of microfiltration (Mulder, 1996)

membranes	symmetric or asymmetric porous
thickness	10000-150000 nm
pore size	50-10000 nm
driving force	pressure (under 2 bar)
separation principle	sieving mechanism
membrane material	polymeric, ceramic

### 7.4 Ultrafiltration

Fundamentally, ultrafiltration (UF) process is very close to microfiltration. Size exclusion plays a key role in both processes. However, ultrafiltration is a finer separation than MF due to the fact that the nominal pore size can be as little as 0.002  $\mu\text{m}$ . MWCO is between 1000 and 10000 Da. Considering small sizes of pores, pressure is required to be 2 – 10 bars. The greatest difference between ultrafiltration and microfiltration is in the symmetric property of the

membranes. In UF the vast majority of membranes are asymmetric. It means that UF membrane has several layers with different selectivity and permeabilities. (Baker, 2004)

An example of an asymmetric membrane is depicted in Figure 7.4.

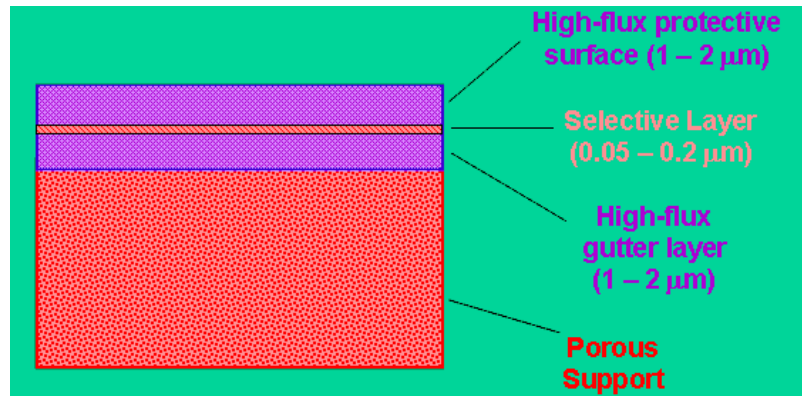


Figure 7.4 A schematic description of an asymmetric membrane (Fumatech.com, n.d.)

The layer with the finest selectivity is usually placed on the top of the membrane. The top layer, which is always less than 1  $\mu\text{m}$  thick, restricts permeability and selectivity of the whole process. The rest of the layers hardly contribute to separation, being mostly support-layers. Thus, hydrodynamic resistance does not depend on the thickness of the whole membrane. In microfiltration the correlation between the thickness of the membrane and a hydrodynamic resistance is direct. (Mulder, 1996)

Ultrafiltration is preferentially exploited in macromolecules separation (in many cases, proteins separation). In recent years, it is commonly used in membrane bioreactors, processes of potable water reuse, sterilization of water, separation of biomass. (Fumatech.com, n.d.)

A brief summary of ultrafiltration is presented in Table 7.4.

Table 7.4 Summary of ultrafiltration (Mulder, 1996)

membranes	asymmetric porous
thickness	approximately 150000 nm
pore size	1-100 nm
driving force	pressure (1-10 bar)
separation principle	sieving mechanism
membrane material	polymeric (e.g. polysulfone)



## 7.5 Nanofiltration

Nanofiltration (NF) is placed in a so-called “Transitions Region” (Baker, 2004). It means that this process is a transit process from ultrafiltration to reverse osmosis. Ultrafiltration is a typical pore-flow process where retention takes place mostly based on sieving mechanism. Reverse osmosis is a solution-diffusion model process where small size molecules such as chlorides and sulphates are retained based on the charge of the membrane. As a result, nanofiltration process is 100% efficient in divalent ions rejection and only 20-70% efficient in monovalent ions rejection (Labban et al., 2017).

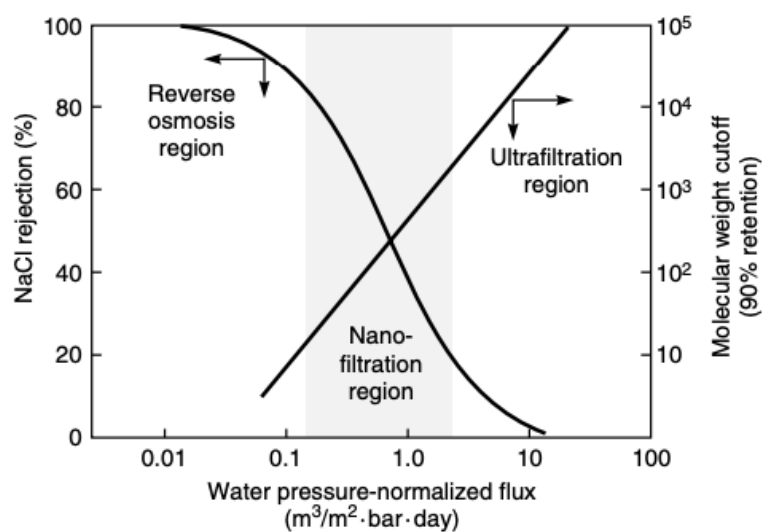


Figure 7.5 Diagram of nanofiltration characteristics in relation to reverse osmosis and ultrafiltration (Baker, 2004)

According to Figure 7.5, the water flux through UF membrane is significantly higher than the flux through the dense non-porous reverse osmosis membrane. Nanofiltration flux is between RO and UF fluxes. Pore size of NF membrane is around 0.001  $\mu\text{m}$ . MWCO is between 200 and 1000 Da. Typical salt rejection for nanofiltration is between 20 – 80%. (Labban et al., 2017)

Main application NF membranes is water hardness removal. That is the reason why NF membranes are also called as “softening membranes”. (mrwa.com, n.d.)

## 7.6 Reverse Osmosis

Osmosis should be introduced in order to understand the principle of a reverse osmosis separation. Osmosis phenomena occurs when two liquids separated by a semipermeable membrane have different concentrations. Water from the part with low concentration would tend to the part with higher concentration. The difference in levels of liquids would represent

an osmotic pressure. If a pressure, which is bigger than osmotic pressure, would be introduced to the liquid with a higher concentration, water will flow to another part of the system. (Baker, 2004)

This is a principle of reverse osmosis (RO) and it is illustrated in Figure 7.6.

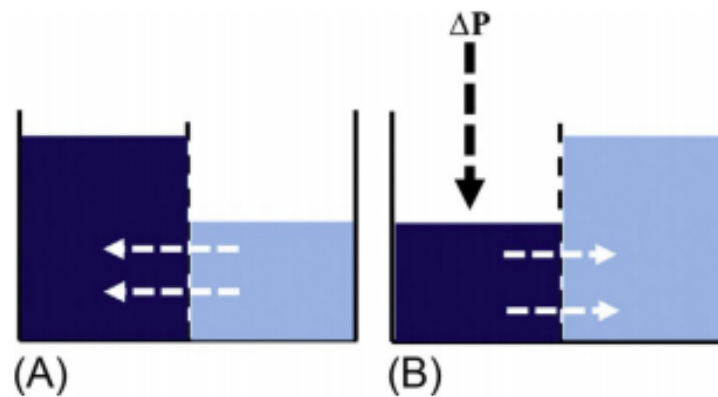


Figure 7.6 Schematic descriptions of osmosis (A) and reverse osmosis (B) (Ibrahim et al., 2020)

In comparison with other pressure driven processes, the pores of RO are extremely small, the membrane is asymmetric and very dense, which leads to a high pressure demand. Applied pressure in reverse osmosis varies between 20 and 100 bars. Rejection of dissolved salts can be up to 99%. Molecules with a weight more than 100 Da are retained on 100%. Molecules smaller than 100 Da can partly pass the membrane. This process effectively retains viruses, bacteria, pesticides and almost all contaminant ions and dissolved non-ions. Reverse osmosis follows a solution-diffusion model, the charge of separated ions can be as important as their size and weight. It is determined that the higher the charge of the ion, the better it is retained. (Ibrahim et al., 2020)

A brief summary of reverse osmosis process is presented in Table 7.5.

Table 7.5 Summary of reverse osmosis (Mulder, 1996)

membranes	asymmetric or composite
thickness	sublayer 150000 nm; top 1000 nm
pore size	under 2 nm
driving force	pressure (20-100 bar)
separation principle	solution-diffusion
membrane material	cellulose triacetate, aromatic polyamide

## 7.7 Polarization Phenomena and Membrane Fouling

Quite frequently a significant flux decrease is observed through a filtration time. This deterioration of filtration performance is usually caused by gel layer formation, adsorption, and a pore plugging. Concentration polarization phenomena occurs when a big number of retained molecules are accumulated near the surface of the membrane. A so-called “boundary layer” formation hinders the flux through the membrane (Baker, 2004). One of the main characteristics of concentration polarization is the modulus. It is expressed as  $c_m/c_b$ , where  $c_m$  is a concentration of a solute in a boundary layer and  $c_b$  is a concentration of a solute in a bulk. Concentration polarization can lead either to higher or lower retention, but it always leads to a lower flux (Mulder, 1996). After a decrease in flux due to concentration polarization, a steady state condition should be reached. However, subsequently to attainment of a steady state condition, a further decrease can be observed. This phenomenon is called fouling. Fouling can be reversible or irreversibly. It happens because of the deposition of organic/inorganic particles and molecules on the surface and in pores of the membrane (Baker, 2004). Reversible fouling can be cleaned by one of three methods – hydraulic cleaning, mechanical cleaning and chemical cleaning.

## EXPERIMENTAL PART

### 8 EXPERIMENTAL EQUIPMENT AND TEST PROCEDURES

The further described experiments were implemented at Lappeenranta-Lahti University of Technology in the laboratory of Membrane technology.

#### 8.1 Materials

Spent DES for the experiments was obtained from a treatment of both hardwood and softwood samples with the DES. DES was prepared from Choline Chloride (CAS: 67-48-1) and 90% Lactic Acid (CAS: 50-21-5), supplied by Alfa Chemistry. The molar ratio of choline chloride to lactic acid was 1:10. Wood treatment was conducted at 120 °C for 6 hours with mass ratio of solid phase to liquid phase of 1:10. The filtration experiments were done with the RC70PP membrane. The RC70PP membrane is an ultrafiltration membrane of which skin layer is made from regenerated cellulose. Main properties of this membrane are presented in Table 8.1. Ethanol was exploited in two ways; for solution preparation and washing. For the preparation of solutions, a 99% ethanol (ETAX A) was used. For washing, a 92.4% ethanol (ETAX B) was used. 99.5% acetone was exploited in after treatment as the final washing of biomass. Polyethylene glycol (PEG, approx. Mw. 4000 g/mol, CAS: 25322-68-3), supplied by Fluka AG (Switzerland), was utilized in the retention experiments.

Table 8.1 Main properties of RC70PP membrane

Property	Value
Support material	Polypropylene
Characteristics	Regenerated cellulose acetate
Company	Alfa Laval
MWCO	10 kDa
pH range	1 – 10
Typical operating pressure, bar	1 – 10
Temperature, °C	5 – 60

##### 8.1.1 DES preparation

In the current research, DES based on the mixture of choline chloride and lactic acid in molar ratio of 1:10 was used as solvent in the biomass treatment. The constituents as well as the precise ratio remain constant through the whole experimental part. DES had been prepared in

1 L Duran bottle and then kept at laboratory room temperature  $\sim 21$  °C. The procedure of DES preparation involved transferring 139.6 g of choline chloride and 900.8 g of lactic acid into 1 L bottle with further mixing at 250 rpm and heating at 100 °C for at least 1 hour. A homogeneous state of solution can be reached in about 30 minutes. However, DES homogeneity is vital, thus, mixing and heating of DES was continued for another 30 minutes to ensure a complete dissolution of Choline chloride and to reach a complete homogenous mixture. Thus, the whole procedure took at about 1 hour.

### **8.1.2 Membrane pretreatment**

Circular shaped sheets of 76 mm in diameter of the membrane were cut, washed with water, and stored in the fridge at 4 °C, one day before the planned filtration.

## **8.2 Design of experiments**

Two groups of experiments can be observed in this experimental part. First group had its aim in investigation of the best parameters of ultrafiltration process which was examined as a process for effective DES recycling. Second group of experiments was set up in order to observe the influence of pure DES over the RC70PP membrane and the influence of 60% solution of pure DES in ethanol (ETAX A) over the RC70PP membrane. The knowledge from these experiments will be of great value in estimating the perspectives of using the RC70PP membrane in DES recycling.

Thus, the sequence of experiments obeyed the following order: birch chips treatment with DES, separation of spent DES from the treated biomass, preparation of solutions of spent DES in ethanol, ultrafiltration of the solutions. Parameters of the birch treatment process were constant, preparation of solutions of spent DES in ethanol was always the same, although each time different concentrations were tried. For the ultrafiltration of spent DES solutions, the temperature of filtration, the concentration of solution and the presence of the initial suspended solids were the only variables. At the same time the mixing speed, pressure, membrane's type, size and shape and the eventual amount of permeate were kept constant. The impact of pure DES and 60% solution of pure DES in ethanol on the RC70PP membrane was examined in the second group of experiments. The impact was evaluated based on the changes in pure water flux behavior of the membranes which were exposed to DES and the solution of DES for different time periods. The only variable was a time of exposure of the membrane to pure DES or to the solution of DES and ethanol (from 1 to 4 weeks).

