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Forward osmosis for concentration of tannin containing bark extract

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ABSTRACT

Modern pulp mills can produce biofuels and value-added bio-products, such as lignin products. However, these bio-products are often present in solutions that are too dilute to be separated in a cost-efficient manner, and concentration by filtration is difficult due to their high fouling properties. In this research, challenging liquor, tannin-containing spruce bark extract, was concentrated by forward osmosis using soda ash from the soda recovery boiler as a draw solution. Soda ash, which consists of about 90% sodium sulphate, could be considered as a cost-free draw solution, since part of it needs to be discharged daily in order to prevent enrichment of potassium and chloride in the chemical circulation of pulp mills. Draw properties of soda ash solution were compared with the properties of pure salts, namely sodium sulphate and sodium chloride. Soda ash generated the same osmotic pressure and similar flux than sodium sulphate, but was a weaker draw solution compared with sodium chloride. When the draw solution concentration was 20% at 40°C, the flux was 16 and 13 LMH with soda ash and sodium sulphate, respectively. Using FO, water recovery over 80% could be reached, which is double compared with water recovery obtained by nanofiltration. However, the salt concentration of the feed solution was increased due to the reverse salt flux of the draw solution, which may hinder the further processing of tannin-containing spruce bark extract.

Keywords: Soda ash; Draw solution; Energy saving; Forward osmosis; Fouling; Bio-product; Tannin; Sodium sulphate

1. Introduction

Nowadays, modern pulp mills are designed to be resource efficient bio-product mills that utilize all the materials. In addition to pulp, mills could produce biofuels and several high value-added by-products such as phenols, lignin, organic acids, and hemicellulose, which are traditionally burnt to recover their energy content [1]. Phenolic tannins (MW 500–3,000 Da), extracted from spruce bark, can be used to replace fossil fossil-based phenol in many applications such as plastics, resins, insulating foams and adhesives [2–5]. The low concentration of the by-product in the process streams makes separation of the products infeasible [6,7]. Due to the high organic matter content, concentration of products is challenging using conventional, pressure-driven membrane processes [5]. Fouling and cleaning increase both the operating and investment costs of the membrane process [7].

Forward osmosis (FO), which is driven by the osmotic pressure difference between two liquids on the opposite sides of a semi-permeable membrane, has proven to be interesting from the fouling point of view. Fouling in FO is less and cleaning is easier due to the lack of high hydraulic pressure for the separation process [8–10]. The initial water flux of FO is usually lower than those of the pressure driving process, such as reverse osmosis (RO) or nanofiltration (NF), but because of its reduced fouling propensity, the achieved water recovery and concentration factor can be excellent with FO for challenging feeds [11]. However, FO has its own challenges, one being the product of FO is not potable water, but a diluted draw solution. The overall economy and energy requirements of a combined FO/draw solution regeneration are usually higher when compared

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with RO alone [10,12]. If the diluted draw solution could be used directly at the site, no draw solution regeneration is required and energy consumption of FO could be very low.

In pulp mills, waste (black) liquor is burned in the soda recovery boiler and the inorganic cooking chemicals, namely sodium hydroxide and sodium sulphide, are recycled. The fly ash from the soda recovery boiler is separated by an electrostatic precipitator from the gas stream [13]. Fly ash, also called electrostatic precipitator dust and soda ash, contains sodium sulphate (Na_2SO_4) as a dominating salt having some sodium carbonate, chloride and potassium salts as impurities [14]. Due to controlling corrosion problems, a portion of soda ash needs to be purged periodically to lower chloride and potassium levels in chemical circulation. If the purged ash will be washed and the rinsed salt cake is returned back to the chemical cycle, the loss of process chemicals will be reduced [13]. The rinsing water of waste salt, which also contains Na_2SO_4, can be utilized as a feed solution for the electrodialysis process. Na_2SO_4 is then split to an acid and base and the produced dilute process chemicals can be used on-site at the mill without concentration. In the mill area, produced caustic soda could replace a portion of the purchased sodium make-up, which is needed for controlling the sodium/sulphur balance [15].

