Membrane Water Treatment, *Vol. 7, No. 5 (2016) 433-449*
DOI: http://dx.doi.org/10.12989/mwt.2016.7.5.433

Fouling and cleaning of a tubular ultrafiltration ceramic membrane

Farrukh Arsalan Siddiqui [1,2a] and Robert W. Field [*1]

[1] *University of Oxford, Department of Engineering Science, OX13PJ, United Kingdom*
[2] *Bahauddin Zakariya University, Department of Mechanical Engineering, Multan 60800, Pakistan*

(*Received August 09, 2015, Revised May 03, 2016, Accepted May 16, 2016*)

Abstract. The successful application of cleaning protocols is vital for optimized filtration processes. A series of experiments with an ultrafiltration ceramic tubular membrane were carried out for the foulants dextran and carboxymethyl cellulose. Firstly, the impact on fouling of concentration changes was investigated with the increase in resistance being used as the key parameter. In the second phase, removal of reversible fouling was also investigated by employing intermittent rinsing consisting of a cold water rinse followed by a hot one. A comparative analysis for both foulants is reported. Across a range of concentrations and for both foulants, the reduction in resistance due to rinsing was found to depend upon concentration (C); it changed as C^n where n was found to be 0.3. A plausible semi-theoretical explanation is given. Thirdly, for both foulants, the application of a combination of strong alkaline solutions with oxidizing agent (mainly sodium hypochlorite) followed by acid was found to be appropriate for cleaning of the ceramic membrane. The effect of increased temperature for cleaning agents followed by a warm water rinse contributed positively to the cleaning capability.

Keywords: membrane cleaning; reversible & irreversible fouling; dextran; carboxymethyl cellulose

1. Introduction

The early years of membrane development were dominated by polymeric membranes but for the last 25 years inorganic membranes have found commercial application in applications where chemical aggressive feeds are handled or aggressive cleaning is necessary. Examples from the 1990's include applications in argo-food, biotechnology and pharmaceuticals (Burggraaf and Lot 1996). Today, with the price of ceramic membranes having fallen dramatically, consideration is being given to certain water treatment applications because of the longevity of ceramic membranes.

Membrane fouling is the major factor responsible for the decrease in membrane efficiency; with time and at constant transmembrane pressure (TMP) it decreases the flux and increases the resistance. Fouling happens by deposition on the membrane surface and/or inside the membrane pores and this creates resistances in addition to the membrane resistance (R_m). Now the fouling is classified into reversible and irreversible with the former being easily removed without the use of chemicals. The performance of the membrane can be restored by efficient cleaning which depends

---

[*] Corresponding author, Professor, E-mail: robert.field@eng.ox.ac.uk
[a] Ph.D. Student, E-mail: farrukh.siddiqui@eng.ox.ac.uk

http://www.techno-press.org/?journal=mwt&subpage=7 ISSN: 2005-8624 (Print), 2092-7037 (Online)

mainly on the type of fouling and the membrane material. This implies that membrane cleaning is an essential part of the membrane filtration operation. Normally, the cleaning procedure is advised by the manufacturer. There are some factors which are of prime importance like cleaning agent type, its concentration, cleaning time and its impact on membrane material. Inadequate handling of these cleaners and their procedure used may affect the membrane operation or in a severe case may damage the membrane.

Field *et al*. (2008) categorized the cleaning agents used for cleaning microfiltration membranes into three broad categories: strong bases such as sodium hydroxide (NaOH), strong oxidising agents i.e., sodium hypochlorite (NaOCl) which is a source of free chlorine, and strong acids e.g. hydrochloric acid (HCl). The strong base brings change in pH and is responsible for increasing the electrostatic repulsion between membrane and the foulants. Hydrolyzing of the foulant occurs in the presence of strong oxidising agents like NaOCl. It is widely accepted that chemical cleaning is quite effective at zero TMP with little influence of crossflow velocity. More broadly membrane cleaning chemicals can be divided into five categories namely caustic, oxidants/disinfectants, acids, chelating agents and surfactants (Liu *et al*. 2006). However, the hypochlorite normally remains a preferred choice due to multiple reasons including availability, price and efficient cleaning of bio-fouling.

Tomaszewska and Białończyk (2012) working with the similar membrane type and fouling category found an effective cleaning combination to be sodium hydroxide, phosphoric acid and sodium hypochlorite as a disinfectant. Ogunbiyi *et al*. (2008) discovered an effective cleaning impact on microfiltration processes in ceramic membranes again through a combination of chemicals. The solutions used were NaOH, NaOCl and nitric acid. Vanysacker *et al*. (2014), compared citric acid cleaning to that with sodium hypochlorite; the latter has a significantly higher cleaning efficiency. Whilst the cleaning efficiency of hypochlorite solutions is excellent, precision in chlorine concentration is also very important as frequent use of these solutions weakens the membrane material and results in deterioration in the mechanical strength of membranes which may cause a much earlier loss in membrane integrity than that stated by the manufacturer (Arkhangelsky *et al*. 2007). Regarding membrane cleaning there has been a number of other researches (e.g., Shi *et al*. 2014, Vaisanen *et al*. 2002, Astudillo *et al*. 2010).

The preliminary research herein is focused on the cleaning and fouling of an ultrafiltration ceramic membrane by dextran and carboxymethyl cellulose (CMC) solutions. The latter is a derivative of cellulose and is formed by its reaction with sodium hydroxide and chloroacetic acid. The introduction of a number of sodium carboxymethyl groups ($-CH_2COONa$) promotes water solubility (Biswal and Singh 2004). It continues to be used in membrane fouling studies involving colloidal foulants (Zuriaga-Agustí *et al*. 2014). Now dextran is also widely used as model foulant (e.g., Howell *et al*. 1996, Zator *et al*. 2007, Latulippe *et al*. 2007) and being a sugar it generally has less interfacial interactions with the membrane than proteins. An important part of the current paper was the removal of reversible fouling through rinsing and analysis of resistance as an indicator of fouling.

2. Materials and methods

2.1 Membrane structure

The membrane had a hexagonal cross section that contains 19 parallel cylindrical channels, each 4 mm in diameter and 1020 mm long resulting in a total surface area of 0.24 m^2. The

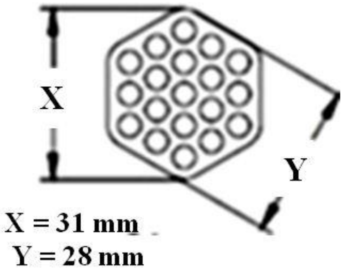


Fig. 1 Cross-sectional view of hexagonal channel of the ultra- filtration membrane element

membrane element is a made from ultrapure aluminium oxide (Al_2O_3) with zirconium oxide (zirconia) and a titanium oxide (titania) in the filtering layers. Its multi-layered structure has a thin filtering layer on the surface, which will only let through particles below a certain molecular weight cut off (MWCO). The general definition of MWCO is: the molar mass of a globular protein which is 90% retained by the membrane.

