Flexographic Newspaper Deinking: Treatment of Wash Filtrate Effluent by Membrane Technology

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Ultrafiltrationwas investigatedas a means to removeflexographic inkpigmentsfrom washfiltrate efluent generatedfrom various mixtures offlexographic and offset old newspapersfrom deinking operations. Membrane separation efficiency was assessed from permeate fluz, fouling rate, and ease of membrane regeneration (cleaning). Ultrafiltration was capable of completely removing ink pigmentsfrom effluent streams. Permeateflux decreased significantly with time due to membranefouling and concentrationpolarization. Flocculation by acidification of theflexographic ink of effluentscontaining highflexo ink content improved significantly thepermeation rate and reduced thefouling duepossibly to a morepermeable cakeformation near the membrane suface. Ultrafiltrationproduced betterwater quality compared to standard jar tests.

L'ultrafiltration (UF)a été analysée comme moyen d'extraire les pigments d'encre flexographiquedes filtrats de lavage de mélanges variés de vieuxpapierjournal offset etflexographique mélangés, produits lors du désencrage. Nous avons évalué l' efficacité de la séparation par membrane en considkrant le dkbit de permkation, la vitesse d'encrassement et la facilité de régénération de la membrane (nettoyage). L'ultrafiltration a permis d'extraire tous les pigments d'encre de l'effuent. Le dkbit de permkation a considkrablement diminud avec le temps, en raison de la polarisation de la concentration et de l'encrassementde la membrane. Lafloculation par acidification de l'encre flexographique des effluents à teneur élevée en encre flexographique a amdliord considérablement le ddbit de perméation et réduit l' encrassement possiblement en raison de laformation d'un gateauplus permkable prés de la surface de la membrane. L'ultrafiltration a produit une meilleure qualité d'eau comparativement aux essais defloculation Jar-Test.

INTRODUCTION

Water-based inks used in flexographic news printing remain one of the most troublesome contaminants and present a unique challenge to the deinking operation. Most newspaper deinking plants are designed to remove the oil-based inks most commonly used in newsprint publication. These facilities tend to rely on froth flotation for ink removal. However, it is well established that the conventional flotation process is ineffective at removing flexographic inks [1-4]. Under alkaline repulping conditions, flexographic inks form colloidal dispersions of small hydrophilic particles (<5 μm) [3,5,6] stabilized by the ionized binder via an electrosteric mechanism [5-7]. Flexographic ink particles dispersed in the pulp suspension are then too small and/or too hydrophilic to float at a good rate in flotation cells.

Since flexographic inks form very small hydrophilic dispersions under alkaline repulping conditions, they are particularly well suited to removal by washing deinking technology [3,8]. However, large quantities of filtrate are produced by washing which cannot be directly recycled to the process without detrimental effects on brightness of the deinked pulp or discharged to the environment. However, the deinking efficiency of a wash deinking process is strongly dependent on removal of the ink from the washer effluent [9]. Therefore, the wash effluent must be clarified of the flexographic pigments. In practice, most deinking plants have some process water clarification as part of a washing stage.

Dissolved air flotation (DAF) is one of the most common types of process water clarification used in deinking mills. However, the presence of flexo-printed materials in the furnish seriously impacts DAF clarification and necessitates significantly higher levels of coagulant to achieve a proper clarified water quality [10,11].

Membrane separation technology is a potentially attractive method for the removal of flexographic ink residues from the wash filtrate effluent of deinking mills [12].

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Deinking of mixed old newspaper furnish would rely on both froth flotation and washing processes, with the wash filtrate clarified by ultrafiltration before being recycled to the process. A research program at Auburn University has been undertaken to study the potential application of membrane technology for the treatment of wash deinking effluents [13]. Results showed that ultrafiltration and microfiltration were both capable of completely removing flexographic pigments from aqueous dispersions [14,15].

Although the use of flexo-printed newspapers is increasing, limited studies on the application of membrane technology for the removal of ink pigments for real deinking effluents have been reported in the literature[16]. Concerns about the feasibility and commercial implimentation of the method must also be considered for the potential application of ultrafiltration technology. Therefore, the objective of this work is to investigate the potential of ultrafiltration to clarify process water from a flexo-printed newspaper deinking facility. Several experiments with different mixtures of newspapers printed with flexographic and oil-based inks were conducted with laboratory deinking equipment in order to generate wash effluents. A bench-top ultrafiltration apparatus was then used to evaluate the performance of ultrafiltration (UF) membranes. Membrane separation efficiency was assessed from permeate flux, fouling rate and ease of membrane regeneration (cleaning). Carbon black pigment removal was also measured and compared to standard dissolved air flotation clarification as indicated by jar tests. A spectrophotometric method was used to determine carbon black removal efficiency.

EXPERIMENTAL

Materials

Flexo-printed newspapers were obtained from a newspaper printer, and offset newspapers were obtained from a deinking mill. Papers have been stored in a temperature- and humidity-controlled room prior to their use. The newspapers were approximately four months old.

Membrane

Ultrafiltration experiments were performed with a polysulphone hollow fibre ultrafiltration membrane, with a nominal molecular weight cut-off of 500 000 (UF500), supplied by Koch Membrane System, Wilmington, MA, USA. The experiments were carried out with a bench-top membrane filtration apparatus described in a previous paper [15].

Deinking

A schematic diagram of the basic steps involved for deinking old newspapers (ONP) is presented in Fig. 1. Mixtures of flexo-printed and offset newspapers (0, 10, 20, 50 and 100%) were repulped using tap water for 15min in a laboratory pulper operated at a pulp consistency of 3% and a temperature of 45°C. A standard chemical recipe (1% sodium hydroxide, 1% sodium silicate, and 0.1% nonionic surfactant) was used for all deinking trials. All chemical dosages were based on an oven-dry paper basis. Pulper pH was adjusted to 10.5.

