

T. Y. CHIU*, M. V. LARA DOMINGUEZ*, A. E. JAMES***

NON-CIRCULAR CERAMIC MEMBRANES FOR USE IN WASTEWATER TREATMENT

An extensive use of membrane bioreactors in wastewater treatment often produces the effluent quality far beyond the current regulatory requirements for discharge to the environment. However, like other processes involving membranes, the severest constraint is the problem of fouling, the extent of which can be reduced by changing the flow pattern (maintaining in turbulent conditions) within the channels. In this study, the treatment of effluent from synthetic sludge production was investigated employing membrane bioreactors utilising non-circular multi-channelled membranes. Very high chemical oxygen demand (COD) and suspended solids (SS) removals were obtained for the range of pore sizes employed, up to 94% and 98%, respectively. As the pore size was increased, a decrease in efficiency was observed. Differences in the rejection behaviour are attributed to the difference in the characteristics of cakes which were formed. Specific cake resistance seems to increase moderately with diminishing pore size. The critical flux was found to be dependent on cross-flow velocity, introduction of inserts and pore size. Critical flux increased to about $82.5 \text{ l m}^{-2} \text{ h}^{-1}$ at a cross-flow velocity of 2.0 m s^{-1} . The high critical flux can be attributed to the non-circular geometry of the channels which seems to promote turbulent flow, depolarising the solute built-up, even at low cross-flow velocity. Finally, the present paper demonstrates ways in which hydrodynamics and colloid interactions affect the critical flux.

Keywords: *non-circular membranes, activated sludge, microfiltration, COD removal, hydrodynamics*

1. INTRODUCTION

Membrane bioreactors (MBRs) are extensively used for diverse applications in wastewater treatment [1] which combines both a membrane separation and an activated sludge system. Typical advantages of MBR over conventional biological treatment processes lie in their higher standards (free of bacteria and substantially reduced virus content) and reduced land requirements [2]. However, when utilising mem-

* School of Chemical Engineering and Analytical Science, The University of Manchester, P.O. Box 88, Manchester M60 1QD, UK.

** Corresponding author. Tel: + 44 0161 200 4368. Fax: + 44 0161 200 4399. E-mail address: alec.e.james@manchester.ac.uk

branes, flux reduction continues to be the major constraint as a result of concentration polarization and fouling. One of the ways to avoid flux limitations is to work under the critical flux J_{crit} also known as the non-fouling regime [3]. J_{crit} depends on the membrane characteristics, physicochemical nature of the colloidal system and the hydrodynamics of the system. This concept has been recognised as a convenient parameter for performance assessment of the different MBR and non-MBR systems [4]. It is necessary in MBR systems to maintain a constant sludge condition for the optimum biological treatment and removal of organic materials using microorganisms [5]. Physicochemical dependence of J_{crit} in such a system would thus appear to play a minor role. Efforts to improve J_{crit} through manipulating the other kinds of influence such as membrane characteristics (pore size) and hydrodynamics would seem to be the best strategy. The dependence of J_{crit} on pore size of MBR still remains unclear [6] as results from various filtration tests in MBR system that have shown very different dependencies of fouling on pore size. MADAENI et al. [7] observed similar values of J_{crit} for the membranes of different pore sizes (d_p) but they varied, depending on the membrane hydrophobicity. CHANG et al. [8], however, found the smallest pore to exhibit the greatest initial fouling when comparing non-woven polypropylene membranes of different pore sizes. Little work has been undertaken in MBR systems regarding J_{crit} using corrugated multi-channelled ceramic membranes even though they possess the ability to cause fluid instability which can be useful in overcoming concentration polarization and membrane fouling [9]. This work sets out to study (i) the relative significance of pore size to critical flux, (ii) the influence of cross-flow velocities on critical flux using non-circular channelled membranes, (iii) the use of inserts in order to enhance J_{crit} and finally the performance of these membranes, i.e. the treatment capacities in relation to COD removal.