Below the filtering layer, there is an intermediate layer with larger pore size and finally a supporting structure that makes up the majority of the membrane element. It is enclosed in a cylindrical stainless steel module with a feed input at the base, an outlet of the retentate at the top and a permeate outlet on the side, just above the base. The ceramic membrane is hydrophilic in nature having a contact angle around 30° (Cheryan 1998). Fig. 1 shows the cross-section of a typical membrane element; this type was used in the current work.

2.2 Experimental set-up

Fig. 2 shows a schematic view of the apparatus including the peristaltic pump, pressure gauges and flow meters. The membrane element and casing, collectively called the module, is mounted vertically. There is a 6 litre cylindrical feed tank with a removable lid to which both permeate and retentate lines are attached. The lines can be detached in order to separate the two streams. There is a valve in the retentate line that allows the outlet pressure, and thus the transmembrane pressure to

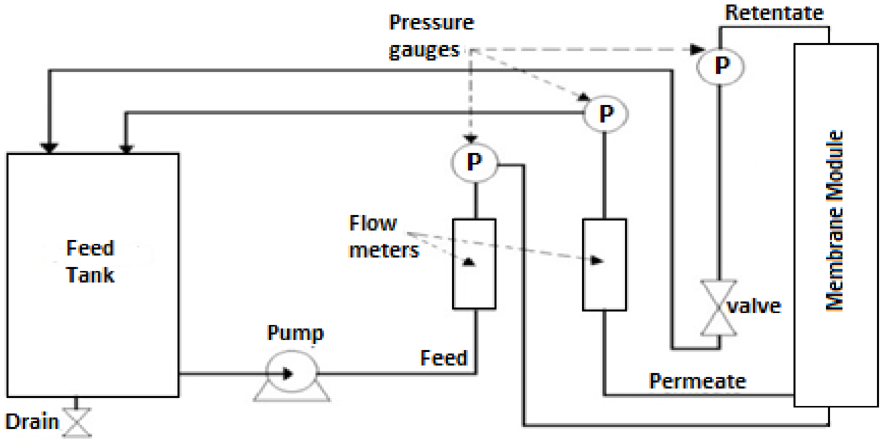


Fig. 2 Schematic view of ultrafiltration rig

be controlled. The peristaltic pump (Watson-Marlow 520S) has a range of 20 to 220 rpm in 0.1 rpm intervals and produces a pulsed flow. Flow meters (CT Platon glass tube and float) on the feed line and permeate gives an indication of the feed flow rate but because of the pulsed flow, they give fluctuating readings, as do the pressure gauges.

2.3 Cleaning procedure

2.3.1 Restoration of membrane permeability

Previously there had been some historical longstanding dextran fouling of the membrane. In this part of the work fluxes at different values of transmembrane pressure were recorded before and after various cleans which sought to restore the original permeability. The membrane was initially treated with a strong alkaline solution of NaOH (2% w/w) for 60 min keeping the crossflow velocity constant at 0.11 m/sec. The permeate valve was kept closed in order to have zero TMP between two ends of the module. After the prescribed time, the alkaline solution was drained and membrane was rinsed with deionised water twice. Next, the membrane was treated with solution of sodium hypochlorite (NaOCl) with 0.1% free chlorine. This operation was undertaken for 60 minutes with the permeate valve closed. The crossflow velocity was 0.11 m/sec. After cleaning with NaOCl solution, the membrane was again rinsed twice with DI water to remove the chlorine effects. In the similar way as before, the flux was recorded and membrane resistance calculated. The membrane was given a second run with NaOCl solution at the same parametrical conditions.

Then the membrane was cleaned with a solution consisting of a mixture of 2% w/w alkaline solution of NaOH and NaOCl with 0.1% free chlorine. Equal amounts of both solutions were mixed thoroughly with a magnetic stirrer. The membrane was run with this solution at 0.11 m/s for 1 hour again with permeate valve closed.

The solution was drained and the flux recorded after rinsing twice. After the application of alkaline solution and oxidizing agent, the membrane was cleaned with HCl (1% w/w) at 0.11 m/sec for 60 minutes. The membrane was then washed twice with DI water. The flux was then recorded using clean water. The membrane cleaning with HCl (1% w/w) was then repeated under conditions. In order to achieve the targeted clean water flux, the membrane was re-treated with the same cleaning chemicals heated up to 40°C. For each application, the permeate valve was kept closed until near the end when it was gently opened. In between each run, the membrane was washed with pre-heated DI water (up to 40°C) to remove any effect of the previously used chemical.

2.1.2 General cleaning procedure

During the second part of the work, reversible fouling was removed intermittently by use of water rinsing. The fouled membrane was rinsed first with cold and then hot water. The removal of fouling (regarded as the reversible fouling) was observed by noting the change in foulant resistance.

2.2 Preparation of feed solutions of Dextran and carboxymethyl cellulose

The solutions of Dextran (average MW 19,500 Da) and carboxymethyl cellulose (average MW of 90,000 Da) were prepared with percentages (w/w) of 0.03, 0.05, 0.1, 0.15 and 0.2. Each solution was prepared in a quantity of 5L and thoroughly stirrer using a magnetic stirrer.

2.3 Filtration process

2.3.1 Without intermittent rinsing

The solutions were filtered through the tubular ultrafiltration membrane at crossflow velocity of 0.11 m/s at room temperature with intermittent stepping of transmembrane pressure. Permeate collected per minute was analysed carefully and flux recorded. The membrane was rinsed thoroughly after each complete test with strong alkaline solution of NaOH (2% w/w), a solution of NaOCl with 0.1% free chlorine and 1% w/w HCl. Before each chemical rinse, the membrane was washed with de-ionized water to clear any impact of the previously used chemical. It was observed that using the chemical cleaners and the water rinsing with raised temperature (up to 40°C) resulted in better cleaning than that at room temperature. To avoid pore blocking by fragmented foulant particles that are freed from the membrane surface each cleaning was done mainly with the permeate valve closed; it was gently opened for the cleaning inside the pores towards the end of each cleaning period. The clean water flux was considered as the yard stick and if necessary, cleaning procedures were repeated.

