ELSEVIER

Dyes and Pigments, Vol. 35, No. 4, pp. 387–401, 1997

PII: S0143-7208(96)00076-9 0143-7208/97 $17.00+0.00

Analysis of the Quality of Permeates Obtained by Ultrafiltration of Water-based Stain Through YM5 and YM100 Membranes

V. Tišler,[a] V. Mihevc,[a] D. Kornhauzer,[a] J. T. Guthrie,[b] M. Kunaver[c] & A. Ivanuš[d]

[a]Department of Wood Science and Technology, University of Ljubljana, Rožna dolina c. 34, VIII/34, 1000 Ljubljana, Slovenia
[b]Department of Colour Chemistry and Dyeing, University of Leeds, Leeds LS2 9JT, UK
[c]Color, Komandanta Staneta 4, 61215, Medvode, Slovenia
[d]Pulp and Paper Institute Ljubljana, Bogošičeva 8, 1000 Ljubljana, Slovenia

(Received 10 July 1996; accepted 8 August 1996)

ABSTRACT

The possibility of using ultrafiltration in the treatment of waste water from wood staining operations was investigated. The study was confined to water-based stains, because their use in woodfinishing is on the increase. In the ultrafiltration process Recombined Cellulose Ultrafiltration membranes type YM100 and YM5 were used. The changes of each membrane was evaluated using scanning electron microscopy. To ascertain how the flow rate was changing as a function of time of filtration the quantity of permeates was measured every hour. By studying the permeate (BOD, COD, GC/MS), information about permeability of the membranes and about purity of the filtrate and its environmental acceptability were obtained. © 1997 Elsevier Science Ltd

INTRODUCTION

Ultrafiltration is now being extensively utilised in the food industry for purifying water such that it is drinkable, in separating and concentrating dairy products, and in the machinery industry for recovering paint, etc. [1].

Camatta has reported the application of ultrafiltration in effluent treatment. The effluents of a paper or board coating plant contain all the residues of the coating colours and of the raw materials swept along by the washing waters of the various equipments, from the kitchen to coating stations.

It has been established that the process has two determining economic and technical advantages viz.,

(i) the result of the separation is totally guaranteed, being independent from the load of effluent and allows the re-use of water for washings;
(ii) the separation is achieved without chemical additives and permits the recycling of the recovered coating raw materials [2].

The use of ultrafiltration in waste water cleaning in the textile-colouring industry has also been mentioned [3]. The research, including pilot tests, was performed on reactive textile dyes. It has been found that this method is economical and highly effective for these kinds of waste waters.

The finishing of wood and wood-based materials has drawbacks both with regard to health and to environmental protection. Liquid coating materials, such as stains, lacquers, paints, oils and waxes (which are mainly used during the finishing of furniture, joinery and carpentry) contain a considerable degree of organic solvents. Some years ago, the pertinent regulatory framework was largely aimed at ensuring that waste disposal was as harmless as possible [4].

Nowadays, the tendency is towards decreased introduction of harmful substances into production processes, with a view to reducing resulting waste materials. Thus, production processes need to be designed to allow for recycling, by formulating systems and selecting materials and methods of application accordingly [4].

By using water-based stains, which contain a dyeing agent as well as a water-soluble binder, uniform colouring can be ensured. Water-based stains normally also contain water-soluble organic solvents, which reduce grain raising [5]. The use of water-based stains has become quite widespread in spite of their known shortcomings [6]. In booth-spraying, the use of a water curtain produces considerable waste water.

Ultrafiltration is a method characterised by low energy consumption. By choosing a selectively permeable membrane of an appropriate type, the desired composition of the retained solution (retentate) and purity of the filtered solution (permeate) can, in the process of concentration, be achieved. Membrane pores are capable of retaining molecules of molecular weight of 100 g mol^{-1} to 100 000 g mol^{-1}, depending on the membrane characteristics [7]. The molecular weight cut-off is defined such that 90% of the (macro) molecular solutes are rejected by the membrane. Solute rejection of membrane characterisation should be considered with care. Two phenomena are strongly involved, viz., concentration polarisation, and deformation of flexible chains. These factors need to be taken into account during consideration of membrane design, filtration assembly and process conditions [7, 8].

Studies of membranes have been undertaken and several excellent reviews are available.

