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THE COMBINED APPLICATION OF ULTRAFILTRATION AND REVERSE OSMOSIS FOR WATER AND BY-PRODUCT RECOVERY

1. INTRODUCTION

One of the concepts for solving a problem of membrane treatment is to combine the ultrafiltration and reverse osmosis into one technological process justified by both economical and technological considerations. Due to application of the ultrafiltration as a preliminary stage in membrane treatment, particularly in case of tubular modules, the stage of thorough preliminary filtration can be limited or eliminated altogether. The ultrafiltration membranes which totally retain colloidal substances, prevent the formation of

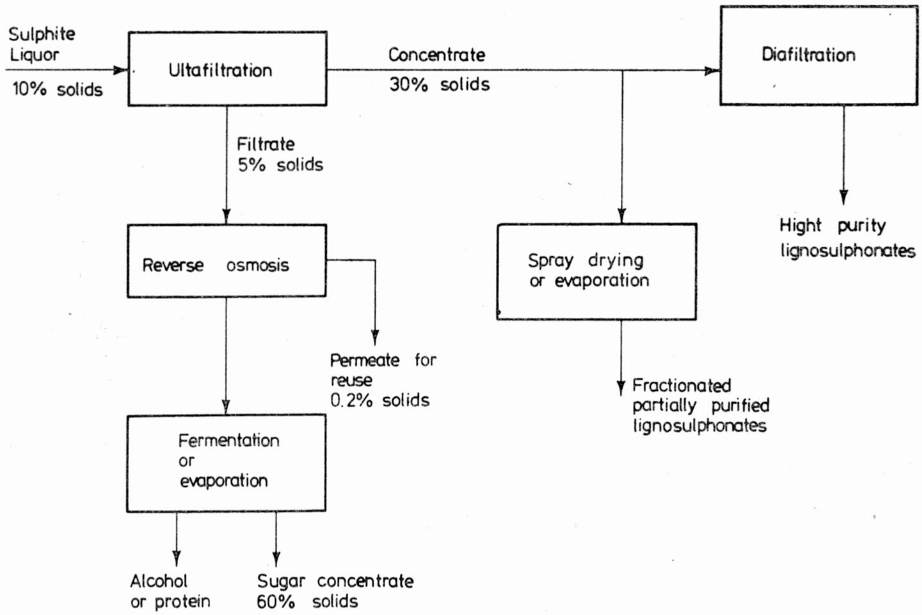

Fig. 1. Fractionation and concentration of spent sulphite liquor by membrane processes

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a film on less resistant reverse osmosis membranes, as well as enable to use capillary or spiral modules for the other stage. A thorough initial treatment, including colloids removal, is a fundamental condition to ensure a continuous operation of the reverse osmosis membranes, therefore increasing their life-time. In case of combined application of ultrafiltration and reverse osmosis the fractioning of components from the separated solution to recover useful substances is of considerable significance. These concepts will be presented here basing on examples of cellulose pulp wastes, emulsion wastes and whey effluents.

Spent sulphite liquors contain about 50% of initial amount of wood raw material in the form of lignosulphonic acid, wood sugars and other products of chemicellulose hydrolysis and wood extraction. The application of the combined ultrafiltration and reverse osmosis allows the recovery of lignin substances, sugars and water through fractioning digester liquors [1–3]. Separation of ligniosulphonates from sugars by the two processes is presented in fig. 1.