2.3.2 With intermittent rinsing

For the analysis of the reversible fouling, the prepared solutions for the foulants of Dextran and carboxymethyl cellulose with concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2% respectively were filtered with intermittent water rinsing being undertaken after each TMP rise. During the rinsing phase, the membrane was rinsed with cold and then hot water each for 30 minutes. The flux was checked after each rinse. The change in foulant resistance was noted. The membrane was thoroughly cleaned with chemicals after each test.

3. Results and discussion

3.1 Cleaning

Table 1 shows the comparative results of the chemical cleanings with NaOH, NaOCl, HCl and their respective solutions to restore membrane permeability. After the treatment with the NaOH solution (2% w/w) for an hour at 0.2 bar and 0.11 m/sec, the permeate flux was observed to have recovered slightly (10.3%). The repeated treatment of membrane with sodium hydroxide failed to show increasing improvement in flux indicating that the capacity of cleaning with NaOH solution had reached its limit. Application of sodium hypochlorite (0.1% chlorine w/w) resulted in a further small improvement of flux i.e., 4.9%. The repeated treatment of membrane with the oxidizing agent NaOCl (0.1% free chlorine w/w) with same parametrical conditions did not show any improvement in the flux recovery indicating that the NaOCl solution too had exhausted its capacity for further cleaning. Then the 50:50 mixture of NaOH (2% w/w) and NaOCl solution (0.1% of free chlorine) was used. This resulted in a further recovery of 6.0%. The membrane was further treated with the same chemicals with the temperature raised to 40°C. A notable flux recovery was experienced namely 34.5%.

It is widely accepted that the cleaning agents are unable to achieve 100% flux recovery. According to Field *et al*. (2008), this can be related to two reasons i.e., relatively low concentration of cleaning solutions and the cleaning was undertaken at low temperature. Ceramic membranes have a capacity to bear high pressure as well as having a good ability to deal with strong cleaning agents. The cleaning is as important as the filtration through the membrane.

Table 1 Decrease in resistance of fouled membrane after various chemical cleans

Sr. No.	Application	Foulant resistance (m^{-1})	Percentage decrease in foulant resistance
1.	Before cleaning	13.6×10^{12}	-
2.	After cleaning with NaOH solution (2% w/w)	12.2×10^{12}	10.3
3.	After cleaning with NaOCl solution (0.1% chlorine w/w)	11.6×10^{12}	4.9
4.	After cleaning with solution of NaOH (2% w/w) and NaOCl (0.1% Chlorine w/w)	10.9×10^{12}	6.0
5.	After cleaning with HCl (1% w/w)	8.4×10^{12}	22.9
6.	After cleaning with heated chemical mixtures	5.5×10^{12}	34.5

Therefore, it is needful to use a combination of strong cleaning agents to recover flux and remove the historic fouling that had been inherited. Table 1 shows the decrease in resistance for the filtration after cleaning tests. The application of hydrochloric acid in the cleaning resulted in notable flux recovery of 22.9%. The reason behind this good recovery is that the acids can weaken and then break the bonds between the foulants and the membrane surface (Lim and Bai 2003). However, it is very important to select the appropriate concentration of the acid as excessive amounts may damage the membrane surface. The technique of using the preheated chemicals had a very positive impact and was further applied during the filtration experiments.

3.2 Constant TMP experiments

3.2.1 Without intermittent rinsing

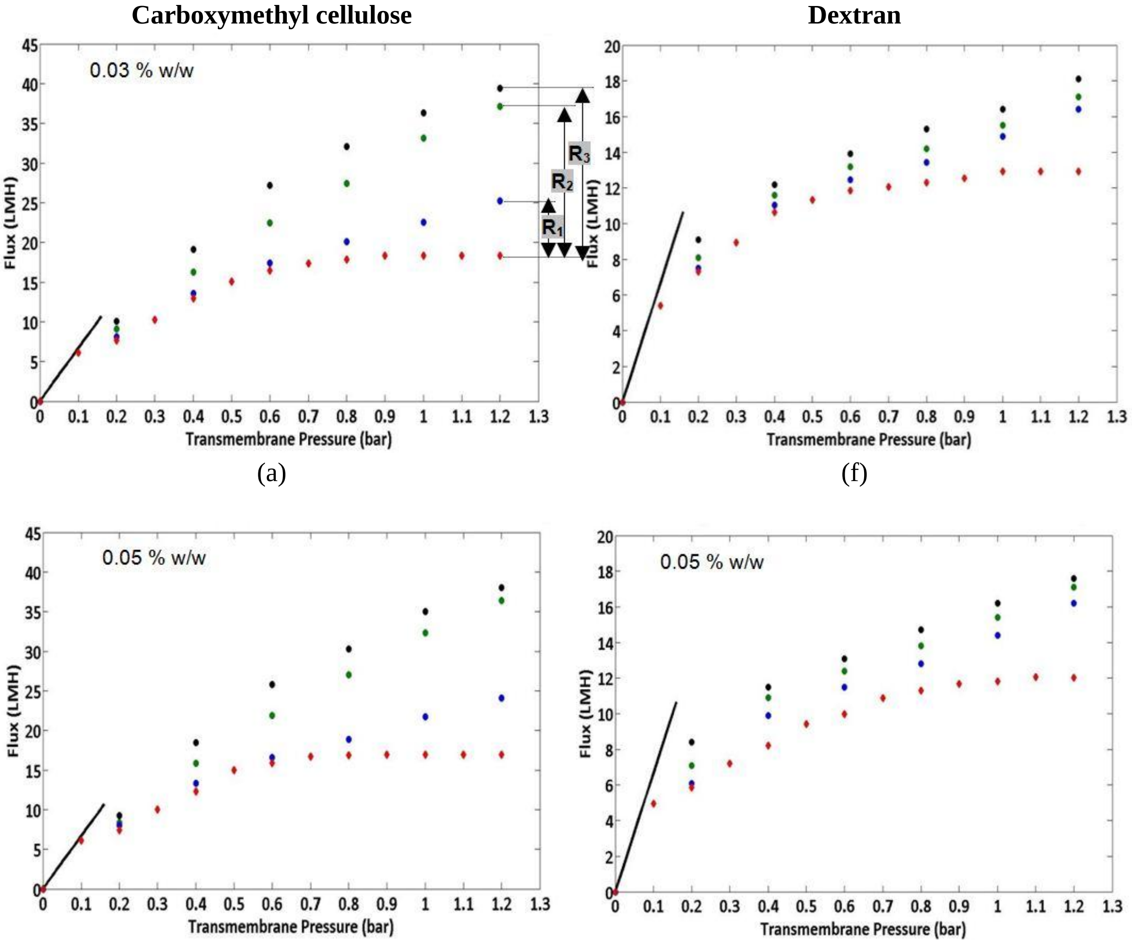
After the thorough cleaning detailed above the rig was used for the fouling experiments starting with a solution of Dextran for which some of the rheological properties of the solution were analysed using a rheometer (Physica MCR 301). The permeate pressure was set to zero and the TMP was raised step wise recording the flux at each step. A series of solutions of carboxymethyl cellulose (Fisher Chemicals) were performed at identical conditions. The experiments were repeated for the concentrations (w/w) of 0.03, 0.05%, 0.1%, 0.15% and 0.2% respectively.