Since soda ash needs to be purged and washed, it is studied in this project as a draw solution in FO with no regeneration requirements. Apart from the possibility as a cost-free draw solution, FO is an interesting technology in the pulp and paper industry, since plenty of waste heat is available. The high temperature of feed and draw solutions could assist FO by lowering the viscosity of water, increasing diffusion of solutes, increasing the solubility of soda ash and osmotic pressure of the draw solution [8,16]. In this research, tannin-containing hot water extract from spruce bark originating from the pulp mill was selected as a feed solution (FS), which requires concentration steps for recovery. All the needed materials and products can be found and used at the same mill site. The performance of soda ash was compared with pure draw solutions, sodium chloride (NaCl) and Na_2SO_4. Also, the effect of temperature on FO performance was tested and reverse salt flux was studied.

2. Materials and methods

2.1. Membranes

The Filmtec NF270 membrane was selected for NF tests. The membrane manufacturer reports 50% sodium chloride rejection and 98% magnesium sulphate rejection [17]. According to the membrane supplier, Filmtec NF270 membrane is, besides other applications, also meant for removing a high percentage of total organic carbon with medium to high salt passage and medium hardness passage [18].

HTI's thin film composite (TFC) membranes with embedded polyester were selected for FO experiments. According to the technical sheet of the membrane [19], water flux is 17 LMH and NaCl salt rejection is 99.4% when the membrane was tested using a 1 M NaCl draw solution at 25°C in the active layer facing the feed solution orientation (commonly known as FO mode).

2.2. NF testing

NF was carried out using a commercial SEPA module with a membrane area of 140 cm^2. The cross-flow NF module was equipped with on-line flux, temperature and pressure measurements. Filtration tests included characterization of a membrane, that is, determination of fluxes during pure water and 2 mg/L NaCl solution filtration. The measured NaCl rejection of the membrane sample was 56%. The tannin's filtration operational parameters were: 5 bar pressure, 25°C temperature and 6.5 kg/min flow of feed. Crossflow velocity was adjusted to 90 cm/s, because the spruce extract solution had a severe fouling tendency and no pre-treatment was done before membrane filtration.

2.3. FO testing

FO tests were performed using laboratory scale equipment (Fig. 1). For each test, a TFC membrane of 140 cm^2 was placed in the FO membrane cell with its active layer facing the feed solution. Feed solution and draw solution tanks were on the balance. Pressure and conductivity were measured after the FO module from both solutions and temperature measurement/control was done in the feed tank. The conductivity of the draw solution was kept constant by adding salt to solution during filtration.

2.4. Feed and draw solutions

The draw solution was made from soda ash taken from a Finnish pulp mill and it was compared with pure sodium chloride (VWR International Oy, Belgium) and sodium sulphate (≥99%, Merck, Germany). The feed solution was extracted from a 11.3% spruce bark solution at 75°C–80°C. The pH of the tannin-containing extract was 4.9 ± 0.1, conductivity 1.0 ± 0.2 mS/cm, dry solids content 1.3% ± 0.1% and viscosity 75 ± 13 cP. The tannin concentration of the solution was 4.4 g/L and ash content of the freeze-dried dry matter was 5.6% (lyophilization). The inorganic content of spruce hot water extract and soda ash was analysed using inductively coupled plasma optical emission spectrometry (ICP-OES; Table 1) using a standard SFS-EN ISO 11885.

2.5. Testing procedure

The membrane was soaked overnight in deionized water at 4°C before filtration tests. The condition of the membrane piece was tested before and after the FO experiments at 25°C using 1 M NaCl as a draw solution and deionized water as a feed solution. If the flux was 14 ± 1 l/m^2h and the conductivity of the FS increased less than 1 μS/cm in minute, the FO membrane was accepted for further experiments. The selected process conditions are shown in Table 2.