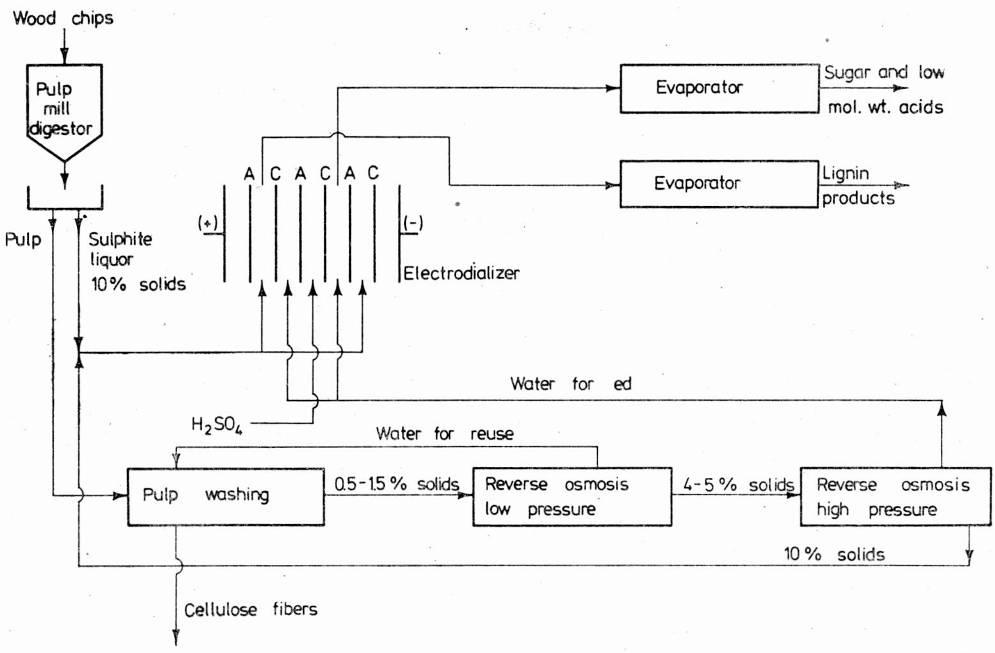
2. THE CELLULOSE PULP WASTES

At the first stage when the ultrafiltration is used, the substances present in digester liquor are separated into two fractions: a filtrate containing hydrolized sugars and a concentrate enriched in lignosulphonate substances. From sulphite liquor, containing 10% of dissolved substances, a lignosulphonate, concentrate with 30% of dissolved substance is obtained that can be further directed for further concentration at the distillation plant, drying or dialysis refining.

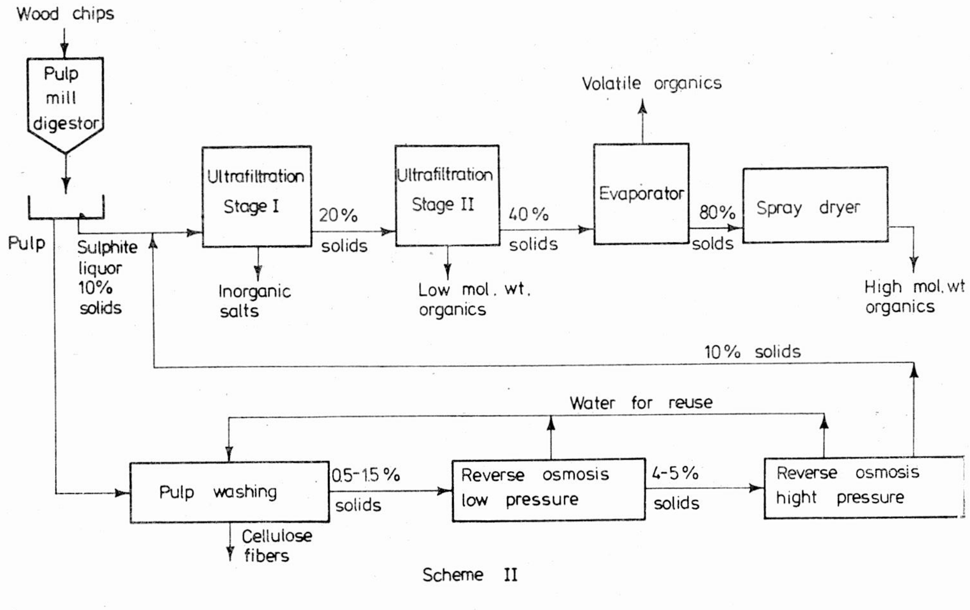
A fraction rich in sugars is then concentrated in the reverse osmosis installation, where concentration increases from 5 to 20%. The filtrate obtained at this stage can be directly reused instead of fresh water. A concentrate is directed for further processing through either alcohol or protein fermentation or is concentrated by evaporizing up to 60%. In an American pilot-plant research [2–3] cellulose acetate membranes have been applied in both stages of processing. The possibilities of using the combined membrane processes for water and useful product recovery from washing sulphite wastes have also been studied. CHANNABASAPPA [6] suggests that the ultrafiltration, reverse osmosis and electro-dialysis should be used for this purpose. Figure 2 shows two variants of washing sulphite wastes and digester liquor treatment using these processes. In both cases the water after cellulose washing contains 0.5–1.5% of the dissolved substances, then it is concentrated up to 10% in reverse osmosis and ultrafiltration-installation. Variant I applies electrodialysis to separate the compounds of low-molecular particles from those of high-molecular, but to do the same in Variant II the ultrafiltration is suggested. In Variant I chemicals for dissolving cellulose are obtained, being then directed to the digester.