A plateau in the flux-TMP relationship was found beyond 0.3 bar for Dextran and 0.2 bar for carboxymethyl cellulose (CMC). The values were essentially independent of concentration.

3.2.2 With intermittent rinsing

In the second phase of experiments, the membrane was intermittently rinsed with cold and hot water. Again the concentrations (w/w) of both solutions were 0.03%, 0.05%, 0.1%, 0.15% and 0.2% respectively. A notable increase in flux was observed after each intermittent rinse. The corresponding decrease in foulant resistance was noted. Flux-TMP graphs in Figs. 3(a)-(e) are for increasing concentration of CMC. These illustrate the improvement in flux due to intermittent rinsing with cold water followed by the hot one. Figs. 3(f)-(j) refers the same for the dextran.

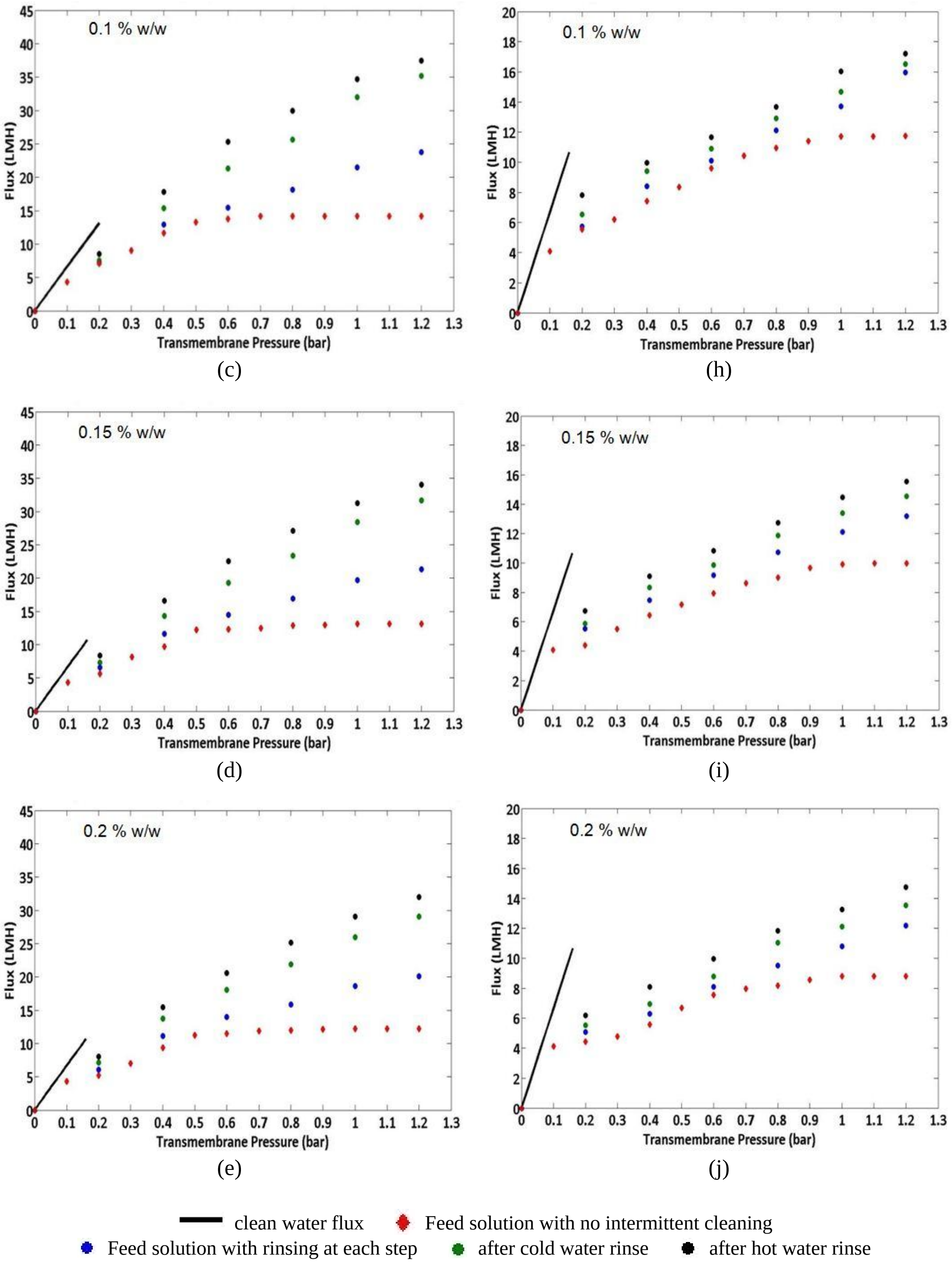
It is evident from the graphs that water rinsing has more impact with CMC solutions than the dextran solutions. This suggests that CMC molecules are more loosely attached to the membrane walls and are more easily removed by rinsing than dextran molecules. However, in both cases some foulant particles are unable to be removed by mere rinsing and these contribute to the irreversible fouling. Analysis indicates that as a percentage of overall resistance, reversible fouling decreases as the concentration increases. The reason behind this could be that during filtration of a more concentrated solution, dense cake layer are formed. For the plants running at commercial scale, the application of intermittent rinsing may have a vital role. It can be queried as to whether this makes economic sense and for each application a case study would be required. One area where it might well make sense is in argo-food. Typically these plants are run in production for two shifts per day and cleaned during part of the night shift. Thus time is available and attention to extensive rinsing might well enable the use of NaOH and acid to be reduced. The strength of ceramic membranes lend themselves to the application of short sharp backwashes and as noted by Wu *et al*. (2008a) for fouling mitigation the effect of backwashing strength can be more significant than the duration or interval of backwashing.