2. EXPERIMENTAL

A schematic diagram of the MBR used in the present study is shown in figure 1. The figure shows a 5 dm³ bioreactor and a vertically mounted star-shaped tubular ceramic microfiltration membrane module. These membranes (0.3 m long, seven star channels of 4.6 mm outer diameter and 2.8 mm inner diameter), supplied by courtesy of Fairey Industrial Ceramics Ltd, England, have a filtration area of 0.03 m². The suspensions were fed to the membrane from the collection tank via a variable speed peristaltic pump and its transmembrane pressure was monitored using two pressure gauges at either ends of the membrane module and controlled by closing the valve A to generate the backpressure. The motor setting was changed to achieve different cross-flow velocities. The filtered suspension, whose biological characteristics is shown in table 2, was the effluent of activated sludge produced using the "Porous Pot" system as proposed by the Organisation for Economic Coordination and Development (OECD)

guidelines 302A and 303A [10] and described elsewhere [11]. The pH of suspensions, within the collection tank, was controlled by adding appropriate amounts of hydrochloric acid or sodium hydroxide and its temperature was kept within the recommended range [10] of 20–25 °C using a water bath thermostat. The particle size of the suspension was quantified with a laboratory particle-size analyser (HYDRO 2000SM, Malvern Instruments, UK) and the average particle size (by number) is 4.0 μm . The chemical oxygen demand (COD) was analysed in accordance with method 508C of standard methods [12]. Total suspended solids (TSS) and suspended solids (SS) were determined in accordance with method 209 of standard methods [12]. The critical flux measurements and cleaning methods were given previously [9]. In the course of the study, the changes in the distilled water flux through cleaned membranes were slight (<1%). Each J_{crit} measurement was repeated several times and the average value is reported. All J_{crit} measurements show good reproducibility.

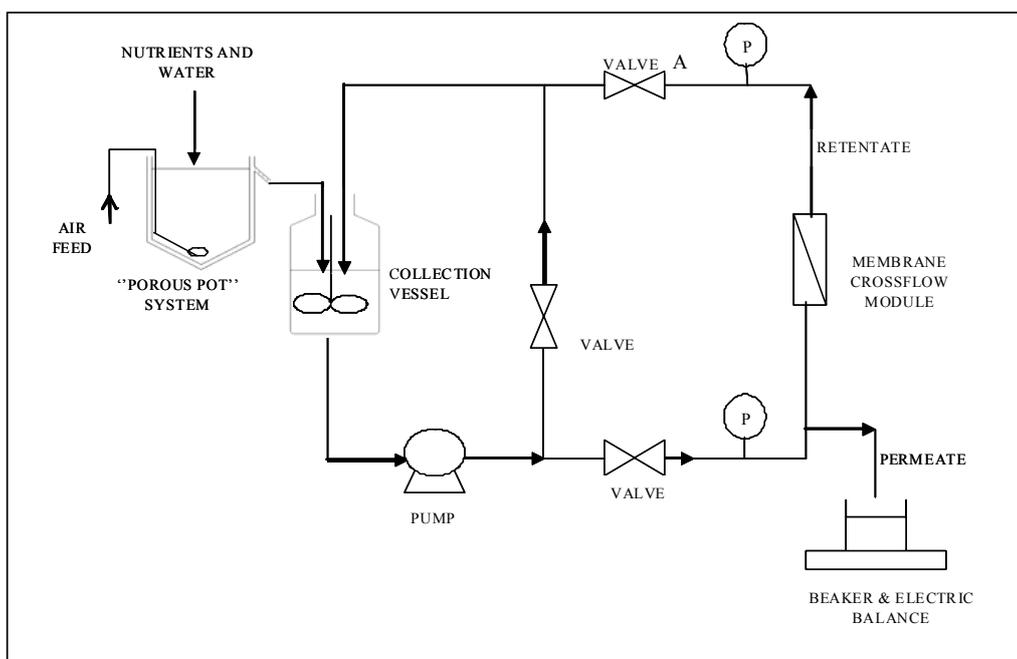


Fig. 1. Experimental setup of membrane bioreactor

Table 1

Biological characteristics of the filtered suspension

Parameters	
COD (mg dm^{-3})	68.7
SS (mg dm^{-3})	313.3
TDS (mg dm^{-3})	582.7

TS (mg dm ⁻³)	896.0
---------------------------	-------

Table 2

Critical fluxes as a function of various operating conditions

Operating parameters		J_{crit} (dm ³ m ⁻² h ⁻¹)
Pore size (μm)	0.2	72.5
	0.35	125
	0.5	165
Cross-flow velocities (m s ⁻¹)	0.60	50.4
	1.19	57.5
	1.59	72.5
	2	82.5
Inserts*	Static rod inserts (0.9 mm)	56.4

* Inserts at hydraulic dissipated power of 0.83 W equivalent to an empty channel with a cross-flow velocity of 0.60 m s⁻¹.