After repulping, the pulp slurry was diluted with tap water to 0.8% consistency. The pH was adjusted to 9.5. Flotations were then carried out in a Denver D12 flotation cell for 5 min at 1200 rpm and 45°C in a 10 L stainless steel container. Foam was manually scraped off from the surface of the cell. The accepted pulp from the flotation cell was kept for thickening and washing.

The pulp suspension (accepts) was diluted with tap water to 0.45% consistency prior to thickening. Thickening of the pulp was carried out using a 150 mesh screen in order to increase the pulp consistency from 0.45 to about 10%. The filtrate was collected for ultrafiltration experiments.

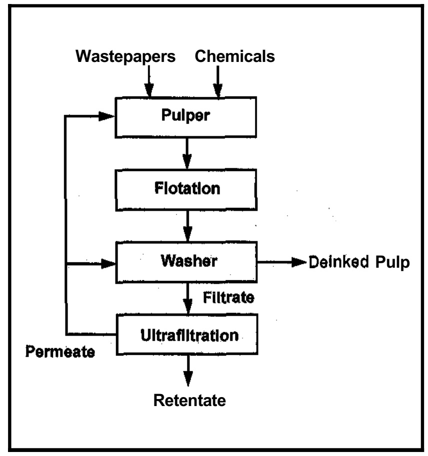

Fig. 1. Basic steps involved for deinking old newspapers.

Wash Filtrate

Wash filtrate effluents collected during thickening and washing were prefiltered using a bag filter with a nominal pore size of 100 µm to remove fibres and fines. Filtered streams were collected and stored at 4°C prior to their use in ultrafiltration experiments.

Ultrafiltration Experiments

Flux vs time

Permeation rates are reported as flux, with units of volume per unit of membrane area per unit time ($L/m^2{\cdot}h$). To study the effect of flexo ink content on fouling of the ultrafiltration membrane, flux decay vs time experiments were carried out with wash filtrate effluents produced from deinking of mixed ONP furnishes.

All ultrafiltration experiments were performed at 45°C, at a constant trans-membrane pressure (ΔP_{TM}) of 172 kPa and feed flow rate of 3.78 L/min which corresponds to an average flow velocity across the membrane of approximately 1.0 m/s, (Re = 1100). The pH of feed solutions varied between 8.5 and 9.5. In several experiments, the pH of feed effluents was adjusted between 3.5 and 4.5 before ultrafiltration. Both retentate and permeate were recirculated to the feed container in order to keep a constant feed concentration during experimentations. Flux was measured by the timed collection of permeate in a tared beaker which rested on a balance. The specific gravity of the permeate was determined to be 1.0. After the flux measurement, the collected permeate was returned to the feed tank.

Cleaning of membranes

The cleaning procedure has already been described in a previous paper [15]. The effectiveness of the cleaning procedure on restoring membrane performance was determined by calculating the reduction of the pure water flux before experiment and after cleaning the membrane as follows:

$$E_c = \left(1 - \frac{J_{Wc}}{J_{Wi}}\right) \times 100 \qquad (1)$$

where

E_c = efficiency of the cleaning procedure, %

J_{Wc} = pure water flux after cleaning, L/m2·h

J_{Wi} = pure water flux before filtration, L/m2·h

Jar Tests

Water clarification was simulated using jar tests to compare the efficiency of water clarification with ultrafiltration results. A sample of wash filtrate effluent before bag filtration (300 mL) was poured in a beaker. The effluent was agitated using a magnetic stirrer. The appropriate dosage of coagulant was injected in the vortex and mixed at 100 rpm for 3 min. Mixing was then reduced to 40 rpm and the appropriate dosage of flocculant was added. The solution was mixed at low speed for an additional 3 min. Mixing was then stopped to allow settling of the flocs for 5 min. At the end of the settling time, transmittance of the supernatant was measured at 457 nm using a Spectronic 20D spectrophotometer. Coagulants and flocculants were kindly provided by Buckman Laboratories, Memphis, TN, USA.

Analysis

Transmittance

Transmittance of both feed and permeate samples were measured with a spectronic 20D spectrophotometer using the method described for jar tests. Carbon black pigment removal efficiency by ultrafiltration was calculated as:

$$E_{UF} = \frac{T_p - T_f}{100 - T_f} \times 100 \qquad (2)$$

where

E_{UF} = carbon black removal efficiency by ultrafiltration, %
T_p = transmittance of the permeate sample, %
T_f = transmittance of the feed sample, %

Total solids content

Total solids content of both feed and permeate samples was determined gravimetrically after drying samples in pyrex evaporating dishes at 105°C overnight. Total solids content were used to determine apparent rejection of total solids by UF membranes. Apparent rejection of total solids was calculated by:

$$E_r = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (3)$$

where

E_r = apparent rejection efficiency, %
C_p = total solids concentration in permeate, %
C_f = total solids concentration in feed, %

RESULTS AND DISCUSSION

Ultrafiltration Experiments

Permeate Flux

Ultrafiltration experiments were carried out consecutively with feed containing a decreasing amount of flexo content, i.e. from 100 to 0%. The membrane was cleaned between experiments. Figure 2 presents permeate flux vs time curves for five feed solutions containing various flexo ink contents. In all cases, a rapid decrease of the flux is observed within 10 min of operation. After this rapid initial decay, the rate of flux decline progressively lessened until a near-equilibrium filtration rate was achieved corresponding to the stabilized flux (steady-state).