### 8.3 Treatment of wood chips with DES

Treatment equipment consisted of a heating magnetic electric plate with digital thermoregulator, a reactor with mixing system and a system which ensures uniform temperature distribution. Electric plate was used to heat the mixture inside the reactor to a required temperature. The required temperature was preset manually. The reactor was a Duran bottle with a temperature resistant cap. Mixing system was a magnet inside the bottle. It was used to ensure the contact between phases. The system, which provided uniform temperature distribution, included a beaker with technical oil. Temperature detector was placed inside the oil, between the walls of the bottle and the beaker. After the treatment a solid-liquid separation was carried out. During this process a liquid spent DES was separated from the treated biomass. The solid-liquid separation equipment consisted of an electric vacuum pump, a Büchner flask, a funnel, a sieve with 180  $\mu\text{m}$  pore size and a hose. Eventually, the obtained spent DES was used further in the ultrafiltration experiments. The setup for the treatment of wood samples with DES is depicted in Figure 8.1.

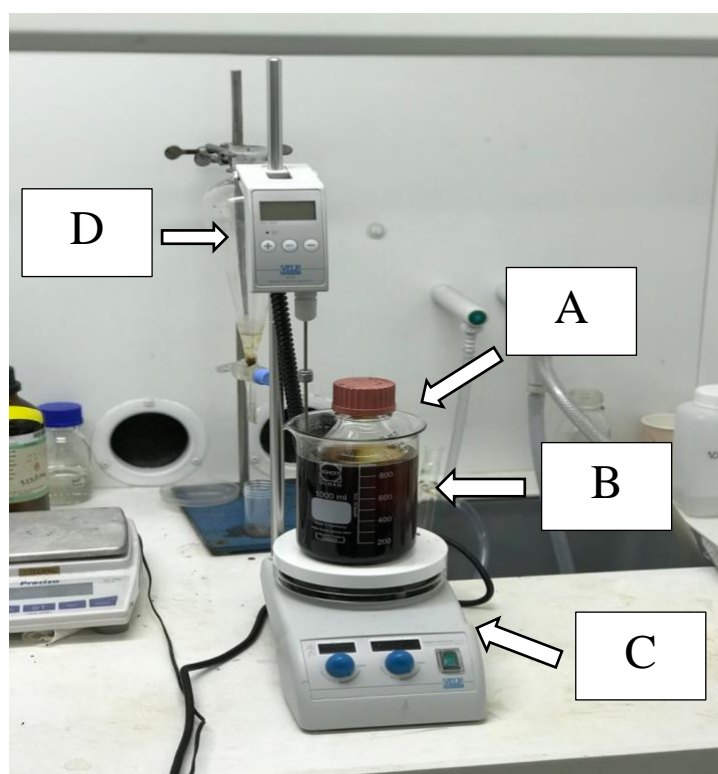


Figure 8.1

The used wood treatment equipment with the bottle with temperature resistant cap (200 °C max.) and magnetic stirring (A), uniform temperature distribution system with technical oil (B), heating magnetic electric plate (C) and digital thermometer (D).

### 8.3.1 Solid-liquid separation equipment

Figure 8.2 describes solid-liquid separation equipment. 2000 ml Büchner flask was used to collect liquid spent DES. Sieve with 180  $\mu\text{m}$  pore size was used to retain biomass. An electric vacuum pump was connected to the Büchner flask by a hose.

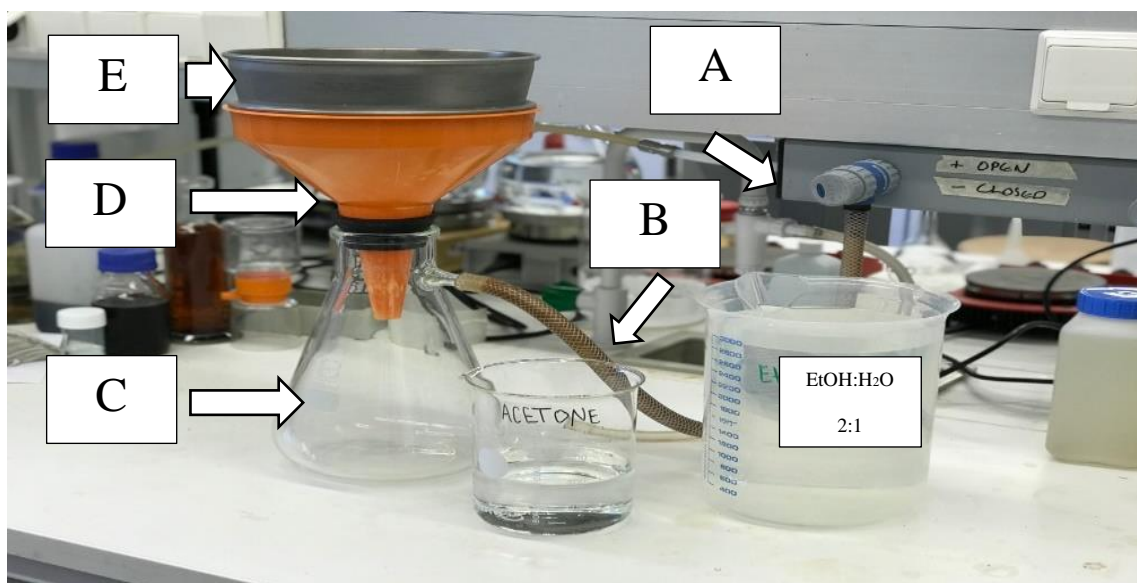


Figure 8.2 Used solid-separation equipment with electric vacuum pump (A), hose (B), Büchner flask (C), funnel (D) and sieve (E) are shown.

### 8.3.2 DES treatment procedure

30 grams of birch were taken and mixed with DES according to the following mass ratio: 1:10. The bottle with the sample and the DES was then placed inside the beaker on a plate. Using the digital thermoregulator, the required temperature of treatment was set to be at 120 °C. Following that, a speed of stirring and a rate of temperature's increase were set. The duration of the treatment was 6 hours. At the end of the treatment time of 6h, the flask was taken out and allowed to cool down slightly, before a solid-liquid separation part was carried out. Finally, the spent DES was collected in a Büchner flask. Solid undissolved biomass (pulp) was then washed to remove residual dissolved compounds and residual spent DES. In the beginning, the cake was washed by solution of ethanol in water (volumetric ratio 2:1 respectively). Subsequently, the pulp (treated wood sample) was washed with 400 ml of acetone. When the washing was completed, pulp was dried in the laboratory oven at 65°C for 16 hours. The appearance of the produced biomass cake is presented in Figure 8.3.

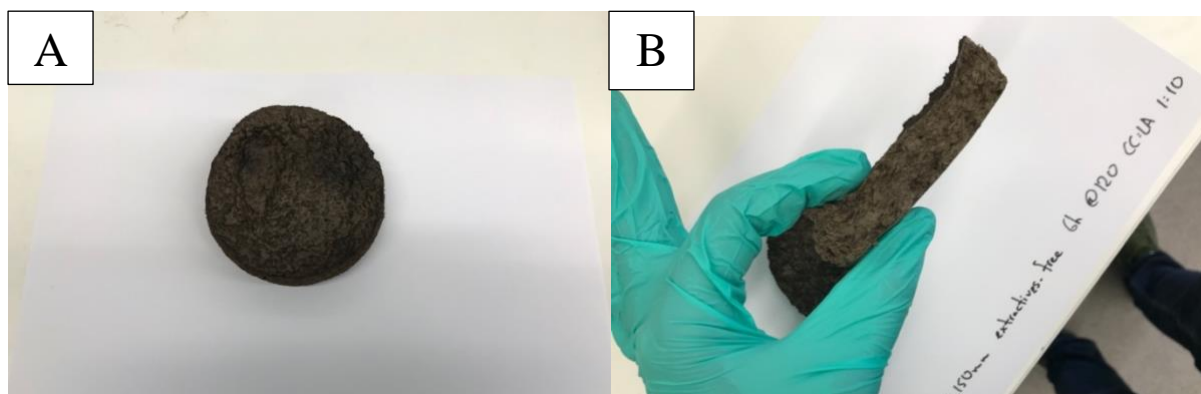


Figure 8.3 Formed biomass cake after the treatment of birch sample with DES where the left part depicts cake's appearance from above (A) and the right part depicts the inside of the cake (B).

## 8.4 Ultrafiltration of the solutions of spent DES in ethanol

As it was initially mentioned, the RC70PP UF membrane was used in all the experiments. A range of ultrafiltration experiments was set up in order to investigate the ability of RC70PP to concentrate lignin in spent DES. Concentration process presented a great interest from two points of view. Firstly, concentration process can reduce the volume of spent DES which leads to lower operational costs and lower amount of anti-solvent needed for lignin precipitation. Secondly, concentration process leads to obtaining DES with low lignin content (as permeate). This recycled DES can be used in the mixture with fresh DES, thus, reducing the amount of fresh DES and, consequently, reducing the cost of production. The most prominent difficulty that must have been tackled during all the ultrafiltration experiments was the high viscosity of spent DES. Two significant steps have been undertaken to lower a spent DES viscosity: 1) making solutions with ethanol and 2) raising filtration temperature. Regarding an optimal concentration of a spent DES solution, a variety of concentrations (from 10% to 90%) were made and tried. Regarding temperature, samples were firstly filtered at room temperature, then the samples of the same concentrations were filtered at 45 °C. Additionally, a filtration with initial suspended solids was carried out to compare it with filtration without initial suspended solids. This experiment could provide understanding on whether a solid-liquid (precipitate) separation was compulsory before ultrafiltration. After ultrafiltration experiments, both the obtained permeates and retentates were analyzed, for suspended solids, as well as for chemical content.

### 8.4.1 Research on optimal spent DES concentration in ethanol

Ultrafiltration cannot be conducted with pure DES due to its high viscosity. Hence, spent DES should be diluted with an organic solvent. A 99% ethanol was chosen because of its availability



and simplicity of operation with it. The purpose was to find an optimal spent DES/ethanol concentration. Precipitation at optimal concentration should be acceptable for ultrafiltration. The following spent DES/ethanol concentrations were prepared during the experiments – 10 vol%, 20 vol%, 40 vol%, 50 vol%, 60 vol%, 80 vol% and 90 vol%. All concentrations were volumetric. All of them were analyzed for suspended solids.

#### 8.4.2 Ultrafiltration equipment

The ultrafiltration experiments were conducted in Amicon dead end stirring cell equipment (Millipore, USA, Cat No.: XFUF07611, diameter of the stirring device 60 mm). The circular coupon cut from membrane batch was placed in the Amicon filtration cell between the spacer and the rubber O-ring for the better fixation of a coupon. Then the filtration cell was put together and filled with approximately 300 ml of DI water. The equipment is presented in Figure 8.4.

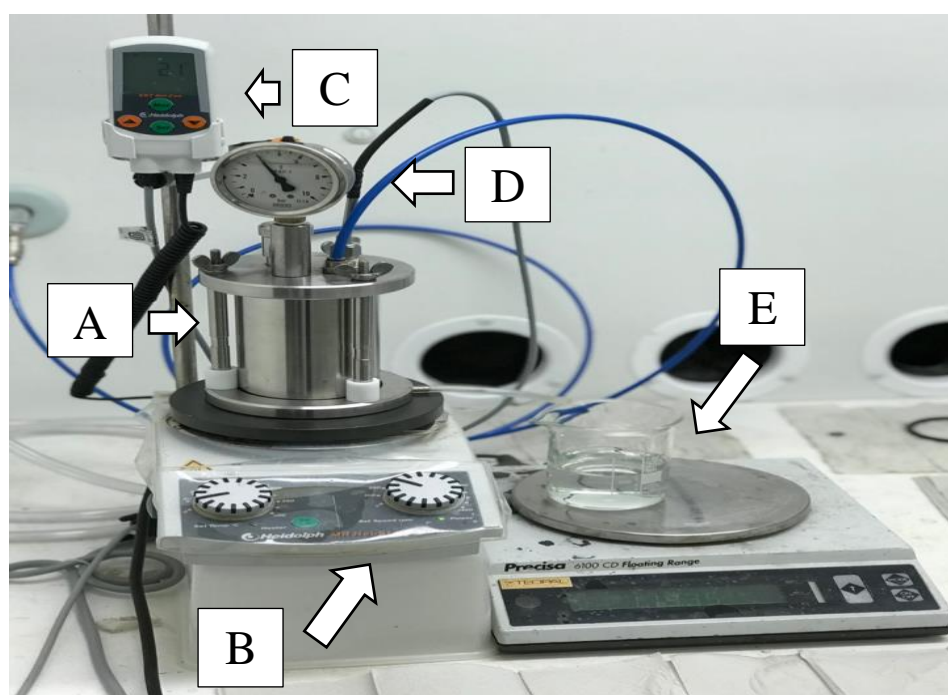


Figure 8.4

Used ultrafiltration equipment with Amicon filter with magnetic stirring (A), electric plate with stirring speed and temperature rate controllers (B), digital thermoregulator (C), compressor (not depicted) with barometer (D) and scales (E) is shown.