Preliminary studies within the discussed range of applications have also been done by the authors [4]. Two-stage-waste-recovery of the products after cellulose sulphite pulp washing was also done on an installation for reverse osmosis and ultrafiltration in a static system [5]. In the first stage the raw wastes of 2.5–8.5 kg/m^3-concentration undergo an ultrafiltration process using "open" UF-17 ultrafiltration membranes [8], at pressure of 0.75 MPa until they reach an 80% ultrafiltration-recovery-level. Two fractions were received: a 20%-concentrate of initial waste volume containing, in the first place, high-molecular lignosulphonate compounds and an ultrafiltrate mainly containing carbohydrates, low-molecular lignin compound and inorganic substances. In the second stage the ultrafiltrate received has undergone a process of concentration by applying reverse osmosis at pressure of 4.0 MPa, on "dense" osmotic membranes, type Batch-301 [9], modified at 70°C or 80°C. At this stage the dissolved substances in the ultrafiltrate are several times concentrated, the outcoming permeate being characterised by a low pollution content.

The table shows the results of the combined waste processing coming from the cellulose pulp washing for various sulphite waste concentrations. The results obtained indicate that ultrafiltration allows 95% colour removal over 82% COD removal and 80% total dissolved solids (TDS) removal. The concentrate received at this stage, compared to ultrafiltrate is characterized by a 8-fold-higher TDS contents and 20-30--fold-higher-colourized-substance-content. In the second-stage-treatment the application of modified membranes at 80°C retains 90% of the dissolved substances in the ultrafiltrate. This leads to a 4-fold concentra-



Scheme I



Scheme II

Fig. 2. Treatment of spent sulphite liquor and pulp wash waste by combined membrane processes [6]

A combined treatment of sulphide wastes by ultrafiltration and reverse osmosis

Type of treatment	Pollution indicator	Dilution of liquor 1+35					Dilution of liquor 1+17.5					Dilution of liquor 1+10				
		W	F	C	R_1	R_2	W	F	C	R_1	R_2	W	F	C	R_1	R_2
I Ultrafiltration UF-17 membrane pressure — 0.75 MPa. Feed: raw wastes recovery of filtrate — 80%	Flux rate, $m^3/m^2 \cdot d$	—	2.38	—	—	—	—	1.43	—	—	—	—	1.03	—	—	—
	TDS g/m^3	2570	1075	8150	79.8	—	5130	2480	16450	76.9	—	8470	3925	29600	79.5	—
	Colour g Pt/m^3	1070	144	4960	95.2	—	1940	378	9920	93.7	—	3585	534	18700	95.5	—
	COD, g O_2/m^3	2940	1370	12500	82.2	—	5600	3100	32500	83.7	—	11100	4210	42800	84.5	—
	Conductivity, μS	680	420	13100	57.9	—	1200	880	2400	51.0	—	1820	1200	3700	56.5	—
II-a reverse osmosis B-301 membrane, modified at 70°C pressure — 4.0 MPa. Feed: ultrafiltrate recovery of permeate: — compared to ultrafil. 80% — compared to waste 64%	Flux rate, $m^3/m^2 \cdot d$	—	0.540	—	—	—	—	0.430	—	—	—	—	0.369	—	—	—
	TDS	—	393	2800	79.7	84.9	—	1170	6215	73.1	77.1	—	2030	11900	74.2	76.1
	Colour g Pt/m^3	—	29	592	92.2	97.2	—	77	1670	92.5	96.0	—	98	2920	97.0	97.5
	COD, g O_2/m^3	—	622	3080	72.1	78.9	—	1190	4220	67.5	78.7	—	2000	5840	60.0	81.9
	Conductivity μS	—	200	1075	72.5	70.6	—	432	2195	76.9	64.0	—	720	3010	67.4	60.4
II-b Reverse osmosis B-301 membrane, modified at 80 °C Pressure — 4.0 MPa. Feed: ultrafiltrate recovery of permeate: — compared to ultrafiltrate 80% — compared to waste 64%	Flux rate $m^3/m^2 \cdot d$	—	0.246	—	—	—	—	0.215	—	—	—	—	0.169	—	—	—
	TDS g/m^3	—	193	3490	91.7	92.6	—	400	8370	92.6	92.2	—	611	13300	93.1	92.7
	Colour g Pt/m^3	—	22	680	94.5	98.3	—	43	1520	95.5	98.0	—	40	2030	96.8	99.0
	COD, g O_2/m^3	—	232	3680	90.8	92.2	—	572	8450	90.1	90.0	—	600	15100	90.5	91.7
	Conductivity, μS	—	93	1280	89.2	86.5	—	182	2550	89.3	84.6	—	258	3730	90.0	85.7