Our results indicated stabilized flux values between 75 and 90 $L/m^2 \cdot h$, except for the case with 100% flexo which gave a stabilized flux of about 120 $L/m^2 \cdot h$. Although initial values of the permeate flux decreased for each flexo content level, steady-state permeation rates seemed to be independent on flexo ink content. A similar phenomenon has been observed by Upton et al. [15] for low-concentration flexographic ink dispersons.

Figure 2 shows that, for all flexo/offset mixtures studied, a rapid decrease in flux is observed. This flux behaviour is typical of membrane filtration processes and is consistent with other studies [14,15,17,18]. Our results suggest that flux decay with time is probably a combination of both concentration polarization and membrane fouling occurring simultaneously. Both phenomena result from the presence of suspended and dissolved materials in feed streams. Most deinking effluents contain various colloidal suspended and dissolved solids such as lignin fragments, wood resin and hemicelluloses as well

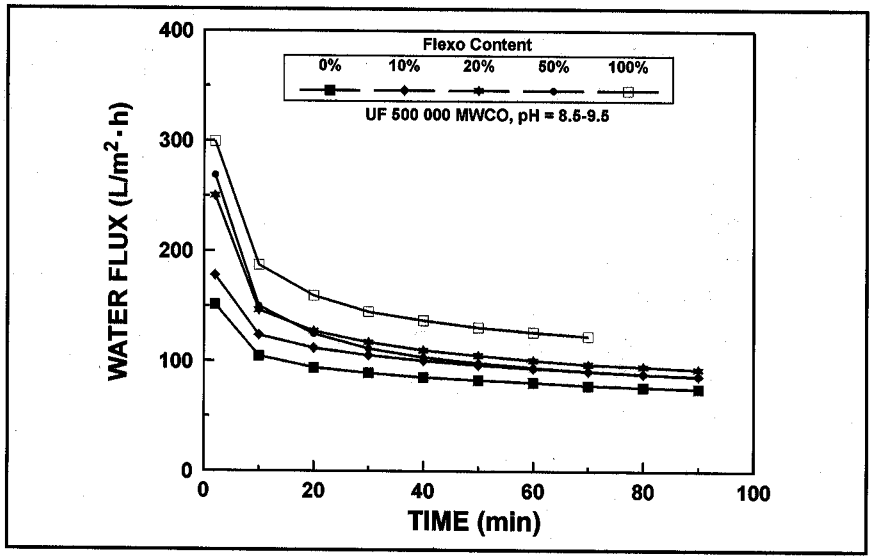

Fig. 2. Permeate flux decline for feed solutions Containing various proportions of flexo-printed newspapers.

compounds and silicates. They also contain variable proportions of water-soluble and oil binders from the inks. Newsprint also contains various additives such as pitch dispersant, fillers, retention aids and bentonite [19,20]. Ash content of offset newspapers used in this study was found to be higher than ash content in flexo-printed newspapers (5 vs 1.5%). Studies have shown that the predominant size of the colloidal materials present in the recycling system are in the range 0.01–1 µm [21]. Therefore, it is likely that the presence of colloidal suspended solids and polymeric materials of various molecular weight, specifically the low molecular weight components, could be responsible for the flux decline observed in Fig. 2.

Fouling depends on the nature of the solutes and is mainly caused by adsorption of the effluent components on the walls of the membrane pores and pore plugging, or by the deposition of solute molecules at the surface of the membrane where a cake is formed [17,18,22]. When the feed solution is processed through the membrane, effluent components such as small ink particles and colloidal materials are drawn toward the filtering surface of the membrane by convective flow of the filtrate through the membrane pores. Feed solutions may contain low molecular weight solutes small enough to enter the membrane pores, or molecules that are adsorbed on the pore wall, and this will restrict the effective pore diameter. As a consequence, these phenomena result in a significant flux decrease. Adsorption is determined by the membrane material and solute interactions, whereas the degree of pore plugging depends on the relative size of solute and pore [23]. Moreover, solutes are more readily adsorbed onto hydrophobic membrane surfaces such as the polysulphone membrane used in our study [22]. Since the UF membrane used was a hydrophobic polysulphone membrane with a molecular weight cut-off (MWCO) of 500 000 Daltons, it means that any dissolved material with a molecular weight lower than 500 000 could permeate through the pores with the solvent and subsequently interact with the membrane surface. It is thus likely that such colloidal materials could be responsible for membrane fouling. According to Cohen and Probstein [24], the initial fouling of the membrane is very fast. They estimated that the reaction time scale is of the order of less than 1 s, which implies that most of the pore plugging and adsorption is essentially instantaneous.

Results in Fig. 2 show that the initial permeate flux for each trial was different although the behaviour of each curve showed similar general characteristics. Since experiments have been performed successively in a reverse order of flexo ink content, i.e. from 100 to 0%, it is clear that addition of offset newspapers in the raw material had a significant effect on initial flux values. These results suggest that irreversible fouling of the membrane had occurred when processing feed containing an increasing proportion of offset newspapers, thus resulting in a gradual decline in productivity.