(a) (f)

(b) (g)

Figs. 3 (a)-(j) Flux-TMP diagrams for foulants of CMC and Dextran for 0.03%, 0.05%, 0.1%, 0.15% and 0.2% solutions (w/w) with and without water rinsing. 3(a)-(e) are for increasing concentration of CMC whilst Figs. 3(f)-(j) refers the same for the dextran. Fig. 3 (a) shows R1, R2 and R3. These represent the changes in fouling that are referenced in Section 3.3



(c) (h)

(d) (i)

(e) (j)

Figs. 3 Continued

Foulant resistance

Based upon Darcy's law and neglecting the osmotic pressure effects the clean water flux (i.e., the flux before any fouling) is given by

$$J = \frac{\mathrm{TMP}}{\mu R_m} \tag{1}$$

As the fouling occurs, the foulant resistance, which is shown as $R_{f(t)}$, needs to be added

$$J = \frac{\mathrm{TMP}}{\mu(R_m + R_f(t))} \tag{2}$$

Where, J is the flux at any instance, μ is the dynamic viscosity, R_m represents the resistance of the membrane while $R_f(t)$ is the resistance of the foulants at a time 't'. When some of the particles adhere before the start of actual filtration due to electrostatic interaction or van der Waals forces etc. resulting in additional resistance (R_{ads}) one may distinguish between this initial amount of fouling and that which occurs later. So after the membrane has equilibrated with the feed but before filtration

$$J = \frac{\mathrm{TMP}}{\mu(R_m + R_{ads})} \tag{3}$$

If, but only if there is no additional increase in resistance up to a certain flux, then the filtration is said to be operating below a critical flux (weak form) – Field *et al.* (1995). From the point on, as more fouling occurs due to flux, the general equation becomes

$$J = \frac{\mathrm{TMP}}{\mu[R_m + R_{ads + R_f(t)}]} \tag{4}$$

In this work R_{ads} was not separated from a general fouling resistance. The graphs in Figs. 4-5 indicate that the relationship between fouling resistance, concentration and TMP is complex. Whilst the fouling resistance vs. TMP relationship for dextran is quite linear that for CMC shows a sharp change in gradient at 0.5 TMP. In general the gradients are greater for dextran than CMC. With regard to CMC, up to 0.5 bar, the gradient of resistance with respect to TMP is around 1.5×10^{13} m^{-1} per bar. These values are for 0.1 w/w% CMC. The curve for dextran is almost straight; for 0.1% w/w, the value is around 3×10^{13} m^{-1} per bar. In Figs. 4-5, the solid lines were added for visualisation and the dotted lines indicate boundaries between different regions.

Hchaichi *et al.* (2014) conducted simulations to predict super saturation along reverse osmosis. In present, for a specific concentration of CMC, a linear relationship between the foulant resistance and TMP exists for TMP greater than 0.5 bar. The data can be represented by

$$R_f = R_{f\text{-}0.5} + b\,(\mathrm{TMP} - 0.5) \tag{5}$$

where, $b = 4.5\,C^{0.3}$ with C being the percentage concentration. The fit to the data is excellent (Fig. 4).

For dextran the gradient was found to be essentially independent of concentration, the gradient of the concentration data set shows a very moderate dependency upon feed concentration as shown in Fig. 5 and modelled through Eq. (6)

$$R_f = R_{f\text{-}0.3} + b\,(\mathrm{TMP} - 0.3) \tag{6}$$

Here, $b = 2.8\ C^{0.05}$ with C being the percentage concentration. Given the weak dependency upon concentration, it is reasonable to say that in region 5, the gradient is essentially independent of *C*. The fit is reasonable in Region 3.

In Fig. 4, region 1 is the one where the foulant resistance is independent of the concentration of CMC. Region 2 is a transition region from region 1 to region 3 in which concentration has an influence. In region 3 the resistance is roughly constant for a given concentration whilst in region 4, Eq. (5) applies and the fouling resistance increases with TMP. Eq. (5) is not independent of

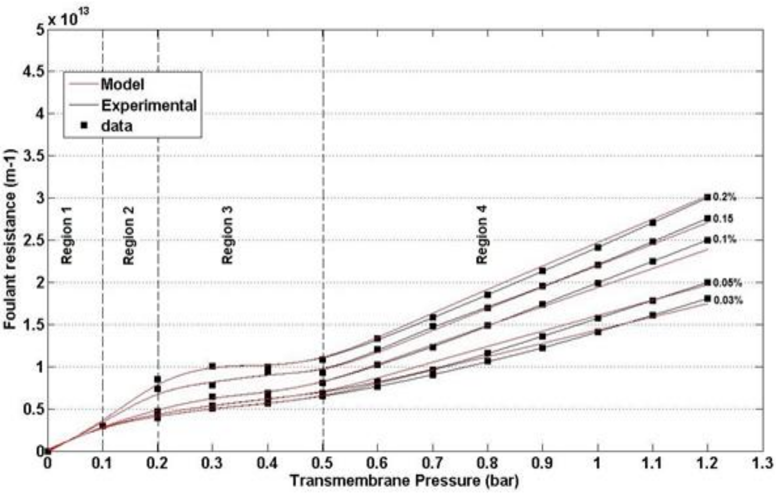


Fig. 4 Fouling resistance vs transmembrane pressure for solutions of carboxymethyl cellulose for concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2%

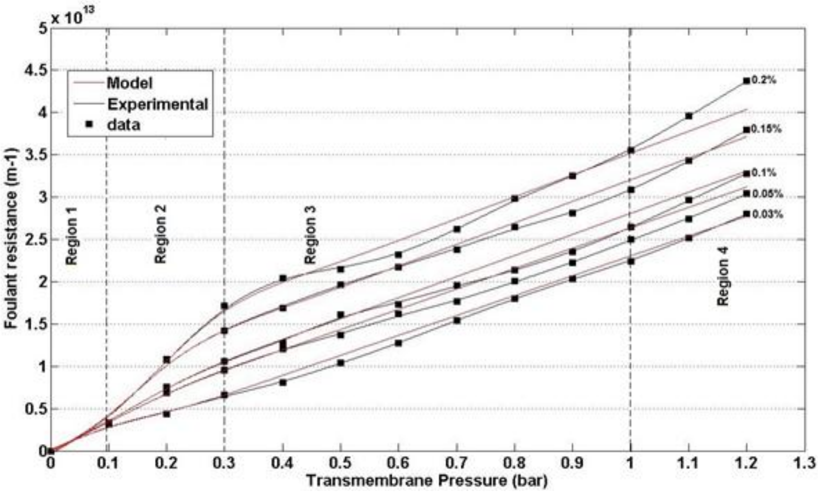


Fig. 5 Fouling resistance vs Transmembrane pressure for solutions of dextran for concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2%

concentration as the gradient has a modest dependency upon C. The change in gradient between region 3 and 4 suggests that at these points, there are threshold conditions as described by Field and Pearce (2011).