#### 8.4.3 Ultrafiltration Procedure

There were 3 batches of spent DES solutions. Each batch consisted of solutions of different concentrations of spent DES in ethanol. For the first batch concentrations were 10 vol%, 20 vol%, 40 vol%, 50 vol% and 60 vol%. For the second batch concentrations were 40 vol%, 50 vol%, 60 vol%, 80 vol% and 90 vol%. For the last, the third batch, concentrations were

20 vol%, 40 vol%, 60 vol% and 80 vol%. The second batch was conducted under the same conditions as the first batch, and only the temperature was different – 45 °C instead of 21 °C. A third batch was conducted under the same conditions as the second, but all the solutions in the last batch were filtered with the initial suspended solids content. Except for the mentioned differences in temperature and the presence of suspended solids, the procedure remained constant. Prior to ultrafiltration, suspended solids were separated from all the prepared solutions of spent DES (this separation was not carried out for the solutions from the third batch). All filtrations were carried out under the constant mixing at 250 rpm. Ultrafiltration was conducted in the Amicon filter. All filtration experiments began and finished with pure water flux measurement. Pure water flux was carried out according to the following rules: 10 minutes of filtration of deionized water at each pressure starting 2 bars in increments of 1 bar until 5 bars. In total, 40 minutes of pure water flux measurement. Prior to pouring spent DES solution into the filter chamber, it was washed with ethanol in order to remove the rest of the water after pure water flux measurement. When a spent DES solution was inside the chamber, temperature was set according to the temperature requirements for the current batch of solutions. The pressure was applied only when the temperature had reached the required value. The pressure value of ultrafiltration was constant for all batches of solutions – 3.5 bars. The information on the mass change of permeate during filtration was transferred from the scales to the computer and recorded there with the MassFlux software. Prior to the final pure water flux measurement, filter chamber was washed with ethanol and then with deionized water to eliminate the residues of the retentate.

## **8.5 Exposure of membranes to DES**

Membranes were exposed to DES in order to examine their ability to withstand the solvent. Resistance of the RC70PP to the pure DES and DES/ethanol solution was important to be studied. Knowledge on this topic can alter ultrafiltration process parameters as well as the membrane choice. Therefore, two purposes were pursued in this group of experiments: 1) observation of the interaction between DES and RC70PP; 2) observation of the interaction between 60% pure DES solution in 99% ethanol and RC70PP. Achievement of these purposes was implemented by the following methods: comparison of pure water fluxes measured before and after the membranes were exposed to pure DES (first batch of membranes) and 60% DES in ethanol -solution (second batch of membranes) for different time periods (1 week, 2 weeks, 3 weeks, 4 weeks); comparison of FTIR spectra of membranes before and after the exposure

and comparison of the retention values of membranes before and after the exposure. Filtration experiments were carried out using Amicon dead end stirring cell equipment.

There were two batches of membranes. One batch was exposed to pure DES while the other one was exposed to 60% solution of DES in ethanol. Every batch contained four membranes. Each membrane was exposed for a period of 1 week, 2 weeks, 3 weeks or 4 weeks. Exposure took place in glass beakers of with the membrane completely submerged in the solution. The beakers with the membranes are presented in Figure 8.5. Pure water flux measurement was conducted in accordance with the procedure mentioned in the Ultrafiltration of solutions of spent DES in ethanol section (see the paragraph 8.4).

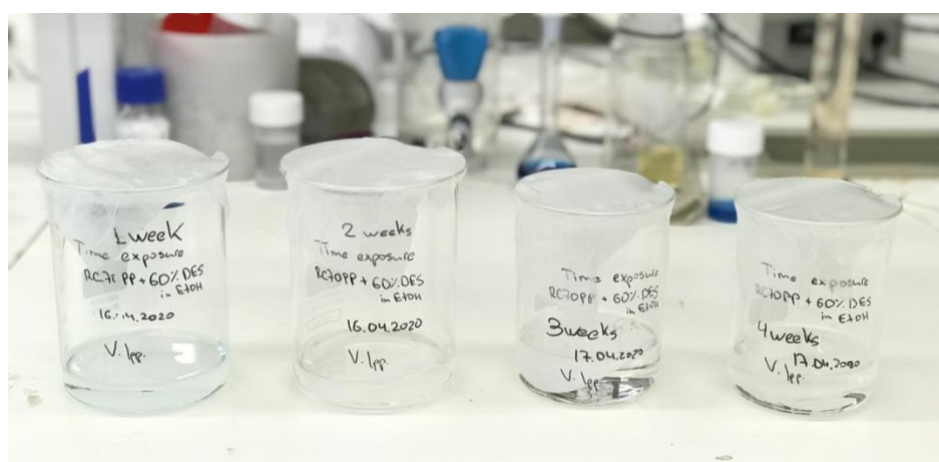


Figure 8.5 Four beakers with RC70PP membranes and DES solutions are shown.

## 8.6 Analyses

Analyses were conducted since, the initial and secondary suspended solids, the influence of DES and 60% DES solution on the membrane's surface and the influence of DES and 60% DES solution on the membrane's retention were unknown. The results of all these analyses would provide information to draw conclusions on the optimal concentration of spent DES in ethanol, on the efficiency of lignin separation by ultrafiltration, on the possible limitations of using the RC70PP membrane in DES recycling and on the changes of the membrane's performance within time.

### 8.6.1 Initial suspended solids in ethanol solutions

During the ultrafiltration experiments solutions of spent DES in 99% ethanol of the following volumetric concentrations were prepared: 10%, 20%, 40%, 50%, 60%, 80% and 90%. It is known that lignin is primarily solubilized in DES during the treatment (Zhu Chen et al., 2020). Solubilized lignin then precipitates with addition of water (Dion Smink et al., 2020). Solutions of spent DES in ethanol, which were prepared to lower spent DES viscosity, should have

contained some amounts of suspended solids, at least since, ethanol must contain some amount of water. Suspended solids, formed in solutions of spent DES and ethanol, were identified as initial. Determination of initial suspended solids in solutions was important because they affected ultrafiltration process. The analysis was conducted as vacuum filtration of the examined solutions through Glass microfiber filter of 110 mm in diameter and the pore size of 1.6  $\mu\text{m}$ . The cakes, formed on the surface of filters, were washed with 92.4% ethanol to make sure that all residual DES were filtered off. Subsequently, the filters with solids were dried in an oven at 65 °C for 16 hours. The weight of solids on the filters was used in calculations of initial suspended solids (Eq 4).

$$ISS = \frac{\text{weight of filter with solids} - \text{weight of filter without solids}}{\text{Volume}} \quad \text{Eq (4)}$$

Where, *ISS* stands for Initial Suspended Solids (mg/l);

*Volume* was constant for all solutions and it equaled to 0.1 L.

### 8.6.2 Secondary suspended solids in water solutions

Suspended solids, that were formed by mixing spent DES solutions with water, were identified as secondary suspended solids. If the previous analysis was aimed at determination of the optimal concentration of spent DES in ethanol, secondary suspended solids analysis was aimed at displaying the efficiency of ultrafiltration in terms of lignin separation. After ultrafiltration of 10%, 20%, 40%, 50%, 60%, 80% and 90% spent DES in ethanol solutions, their permeates and retentates were collected. Water solutions for determination of secondary suspended solids were prepared by taking 10 ml of each permeate and retentate separately and mixing each of them with 90 ml of deionized water. Then the solutions were kept at room temperature (21 °C) for 16 hours to precipitate. Eventually, 10% solutions of permeates and retentates in pure water with precipitated solids were obtained. All solutions are depicted in Figure 8.6.

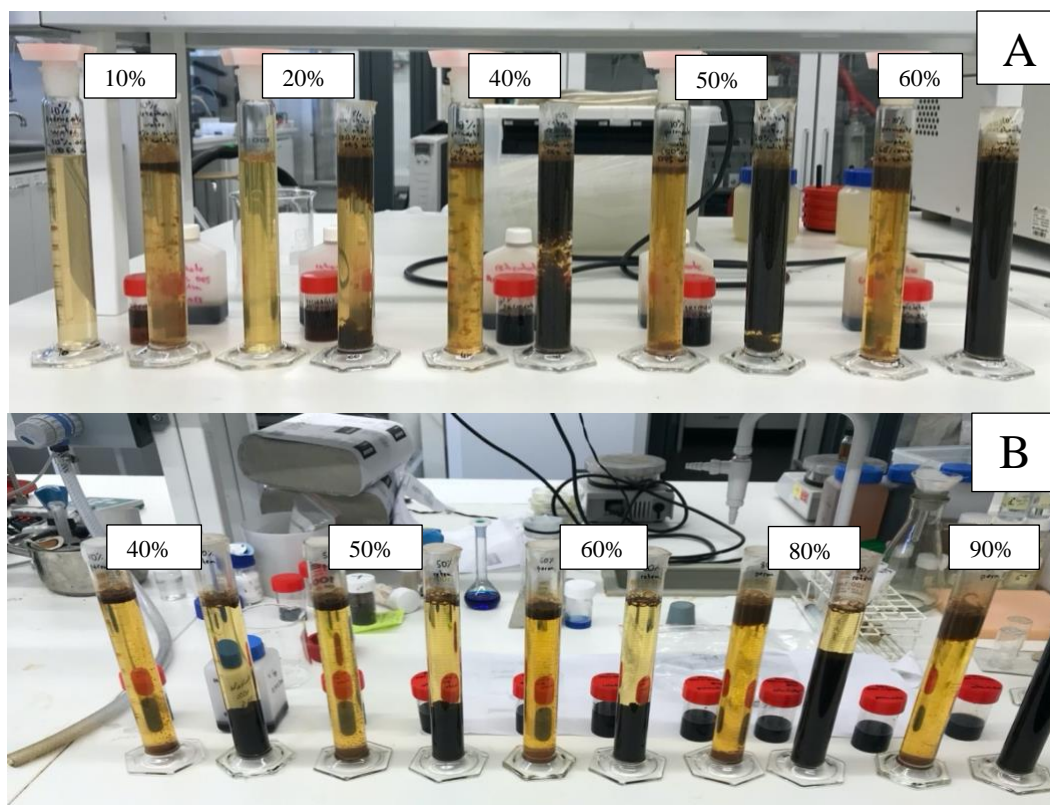


Figure 8.6 10% Solutions of retentates and permeates in pure water after being left to precipitate overnight. Solutions from the first batch (A) and the second batch (B) are shown. Solutions of permeates alternate with solutions of retentate. Each second solution from the left is a retentate solution.

The process of solid-liquid separation was conducted exactly in the same way as the solid-liquid separation process from the determination of initial suspended solids analysis. Calculations were based in the same Eq 10.

### 8.6.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis of secondary suspended solids in permeates and retentates

FTIR analysis was carried out in order to investigate the differences in chemical content between permeates and retentates. Dried solids residuals were collected from the solutions of permeates and retentates in water after filtration. Solid-liquid separation was performed likewise the described above procedure for the initial and secondary suspended solids collection. However, the earlier mentioned Glass Microfiber Filter was not suitable for scrubbing the solids from it. Due to this fact, the different type of filter was used – Nylon Membrane Filter of 47 mm in diameter and the pore size of 0,2  $\mu\text{m}$ . FTIR analysis was performed by the Perkin Elmer Frontier spectrometer with a universal ATR module with a diamond crystal. For all the analyses, FTIR spectra was measured in the wavelength range of 4000-400  $\text{cm}^{-1}$  with the spectra resolution of 4  $\text{cm}^{-1}$  in the absorbance mode. For the use of

final interpretation of the results, ATR correction, baseline correction, normalization and smooth correction (smooth factor 20) were performed on the spectra results.

#### **8.6.4 Fourier Transform Infrared Spectroscopy (FTIR) Analysis of the membranes exposed to DES**

Four membranes each were either exposed to DES or to 60% solution of DES in 99% ethanol, the duration of the exposure was between 1 to 4 weeks. All membranes were completely submerged into liquid. Each week one membrane from each group was taken, properly washed with deionized water for at least 1 minute to remove DES and analyzed by FTIR.