Pure water flux of the membrane measured before experiments, J_{Wi}, and after cleaning the membrane, J_{Wc}, also indicate that irreversible membrane fouling had occurred during treatment of feed solutions. Figure 3 shows a significant decrease of the pure water flux between feed solutions containing 100 and 50% flexo content. Pure water flux decreased from 600 to 350 $L/m^2 \cdot h$, respettively. This decrease was mostly attributable to irreversible fouling that occurred during independent trials performed between those two series of experimentations, and was not entirely related to the present series. Therefore, the lower pure water fluxes observed for experiments with offset newspapers should be higher. How-

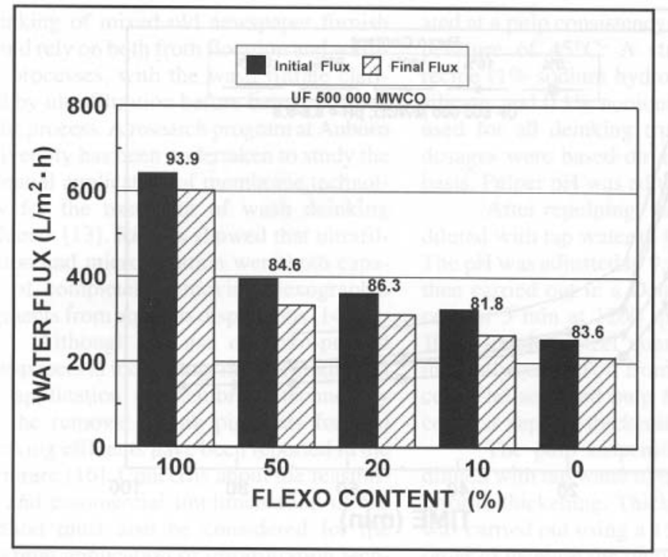

Fig. 3 Pure water permeation rate before experimentation and after cleaning the ultrafiltration membrane. Values reported on the top of the bars are the cleaning efficiency E_C of the membrane after processing feed effluents.

TABLE I
FRACTIONAL RESISTANCES TO PERMEATE FLOW DURING ULTRAFILTRATION OF ALKALINE FEED SOLUTIONS CONTAINING VARIOUS PROPORTIONS OF FLEXO-PRINTED NEWSPAPERS

Flexo Content (%)	R_m (N-h/L)	R_p (N-h/L)	R_{bl} (N-h/L)		R_{bl}/R_T (%)
0	676.8	462.5	1152.9	2292.1	50.3
10	532.0	437.4	1016.4	1985.8	51.2
20	477.3	212.1	1165.9	1855.4	62.8
50	436.5	205.2	1355.6	1997.3	67.9
100	268.7	307.4	859.1	1435.2	59.9

ever, it is clear that treatment of feed solutions containing higher offset newspaper content decreased the membrane permeability due to membrane fouling.

Cleaning efficiency of the membrane, E_C, is also reported and ranged between 82 and 94%. The cleaning process is considered successful when cleaning efficiency reached a value over 80%. Even though the cleaning efficiency of the membrane remained relatively high (80-94%), the membrane permeability steadily decreased with subsequent experimentations, which indicates that foulants were not completely removed during the cleaning process. Lindau et al. [25] have shown a similar phenomenon with low molecular weight hydrophobic solute (octanoic acid) and polysulphone ultrafiltration membranes. They showed that the pure water flux of a membrane can be regained even if the foulants were not completely removed. Therefore, it is possible that an unidentified low molecular weight hydrophobic solute present in feed solutions be strongly adsorbed on the membrane surface and/or inside the pores and could not be removed by the cleaning process. No attempt has been made yet to identify the exact fouling mechanisms involved.

Concentration polarization is also a typical phenomenon associated with membrane filtration. During ultrafiltration, solutes large enough to be retained by the membrane accumulate on the membrane surface forming a boundary layer due to convective transport of materials as solvent permeates through the membrane resulting in a higher local concentration of retained solids at the membrane surface as compared to the bulk suspension. The rejected matter near the membrane surface can be transported back to the bulk of the liquid by diffusion as a result of Brownian motion, shear-induced lift, or electrostatic repulsion [17,26]. After a given period of time, steady-state conditions are reached and the convective solute flow to the membrane surface is balanced by the solute flux through the membrane and the diffusive flow from the membrane surface to the bulk. A concentration boundary layer is thus formed which separates the region of higher concentration near the membrane surface from the more uniform concentration in the bulk of the fluid. Flow of fluid parallel to the membrane surface promotes the back transfer of accumulated material into the bulk fluid controlling the boundary layer thickness [26]. Therefore, this polarized layer also contributes to the total flux decline of permeate during ultrafiltration.

Membrane flux decline observed during ultrafiltration of feed solutions (Fig. 2) is thus a cumulative effect of several mechanisms. All those factors induce additional resistances to the permeation across the membrane. In an attempt to quantify the relative contribution of fouling and concentration polarization to flux decline, a resistance in series model was used.

The total resistance to permeation through the membrane is given by:

$$R_T = R_m + R_p + R_{bl} \tag{4}$$

where

RT = total resistance, N-h/L
R_m = membrane resistance. N-h/L
Rp = resistance due to pore plugging, N-h/L
Rbl = resistance due to the boundary layer, N-h/L

The membrane resistance, Rm, can be calculated from the relation:

$$J_{Wi} = \frac{\Delta P}{R_T} \tag{5}$$

where

J_{Wi} = pure water flux, L/m^2·h
ΔP = transmembrane pressure, kPa

The steady-state permeate flux, J_{SS} during effluent treatment can be defined as:

$$J_{SS} = \frac{\Delta P}{R_T} \tag{6}$$

Assuming that the initial permeate flux with effluent as feed, J_i (measured 2 min after the start of the experiment) is a measure of $R, \ + R_p$, then the resistance due to the boundary layer can be calculated by:

$$R_{bl} = \Delta P \times \left[\left(\frac{1}{J_{SS}} \right) - \left(\frac{1}{J_i} \right) \right] \tag{7}$$

Table I presents the fractional resistances to permeation calculated for feed solutions containing various proportions of flexo ink and gives a relative measure of the various contributions to the total hydraulic resistance.

Results show that the total resistance to permeation, R_T, increased when offset newspapers were added to the furnish, in agreement with our previous findings. However, lower values would have been obtained if the membrane permeability had not been reduced during independent trials carried out before the test with 50% flexo content, as discussed previously. Our results clearly showed that the intrinsic membrane resistance, R_m, almost doubled during these tests due to irreversible fouling.