EXPERIMENTAL

Materials

The experimental procedures were performed with a view to providing information of relevance to the environmental acceptability of permeates, and to ascertaining the suitability of ultrafiltration systems for treating waste water resulting from the process of staining wood in a spray-booth with a water curtain.

For testing purposes, the water-based stain was used as a dispersion. Samples were simulated in laboratory, by mixing distilled water and stain in the ratio of 16:1.

The solvent composition of the stain used in the experiments was- water (74%), butyl glycol (2,4%), ethanol (10%), propylene glycol (7%) and methoxybutanol (0,3%).

Procedures

Scanning electron microscopic studies

The upper and lower surfaces of the membranes were observed by scanning electron microscopy (SEM). Air-dried membrane samples were used. Cut specimens were sputter-coated with gold before SEM photographs were taken; photographs were obtained using a Joel LSM-820 unit at an operational voltage of 15 kV.

Ultrafiltration

Ultrafiltration was carried out by means of an Amicon Stirred Cells 8400 laboratory ultrafiltering unit, at a constant nitrogen pressure of 3.7 bar, with continuous stirring. Amicon Diaflo, Recombined cellulose Ultrafiltration Membranes type YM100 and YM5 were used. YM100 membranes are designed to retain molecules of molecular weight of not less than 100 000 g mol^{-1}. YM5 membranes are designed to retain molecules whose molecular weight is not less than 5000 g mol^{-1}.

Filtration through YM100 and YM5 membranes was carried out over ten days, for nine hours each day. Every hour, the quantity of waste water in the filtering unit was replenished up to level of 250 cm_3. On completion of filtration, the membrane was rinsed with water and then stored in distilled water.

Analysis by gas chromatography/mass spectrometry

Qualitative and quantitative analyses of the permeates obtained by filtration through YM100 and YM5 membranes were carried out using a Hewlett-Packard type 5890 gas chromatography unit coupled with a Hewlett-Packard type 5970 selective mass detector.

The relevant details are: A capillary column (HP-FFAP) length 50 m, 0.2 mm (external diameter), was used; helium was used as the carrier gas and the injection temperature was 70°C.

Spectroscopic examinations of permeates, obtained by filtration through YM100 and YM5 membranes, were performed on a Perkin-Elmer 1740 FTIR unit using flat contact sampling *via* horizontal ATR.

BOD_5-BIOCHEMICAL OXYGEN DEMAND AND COD-CHEMICAL OXYGEN DEMAND

The term BOD_5 refers to the 5-day biochemical demand for oxygen (mg/dm^3 or ppm) used by bacteria in the oxidation of organic matter. In water, the latter may be encountered in the dissolved state or in the form of suspension. Over five days, the bacteria mainly oxidised soluble organic substances, whereas very little solid matter was oxidised. BOD measurement was made using the manometric method, where oxygen consumption is measured directly. Oxygen used up by the sample was replaced with air from above the sample. Continuous detection of used-up oxygen is an important feature of this method. On the basis of graphical representation, specific values, with reference to specific period of time, are obtained [9].

Toxicity characteristics of waste water and permeates were measured by the Offhaus method [10]. This is a method in which a test organism is a mixed bacterial culture and in which we are detecting the influence of the sample on the biochemical decomposition of a known test substance (peptone). Toxicity is expressed as % inhibition of the biochemical decomposition of peptone. Inhibition is shown in Figs 12–14.

For the calculation of inhibition, the surfaces limited by the following curves are compared:

(i) a theoretical curve obtained by the addition of the BOD value for peptone and the BOD value for the sample, and,

(ii) a curve of inhibition, which is the difference between a practically obtained value of the BOD for the sample with pepton, and the theoretical value.

If the tested sample contains toxic substances, these will effect the activity of the mixed bacterial culture. This effect will be reflected indirectly in the inhibited decomposition of the peptone.

The BOD measurements were carried out by means of a BPK5-Mikropolo unit, with pepton from meat digested (Kemika, Zagreb).

The COD was measured according to the standard ISO 6060 procedure [11].

RESULTS AND DISCUSSION

The above mentioned methods of testing permitted selected the analysis of the permeates obtained after filtration through YM100 and YM5 membranes. It was hoped that the results would provide information concerning the environmental acceptability of the permeates, as well as yield useful information concerning the ultrafiltration system itself, together with any effect of the membranes (with different cut-off values) on the permeate purity.