#### **8.6.5 Total Carbon analysis**

The effect of DES on the performance of the membrane was also examined by their polyethylene glycol (PEG) retention. This was done by studying their PEG retention before and after exposure in either pure DES or 60% DES in ethanol solution using a PEG (4 kDa) solution of 300 ppm at 2 bar and at 21 °C in the Amicon module. PEG solutions did not contain inorganic carbon, and thus, the amount of total carbon was the same as the amount of total organic carbon. Retentates and permeates were analyzed with the TOC-L, Shimadzu Total Organic Carbon Analyzer.

## 9 Results and discussion

Two major types of results have been obtained during the experimental part: 1) results from the experiments to determine the concentration of spent DES in 99% ethanol which leads to the greatest efficiency of the following ultrafiltration process ; 2) results from the long-time exposure of membranes to pure DES and also to 60% solution of pure DES in 99% ethanol.

An optimal concentration of spent DES in ethanol has been critically important to investigate due to several reasons: 1) spent DES is a highly viscous substance, hence, filtration requires high pressure and great energy consumption so the viscosity should be lowered; 2) significant amount of solvent, such as 99% ethanol, leads to higher loadings and thus, to greater stress on the whole system, so the amount of solvent should be minimized or at least its recycling should be possible; 3) spent DES is rich in dissolved compounds, such as lignin, which can precipitate even in 99% ethanol. Precipitation of dissolved compounds is not desirable during the membrane filtration process due to fouling risks, so the amount of ethanol should not induce precipitation during the filtration. Using the these set requirements, the following results have been analyzed: a comparison of fluxes of spent DES solutions through the RC70PP membrane of the wide range of concentrations (10 - 90 vol%); a comparison of fluxes of spent DES solutions through the RC70PP membrane under different temperatures (20 °C or 45 °C); a comparison of fluxes of spent DES solutions through the RC70PP membrane with and without precipitated suspended solids in the feed; a comparison of the amounts of precipitation in spent DES solutions of different concentrations; a comparison of the amount of precipitation in permeates and retentates produced in the ultrafiltration of spent DES solutions; a comparison of chemical contents of permeates and retentates produced in the ultrafiltration of spent DES solutions. The results also allow to draw a conclusion on the stability of the RC70PP membrane in the exposure to DES used in this study.

### 9.1 Ultrafiltration of spent DES in ethanol

In this part 6 kinds of results are discussed: precipitation in spent DES solutions, influence of spent DES concentration on flux, influence of temperature on flux, influence of precipitate's presence on flux, separation efficiency and chemical content of precipitates in permeates and retentates after ultrafiltration. The results should show the feasibility of recycling spent DES via ultrafiltration and also the most optimal concentration of spent DES in 99% ethanol.

#### 9.1.1 Influence of ethanol addition on precipitation in DES solutions

Eight different concentrations of spent DES in 99% ethanol have been prepared. They included 10 vol%, 20 vol%, 40 vol%, 50 vol%, 60 vol%, 80 vol%, 90 vol% and 100 vol% (pure spent

DES). All the solutions were analyzed for initial suspended solids. Solution with an optimal concentration of spent DES and ethanol should have considerably small amount of suspended solids along with relatively low viscosity. These two factors should lead to filtration with bigger flux. Correlation between the amount of suspended solids and concentration of the spent DES solutions is presented in Figure 9.1.

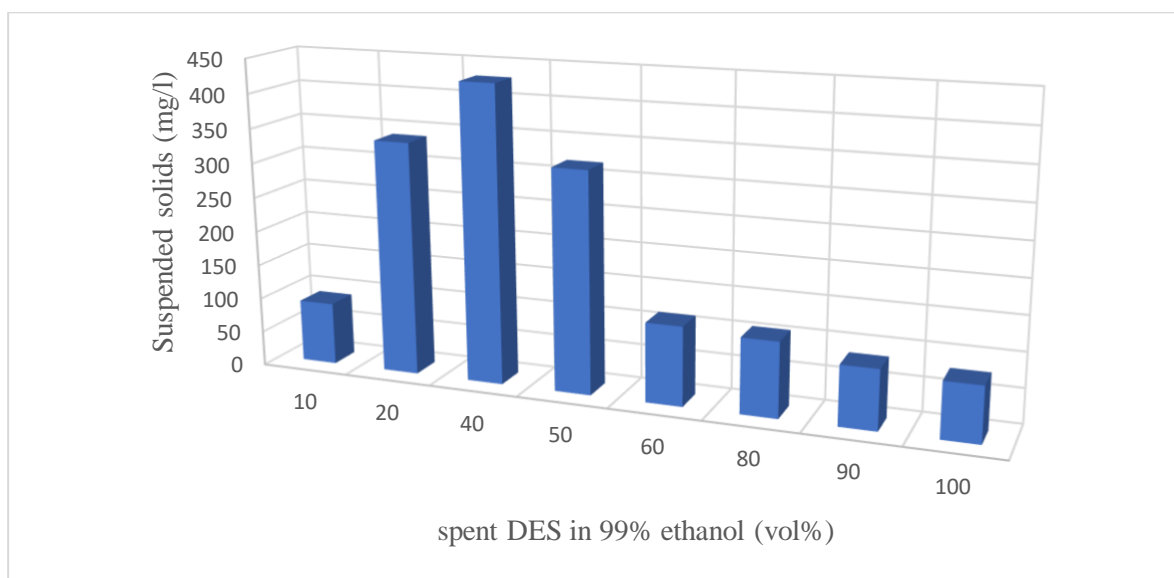


Figure 9.1 Quantities of initial suspended solids in different spent DES solutions

Fig 9.1 shows the pattern of initial suspended solids in spent DES solutions. The maximum concentration of suspended solids was found in 40% solution – 429 mg/l. The 20% and 50% solution also have considerable amount of suspended solids – 338 mg/l and 319 mg/l respectively. The rest of the solutions show low amount of suspended solids (below 120 mg/l). The 10% solution can be eliminated from consideration since, it requires the greatest amount of solvent. Consequently, a loading rate and a stress level on filtration system will be more significant. The 100% spent DES can be omitted from consideration as it exhibits the highest viscosity among all. The choice for an optimal concentration should lie among the three solutions – 60%, 80% and 90%. Suspended solids values for these solutions are 114 mg/l, 108 mg/l and 86 mg/l, respectively. These three solutions were taken further to the filtration experiments.

One disadvantage presented in Figure 9.1, was that bar chart displays the amounts of initial suspended solids in the solutions which have been prepared using different amounts of spent DES and different amounts of 99% ethanol. For better visualization of the influence of ethanol on precipitation of solids, the amount of suspended solids should be recalculated, whereby the amount of spent DES in all solutions are equal. In other words, concentrations of the solutions



remain constant, spent DES volume remains constant so there is only the one variable parameter – the volume of ethanol. It was decided to recalculate all the solutions to 10 ml of spent DES. Calculations are based on Eq 5.

$$RSS = \frac{10 \text{ ml} \cdot \text{Suspended solids in solution}}{\text{Volume of spent DES in solution}} \quad \text{Eq (5)}$$

Where, *RSS* stands for Recalculated Suspended Solids in the solution (mg/l);  
 10 ml is constant volume of recalculation;  
*Suspended solids in solution* displays the amount of suspended solids in the solution (mg/l);  
*Volume of spent DES in solution* displays the volume of spent DES in the solution of (ml).

Recalculated bar chart is depicted in Figure 9.2.

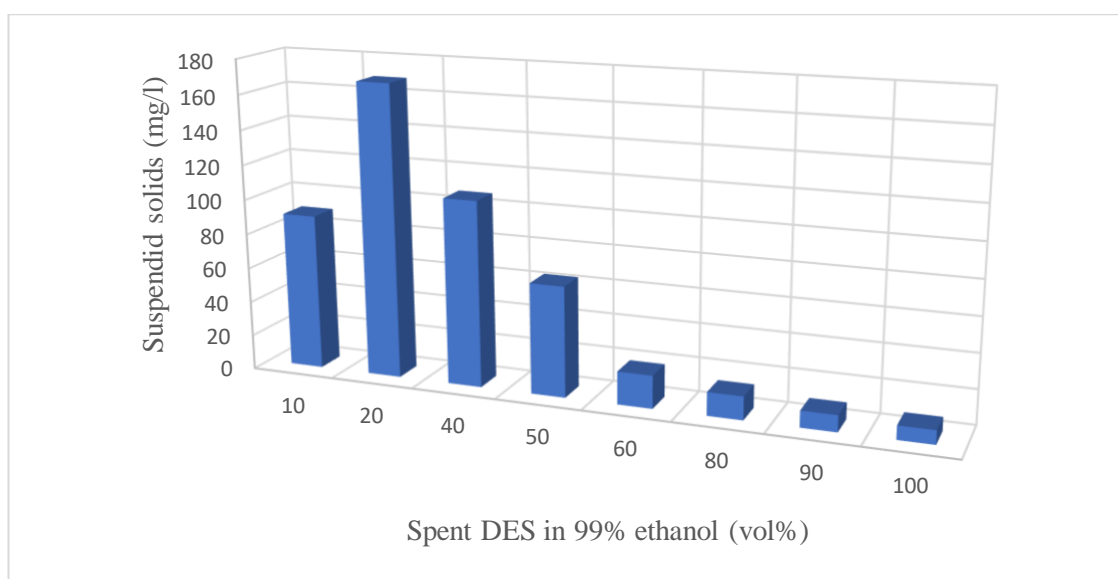


Figure 9.2 Recalculated per 10 ml quantities of suspended solids in different spent DES solutions

The peak of suspended solids quantity is shifted from 40% solution to 20% solution. According to Figure 10.2, there were 4 solutions that has considerable amounts of suspended solids – 10%, 20%, 40% and 50% solutions having 90 mg/l, 169 mg/l, 107 mg/l and 64 mg/l of suspended solids respectively. 100% of spent DES is still out of debate due to its viscosity. Thus, 60%, 80% and 90% solutions resulted in 19 mg/l, 14 mg/l and 10 mg/l of suspended solids respectively.

### 9.1.2 Influence of spent DES concentration on flux

Ultrafiltration was conducted for all the solutions. Solutions from 10% to 60% were filtered at 21 °C. Filtration of 50% and 60% solutions was quite time-consuming due to the very low flux so the next batch of solutions – from 40% to 90% – was filtered at 45 °C. Despite the difference in temperatures of filtration between solutions, the influence of spent DES concentration on flux can still be observed by comparing patterns of flux behavior over concentrations. The graphs are presented in Figure 9.3.

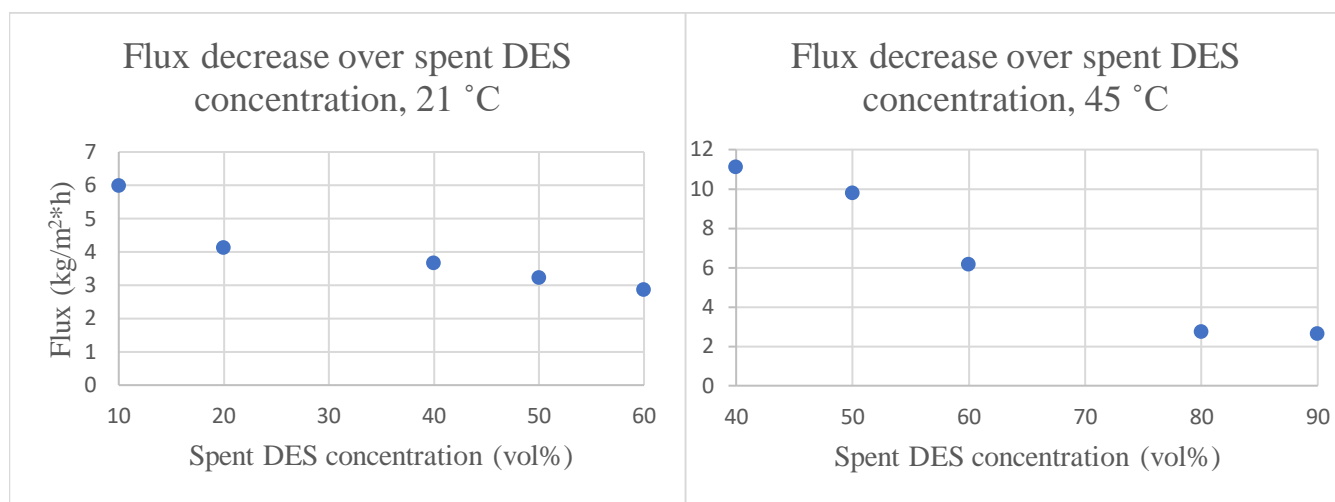


Figure 9.3 Relation between flux and concentration under 21 °C and 45 °C filtration in Amicon with the RC70PP membrane at 3.5 bar and 250 rpm

It is noticeable that patterns for fluxes at different temperatures are non-linear. In each graph there is a point after which the gradient of flux decrease becomes much smaller than it was before. In other words, when filtrating solutions of different concentrations, gradient of flux decrease is changing in an unstable manner till the point (the solution of specific concentration) after which flux decreases in a stable and steady manner. For the left graph, 20% solution is a threshold after which no significant decrease is observed. For the right graph, 80% solution represents this point.