Analysis of the various resistances showed that the predominant resistance to permeation was attributed to the concentration polarization phenomenon as indicated by higher R_{bl} values. The relative contribution of the boundary layer resistance to the total resistance, R_{bl}/R_T, increased from 50 to 68% with addition of offset newspapers in the feed solution, indicating that a less permeable cake was deposited on the membrane surface resulting in lower fluxes. Even if the boundary layer was the main resistance for permeation, fouling-effect resistance, R_p (pore plugging), and membrane resistance, R_m, were also significant. The membrane resistance, R_m, increased steadily with increasing addition of offset newspapers. Therefore, it is clear that treatment of feed effluents containing a higher proportion of offset newspapers reduced the

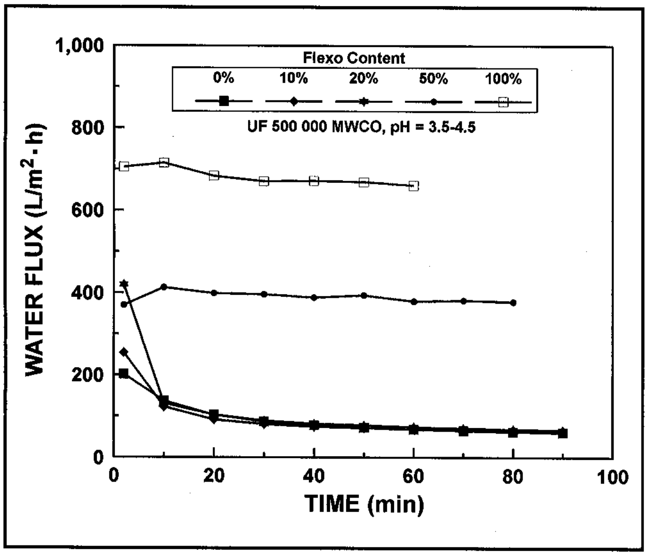

Fig. 4. Permeate flux for feed solutions containing various proportions of flexo-printed newspapers. Feed effluents were acidified between pH 3.5 and 4.5 before ultrafiltration.

TABLE II
FRACTIONAL RESISTANCES TO PERMEATE FLOW DURING ULTRAFILTRATION OF ACIDIFIED FEED SOLUTIONS CONTAINING VARIOUS PROPORTIONS OF FLEXO-PRINTED NEWSPAPERS

Flexo Content (%)	R_m (N-h/L)	R_p (N-h/L)	R_{bl} (N-h/L)	R_T (N-h/L)
0	773.6	78.8	1991.9	2844.4
10	608.4	68.6	2063.3	2740.4
20	354.5	56.0	2173.7	2584.2
50	512.4	–46.0	–10.8	455.5
100	271.5	–26.8	17.8	262.5

membrane permeability (Fig. 3), resulting in lower permeation rates (Fig. *2).*

Effect of pH on Permeate Flux

Experiments have been carried out to minimize the effects of concentration polarization and membrane fouling on ultrafiltration performance. It was thought that decreasing the pH of feed solutions containing flexographic ink particles to acidic values would improve the permeation rate of the ultrafiltration membrane. Therefore, pH of feed solutions containing various proportions of flexographic and offset newspapers were adjusted between 3.5 and 4.5 before ultrafiltration. Results are presented in Fig. 4.

Results show that permeate fluxes for feed effluents containing a high proportion of flexo-printed newspapers (50 and 100%) were improved significantly, whereas no improvement was found for lower flexo-printed content. Surprisingly, for high flexo-printed content, permeate fluxes did not decrease compared to the pure water flux measured before ultrafiltration and remained constant with time. Therefore, no fouling of the membrane occurred during ultrafiltration. The fractional resistances to permeation were also calculated (Table II) and clearly showed a significant decrease of the total resistance to permeation resulting from the elimination of the boundary layer and pore-plugging resistances. Negative values were assumed to be equal to zero.

This spectacular result is thought to be the consequence of the destabilization and the aggregation of small flexographic ink particles into larger ink aggregates, to the reduction of ink particle's charge, and also to the enhancement of back-diffusion of these larger aggregates which resulted in thinner cake layer. Dorris and Nguyen [5] and Fernandez et al. [6] have shown that, at low pH, the zeta potential of flexographic ink dispersions was reduced from -60 to –20 mV which promoted the aggregation of fine ink particles into larger aggregates roughly 10–50 µm in size. During ultrafiltration, larger ink aggregates can form deposits on the membrane surface with lower specific resistance, which facilitates the permeation of the solvent through the cake layer as indicated by the low boundary layer resistance values (Table II) [27]. It is also known that shear-induced lift which promotes back-diffusion of deposit materials on the membrane surface increases with increasing particle size (above 10 pm), resulting in a thinner cake layer [28]. Although lower zeta potential could promote the formation of adsorptive hydrophobic ink aggregates at the membrane surface, it is likely that this phenomenon had been outweighed by the lower cake layer specific resistance and the enhanced back-diffusion mechanisms that occurred under acidic conditions.