Figures 1–8 show the upper and the lower surface of membranes prior to, and subsequent to, filtration.

Figures 1, 2, 5 and 6 show the upper surface of the membranes, whilst Figs 3, 4, 7 and 8 relate to the lower surfaces. The nature of the asymmetry is clearly apparent. This asymmetry is designed to provide a combination of rapid flux and effective separation in each case.

The upper surface can be seen to have undergone substantial changes in the course of filtration, with pores nearly invisible. The lower surface, on the other hand, shows practically no signs of change.

It was suspected that changes to the upper surface could be due to one or more of the solvents present in the stain. To establish whether any component in the stain could cause membrane surface changes, an experiment was devised in which pieces of the membranes, YM100 and YM5, were soaked in mixtures of distilled water and in individual solvents whose percentage corresponded to the percentage of the respective solvent in the stain. The experiment showed that upper surface changed in all cases. Even when soaking the membrane only in distilled water, changes became apparent after one hour. For example, the surface of a membrane which has been simply soaked in distilled water and ethanol is shown in Fig. 9.

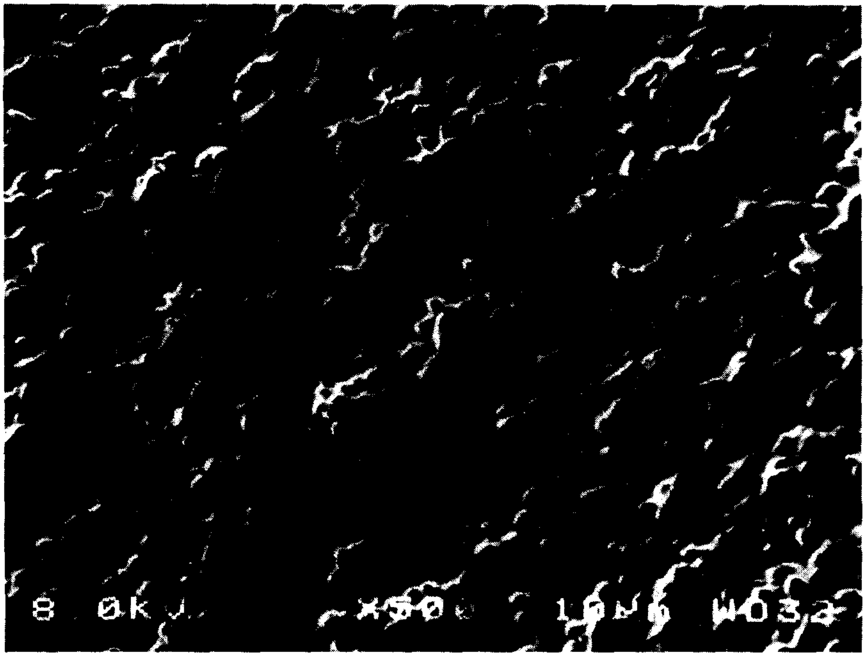

Fig. 1. SEM of a membrane YM100—unused (upper surface).