W — waste
F — filtrate
C — concentrate
R_1 — average rejection ratio compared to feed
R_2 — rejection ratio compared to raw wastes

tion increase of the dissolved substances, including carbohydrates. The permeate received during concentration is characterized by a low pollution load (e.g. colour 22–40 g Pt/m^3, TDS 193–600 g/m^3, conductivity 93–285 μS) and it can be recommended for use as a technological water instead of fresh water. Application of a more "open" membrane modified at 70°C in the second-stage-treatment produces somewhat worse results; the colourized substances are retained at about 90% or over, COD about 60%, TDS about 73%.

In summary the two-stage-treatment of wastes resulting from the washing of cellulose sulphite pulp allows to obtaining of three fractions: concentrate from the ultrafiltration stage (a 20% raw-wastes-volume) enriched with high-molecular-lignin-compounds; concentrate from the reverse osmosis stage (a 16% wastes-volume) enriched with carbohydrates and other low-molecular organic and inorganic compounds; water (64% wastes-volume) low in TDS and adequate for recycling.

3. EMULSION WASTES

One of the latest trends in applying ultrafiltration is to use it for the treatment of hard-to-treat-wastes from metallurgy, oil-refineries, petrochemical and automobile industries. These wastes contain emulsified oils of 1–5% concentration. By using ultrafiltration [7], [12] in place of flotation, adsorption or coagulation it is possible to obtain the water of a low-oil-concentration (< 10 g/m^3) and a concentrate of 50-60% oil which can be reused or burned easily. The process is most often carried out on tubular modules with cellulose acetate or polyamide membranes; at low operation pressures of 0.35–0.50 MPa. The ultrafiltrate is usually higly polluted with the dissolved organic and inorganic substances and needs further treatment prior to stream discharge or reuse. For the second-stage-treatment the reverse osmosis here yields high quality water [6], [7], and appears to be very economical since spiral modules or hollow-fibres can be used, sensitive to membrane surface pollution. Figure 3 shows treatment of emulsion wastes by means of ultrafiltration and the reverse osmosis, such research is conducted by the authors.

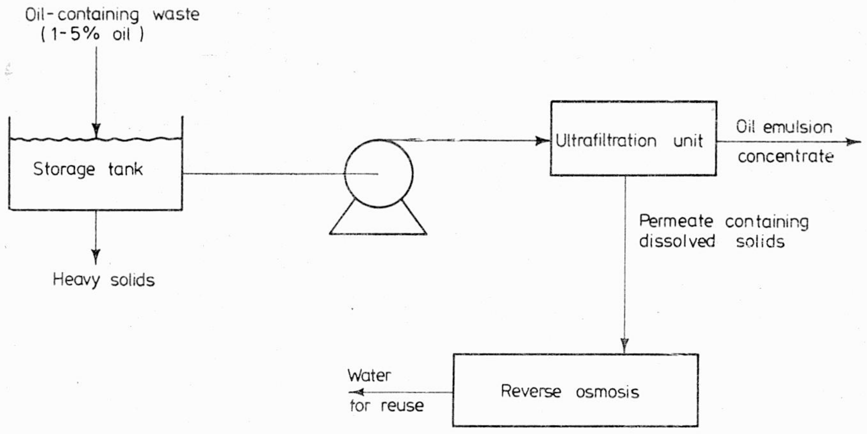
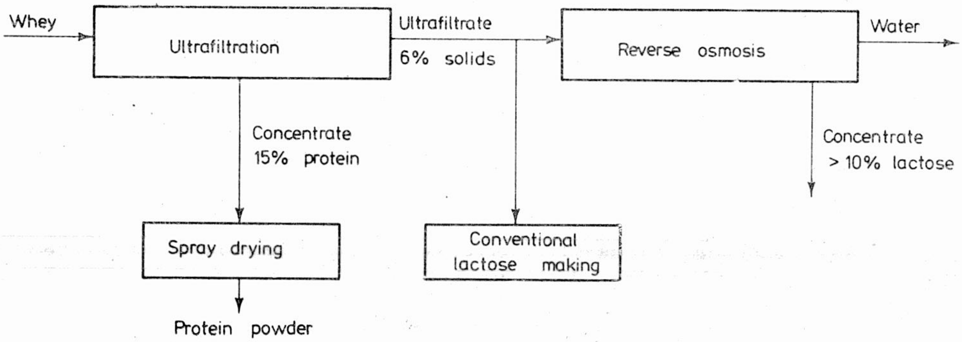