The fouling of the membrane caused by physical or chemical adsorption of certain components present in the feeds could also be reduced due to a minimization of solute–membrane interactions resulting from pH adjustment of the feeds. Kuo and Cheryan [29] have shown subsequent fouling reduction with solutions containing proteins. Coagulation could also reduce the irreversible fouling potential by decreasing the quantity of small particles which could block and/or tightly adsorb onto the membrane pore surface [30]. Unfortunately, the permeate flux improvement was not found for lower flexo content, clearly indicating that other foulant compounds not affected by the pH variation reduced the permeation rate. The same flux decline mechanisms such as added resistances from fouling and concentration polarization as discussed previously for alkaline feed effluents are likely to occur for those specific cases. However, further permeate flux improvement for these feed solutions could be expected with the addition of proper coagulating agents. Studies in the field of food technology and wastewater treatment have shown that coagulation or precipitation of foulant materials present in the feed reduced fouling and improved flux rates [30-32]. Therefore, this approach looks very promising for the treatment of wash deinking effluents containing a higher proportion of organic and inorganic materials.

Carbon Black Pigment Removal and Total Solids Rejection

The two main features of the ultrafiltration process for operational performance are: i) separation or rejection of materials from the liquid phase; and ii) permeate flux. Carbon black removal efficiency was calculated from transmittance measurements, whereas total solids rejection was determined from total solids content of permeate and feed samples. Figures 5 and 6 present carbon black pigments removal efficiency and total solids rejection for various feed solutions treated under alkaline and acidic conditions, respectively. Our results show that carbon black pigments from flexo as well as offset inks are completely removed by ultrafiltration membrane. Therefore, no carbon black pigments were detected in the permeate samples for both operating conditions, indicating that the ultrafiltration membrane used achieved complete retention of pigments and produced clear permeate. These results are in total agreement with results presented by Upton et al. [13-15] for flexographic ink dispersions.

Total solids rejection, which include suspended as well as dissolved materials, are also presented in Figs. 5 and 6. Under alkaline conditions (Fig. 5), total solids rejection ranged between 30 and 55%, with increasing rejection for feed containing a higher proportion of offset ink. These results suggest that treatment of feed solutions containing a higher proportion of offset ink tended to foul the membrane which is in good agreement with previous results presented for permeate flux. Higher total solids and carbon black rejection could be attributed to the reduction of membrane permeability due to partial pore plugging by foulant compounds and/or to the formation

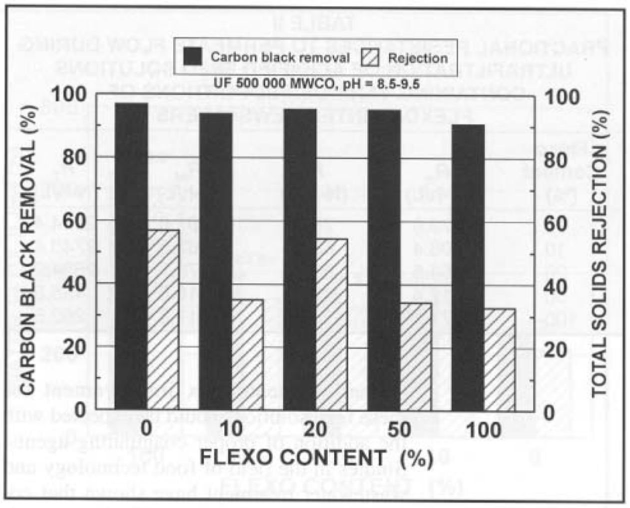

Fig. 5. Carbon black removal efficiency and rejection of total solids by ultrafiltration for alkaline feed solutions containing various proportions of flexo-printed newspapers.

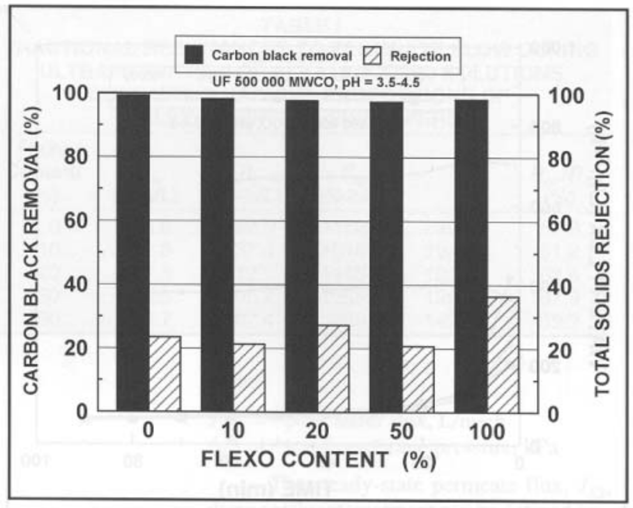

Fig. 6. Carbon black removal efficiency and rejection of total solids by ultrafiltration for acidic feed solutions containing various proportions of flexo-printed newspapers.

of a stronger resistance layer over the membrane during ultrafiltration. It is likely that a less permeable membrane and/or cake layer will retain more materials, irrespective of their sizes. In our case, this phenomenon could be desirable only if an acceptable permeate flux level is maintained. In addition, a permeate containing lower dissolved materials is beneficial because it reduces the chemical build-up in the water loop which could have a negative impact on production and product quality. However, acidic feed solutions treated with the same ultrafiltration membrane showed nearly 100% carbon black pigment removal (Fig. 6) although a slightly lower total solids rejection (20%) compared to alkaline feed solutions as illustrated by Fig. 6. These lower values could be attributed to a lower fouling effect resulting from the treatment of acidic solutions. Although acidic conditions resulted in lower total solids rejection, one must consider the significantly higher flux levels obtained with feed solutions containing 50 and 100% flexo newspapers.