2.6. Analysis

The soda ash and spruce extract were dissolved using microwave-assisted digestion with hydrofluoric acid, nitric acid and hydrochloric acid mixture (SFS-EN 13656:2003 (mod.) standard) and analysed by ICP-OES using method SFS-EN ISO 11885:2009 (mod.). Chloride was dissolved

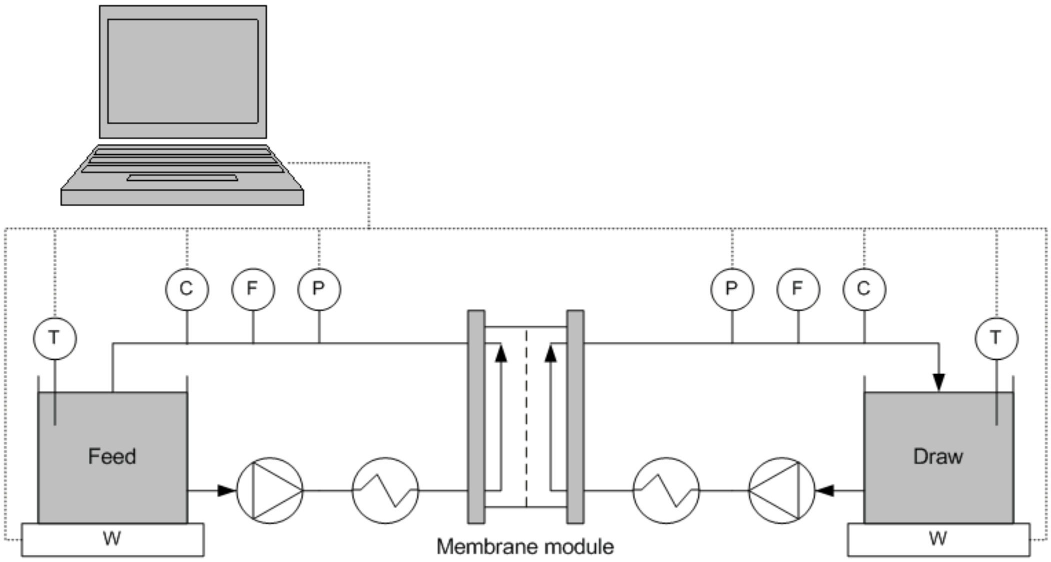

Fig. 1. Schematic figure of a laboratory scale FO testing apparatus with online data collection of weight (*w*), temperature (*T*) and conductivity (*C*).

Table 1
Inorganic content of spruce extract solution and soda ash

	Spruce extract mg/L	Soda ash mg/kg dry solids
Ca	72	160
Mg	29	120
Na	3.4	289,800
K	220	52,400
P	27	44
S	19	202,400
Cu	<0.1	0.6
Mn	9.2	40
Zn	2.3	42
Fe	1.1	17
Al	4.2	15
Cr	<0.1	<0.5
Ni	<0.1	<0.5
Si	2.4	150
Ti	<0.1	2.0
Pb	<0.1	<0.5
Ba	1.6	3.8
Cl	8.6	5,700

using nitric acid and analysed using an anion chromatograph for halogens SFS-EN ISO 10304-1:2009 (mod.). Total dissolved solids (TDS), conductivity, pH and osmotic pressure were analysed from the feed and draw solution before and after FO filtration. TDS was analysed according to SFS-EN 15216. Conductivity of both the feed and draw solutions was measured on-line during the FO process using a Yokogawa Europe B.V., (The Netherlands) and Mettler

Table 2
Selected FO process conditions for tannin (spruce extract) concentration

Temperature, °C	Concentration, %	Draw salt
25	12	Soda ash, NaCl or Na_2SO_4
40	12	Soda ash, NaCl or Na_2SO_4
40	20	Soda ash, NaCl or Na_2SO_4
40	57	Soda ash

DS: draw solution.