Fig. 5 shows that the fouling caused by dextran is broadly similar to that caused by CMC. Similar to CMC, region 1 represents the point where concentration does not have any influence on foulant resistance. Also region 2 is similar in that it is a transition region where both concentration and TMP influence the value of R_f. However, with regard to the other two regions, the fouling phenomenon is somewhat different. For both regions 3 and 4, Eq. (6) is applicable.

3.3 Reversible fouling

It was observed that difference in resistance after each rinse was related to concentration of the solution. Much of the reversible fouling was removed through cold water rinsing and then more by hot water rinsing. If the influence of the concentration of the feed solution is of the form C^n, with n being a suitable exponent, then the difference in foulant resistance (R_{df}) is given by Eq. (7)

$$R_{df} = K_{av}\, C^n \tag{7}$$

where, C represents the feed concentration and K_{av} is the modulus. The value of the latter depends solely upon the transmembrane pressure. The value of n was found to be 0.3 for both foulants.

For dextran as well as CMC, K_{av} was found to be a function of transmembrane pressure and not concentration. K_{av} was calculated for each transmembrane pressure for the following three cases:

(i) The change in resistance without and with intermittent rinsing between each TMP step, represented as R_1 in Fig. 3(a).
(ii) The change in resistance measurements between without rinsing and after cold water rinsing (where rinsing is done at each step), represented as R_2 in Fig. 3(a).
(iii) The change in resistance between without rinsing measuremnts and after hot water rinsing represented as R_3 in Fig. 3(a).

The calculated values of K_{av} are tabulated in Table 2 and trends with TMP shown in Fig. 6. These values of K_{av} reveal that it increases with the increase in transmembrane pressure. However, through rinsing, the reversible fouling is removed as these are loosely attached particles and can be easily freed by mere rinsing.

A plausible semi-theoretical explanation for the 0.3 dependency in Eq. (7) can be represented by the following equations where in ‘spacing’ refers to the average distance between foulant molecules

$$R_{df} \propto \text{Spacing}^{-1} \tag{8a}$$

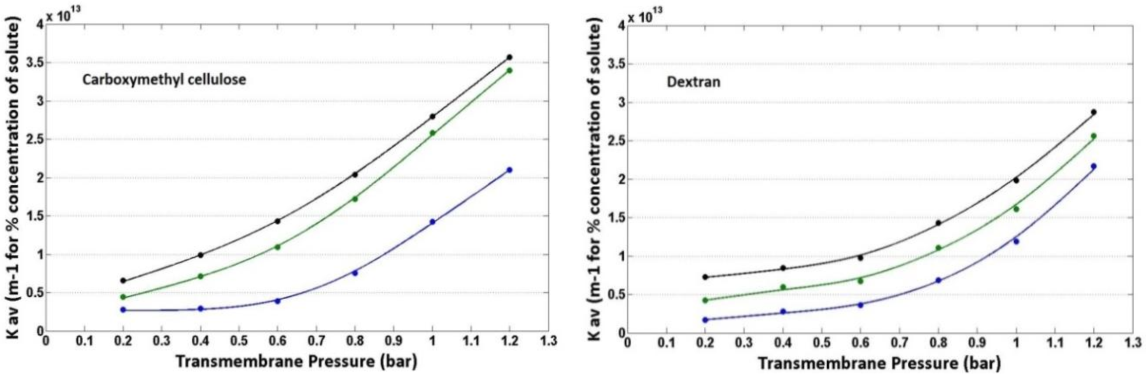
$$\text{Spacing} \propto (1/C)^{-0.33} \tag{8b}$$

$$R_{df} \propto C^{0.33} \tag{8c}$$

The resistance of the loosely attached foulant layer that is removed by rinsing is assumed to have a resistance that is related to the spacing between molecules in the immediate vicinity of the foulant layer i.e., if the molecules are closer together immediately before attachment they will form a denser layer. The fouling tendency might well be inversely proportional to the spacing and

Table 2 Modulus (K_{av}) at different values of transmembrane pressure for dextran and carboxymethyl cellulose solutions

	Trans-membrane pressure (bar)	For change in resistance (R_1) for the feed solutions without and with intermittent rinsing (m^{-1} for % concent. of solute) × 10^{13}	For change in resistance (R_2) for the feed solution without rinsing and after cold water rinsing (m^{-1} for % concent. of solute) × 10^{13}	For change in resistance (R_3) for the feed solution without rinsing and after hot water rinsing (m^{-1} for % concent. of solute) × 10^{13}
Carboxymethyl cellulose	0.2	0.28	0.44	0.66
	0.4	0.30	0.71	0.99
	0.6	0.39	1.09	1.43
	0.8	0.76	1.72	2.04
	1	1.43	2.58	2.80
	1.2	2.10	3.40	3.57
Dextran	0.2	0.17	0.42	0.73
	0.4	0.28	0.60	0.85
	0.6	0.36	0.67	0.98
	0.8	0.69	1.11	1.43
	1	1.19	1.61	1.98
	1.2	2.17	2.56	2.87



(a) (b)

▬ Feed solution with rinsing at each step ▬ after cold water rinse ▬ after hot water rinse

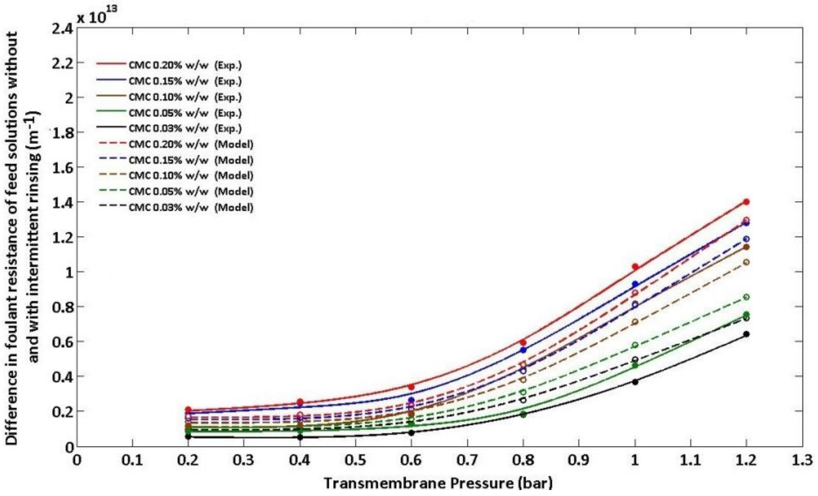
Fig. 6 Modulus (K_{av}) vs. transmembrane pressure for carboxymethyl cellulose and dextran

as shown in Eqs. (8a)-(8c) this suggests that the dependency upon concentration will be $C^{0.33}$ which is close to the dependency found experimentally.