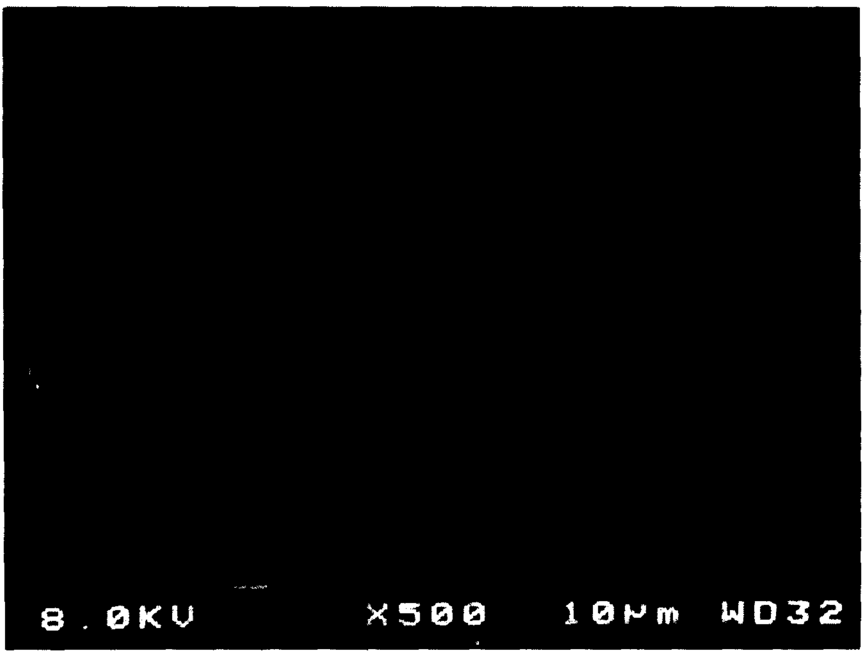

Fig. 2. SEM of a membrane YM100—after 10 days of filtration (upper surface).

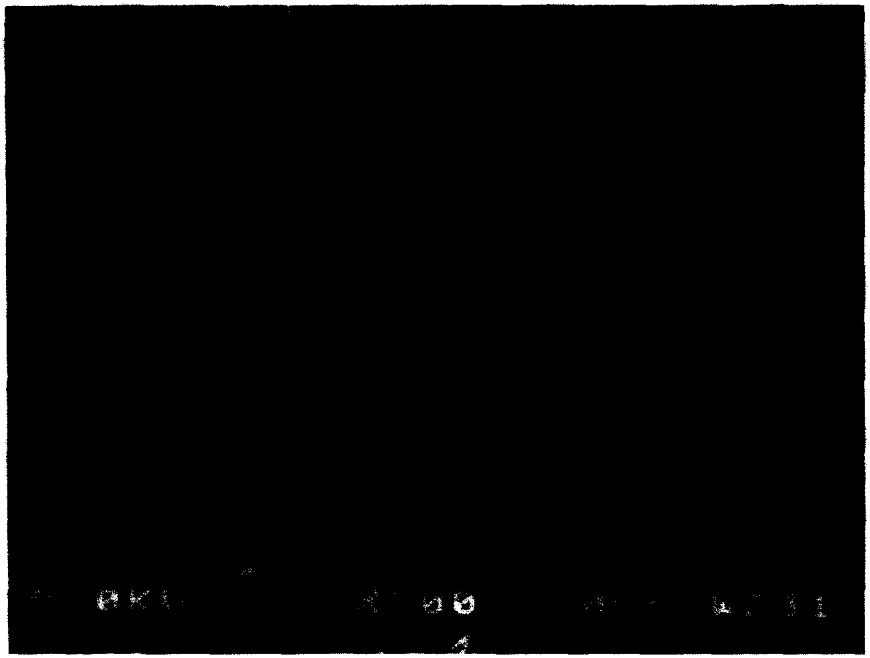

Fig. 3. SEM of a membrane YM100—unused (lower surface).

Fig. 4. SEM of a membrane YM100—after 10 days of filtration (lower surface).

Fig. 5. SEM of a membrane YM5—unused (upper surface).

Fig. 6. SEM of a membrane YM5—after 10 days of filtration (upper surface).

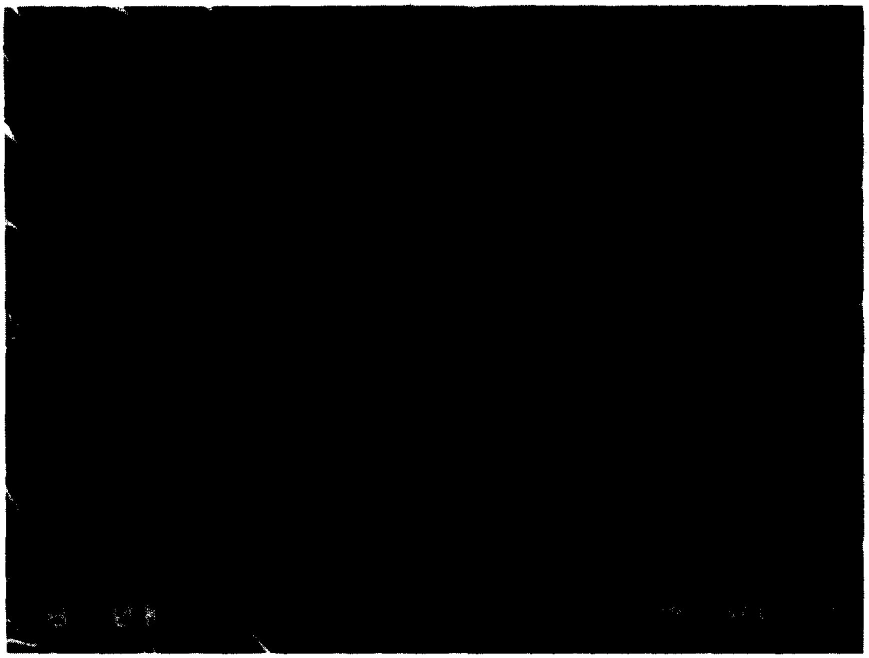

Fig. 7. SEM of a membrane YM5—after 10 days of filtration (lower surface).