3. RESULTS AND DISCUSSION

Table 2 shows an increasing critical flux with increasing cross-flow velocity. The increase in the cross-flow velocity from 1.2 to 2.0 m s⁻¹ led to an increase in the critical flux by 1.4 times. This trend is in agreement with that reported by other workers [7]. The increase in the cross-flow velocity results in an increase in the back transport rate of particles, greater wall shear stresses and a thinner laminar sub-layer [7], [13]. This inhibits the fouling layer development and subsequently delays particle deposition on the membrane. Thus a greater J_{crit} is expected with increased cross-flow velocity. A greater J_{crit} is achieved in the current study when compared to the results of previous workers [7], [14] using activated sludge systems at similar cross-flow velocities. These findings could arise from the geometry of the channels. BELFORT et al. [15] state that either using a well-defined rough surface, i.e. furrowed profile, or placing extended protuberances directly onto the membrane surface at defined separation distances induces increased intensity and size of periodic unsteady flows in the mass transfer boundary layer. The former method is currently used with the star-shaped membrane channels. This causes instabilities to be produced where they are most needed, i.e. in the region of solution–membrane interface, to depolarize the solute buildup [16]. In addition, the initiation of unstable flow could have been faster in this study for non-circular channels at similar circulation velocities. Flow patterns in narrow empty circular and narrow obstructed channels have been studied by SCHWINGE et al. [17] who report that flow in narrow empty channels is laminar for Re of up to 2000 but in the latter case, flow becomes unsteady at much smaller Reynolds numbers. The flow can become unsteady and can show periodic movements at Re as low as 200, depending on the geometry of the

obstructions. This could explain why at similar circulation velocities, the J_{crit} obtained in this study is much greater than the one reported by other workers.

An increase in d_p led to an increase in J_{crit} as shown in table 2. This is in agreement with findings of other workers [18]. The trend of J_{crit} increasing with d_p is suspected to arise from the different types of colloid rejections occurring as suggested by CHEN et al. [18]. At $d_p = 0.5 \mu\text{m}$ a substantial transmission was allowed, whilst most of the colloid particles are retained at the smaller d_p of $0.2 \mu\text{m}$. This initial transmission allows the delay in cake formation which subsequently leads to a greater J_{crit} . LE-CLECH et al. [4] state that a decrease in deposition on the membrane as the pore size increases is at the expense of internal deposition and such internal deposition may not affect the bulk membrane permeability during short-term tests, provided that the amounts of foulant are small. In order to establish whether the initial transmission was indeed causing the trend observed, experiments involving membrane rejection behaviour were carried out at the different d_p .

The retention efficiencies were calculated by comparing the concentrations of the organic matter in the permeate and feed as follows:

$$R = \left(1 - \frac{C_p}{C_f} \right), \quad (1)$$

where R , C_p and C_f are the retention, concentration in permeate and the concentration in feed, respectively.

Table 3

Solid retention efficiencies in terms of COD, SS, TS and TDS at cross-flow velocity of 1.6 m s^{-1} and $\Delta P = 0.1$ and 0.7 bar, transition and steady-state filtration, respectively

Stage in filtration	Pore size (μm)	Permeate C_p (rejection coefficient R)			
		0.2	0.2*	0.35	0.5
Transient filtration (before J_{crit} is reached)	COD (mg dm^{-3})	24.1 (0.65)	–	40.5 (0.41)	48.8 (0.29)
Steady-state filtration (after J_{crit} is reached and plateau in the filtration plot is achieved)	COD (mg dm^{-3})	4.1 (0.94)	4.3 (0.94)	10.3 (0.85)	30.2 (0.56)
	SS (mg dm^{-3})	4.9 (0.98)	4.6 (0.99)	24.6 (0.92)	94.2 (0.70)
	TS (mg dm^{-3})	51.4(0.94)	52.3 (0.94)	170.2 (0.81)	250.9 (0.72)
	TDS / (mg dm^{-3})	46.5 (0.92)	47.7 (0.92)	145.6 (0.75)	156.7 (0.73)

* Denotes COD removal in the presence of inserts.