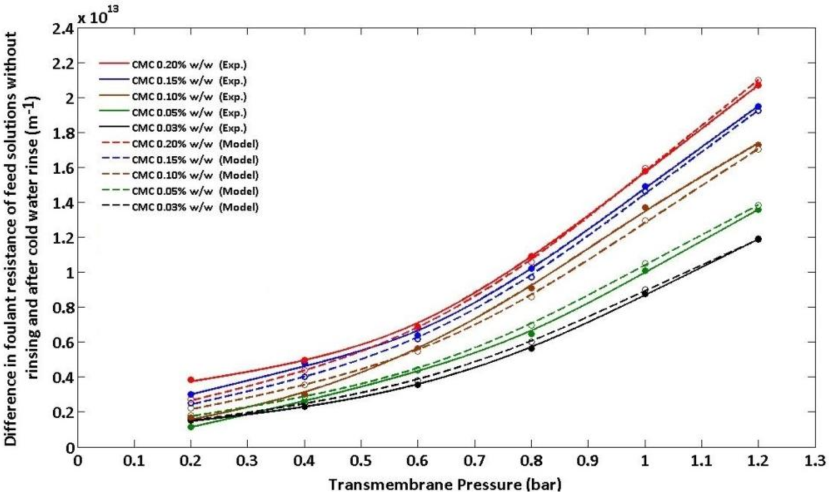
3.4 Trends in reversible fouling

Based on the matrix of K_{av} values, the difference in foulant resistance was calculated using Eq. (7) and compared graphically with the experimental values. For both carboxymethyl cellulose and dextran this was done three ways

(a) for the change in resistance for feed solutions without and with intermittent rinsing,
(b) for the change in resistance for feed solution without rinsing and after cold water rinsing, and
(c) for the change in resistance for feed solution without rinsing and after hot water rinsing

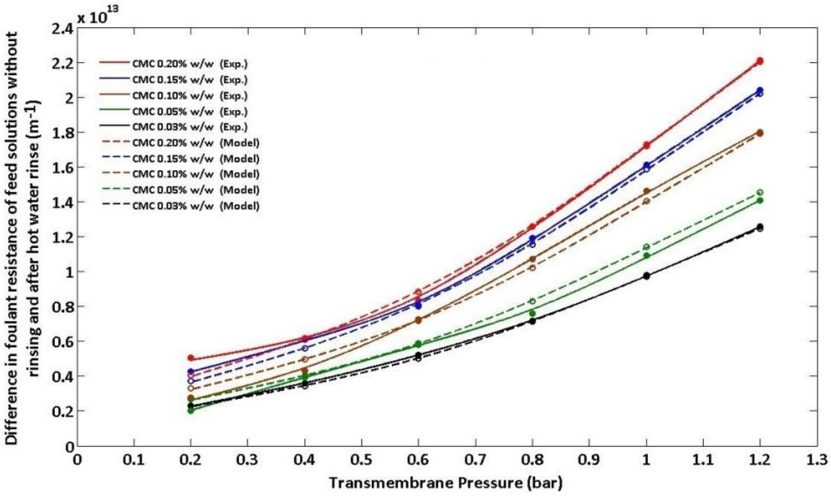


(a) Difference in fouling for the feed solutions without and with intermittent rinsing for carboxymethyl cellulose for concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2% at different values of transmembrane pressure

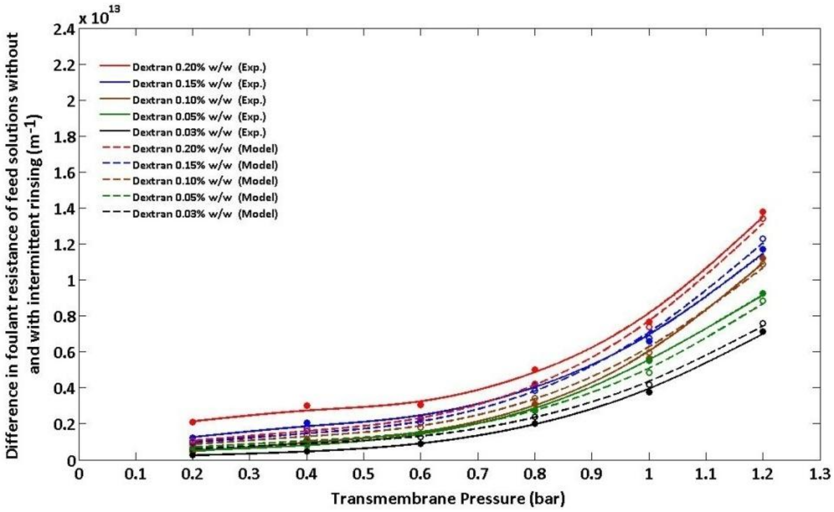


(b) Difference in fouling for the feed solution without intermittent rinsing and after cold water rinse for carboxymethyl cellulose for concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2% at different values of transmembrane pressure

Fig. 7 Change in foulant resistance on account of rinsing with cold and hot water for different concentrations of carboxymethyl cellulose and dextran



(c) Difference in fouling for the feed solution without intermittent rinsing and after hot water rinse for carboxymethyl cellulose for concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2% at different values of transmembrane pressure

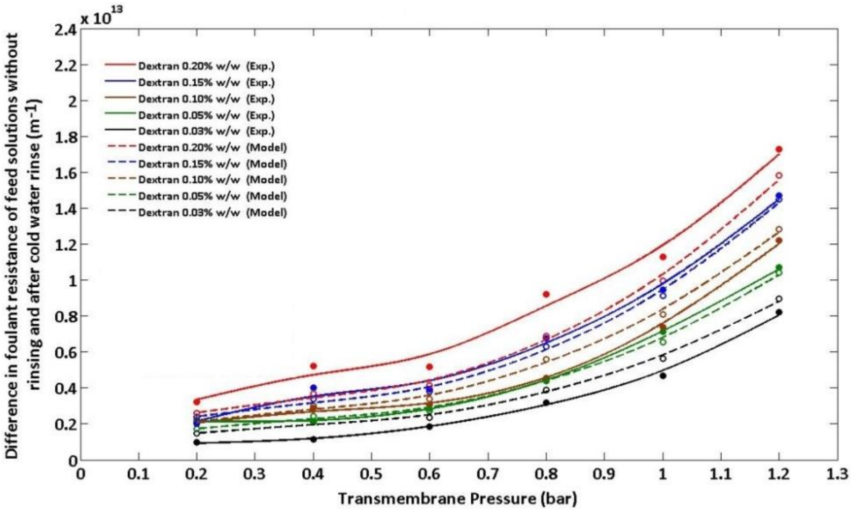


(d) Difference in fouling for the feed solutions without and with intermittent rinsing for dextran for concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2% at different values of transmembrane pressure