### 9.1.3 Influence of temperature on flux

With the objective to investigate the way that temperature affects the flux, the same concentrations of spent DES in 99% ethanol were filtered at two different temperatures – 21 °C and 45 °C. The graphs, which are depicted in Figure 9.4. show comparison of the fluxes of the solutions and the relation between temperature and flux.

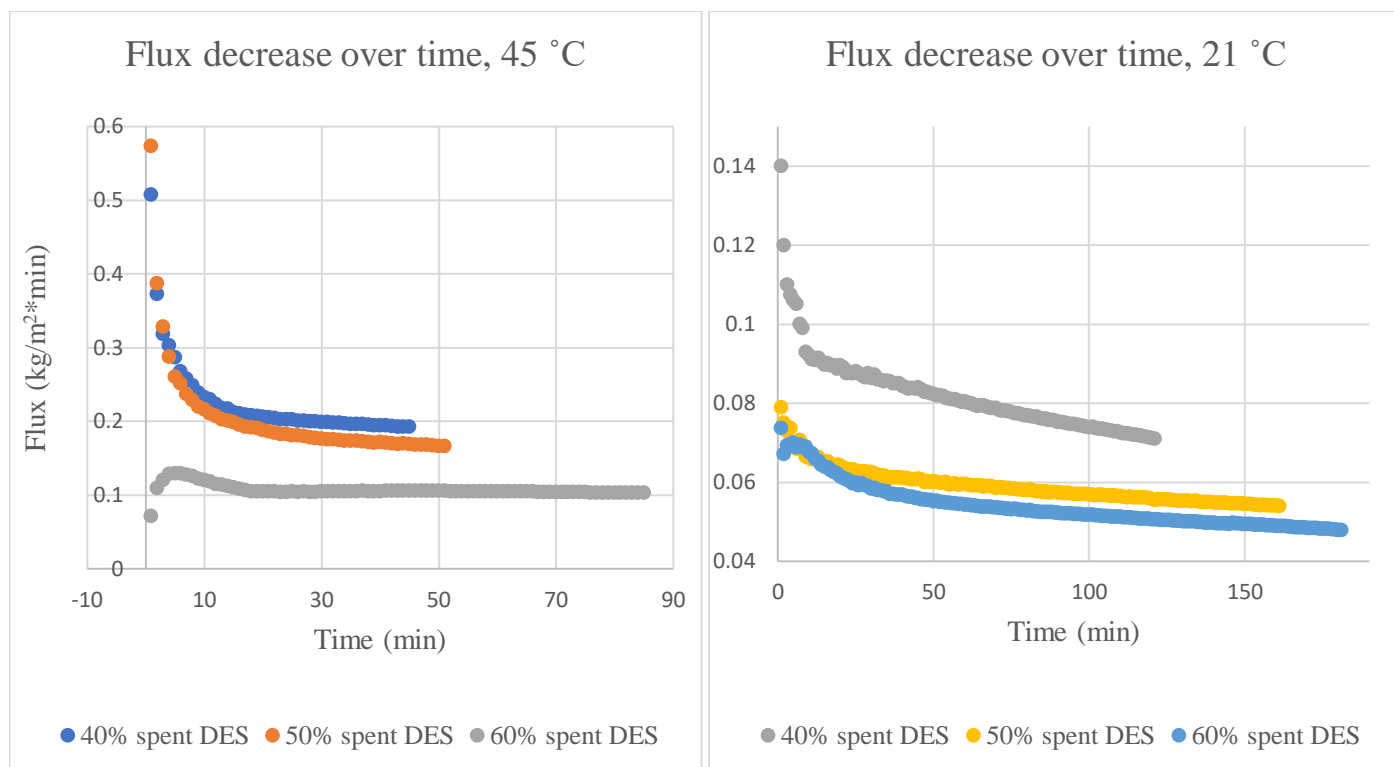


Figure 9.4 Flux behavior over time due to different temperatures for filtration in Amicon with the RC70PP membrane at 3.5 bar and 250 rpm

Both graphs demonstrate the correlation between flux through the membrane and the time, required to collect around 33 grams of permeate. It should be noticed that suspended solids were separated from all the solutions before the membrane filtration. Filtration at 21 °C demonstrates very low fluxes for all studied in this experiment solutions. For 50% and 60% solutions fluxes are even below 0.1 kg/m<sup>2</sup>\*min. Filtration at 45 °C shows bigger fluxes. At this temperature filtration seems more stable. Nevertheless, even at 45 °C 60% solution demonstrated low flux, fluctuating around 0.1 kg/m<sup>2</sup>\*min. Thus, the higher spent DES solution concentration, the higher temperature is required for a stable flux. Generally, filtration at 45 °C resulted to be more efficient for all tested solutions comparing to the filtration at 21 °C.

The second parameter that presents an interest is a length of filtration. The length data is presented in Table 9.1.

Table 9.1 Duration of filtration of spent DES solutions

Spent DES concentration	Time of filtration under 21 °C (min)	Time of filtration under 45 °C (min)
40%	121	45
50%	161	51
60%	181	85

Although the greatest reduction of the filtration time happened for the 50% solution (3 times faster), the rest of the solutions also demonstrate good time reduction values (more than 2 times). It means that raising the temperature of filtration accelerates the process significantly in the range of solutions' concentrations from 40% to 60%. After 45 °C filtration, the membrane did not exhibit any noticeable damages or changes in its appearance (except for some brown dots close to its center), however, pure water flux before and after filtration need to be analyzed in order to observe any impact of temperature and solution concentration on the performance of the membrane and possible fouling. The results on pure water permeabilities before and after the filtration of the spent DES solutions as well as the results on the loss of permeability after filtration of the treated solutions at different temperatures are gathered and presented in Table 9.2.

Table 9.2 Pure water permeability of the RC70PP membrane before and after the filtration of spent DES.

T°	Spent DES concentration	Permeability before (kg/m <sup>2</sup> ·h)	Permeability after (kg/m <sup>2</sup> ·h)	Loss of pure water permeability
21 °C	40%	19	15	20%
	50%	18	15	17%
	60%	18	16	11%
45 °C	40%	16	12	21%
	50%	17	14	18%
	60%	17	15	12%

Fouling is crucial in membrane process because it has a straight effect on the efficiency. Despite, the differences in temperatures, pattern remains constant and the values for each solution are very similar. According to the Table 9.2, the loss of pure water permeability decreases from 40% solution to 60% solution and it seems that the membrane used in the filtration of 60% spent DES in 99% ethanol was least fouled.

#### **9.1.4 Influence of suspended solids on flux**

Solutions of three concentrations – 40%, 60% and 80% of spent DES in 99% ethanol – were chosen for the experiment which was aimed at exploring the impact of the presence of suspended solids on flux through the RC70PP membrane and the impact on membrane's fouling. During filtration, all parameters were constant except for the presence of suspended solids in the first three solutions. The temperature was chosen to be 45 °C because filtration at this temperature was most efficient. Fouling effect was measured similarly to the previous experiment – through comparing pure water permeabilities before and after ultrafiltration of the investigated solutions (see Table 9.4). All the analytical discussion on the investigation are depicted in Figure 9.5. In Figure 9.5 both graphs show the correlation between flux through the RC70PP membrane and the time required to collect 33 grams of permeate. The 40% solution's curve behaves exponentially in both graphs. As was suggested in the previous chapter, the constant exponential movement of the curve was attributed to high amount of suspended solids. Thus, it can be claimed that 40% solution is prone to clog membrane's pore regardless temperature and preliminary separation of suspended solids before filtration. On the other hand, the 60% solution's curves behave differently. When filtrating without preliminary separation of suspended solids, the concentration of solids in the Amicon filter chamber is genuinely high, therefore, flux decreases exponentially.

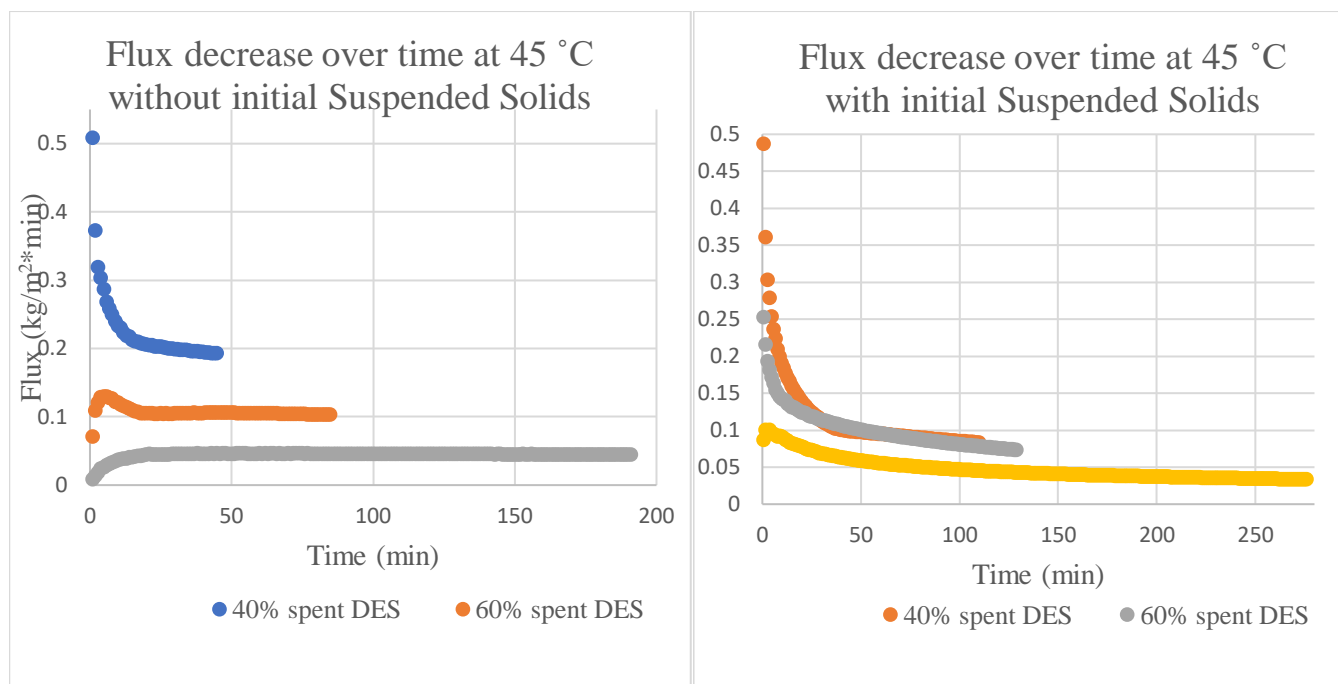


Figure 9.5 Flux behavior over time without and with initial suspended solids during filtration in Amicon with the RC70PP membrane at 3.5 bar and 250 rpm

According to the paragraph 9.1.1, the 80% solution of spent DES contains relatively small amount of suspended solids (for example, 80% solution shows in 8 times per 10 ml less amount of suspended solids than 40% solution). This fact leads to the less intensive pore blocking during filtration with suspended solids.

Considering, that the flux even rises and then levels off in the second graph, it can be suggested that there is no secondary suspended solids formation in the filter chamber in case of 80% solution filtration. It should be noted that filtration of the solutions without initial suspended solids was less time-consuming than without this separation. The data on filtration durations is presented in Table 9.3.

Table 9.3 Duration of filtration of spent DES solutions in Amicon with the RC70PP membrane at 3.5 bar and 250 rpm

Spent DES concentration	Filtration duration with initial suspended solids (min)	Filtration duration without initial suspended solids (min)
40%	110	45
60%	129	85
80%	275	191

Compelling increase in filtration duration is evident. As it was established in paragraph 9.1.1 that 40% solution contains the greatest amounts of suspended solids, it demonstrates the greatest difference in durations – without initial suspended solids it goes 60% faster. For the rest of solutions, the difference is smaller – around 30% faster without initial suspended solids. In order to better estimate the efficiency of ultrafiltration with suspended solids, it is necessary to examine and compare pure water fluxes before and after filtration. The results on permeabilities before and after ultrafiltration as well as the results on the loss of permeability after filtration of the 3 observed solutions are gathered and presented in Table 9.4.

Table 9.4 Permeability of the RC70PP membrane before and after filtration in Amicon at 3.5 bar and 250 rpm

Initial suspended solids	Spent DES concentration	Permeability before (kg/m <sup>2</sup> ·h)	Permeability after (kg/m <sup>2</sup> ·h)	Loss of pure water permeability
Present	40%	19	10	46%
	60%	16	8	49%
	80%	19	7	63%
Absent	40%	16	12	21%
	60%	17	15	12%
	80%	19	15	14%

Values for the loss of pure water permeability for the solutions without preliminary solid-liquid separation are much higher than the values for solutions with a pre-solid-liquid separation. Solutions with initial suspended solids have quite similar values of the loss of permeability for 40% and 60% solutions – 46% and 49% respectively. At the same time, 80% solution with initial suspended solids had a drastic impact on membrane causing 63% of loss of pure water permeability. For the other type of solutions, the pattern is completely different. 40% solution shows the greatest influence on the membrane, 21% of loss of permeability. Meanwhile, 60% and 80% solutions showed similar values of the loss of permeability, 12% and 14% respectively.