Table 3 shows the COD, SS, TS and total dissolved solids (TDS) concentrations in

the permeate collected in the two main stages of filtration, i.e. transient and steady-state filtration with its corresponding rejection coefficients given in parentheses. During transient filtration an increase in the pore size causes a decrease in COD removal. This would imply that the smaller pores allow a worse transmission of chemically oxidising compounds. The best transmission through the pores occurs with 0.5- μm pore size. This seems to strengthen the argument supporting the previous observations relating the increased critical flux to the pore size with respect to the different colloidal rejections. In a steady-state filtration, the rejection coefficient decreases at all the parameters measured, i.e. COD, SS and TS, with increasing pore size. Higher rejection coefficients of both 0.2 and 0.35 μm are achieved compared to 0.5 μm . This observation is in agreement with observations of other workers [19]. These authors suggest that the removal of total solids varied substantially with pore size and was caused by the predominant difference in TDS rejection among the three pore sizes with a very low TDS rejection coefficient at 1.3- μm pore diameter. This explanation is applicable to the present study even though effluent from synthetic activated sludge is used. The difference in the rejection behaviour may result from differences in the cake characteristics. CHANG et al. [20] report that the cake layer deposited over the membrane surfaces plays an important role in solute rejection, i.e. the predominant solute removals are attributed to the sieving and/or adsorption onto the cakes with some parts of solutes being adsorbed into the membrane pores and on their surfaces. If the selective particle deposition is taken into account [21], the critical cut diameter of the particles deposited in cross-flow filtration depends on filtrate flux at the same cross-flow velocity. ZHAO et al. [22] report that the cake on the surfaces of the larger pore-size membranes consists of larger particles and this cake resistance is smaller than that of smaller pore-sized membranes. Specific cake resistance seems to increase moderately with diminishing pore size. This may be explained by the fact that either finer particles are retained by the membranes with smaller pores or the larger pores of the membrane carry a larger percentage of the flow and a smaller steady-state flux is obtained when they are blocked. As a result, voids among cells are filled with these finer particles and/or larger pores are blocked, thereby increasing a cake resistance. This greater cake resistance would result in greater rejection and this is also observed in the current work.

With the introduction of inserts, which were intended to promote turbulence, a slight J_{crit} improvement of 11.9% is found. Our results are in agreement with the results of other workers who studied various ways of enhancing permeate flux through adding inserts. Several workers [23] have reported that rod inserts did not give a very significant flux enhancement and attribute it to the flow pattern which does not "scour" the surface. Normally, these inserts increase the cross-flow velocities [24] which leads to an increase in the shear stress of a membrane wall. In addition, turbulence would at times be produced. This turbulence is known to disturb concentration polarisation and buildup which is responsible for limiting flux. However, calculations

show that the effect of turbulence does not seem to be the influencing factor, since the values of Re drop with the insertion of the rod from 2776 (absence of inserts) to 2248. More effective usage of the filtration area within the star-shaped channel could be responsible for the slight increment. This is supported by the results of our previous work [9] which show that full turbulence, i.e. reaching the ends of the points of the star-shaped channel, results in a much greater critical flux (greater than the asymptotic level). This would result in a delay of particle deposition and hence a greater J_{crit} is observed. However, COD removal seems to be independent of the presence of inserts as shown in table 3. This is somewhat expected since the key membrane properties affecting rejection (COD removal), i.e. pore size, surface charge, hydrophobicity/hydrophilicity and surface morphology, are the same with and without inserts.

4. CONCLUSIONS

The critical flux and rejection behaviour of a MBR were evaluated. Critical flux is shown to be dependent on hydrodynamics and membrane characteristics. An increase in the wall shear stress (increasing cross-flow velocities), pore sizes and the insertion of baffles led to increased critical fluxes. Rejection analysis of the transient filtration stage at the critical flux shows a better initial transmission in larger pores which accounts for the higher critical flux achieved. Rejection performances of MBRs, in terms of COD removal, SS and TDS, were better at smaller pore sizes. The different cake structures leading to a different pore-size distribution account for the observed differences in rejection. COD removal in the presence of inserts remained unchanged since the inserts affect only the hydrodynamics of the system. However, critical flux increment was slight due to the balance between the drop in Re number and an increase in effective filtration area within the star-shaped channels.

ACKNOWLEDGEMENT

The authors are grateful to Universities UK for an Overseas Research Sponsorship award, CONA-CyT, and to Fairey Ceramics Ltd, England, for the supply of the membranes.