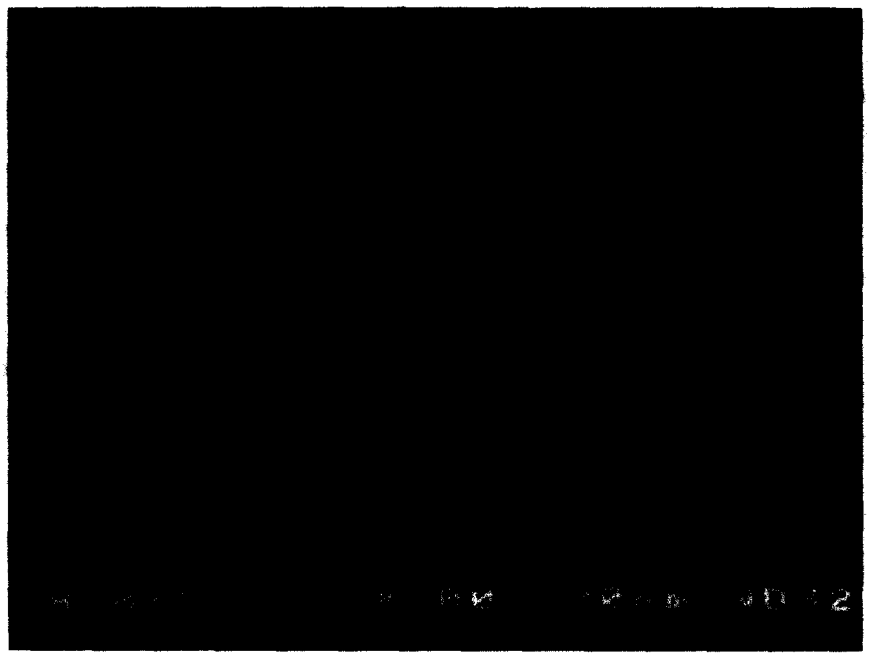

Fig. 8. SEM of a membrane YM5—after 10 days of filtration (lower surface).

Fig. 9. SEM of a membrane soaked in mixture of distilled water and ethanol (after 50 hours).

The question then arises as to how the changes to the surface of the membrane might affect the permeability of the membrane. Relevant information was obtained by monitoring the flow rate over a 10-day period of filtration. Table 1 shows the quantity of permeate filtered out through membranes YM100 and YM5 on the first, fifth and tenth day.

TABLE 1
Quantity of Permeates Obtained by Filtration Through YM100 and YM5 Membranes

	YM100			*YM5*		
	day 1	*day 5*	*day 10*	*day 1*	*day 5*	*day 10*
Time (hour)	*Filtrate (ml)*	*Filtrate (ml)*	*Filtrate (ml)*	*Filtrate (ml)*	*Filtrate (ml)*	*Filtrate (ml)*
1	160	182	170	112	117	111
2	158	147	143	111	110	110
3	157	121	129	111	110	106
4	145	115	108	110	106	105
5	145	110	98	109	105	105
6	125	98	96	107	102	105
7	125	98	97	103	102	103
8	124	98	87	103	102	96
9	110	80	85	96	100	95
sum	1249	1049	1013	962	954	936

It is clear that a gradual and continuous decrease in elution rate occurred over that period, indicating closure of the pores in the membrane.

Figure 10 shows that the total quantity of permeates does not decrease over each day. Some variations occur, and these can be ascribed to the ultrafiltration process. During ultrafiltration, particles come onto the membrane, and a thin layer which disturbs ultrafiltration is produced. In spite of constant mixing, this phenomenon cannot be completely avoided. Dosage of a new waste water in the ultrafiltrator can cause rising of the particles from the bottom of the membrane which on this part of the membrane implies a fast process of filtration and variation in the quantity of the filtered part. Additionally the membranes tend to clog with time, which also causes changes in the flow rate.