In summarizing, it can be reported that ultrafiltration is between 30% to 60% faster when filtrating solutions without the initial suspended solids and that the loss of membrane pure water permeability is 2 to 6 times higher, when filtrating the solutions with the initial suspended solids. Consequently, preliminary solid-liquid separation makes ultrafiltration of spent DES

solutions more efficient. 60% spent DES solution exhibited medium values of the decrease in duration when preliminary solid-liquid separation is introduced (about 34% reduction in the filtration time) and also medium values of the loss of membrane permeability both with and without initial suspended solids – 49% and 12% respectively.

### 9.1.5 Separation efficiency

Discussed hitherto impact of temperature and the presence of suspended solids is very important in terms of analyzing the best parameters of ultrafiltration. However, the efficiency of ultrafiltration process should be discussed. Though the differences of process duration were previously observed, it is just the one aspect of efficiency. The most significant characteristic is separation. Furthermore, results were obtained from mixing separately 10 ml of permeates and retentates from the ultrafiltration experiments with 90 ml of water were analyzed. A range of 10% solutions of permeates and retentates in water was made. A suspended solids formation was observed since, water is an antisolvent (S. Hong et al., 2019). These suspended solids are identified in this work as secondary suspended solids. In order to observe the influence of temperature of ultrafiltration on separation efficiency, the permeates and retentates of three solutions (40%, 50% and 60% solutions), which were previously filtered at 21 °C and 45 °C with preliminary separation of suspended solids, were used in the experiments. Hence, there are two bar charts to compare – one with suspended solids in permeates and retentates after ultrafiltration at 21 °C, and another one with suspended solids in permeates and retentates after ultrafiltration at 45 °C. The bar charts are depicted in Figure 9.6.

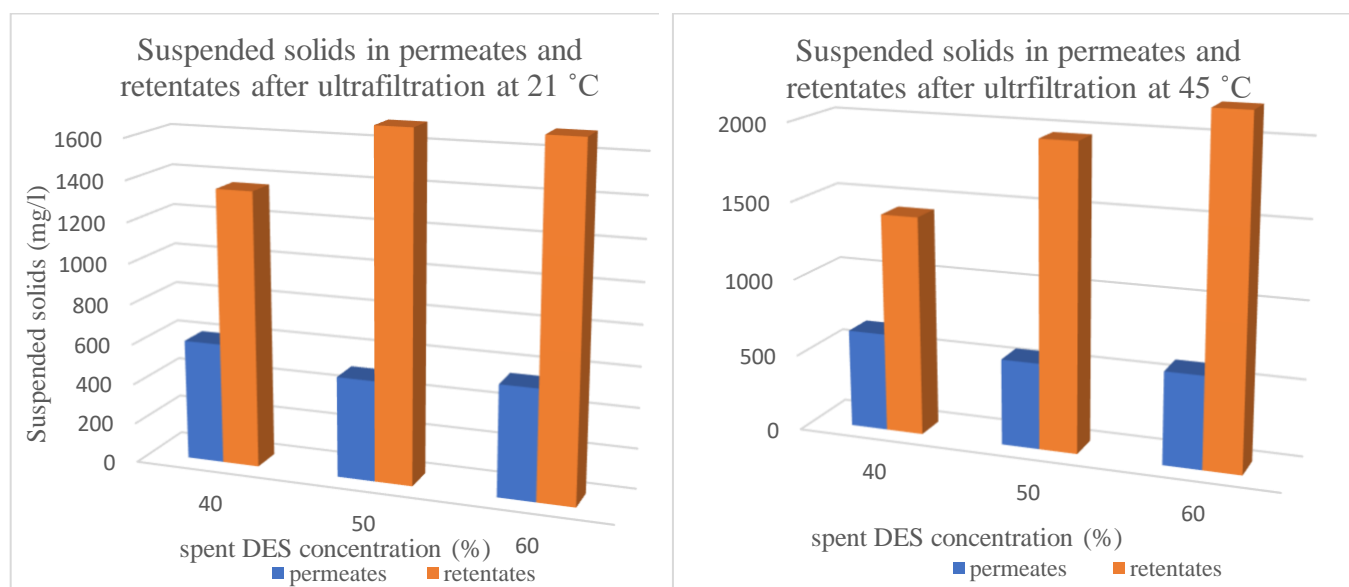


Figure 9.6 Suspended solids content in permeates and retentates after ultrafiltration at 21 °C and 45 °C in Amicon with the RC70PP membrane at 3.5 bar and 250 rpm



It is noticeable that in all pairs the content of secondary suspended solids in retentates is much higher than in permeates. It means that chosen parameters and equipment of ultrafiltration eventually lead to partial lignin separation. According to Figure 9.6, bar charts of suspended solids in permeates and retentates, obtained under different temperatures, are extremely similar to each other. The level of secondary suspended solids in all the permeates fluctuates around 600 mg/l whereas the quantity of suspended solids in retentates rises. The level of suspended solids in permeates fluctuates around one value because of the membrane characteristics. The level of suspended solids in the retentates increases because the concentration of spent DES is rising. The values of suspended solids in permeates and retentates as well as the concentration of retained solids are presented in Table 9.5.

Table 9.5 Separation efficiency for 40%, 50% and 60% spent DES solutions after filtration in Amicon with the RC70PP membrane at 3.5 bar and 250 rpm

T°	Spent DES concentration	Suspended solids in permeate (mg/l)	Suspended solids in retentate (mg/l)	Concentration of retained solids
21 °C	40%	600	1360	69%
	50%	500	1800	78%
	60%	550	2400	81%
45 °C	40%	640	1420	69%
	50%	560	1960	78%
	60%	600	2210	79%

The amount of secondary suspended solids was measured for the pairs of permeates and retentates. The concentration of retained solids was calculated based Eq 6.

$$CRS = \frac{SS \text{ in retentate}}{SS \text{ in permeate} + SS \text{ in retentate}} \cdot 100 \quad \text{Eq (6)}$$

Where, *CRS* stands for Concentration of Retained Solids (%);

*SS in permeate* – the amount of suspended solids in the 10% solution of the permeate in water (mg/l);

*SS in retentate* – the amount of suspended solids in the 10% solution of the retentate in water (mg/l).

In Eq 6 permeate and retentate are obtained from the filtration of solution of spent DES in ethanol. It is apparent that separation efficiency is not affected by temperature of ultrafiltration. The values of concentration of suspended solids in retentates are the greatest for 60% solution regardless temperature. It is then concluded that 60% solution of spent DES in 99% ethanol demonstrates the best separation efficiency. Aside from the mentioned solutions, suspended solids were also measured in permeates and retentates of 10%, 20%, 80% and 90% spent DES solutions. Permeates and retentates from 10% and 20% solutions were obtained by ultrafiltration at 21 °C while 80% and 90% solutions were filtered at 45 °C. The results can be found in Table 9.6.

Table 9.6 Separation efficiency for 10%, 20%, 80% and 90% spent DES solutions after filtration in Amicon with the RC70PP membrane at 3.5 bar and 250 rpm

T°	Spent DES concentration	Suspended solids in permeate (mg/l)	Suspended solids in retentate (mg/l)	Concentration of retained solids
21 °C	10%	10	200	95%
	20%	100	500	83%
45 °C	80%	660	2482	79%
	90%	700	2800	80%

Presented in Table 9.6 four solutions demonstrates quite high levels of efficiency in terms of retention. 10% and 20% solutions show 95% and 83% retention respectively. However, these solutions are too diluted in order to consider their usage in practice. 80% and 90% solutions demonstrate 79% and 80% retentions respectively. These values are good but comparable with 60% solution, which have 79% concentration of retained solids. At the same time, 60% solution is much less viscous and thus, it is more promising in terms of membrane filtration.

#### 9.1.6 Chemical content of precipitates

Suspended solids precipitated by water were dried and analyzed by FTIR. The difference in peaks between permeates and retentates will detect the substance that is present either only in retentates or only in permeates. A comparison between permeates' and retentates' peaks is conducted separately for each solution of spent DES in ethanol 40%, 50% and 60%. The peak at 1235 cm<sup>-1</sup> identifies either lignin or hemicellulose. However, hemicellulose is soluble in water (M.T. Holtzapple, 2003). It means that in the analyzed precipitates from water solutions

of permeates and retentates no hemicellulose should be present. Main peaks for lignin and hemicellulose are examined. These values of peaks are presented in Table 9.7.

Table 9.7 Main peaks for FTIR of precipitates from water solutions of permeates and retentates

Absorption peak wave number (cm <sup>-1</sup> )	Biomass component	Characteristic bond and movement
1734	Extractives	C=O vibrations of unconjugated esters, ketones, aldehydes frequently of carbohydrate origin 1,2
1605-1598	Lignin	Aromatic ring stretching in lignin 3,4
1515-1502	Lignin	Aromatic ring stretching in lignin, C=C stretching of the aromatic ring in lignin 3,5
1370-1365	Cellulose/Hemicellulose	CH <sub>2</sub> bending in cellulose and hemicellulose 5,6
1329	Lignin/Cellulose	C-O vibration in guaiacyl and syringyl rings, C-H cellulose 4,7
1235	Hemicellulose/Lignin	Syringyl ring and C=O stretch in lignin and xylan 4
1157-1156	Cellulose/Hemicellulose	C-O-C vibration in cellulose and hemicellulose 4,8

<sup>1</sup> R. Herrera et al., 2014; <sup>2</sup> Z.H.Li et al., 2011; <sup>3</sup> Esteves et al., 2013; <sup>4</sup> Muller et al., 2009; <sup>5</sup> Kocaeft et al., 2008; <sup>6</sup> Missio et al., 2015; <sup>7</sup> H. Chen et al., 2010; <sup>8</sup> Peng et al., 2015.

The comparison of FTIR graphs in case of 40% solution is presented in Figure 10.7.

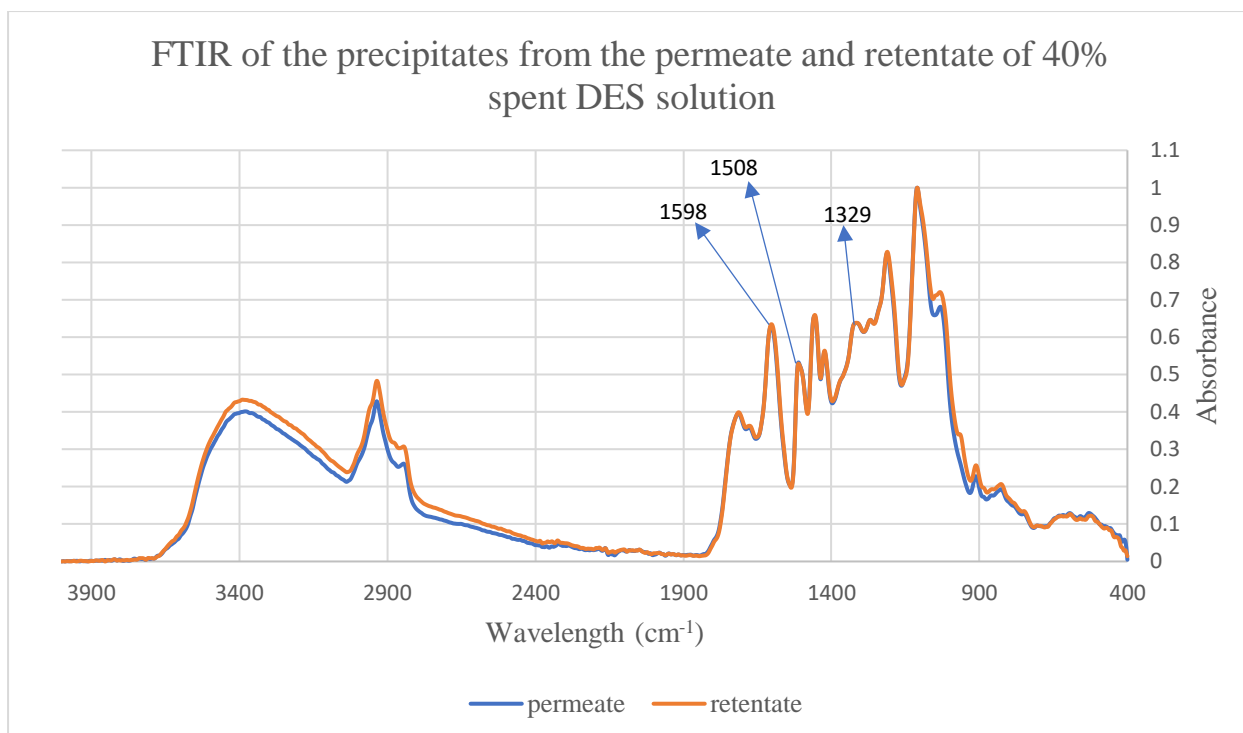


Figure 9.7 Comparison of FTIR graphs of the permeate and the retentate of the 40% solution of spent DES in 99% ethanol

It is noticeable in Figure 9.7 that all the peaks of the permeate completely match to all the peaks of the retentate. Thus, in case of the 40% solution no complete separation of any component was observed based on the FTIR analysis. Chemical content of the permeate is absolutely the same as the chemical content of the retentate. Main peaks for lignin are present in both graphs, though with slight shifts. The peaks for hemicellulose are missing. The comparison of FTIR graphs in case of 50% solution is presented in Figure 9.8. The graphs of the permeate and the retentate in Figure 9.8 also share the same peaks – this pattern has already been noticed in the case of 40% solution.