REFERENCES

- [1] ALMALACK M.H., ANDERSON G.K., *Use of microfiltration in wastewater treatment*, Water Res., 1997, 31, 3064–3072.
- [2] FANE A.G., *Membrane for water production and wastewater reuse*, Desalination, 1996, 106, 1–9.
- [3] FIELD R.W., WU D., HOWELL J.A., GUPTA B.B., *Critical flux concept for microfiltration fouling*, J. Membr. Sci., 1995, 100, 259–272.

- [4] LE-CLECH P., JEFFERSON B., JUDD S.J., *Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor*, J. Membr. Sci., 2003, 218, 117–129.
- [5] METACALF and EDDY, *Wastewater Engineering Treatment and Reuse*, McGraw-Hill, New York, 2003.
- [6] CHANG I.S., LE-CLECH P., JEFFERSON B., JUDD S., *Membrane fouling in membrane bioreactors for wastewater treatment*, J. Environ. Eng., 2002, 128, 1018–1029.
- [7] MADAENI S.S., FANE A.G., WILEY D.E., *Factors influencing critical flux in membrane filtration of activated sludge*, J. Chem. Technol. Biotechnol., 1999, 74, 539–543.
- [8] CHANG I.S., GANDER M., JEFFERSON B., JUDD S., *Low-cost membranes for use in a submerged MBR*, Process Safety Environ. Protection, 2001, 79, 183–188.
- [9] CHIU T.Y., JAMES A., *Critical flux determination of non-circular multi-channel ceramic membranes using TiO₂ suspensions*, J. Membr. Sci., 2005, 254, 295–301.
- [10] OECD, *OECD Guidelines for Testing Chemicals*, Organization for Economic Cooperation and Development, Paris, 1993, Guideline 302A & 303A.
- [11] LARA DOMINGUEZ M.V., JAMES A.E., *Use of floc physical properties in the study of sludge conditioning*, Water Research, submitted for publication.
- [12] APHA, 1992. *Standard Methods for the Examination of Water and Wastewater*, Section 5210, 18th ed., American Public Health Association, Water Works Association, American Water Environment Federation, Washington, DC, 5.1–5.6.
- [13] YOURAVONG W., LEWIS M.J., GRANDISON A.S., *Critical flux in ultrafiltration of skimmed milk*, Trans IChemE, 2003, 81, 303–308.
- [14] OGNIER S., WISNIEWSKI C., GRASMICK A., *Membrane bioreactor fouling in sub-critical filtration conditions: a local critical flux concept*, J. Membr. Sci., 2004, 229, 171–177.
- [15] BELFORT G., DAVIS R.H., ZYDNEY A.L., *The behaviour of suspensions and macromolecular solutions in crossflow microfiltration*, J. Membr. Sci., 1994, 96, 1–58.
- [16] THOMAS D.G., *Forced convection mass transfer in hyperfiltration at high fluxes*, Ind. Eng. Chem. Fundam., 1973, 12, 396–405.
- [17] SCHWINGE J., WILEY D.E., FLETCHER D.F., *A CFD study of unsteady flow in narrow spacer-filled channels for spiral-wound membrane modules*, Desalination, 2002, 146, 195–201.
- [18] CHEN V., *Performance of partially permeable microfiltration membranes under low fouling conditions*, J. Membr. Sci., 1998, 147, 265–278.
- [19] GAN Q., ALLEN S.J., *Crossflow microfiltration of a primary sewage effluent-solids retention efficiency and flux enhancement*, J. Chem. Technol. Biotechnol., 1999, 74, 693–699.
- [20] CHANG I.S., BAG S.O., LEE C.H., *Effects of membrane fouling on solute rejection during membrane filtration of activated sludge*, Process Biochemistry, 2001, 36, 855–860.
- [21] LU W.M., JU S.C., *Selective particle deposition in cross-flow filtration*, Sep. Sci. Technol., 1989, 24, 517–540.
- [22] ZHAO Y., ZHONG J., LI H., XU N., SHI J., *Fouling and regeneration of ceramic microfiltration membranes in processing acid wastewater containing fine TiO₂ particles*, J. Membr. Sci., 2002, 208, 331–341.
- [23] GUPTA B.B., HOWELL J.A., WU D., FIELD R.W., *A helical baffle for cross-flow microfiltration*, J. Membr. Sci., 1995, 102, 31–42.
- [24] YE H.M., CHEN H.Y., CHEN K.T., *Membrane ultrafiltration in a tubular module with a steel rod inserted concentrically for improved performance*, J. Membr. Sci., 2000, 168, 121–133.