GC/MS analyses were performed with a view to identifying the substances that the two membranes failed to intercept and to determine, in what way the content of the substances changed with filtration time.

In the case of water, and its extremely high concentration, various peaks can be observed. The retention time given is the average value of retention times of each individual peak.

Figure 11 shows a GC/MS trace, as described in the legend. The form of all other traces was very similar. In Fig. 11 we have evidence of the presence of ethanol with retention time 4.0 min, water with average retention time 6.1 min, butyl glycol with retention time 10.4 min and propylene glycol with retention time 13.2 min. The mass detector was used to identify individual substances in the permeates. It allows an unequivocal and rapid

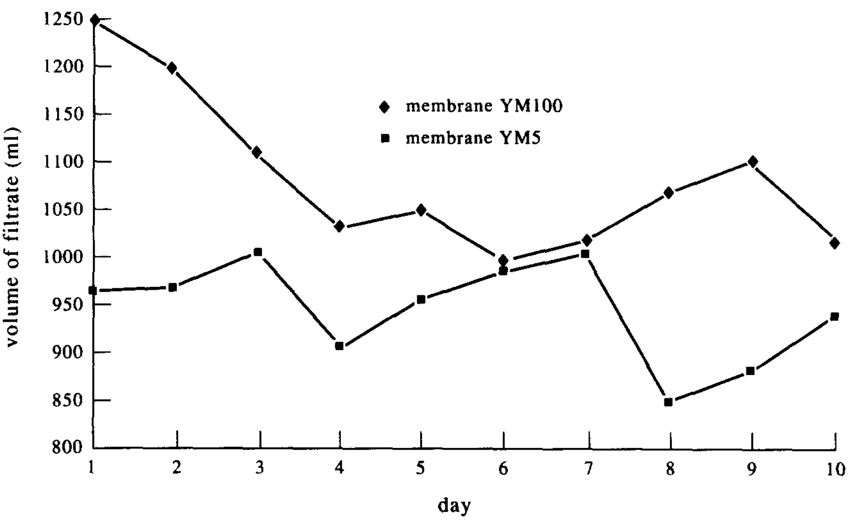

Fig. 10. Total quantity of permeates.

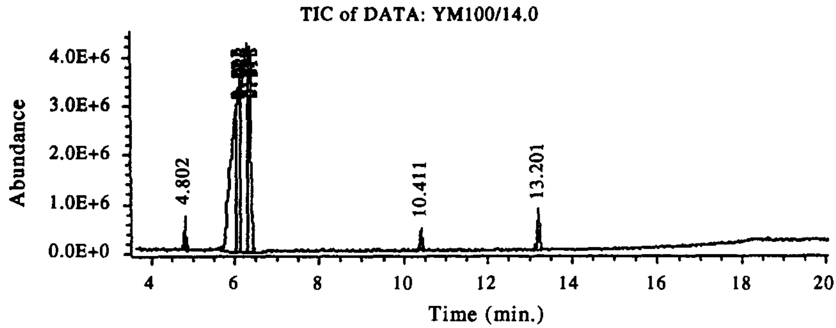

Fig. 11. Chromatographic output data for permeate obtained by filtration through YM100—first day.

determination of substances present in the sample. Table 2 shows the substances and their retention times.

Table 3 illustrates results obtained from analysis of waste waters, after filtration through the membranes YM5 and YM100, for the COD and BOD demand criteria; the level of inhibition is also indicated.

Inhibition of 30% was observed, which is high. Such a figure implies that the treatment plant would not be able to cope with the effluent load.

Inhibition of 18% was observed, which indicates that this parameter was reduced by the use of the YM100 membrane.

TABLE 2
Substances Identified by Mass Spectrometry for Permeate Obtained by Filtration Through YM5 Membrane—Fifth Day

Peak	*Substance*	*Retention time (min)*
1	ethanol	4.8
2	water*	6.2
3	methoxybutanol	10.0
4	butyl glycol	10.4
5	propylene glycol	13.2

TABLE 3
Actual Concentrations of Individual Substances in the Sample

Sample	*ethanol (ppm)*	*water (ppm)*	*butyl glycol (ppm)*	*propylene glycol (ppm)*
YM100-day 1	2000	991 000	1000	6000
YM100-day 5	3000	988 000	1000	5000
YM100-day 10	3000	988 000	1000	6000
YM5-day 1	1000	991 000	1000	8000
YM5-day 5	2000	978 000	1000	8000
YM5-day 10	2000	985 000	1000	6000

By the use of the YM5 membrane, inhibition of 13% was observed.