Toledo, Switzerland (INPRO 7100i/12/425/4435) conductivity meters, respectively. Osmotic pressure was measured using a Vapro 5600XR, Vapor Pressure Osmometer (Wescor Inc., U.S.A.).

The tannin content of the solutions was analysed using acid butanol assay, which is specific for condensed tannins (proanthocyanidins) and described by Gessner and Steiner [20]. The flavonoid subunits of the condensed tannin polymer are oxidatively cleaved to yield anthocyanidin, which absorbs at 550 nm and was measured using a spectrophotometer. The initial viscosity of the tannin solution was measured using a Brookfield LVDV-II+pro Extra rotator viscometer.

3. Results

3.1. Forward osmosis concentration

FO of tannin-containing spruce extract was compared with NF. FS in FO was fed to the membrane module as such without any pre-treatment and the draw solution concentrations were 12 w-% at 25°C. When NF was used, initial flux was the highest (19 LMH) but WR was the lowest. It was possible to filter only 40% of the water from the tannin solution when the NF270 membrane was used (Fig. 2). The fouled NF270 membrane was not able to be cleaned by flushing with deionized water, that is, pure water flux could not be recovered. When FO was used for concentration, it was possible to reach over 80% water recovery (WR) and after flushing with deionized water, the membrane flux was similar to that obtained before concentration. Although the initial flux was lower than when NF was used, the flux of FO was fairly stable throughout concentration. The flux was similar, 4–5 LMH, when using soda ash and pure sodium sulphate as a draw solution. A higher flux of 7 LMH was obtained when NaCl was used as a draw solution.

When soda ash was the draw solution and tannin was the feed solution, WR was 87%. After the test, it could be seen that organic matter of the feed solution accumulated on the surfaces of the FO device. That was also observed when calculating the concentration factor (CF). If the CF was calculated by transported water, it was 7.7 and when calculation was done by measuring tannin concentration, CF was 3.9. Tannin content in the draw solution before and after the test was equal to inaccuracy of the tannin measurement. Thus, it can be concluded that tannin was rejected well by the FO membrane.

3.2. Effect of temperature and concentration of soda ash

Although a lot of water could be removed from tannin-containing spruce extract using FO, the flux in concentration was low. Increasing temperature from 25°C to 40°C improved the flux by decreasing the viscosity of water (correction factor 0.74 [21]), decreasing the diffusion of solutes, thus reducing the internal concentration polarization effect, and increasing the osmotic pressure of salt solution. At the pulp mill, heating of process solutions can be economic since several waste heat sources are available. In tannin solution concentration, the flux was doubled with 12% sodium chloride as draw solution, when temperature was increased from 25°C to 40°C (Figs. 2 and 3). With soda ash and sodium sulphate the effect was smaller. The osmotic pressure (π) is proportional to molarity, π = MRT. The molarity of 12 w-% salt solution was higher when NaCl was used compared with Na_2SO_4 solution, 2.05 and 0.85 M, respectively. Thus, when temperature was higher the effective osmotic pressure was higher for NaCl than for Na_2SO_4, 2.56 bar vs. 1.05 bar, meaning that also flux increase was higher.

When temperature was increased from 25°C to 40°C, it was possible to dissolve more salt to the draw solution and reach higher osmotic pressure. The flux was higher when the salt concentration increased from 12% to 20%, but when the soda ash concentration was increased from 20% to 57%, the flux did not improve further (Fig. 4), since the salt dissolved only partly. The undissolved solids of draw solutions could rather disturb the filtration by blocking the pores in the draw solution. However, in short, FO filtrations solids did not affect the FO performance since solids were flushed away from the membrane pores by water, which was transported through the membrane.