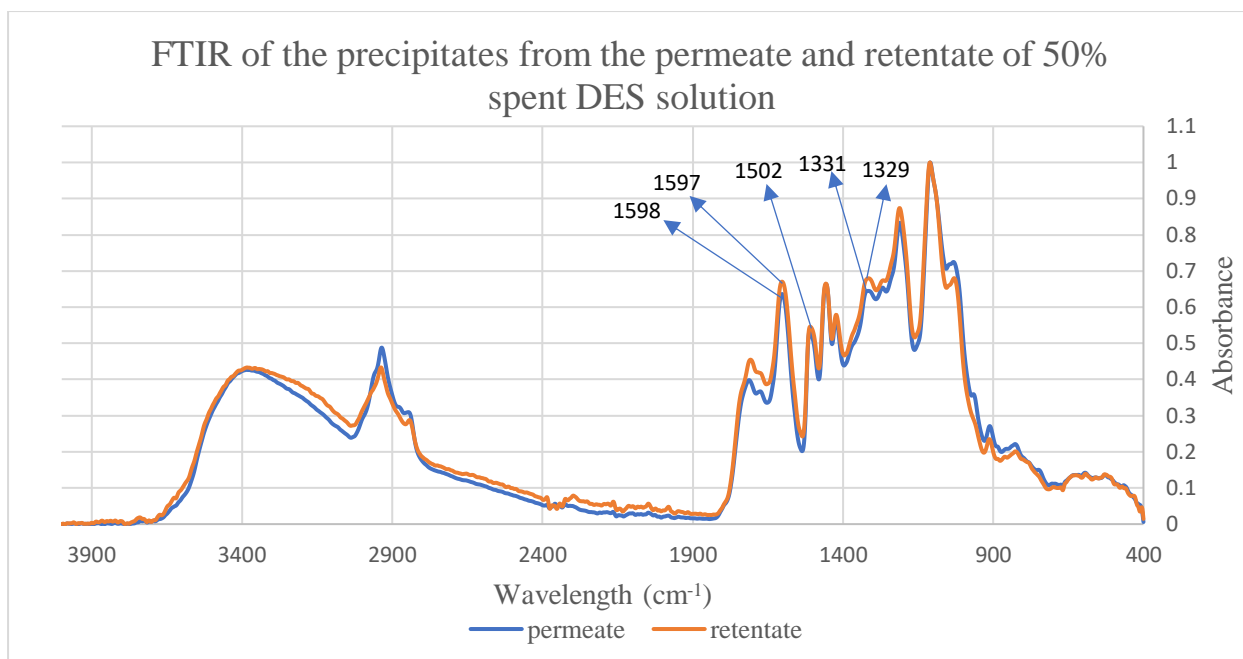


Figure 9.8 Comparison of FTIR graphs of the permeate and the retentate of the 50% solution of spent DES in 99% ethanol

The base peaks for lignin are present. The peaks for hemicellulose are not detected. Generally, the chemical contents of the permeate and retentate after ultrafiltration of 50% spent DES solution are identical. The comparison of FTIR graphs in case of 60% solution is presented in Figure 9.9.

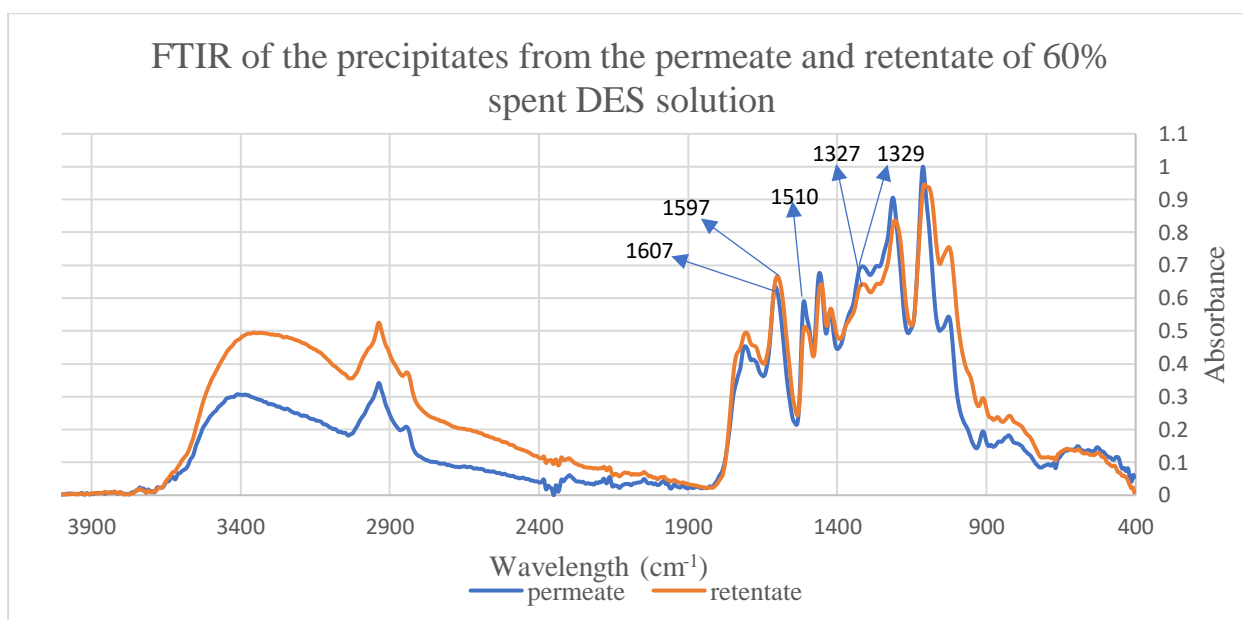


Figure 9.9 Comparison of FTIR graphs of the permeate and the retentate of the 60% solution of spent DES in 99% ethanol

Differences in peaks of the permeate and the retentate are absent. Chemical composition of the permeate and the retentate of 60% solution is the same. Thus, chemical contents in pairs of

permeates and retentates of 40%, 50% and 60% solutions are identical. Apart from 40%, 50% and 60% solution of spent DES, 80% and 90% solutions were also analyzed by FTIR. The results and conclusions based on 80% and 90% solutions are similar to the results obtained from the previously observed solutions. FTIR graphs for the permeates and retentates of 80% and 90% solutions of spent DES in 99% ethanol can be found in Appendices.

## **9.2 Exposure of membranes to DES within time**

This part presents a discussion of the results from the experiment of exposure of the membranes to either pure DES or 60% solution of pure DES in 99% ethanol over the following time periods: 1 week, 2 weeks, 3 weeks and 4 weeks. A strength of membranes' exposure to DES is evaluated by three parameters: changes in the chemical content of the membrane's surface after exposure; changes in the pure water flux after exposure and changes in retention after exposure. All these results would help to make a conclusion on the usability of the RC70PP membrane in DES recycling.

### **9.2.1 Influence of pure DES on membrane's surface**

This session is aimed at identifying the formation of depositions on the membrane's surface due to the pure DES exposure. Pure DES is completely homogeneous so there are no solids which can be precipitated. In addition, all the membranes were thoroughly washed with deionized water before the analyses. Hence, all DES should have been washed away unless some molecules were adsorbed by the membrane or stuck in pores without adsorption. The possibility of absorbance of pure DES molecules by the RC70PP is studied here. The results were obtained by FTIR analysis are, the spectra of membranes exposed to DES are depicted in Figure 9.10. Additionally, Figure 9.10 contains the spectrum of non-exposed membrane.

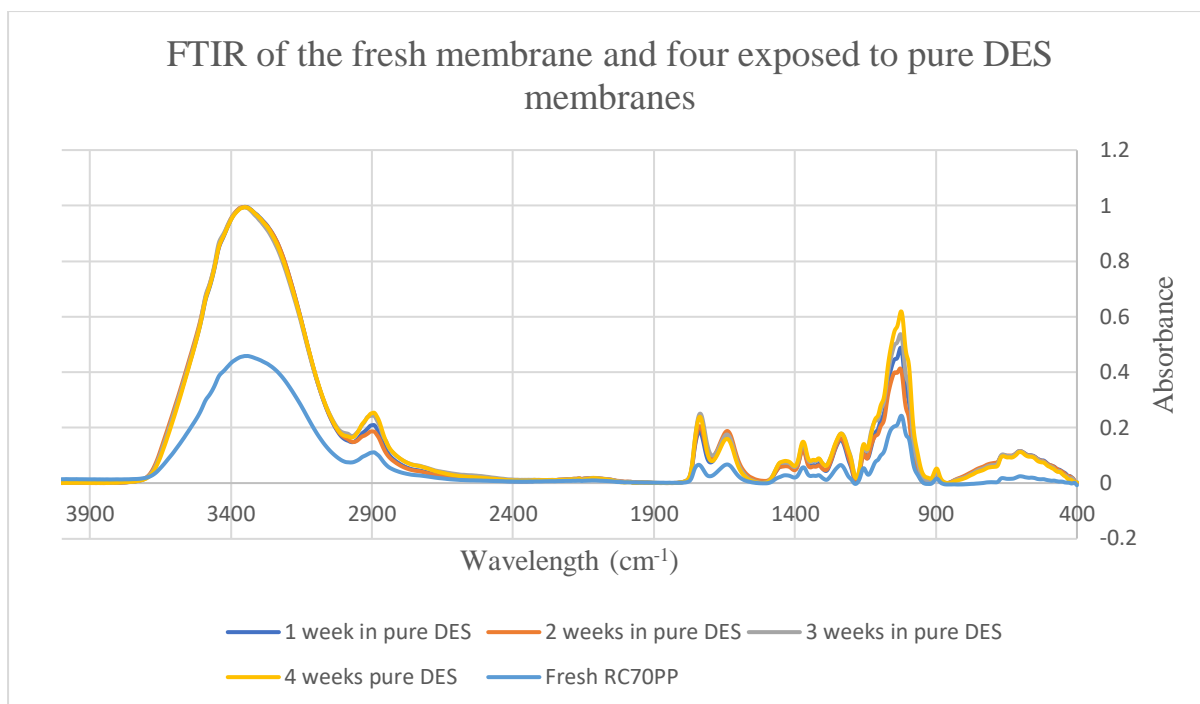


Figure 9.10 Comparison of FTIR graphs of the fresh membrane and the four exposed to pure DES membranes

According to Figure 9.10, the exact same peaks of the fresh membrane are duplicated on the graphs of the exposed membranes. Though the intensities of the peak differ significantly, new peaks on the graphs of the exposed membranes are not detected. In other words, chemical content of the membranes after different periods of pure DES exposure has not been changed. Evidently, absorbance of DES molecules on RC70PP do not take place as well as no signs of membrane degradation were detected.

### 9.2.2 Influence of 60% solution of DES on membrane's surface

The influence of 60% DES solution in 99% ethanol was analyzed in order to establish the difference between pure DES exposure and 60% DES solution exposure. The results of FTIR analysis are presented in Figure 9.11. The absorbance values of the fresh membrane spectrum are place to 0.2 values higher than the graphs of the exposed membranes.