Inhibition is due to the presence of the alcohols identified by GS/MS. From Table 4, it is evident that the COD value of the permeates is about half that of waste water, and that the BOD value is also lower. In the case of permeates obtained by filtration through the YM100 membrane, 18% inhibition

TABLE 4
BOD, COD and Inhibition of Waste Water and Permeate Solutions

Sample	*COD* (mgO_2/dm^3)	*BOD* (mgO_2/dm^3)	*inhibition (%)*
waste water	9120	337	30
permeate YM5	4100	265	13
permeate YM100	4230	283	18

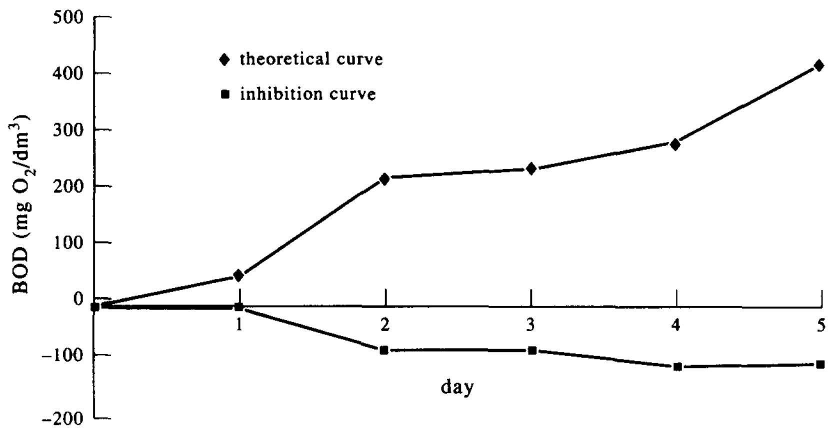

Fig. 12. Inhibition for waste water as a function of time.

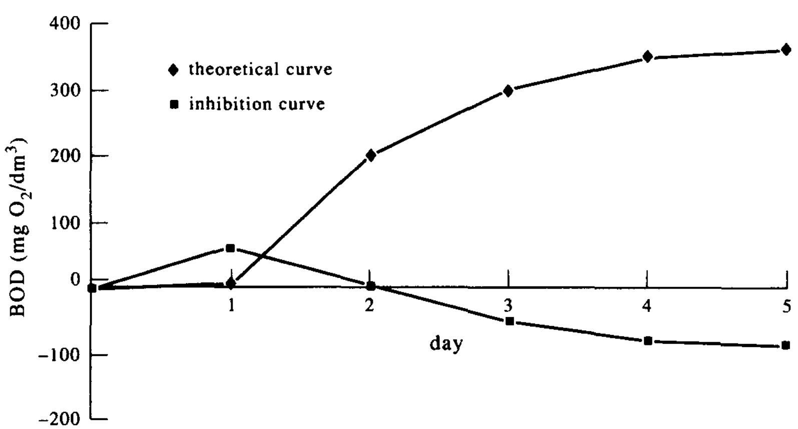

Fig. 13. Inhibition for the permeate filtered through YM100 membrane as a function of time.

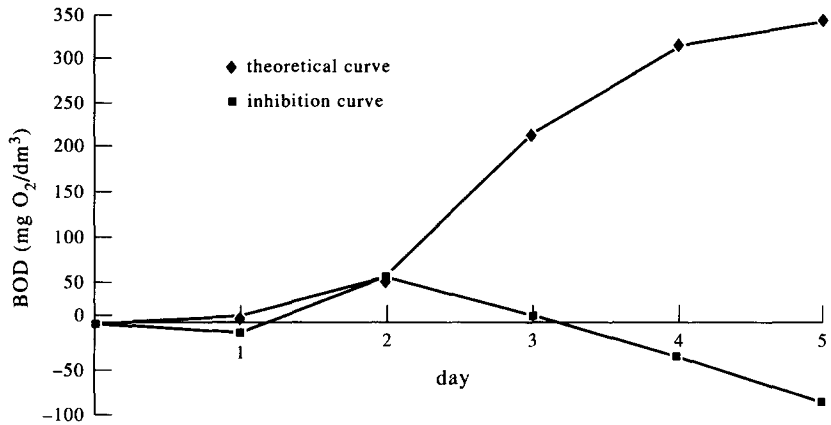

Fig. 14. Inhibition for the permeate filtered through YM5 membrane as a function of time.