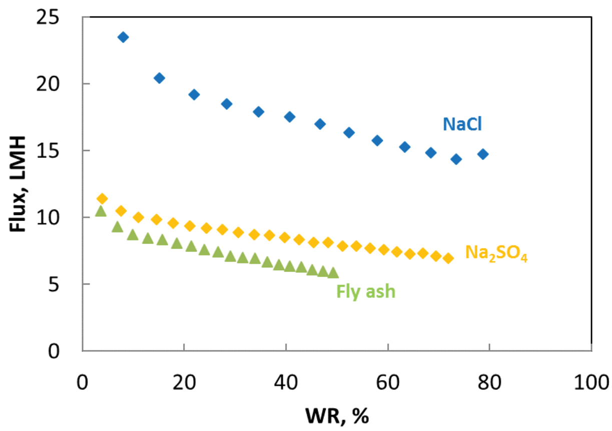

Fig. 3. Concentration of tannin using FO at 40°C. FO's draw solutions were 12 w-% NaCl, Na_2SO_4 and fly ash from a soda recovery boiler.

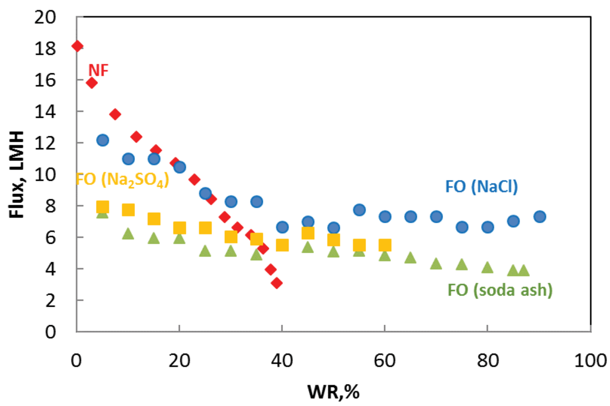

Fig. 2. Comparing membrane concentration methods for the tannin solution, that is, NF and FO, at 25°C. Draw solutions of FO were 12 w-% NaCl, Na_2SO_4 and fly ash from the soda recovery boiler. When NF was used, operation pressure was 5 bar.

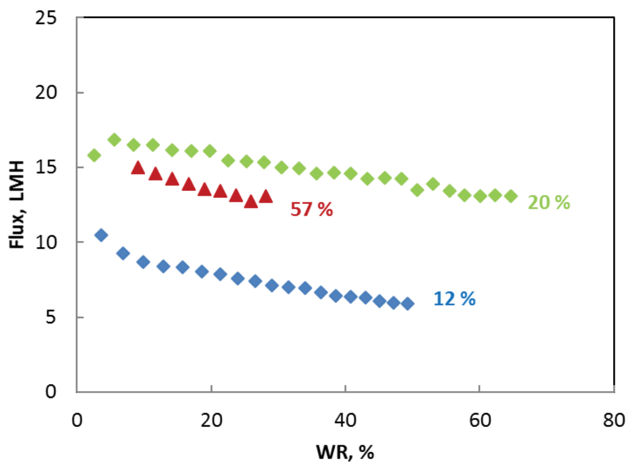

Fig. 4. Effect of the concentration of soda ash on the flux of FO, when the tannin solution acted as a feed solution.

3.3. Reverse salt flux

In the reverse solute flux (RSF) phenomenon, the solute molecules permeate from the draw solution to the feed solution due to the concentration gradient across the membrane. The rate at which solutes diffuse across a membrane depends on membrane properties and diffusivity coefficient of the solutes [22]. In general, diffusivity decreases with

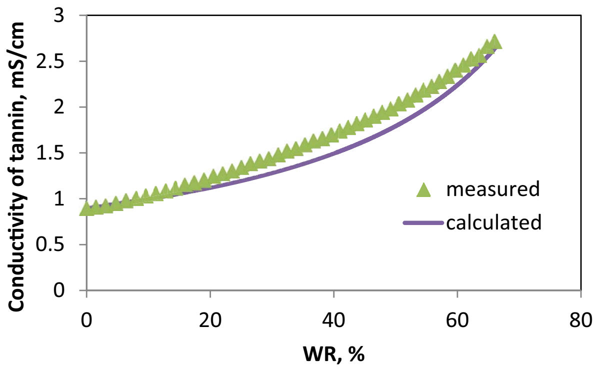

Fig. 5. Measured and calculated (from water recovery) conductivities of the feed solution during the FO process with a 20% soda ash draw solution at 40°C.