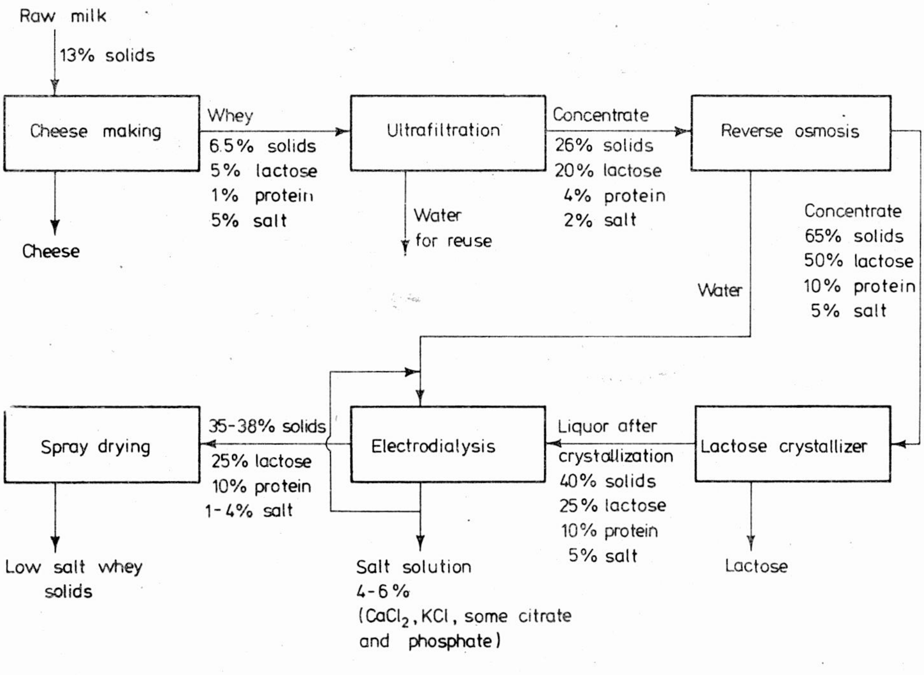
Fig. 3. Membrane process treatment of emulsion wastes

4. THE TREATMENT OF WHEY

The processes of reverse osmosis and ultrafiltration have been applied to treat the wastes of food industry mostly to the treatment of whey [6], [10], [11], a by-product of cheese production. In the production process about a half of the dissolved milk substances get into whey, including most of lactosis, about 20% of pro



Scheme I



Scheme II

Fig. 4. Treatment of whey by utlrafiltration and reverse osmosis processes [6, 11]

tein and a significant amount of vitamins and mineral salts. An animal feed can be obtained through concentrates for pharmatheutical industry and lactic acid for food grade acidulants can be recovered. The ultrafiltration is carried at the pressure of 0.7 MPa, using tubular modules with membranes which retain protein. The concentrate received contains approximately 10% of protein (with 8 times-lower-nonprotein-impurity-content) and is suitable for direct spray drying. The ultrafiltrate thus obtained is concentrated at pressure of 4.0 MPa in the reverse osmosis installation using membranes allow the passage of mineral salts but retain lactose. The final concentrate contains over 10% of lactose, whereas the water needs no further treatment. In another variant of processing [6] a concentrate from the ultrafiltration stage is concentrated in the reverse osmosis installation. The concentration of the dissolved substances in whey increases then from 6.5% to 65% and after spray drying an animal feed is obtained. The application of membranes to electrodialysis allows to remove the salts from a concentrate and to receive whey solids of a low-ash-content which can be used as an additive for foodstuffs. The water from both membrane processes is used again in technological processes. Figure 4 presents the schemes for both whey processing variants.

5. SUMMARY

The presented concepts of a combined application of ultrafiltration and the reverse osmosis in recovery of water and valuable substances can be applied for waste treatment in other branches of industry. A two-stage-treatment of municiapl wastes has been suggested and the application of ultrafiltration as a pre-treatment before reverse osmosis desalination has been demonstrated.

At the present stage of membrane separation technology development the method should be applied only after proving economic feasibility. A practical realization of the tasks lies in a combined use of ultrafiltration and the reverse osmosis as one technological series.

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