was observed; this is presumed to be due to the higher concentration of alcohols, in particular ethanol and propylene glycol. With permeates obtained by filtration through the YM5 membrane, inhibition was 13%. The ultrafiltration process significantly decreases the COD and BOD, which still greatly exceed the standard values for release into the waste pipe. The toxicity of the permeates is also decreased. The barely perceptible toxicity of the permeates implies that the waste water after ultrafiltration, is suitable for biological cleaning, but the possibility of returning the permeates into the varnishing cabin also exist.

SUMMARY

This paper reviews an analysis of permeates obtained by filtration based on the use of YM100 and YM5 membranes. From the results obtained, it may be concluded that ultrafiltration is a method which is suitable for the treatment of waste water resulting from staining operations in which water based stains are used.

Flow rates through membranes decreased as filtration progressed, which could be explained by the fact that pores become impervious with time, rather than by surface changes as identified by the use of SEM.

Waste water which was prepared in the laboratory was of dark colour, and the permeate obtained was colourless, which indicates that the pigments were retained.

GS/MS analysis showed that the membranes did not retain ethanol, butyl glycol and propylene glycol as the cause of inhibition established by the

Offhous method. The permeates obtained by filtration through the YM100 membrane exhibit higher BOD and COD values, and are also characterised by greater inhibition in comparison with the permeates obtained by filtration through the YM5 membrane. Higher BOD and COD values of permeates obtained by filtration through the YM100 membrane should be seen as due primarily to higher content of ethanol and propylene glycol.

Measurements show that, by using the YM5 membrane, toxicity can be reduced to an insignificant level. A disadvantage of this membrane, however, is a low rate of filtration. By the use of the YM100 membrane, the quality of the products obtained is slightly reduced, but inhibition is still satisfactory. The rate of inhibition, however, is higher.

Further research needs to focused on the analysis of the quality of retentates, and on assessment of possibilities for recycling.

REFERENCES

1. *Filters and Filtration handbook.* Elsevier Science Publishers Ltd. UK, 1992, p. 87.
2. Camatta, R., Effluent treatment by ultrafiltration, *Papier, Carton & Cellulose* **41**(1) (1992) 33–36.
3. Tegtmeyer, D., *Possibilities and opportunities for membrane treatment of waste water in textile dyeing.* Melliand Textilberichte, **74**(113)2, pp. 174–178.
4. Kotnik, D., *Površinska obdelava v izdelavi pohištva (Finishing operations in furniture manufacture)*, Ljubljana, Lesarska založba (Wood processing Publishing House), 1992, p. 233.
5. Ljuljka, B., *Površinska obrada drva (Wood finishing)*, Zagreb, Šumarski fakultet (Faculty of Forestry), 1990, pp. 83–94
6. Mihevc, V., Tisler, V., Kunaver, M. and Kornhauzer, D., Ultrafiltracija vodnih lužil (Ultrafiltration of water based stain). *Zbornik gozdarstva in lesarstva (Proceedings of Wood Processing and Forestry)*, Ljubljana, **43**, 1994, pp. 245–257.
7. *Amicon, Products for Separations Technology.* Publication No. 553, Danvers, Amicon Corporation, 96s.
8. Howell, J. A., Sanchez, V. & Field, R.W., *Membranes in bioprocessing*, Blackie Academic & Professional, Glasgow, 1993.
9. International Standard ISO 5815, 1989. *Water quality—Determination of biochemical oxygen demand after 5 days (BOD5)—Dilution and seeding method*, 6s.
10. Oldenfourg, R., *Stand und Entwicklung der Abwasserreinigung Müncher Beitrage zur Abwasser, Fischerei und Flußbiologie*, Band 24, Munchen, 1973.
11. International Standard ISO 6060, *Water quality—Determination of the chemical oxygen demand*, 1989, 4s.