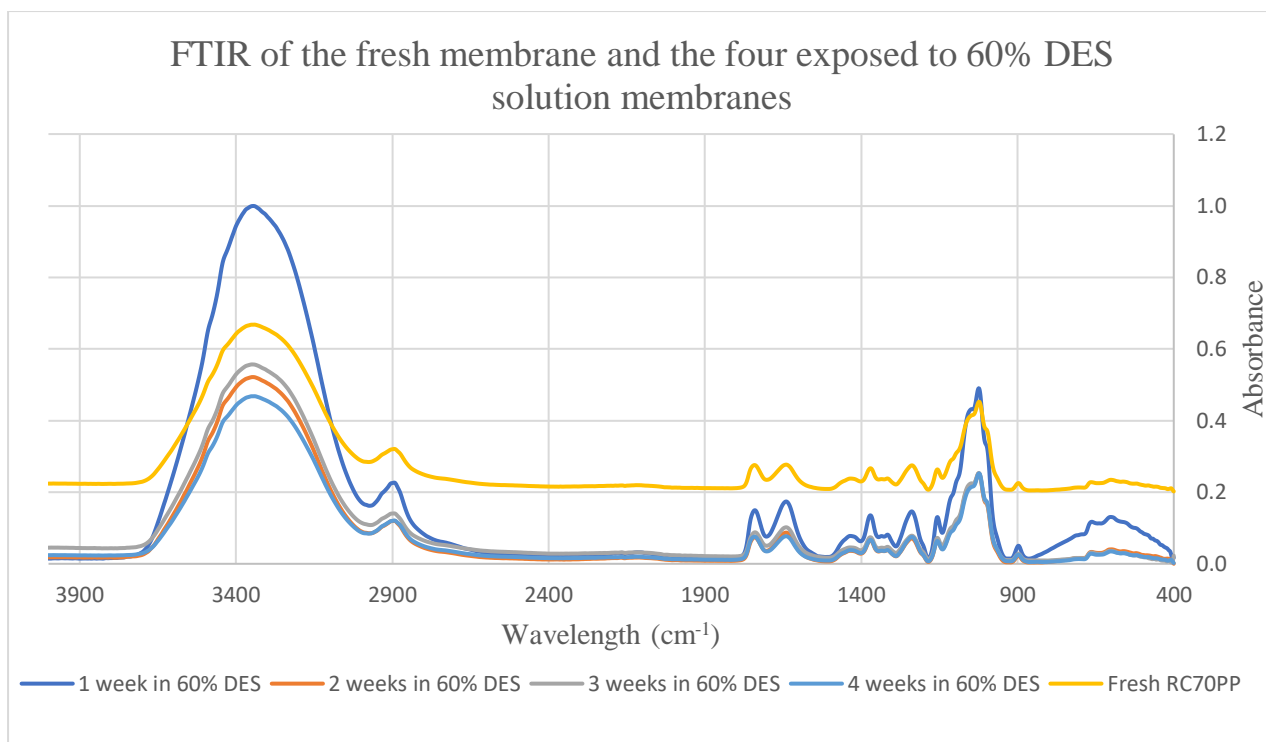


Figure 9.11 Comparison of FTIR graphs of the fresh membrane and the four exposed to 60% DES membranes

The behavior of the graphs of the exposed membranes and the fresh membrane are similar. No new peaks were detected, which means that no new substances appeared. The peaks of fresh RC70PP are duplicated by the graphs of the exposed membranes. To conclude, time exposure of DES in ethanol solution do not have any impact on the membrane's surface. FTIR analysis demonstrated that degradation of the membrane material did not occur during the exposure.

### 9.2.3 Comparison of the impacts of pure DES and 60% solution of DES on pure water fluxes through the membrane

Pure water fluxes before and after the exposure were analyzed in order to get the value of permeability for each membrane. The difference in permeabilities demonstrates the impact of either DES or 60% DES in 99% ethanol exposure. The bar chart, which shows the permeabilities of the membranes that were exposed to pure DES, is presented in Figure 9.12.



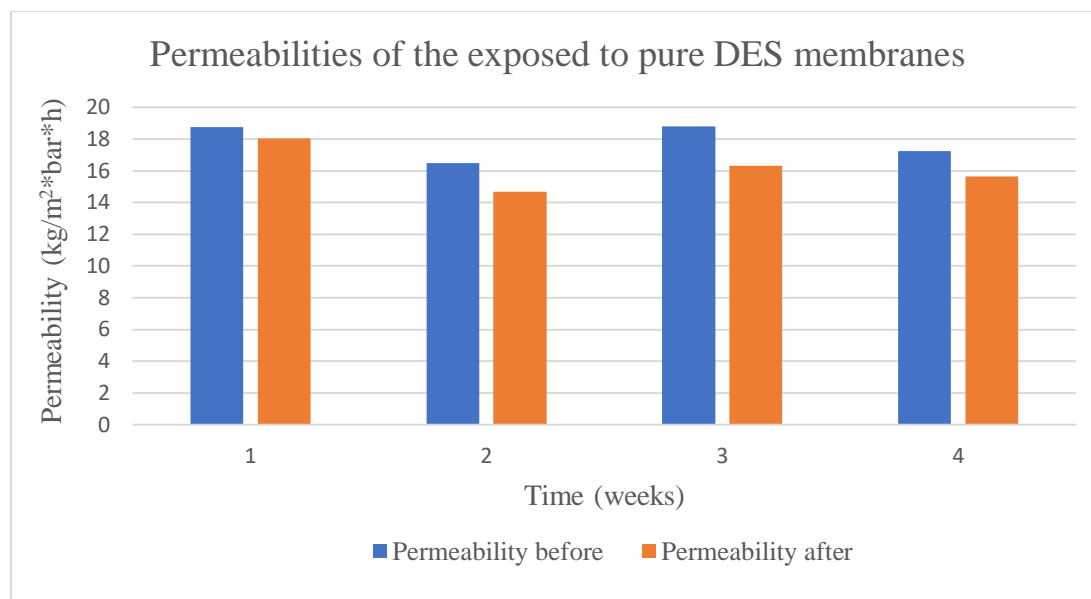


Figure 9.12 Comparison of the permeabilities of the exposed to pure DES RC70PP membranes from filtration in Amicon at 3 bar, 4 bar and 5 bar and 250 rpm

According to Figure 9.12, permeabilities of the membranes were not influenced by pure DES significantly. Loss of permeability of the membranes in percentage is presented in Table 9.8.

Table 9.8 Loss of permeability of the exposed to pure DES membranes

Period of exposure	Loss of pure water permeability
1 week	4 %
2 weeks	11 %
3 weeks	13 %
4 weeks	9 %

The values for the loss of permeability after exposure did not following any pattern. Loss of pure water permeability is less than 10% for the membrane which was exposed to pure DES for 4 weeks means that the RC70PP can withstand pure DES exposure. During the recycling of DES, not only does the membrane contact DES, but also 99% ethanol. That is the reason why the influence of 60% DES solution in 99% ethanol was studied. The bar chart, which shows the permeabilities of the membranes that were exposed to 60% DES, is presented in Figure 9.13.

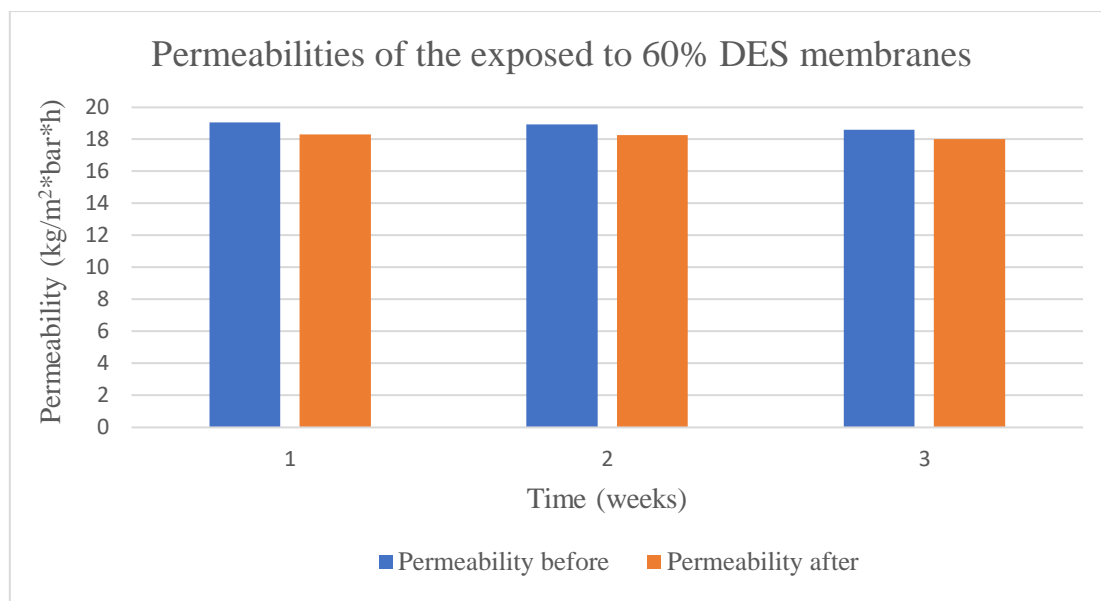


Figure 9.13 Comparison of the permeabilities of the exposed to 60% DES RC70PP membranes from filtration in Amicon at 3 bar, 4 bar and 5 bar and 250 rpm

According to Figure 9.13, permeabilities of the membranes were not influenced by 60% DES significantly, similarly to the result from pure DES exposure. Loss of permeability of the membranes in percentage is presented in Table 9.9.

Table 9.9 Loss of permeability of the exposed to 60% DES membranes

Period of exposure	Loss of permeability
1 week	4 %
2 weeks	4 %
3 weeks	3 %
4 weeks	3 %

It is noticeable that the loss of permeability after 60% DES exposure is around 3 %. This value is not significant. Thus, it was concluded that the usage of RC70PP membrane is feasible in DES recycling.

#### 9.2.4 Influence of 60% solution of DES on membrane's retention

The results of Total Carbon analysis are discussed in order to examine the influence of 60% DES in 99% ethanol solution on the retention of the membrane. TC analysis was conducted for permeates from ultrafiltration of Polyethylene glycol solution and TC was conducted for the feed of ultrafiltration. The calculations of retention were based on Eq 7.

$$Retention = \left(1 - \frac{TC \text{ in permeate}}{TC \text{ in feed}}\right) \cdot 100 \quad \text{Eq (7)}$$

Where, *Retention* (%);

*TC in permeate* – Total Carbon concentration in permeate (mg/l);

*TC in feed* – Total Carbon concentration in feed (mg/l).

Table 9.10 presents the results of the retention calculations for the membranes, exposed to 60% DES solution for 1 week, 2 weeks, 3 weeks and 4 weeks.

Table 9.10 Retentions of membranes before and after 60% DES exposure

Period of exposure	Retention before (%)	Retention after (%)
1 week	95.2	86.6
2 weeks	94.2	94.2
3 weeks	93.2	95.2
4 weeks	93.4	96.8

According to Table 9.10, the values of retention after exposure tend to rise. In other words, the longer the membrane was exposed, the bigger the retention becomes after exposure. At the same time, it was proved in the paragraph 9.1.2 that degradation of the RC70PP does not occur. Thus, the RC70PP is resistant to 60% DES solution in ethanol.

## 10 CONCLUSIONS

The main objective of the thesis was to investigate feasibility of DES recycling with membrane technology after wood fractionation treatment. Since DES is an emerging solvent for wood fractionation, thus, quite few research studies were reported in the area of DES recovery and regeneration. Tackling recyclability problem can usher in a new era in many industries, especially in biorefineries. Experiments were divided into two groups. The purpose of the first group was related to membrane filtration of DES. The experiments included 1) determination of ethanol influence on the initial suspended solids precipitation; 2) determination of concentration of spent DES in ethanol on flux; 3) determination of temperature of filtration on flux; 4) determination of initial suspended solids presence influence on flux; 5) determination of separation efficiency; 6) determination of chemical content of precipitates in permeate and retentate. These experiments showed that filtration of 60% solution of spent DES is more stable. Besides, separation efficiency in that case is greater than separation of other solutions.

Higher temperature of filtration (45 °C) leads to higher fluxes without membrane destruction. At the same time, presence of initial suspended solids negatively affected the flux, increasing the duration of filtration in the case 60% solution by 30%.

The second group of experiments was aimed at determination of the RC70PP resistance to DES. Exposure of the membranes to pure DES and to 60% DES during different time periods did not cause the degradation of the membrane. Moreover, it did not reveal any adsorption. These facts were proved by FTIR analysis. Reduction of pure water flux after the exposure happened to be small. The loss of permeability for exposed to 60% DES membranes varied around 3%. At the same time, the retention values grew within time by 2-3%

Herewith, thesis objectives were achieved. Nevertheless, introduction of a tighter membrane, reuse of spent DES and reuse of permeates after ultrafiltration could be considered as further studies.

## **11 FURTHER RECOMMENDATIONS**

Despite very remarkable results on spent DES concentration with the RC70PP, a tighter membrane with lower MWCO should be examined. Firstly, it could theoretically improve separation. Thus, the content of lignin in permeate would be smaller. Secondly, the average molar weight of retained lignin could increase. In addition, different variations of DES reuse should be tried. In other words, reuse of delignified spent DES after water separation, reuse of delignified permeate and retentate from spent DES ultrafiltration and the following water separation. Lignin removals obtained from bio fractionations with recycled DES would demonstrate the reasonability of the whole membrane-based solvent regeneration. Furthermore, different organic solvents should be examined as alternatives to ethanol. Moreover, it would be reasonable to know membrane fouling behavior for the chosen 60% solution. Possible cleaning methods and their influence on membranes of DES recycling process should be also studied.

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