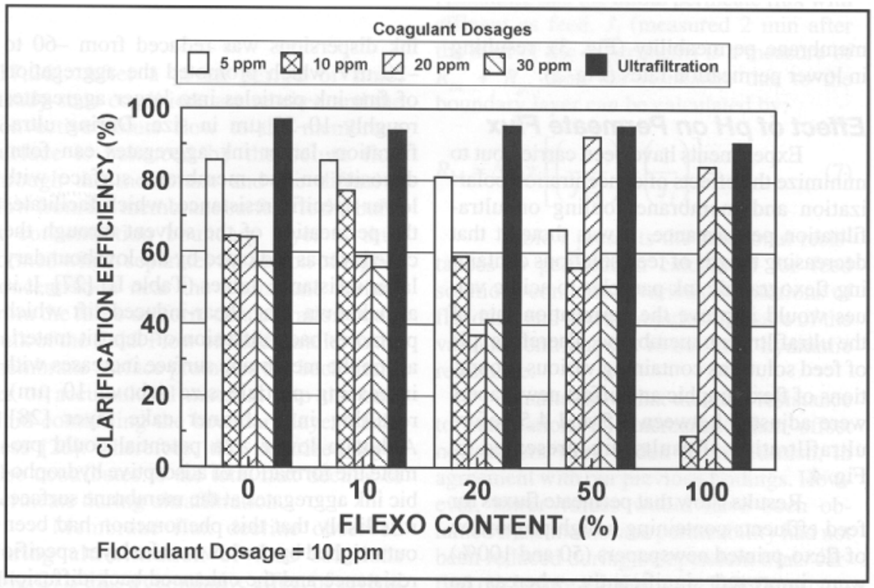

Fig. 7. Clarification efficiency for ultrafiltration and standard jar tests for feed solutions containing various proportions of flexo-printed newspapers.

Clarification Efficiency

Figure 7 presents a comparison of the clarification efficiency obtained by ultrafiltration and conventional jar tests for various mixtures of flexographic and offset newspapers. Results show that ultrafiltration consistently performed better than jar tests at every coagulant and flocculant dosage tested. Ultrafiltration yielded clarification efficiencies over 90% for each flexo/offset feed effluent.

Although several jar tests resulted in clarification values higher than 80%, the clarified water quality never approached ultrafiltration permeate quality. Clarified water turbidity was particularly affected by the presence of fillers in the offset newspapers (5%). It has systematically been found that, as offset content increases, the turbidity of the clarified water increased, indicating the presence of fillers remaining in the clarified water. Hsu [19] has clearly shown that the presence of clay and calcium carbonate fillers in process water before clarification affected the process water clarification requiring higher levels of flocculant.

Figure 7 also clearly shows that when flexo content increased, a higher coagulant dosage was required to improve the clarification efficiency which is in perfect agreement with litterature results [10,11].

CONCLUSIONS

Treatment of wash filtrate effluents, containing various proportions of flexographic ink, by ultrafiltration produced clean permeates free of flexographic ink pigments.

The permeate flux of wash deinking effluents was shown to decrease with time as a result of fouling and concentration polarization. It was shown that the addition of offset newspapers in the raw material had a significant detrimental effect on flux decay and membrane fouling. The flux decrease was controlled mainly by the boundary layer resistance and to a lesser extent by membrane fouling due to adsorption of foulant components of the feed and pore blocking. Although the cleaning procedure appeared to be quite effective, the performance of the membrane could not be totally restored, thereby resulting in a steady decrease of the membrane permeability with usage.

Acidification of effluents was shown to improve permeation rates significantly and reduced membrane fouling when using higher percentages of flexo-printed papers. However, permeation rates decreased with increasing proportions of offset newspapers.

Ultrafiltration produced better clarification than dissolved air flotation. This indicates that ultrafiltration may be successfully applied to clarify the wash filtrate from a deinking process for mixed furnish containing conventional and flexo-printed ONP. However, the feasibility and commercial implimentation of the method must be investigated to validate the practical application of membrane technology in the deinking field.