Table 3
Properties of the tannin solution before and after the FO process at 40°C using fly ash as a draw solution

	Initial	WR 66%
TDS, %	1.43	3.35
Conductivity, mS/cm	0.814	2.338
pH	3.9	5.7
Osmotic pressure, bar	0.95	2.46
Ca, mg/L	72	150
Mg, mg/L	29	63
Na, mg/L	3.4	520
K, mg/L	220	310
P, mg/L	27	63
S, mg/L	19	46
Cu, mg/L	<0.1	0.2
Mn, mg/L	9.2	19
Zn, mg/L	2.3	4.8
Fe, mg/L	1.1	3.6
Al, mg/L	4.2	8.5
Cr, mg/L	<0.1	<0.1
Ni, mg/L	<0.1	0.1
Si, mg/L	2.4	7.5
Ti, mg/L	<0.1	<0.1
Pb, mg/L	<0.1	<0.1
Ba, mg/L	1.6	3.0
Cl, mg/L	8.6	33.5

increasing molecular weight, charge, and hydrated radius of the ion [22] and increasing temperature increases also solute diffusivity [23]. The higher the temperature, the higher the diffusivity of the solutes. The conductivity of feed and draw solutions was measured, and from the collected data it can be concluded that salt leaked more from the draw side to the feed side at 40°C than at 25°C. When multivalent ions, namely Na_2SO_4, were used as a draw solution, diffusion through the FO membrane was less than if monovalent ions, namely NaCl, were used. In addition to Na_2SO_4, soda ash also contains, carbonate chloride and potassium salts. The measured conductivities of feed solution were slightly higher than the calculated values (calculated conductivity = initial conductivity × (100/[100-WR%]), with the difference attributed the RSF (Fig. 5).

Table 3 shows the change of feed composition for an FO water recovery of 66%. TDS of the tannin-containing solution increased from 1.43% to 3.35%, corresponding to a concentration factor of 2.3. ICP-OES results showed that concentrations of all the other elements were about doubled, except for chloride and sodium. Chloride concentration increased 3.9-fold and sodium concentration increased 153-fold, from 3.4 to 520 mg/L, during 6.5 h FO filtration (Table 3). The reverse salt flux of sodium was as high as 5.63 g/m^2h. Part of salt diffuse to feed solution in the form of sodium chloride but it seemed that the most of the sodium was transported via carbonate anion. Also, the increase of pH during FO filtration from 3.9 to 5.7 at the feed solution supports that.

4. Conclusions

In addition to pulp, new modern pulp mills will produce also more valuable products such as biofuels and value-added bio-products, which are often present in too diluted solutions to be separated in a cost-efficient manner. In addition, concentration of dilute solutions by filtration is difficult due to their high fouling properties. In this research, phenolic tannins present in extract of spruce bark were concentrated by forward osmosis using soda ash as a draw solution. Soda ash consists of roughly 90% sodium sulphate. If a diluted draw solution is utilized at the site, for example in process chemical production instead of regeneration, forward osmosis can be a competitive concentration method for producing bio-products. Soda ash can be considered as a cost-free draw solution, since some of it needs to be discharged daily and used in a diluted form to prevent concentration of potassium and chloride in the chemical circulation of pulp mills.

According to the experimental results, the soda ash generates the same osmotic pressure and similar flux than pure sodium sulphate, but it was a weaker draw solution than pure sodium chloride. Temperature increase not only enhanced the flux but also the reverse salt flux. Increased sodium concentration in the feed can hinder the productisation of tannin. When the concentration of draw solution was increased to 20% at 40°C, the flux was 16 LMH with soda ash and 13 LMH with Na_2SO_4. When using forward osmosis in concentration, the water recovery can easily exceed 80%. Water recovery was only ~40%, when nanofiltration was used.

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