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REFERENCES

1. GALLAND, G. and VERNAC, Y., "Deinking of Wastepaper Containing Water-Based Flexo-Printed Newsprint", *Pulp Paper Can.* 96(6):T181–T185 (1993).
2. MAH, T., REID, F. and YAU, T., "Deinking of Flexographic Ink by Flotation Process", Preprints 79th Ann. Mtg., Tech. Sect., CPPA, A119–Al28 (1993).
3. JARREHULT, B., HORACEK, R.G. and LINDQUIST, M.L., "Deinking of Wastepaper Containing Flexographic Inks", Proc. 1989 TAPPI Pulping Conf., 391-405.
4. PUTZ, H-J., SCHRAFFATH, H.J. and GOTTSCHING, L., "Deinking of Oil-and Waterborne Printing Inks: A New Flotation Deinking Model", *Pulp Paper Can.* 94(7): 16–21 (1993).
5. DORRIS, G.M. and NGUYEN, N., "Flotation of Model Inks. Part II. Flexo Ink Dispersions Without Fibres", *J. Pulp Paper Sci.* 21(2):J55–J62 (1995).
6. FERNANDEZ, E.O. and HODGSON, K.T., "Stabilization Mechanism of Water Based Inks", Preprints 82nd Ann. Mtg., Tech. Sect., CPPA, A77–A82 (1996).
7. LIPHARD, M., SCHRECK, B. and HORNFECK, K., "Interfacial Studies and Application Tests on the Flotation of Printing Inks and Fillers", Proc. 1990 TAPPI Pulping Conf., 965–975.
8. RANGAMANNAR, G., GRUBE, G. and KARNETH, A.M., "Behaviour, of Water-Based Flexographic Inks in Newsprint Deinking", Proc. 1992 TAPPI Pulping Conf., 933–939.
9. PHILIPPE, I.J., "Effective Flotation Deinking of ONP With Increasing Levels of Flexographic Print", Proc. 1996 TAPPI Pulping Conf., 805–810.
10. TREMONT, S.R., "Impact of Neutral Deinking Chemistry on DAF Clarification and Sludge Dewatering of Deink Plant Rejects", Proc. 1993 TAPPI Pulping Conf., 749–756.
11. SCHRIVER, K.E. and FRIEL. T.C., "Approaches to Deink Process Water Clarification", Proc. 1992 TAPPI Pulping Conf., 439-443.
12. SKELTON, R., "Experiences in the United States with Ultrafiltration for Treatment of Aqueous Flexographic Ink and Starch Wastes in the Corrugated Container Industry", *Converter* 22(4):14–18 (1988).
13. UPTON, B.H., KRISNAGOPALAN, G.A. and ABUBAKR, S., "Deinking Flexographic Newsprint: Ultrafiltration Technology as a Method for Wash Filtrate Clarification", Proc. 1994 TAPPI Recycling Symp., 17–24.
14. UPTON, B.H., KRISNAGOPALAN, G.A. and ABUBAKR, S., "Flexographic Newsprint: Deinking: Wash Filtrate Clarification by Membrane Filtration", *Progress Paper Recycling* 5(2):36-48 (1996).
15. UPTON, B.H., KRISNAGOPALAN, G.A. and ABUBAKR, S., "Deinking Flexographic Newsprint: Using Ultrafiltration to Close the Water Loop", *Tappi J.* 80(2):155–164 (1997).
16. BRADEAL, J., SELL, N.J. and NORMAN, J.C., "The Use of Membrane Technology to Clean Deinking Effluent", *Prog. Paper Recycling* 6(1):24–31 (1996).
17. RAMAMURTHY, P., POOLE, R. and DORICA, J.G., "Fouling of Ultrafiltration Membranes During Treatment of CTMP Screw Press Filtrates", *J. Pulp Paper Sci.* 21(2):550-554 (1995).
18. TARLETON, E.S. and WAKEMAN, R.J., "Understanding Flux Decline in Cross Flow Microfiltration: Part.1: Effects of Particle and Pore Size", *Trans. IChemE* 71:Part.A, 399-410 (1993).
19. HSU, N.N.-C., "Effects of Fillers in Waste Furnishes on the Clarification of Deinking Process Water", *Pulp Paper Can.* 96(2): 50–53 (1995).
20. BOUCHER, G. and PIKULIK, I.I., "Survey of Additives for Papers Containing Mechanical Pulp", *Pulp Paper Can.* 95(7):41–43 (1994).
21. RORING, A. and WACKERBERG, E., "Characterization of Deinking White Water. Influence on Flotation and Bleaching Efficiency", *Pulp Paper Can.* 98(5):17-21 (1997).
22. JONSSON, A-S. and TRAGARDH, G., "Fundamental Principles of Ultrafiltration", *Chem. Eng. Process.* 27(2):67–81 (1990).
23. DAL-CIN, M.M., McLELLAN, F., STRIEZ, C.N., TAM, C.M., TWEDDLE, T.A. and KUMAR, A., "Membrane Performance with a Pulp Mill Effluent: Relative Contributions of Fouling Mechanisms", *J. Membrane Sci.* 120:273-285 (1996).
24. COHEN, R.D. and PROBSTEIN, R.F., "Colloidal Fouling of Reverse Osmosis Membranes", *J. Colloid Int. Sci.* 114(1):194–207 (1986).
25. LINDAU, J., JONSSON, A-S. and WIMMERSTEDT, R., "The Influence of a Low-Molecular Hydrophobic Solute on the Flux of Polysulphone Ultrafiltration Membrane with Different Cut-Off", *J. Membrane Sci.* 106:9-16 (1995).
26. PORTER, M.C., "Concentration Polarization with Membrane Ultrafiltration", *Ind. Eng. Chem. Prod. Res. Dev.* 11(3):234–248 (1972).
27. McDONOGH, R.M., WELSCH, K., FANE, A.G. and FELL, J.D., "Flux and Rejection in the Ultrafiltration of Colloids", *Desalination* 70:251–264 (1988).
28. WIESNER, M.R. and CHELLAM, S., "Mass Transport Considerations for Pressure-Driven Membrane Processes", *J. Am. Water Works Assoc.* 84(1):88-95 (1992).
29. KUO, K-P. and CHERYAN, M., "Ultrafiltration of Acid Whey in a Spiral-Wound Unit: Effect of Operating Parameters on Membrane Fouling", *J. Food Sci.* 48(4): 1113–1118 (1983).
30. YING, W. and TANSEL, B., "Effect of Coagulation on Fouling Rate and Cleanability of Ultrafiltration Membranes", Proc. 50th Purdue Industrial Waste Conf., Ann Arbor Press Inc., Chelsea, MI, 285–295 (1995).
31. KAISER, J.M. and GLANTZ, C.E., "Use of Precipitation to Alter Flux and Fouling Performance in Cheese Whey Ultrafiltration", *Biotechnol. Prog.* 4(4):242–247 (1988).
32. HENG, M.H. and GLATZ, C.E., "Flux Enhancement in Hollow Fibre Ultrafiltration for the Recovery of Acid Cheese Whey Precipitates", *Biotechnol. Prog.* 6(2):129–134 (1990).

REFERENCE: CHABOT, B., KRISHNAGOPALAN, G.A. and ABUBAKR, S., Flexographic Newspaper Deinking: Treatment of Wash Filtrate Effluent by Membrane Technology. Journal of Pulp and Paper Science, 25(10):337–343 October 1999. Paper presented at the 4th Research Forum on Recycling of the Technical Section, Canadian Pulp and Paper Association in Quebec, QC, on October 7–9, 1997. Not to be reproduced without permission from the Pulp and Paper Technical Association of Canada. Manuscript received July 15, 1997; revised manuscript approved for publication by the Review Panel June 3, 1999.

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