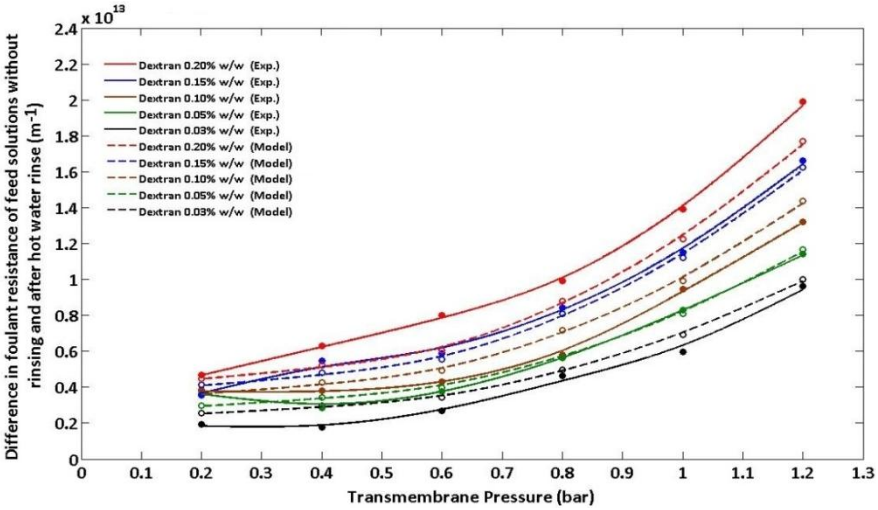
Fig. 7 Continued

It can be recalled that three categories of respective foulant resistance are represented as R_1, R_2 and R_3 in Fig. 3(a). It has already been noted that both the value of 'n' in Eq. (7) is 0.3 and as shown in Table 2, K_{av} values increase with TMP so one can summarise that the average reversible fouling per unit area reflected by the R_{df} in Eq. (7) is increasing with concentration and TMP. The experimental and modelled values for R_{df} vs TMP are illustrated graphically in Figs. 7(a)-(f).

An implication of graphs in Figs. 7(a)-(f) is that there is a considerable increase in flux after



(e) Difference in fouling for the feed solution without intermittent rinsing and after cold water rinse for dextran for concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2% at different values of transmembrane pressure



(f) Difference in fouling for the feed solution without intermittent rinsing and after hot water rinse for dextran for concentrations (w/w) of 0.03%, 0.05%, 0.1%, 0.15% and 0.2% at different values of transmembrane pressure

Fig. 7 Continued

each step of rinsing i.e., reversible fouling is a significant component of the overall fouling. This trend was observed for the solutions of both carboxymethyl cellulose as well as the dextran.

As a final observation there might be a link between optimising intermittent rinsing and optimising intermittent backwash as practised in direct-flow filtration which is the technology of choice for surface water treatment by membranes (Pearce 2011). Relaxation and/or backwashing have been incorporated in many membrane bioreactor (MBR) designs as standard operating strategies to limit fouling and it is therefore no surprise that rinsing under conditions of zero TMP had a beneficial effect. Following Wu *et al*. (2008b) we will in future work give consideration to having an initial short duration period (circa 100s) of elevated high flux followed by a longer filtration for the rest of the filtration cycle. This approach is said (at least for Wu's application) to limit irreversible fouling by having an initial fouling layer that prevents more highly fouling material from attaching onto the membrane surface. The initial layer acts as a filter aid. Whether one can achieve a filter aid situation as opposed to an over-clogging situation will depend upon the feed-membrane combination (Hughes and Field 2006).

4. Conclusions

- The application of a combination of strong alkaline solutions containing oxidizing agent (mainly sodium hypochlorite) followed by acid was found to be appropriate for cleaning of the ceramic membrane previously fouled extensively by dextran.
- The rate of change of foulant resistance with TMP is greater for dextran solutions than CMC solutions. For dextran, a typical gradient is 2.5×10^{13} m^{-1} per bar and does not change with TMP. For CMC, the gradient increases above 0.5 bar but never exceeds 2.0×10^{13} m^{-1} per bar. Below 0.5 bar, it is 1.0×10^{13} m^{-1} per bar.
- The intermittent rinsing improved filtration efficiency at each step for both solutions of CMC and dextran. Rinsing intermittently with cold water followed by the hot one (40°C) removed the reversible fouling quite effectively.
- A modulus (K_{av}) was introduced; this factor relate reversible fouling resistance with concentration. Although, the value of the K_{av} itself depends upon transmembrane pressure, it is interesting to note that at each value of TMP, five of six dependencies of the effect of concentration were of the form $C^{0.3}$. A semi-theoretical justification for this dependency was given.

Acknowledgments

Farrukh A. Siddiqui gratefully acknowledges the financially support from the Higher Education Commission of Pakistan.

References

Arkhangelsky, E., Kuzmenko, D. and Gitis, V. (2007), "Impact of chemical cleaning on properties and functioning of polyethersulfone membranes", *J. Membr. Sci.*, **305**(1-2), 176-184.

Astudillo, C., Parra, J., González, S. and Cancino, B. (2010), "A new parameter for membrane cleaning evaluation", *Separ. Purif. Technol.*, **73**(2), 286-293.

Biswal, D.R. and Singh, D.R. (2004), "Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer", *Carbohyd. Polym.*, **57**(4), 379-387.

Burggraaf, A.J. and Cot, L. (Eds.) (1996), *Fundamentals of Inorganic Membrane Science and Technology*, Elsevier, Amsterdam, The Netherlands.

Cheryan, M. (1998), *Ultrafiltration and Microfiltration Handbook*, (2nd Eition), CRC Press LLC, FL, USA.

Field, R.W. and Pearce, G.K. (2011), "Critical, sustainable and threshold fluxes for membrane filtration with water industry applications", *Adv. Colloid Interf. Sci.*, **164**(1-2), 38-44.

Field, R.W., Hughes, D., Cui, Z. and Tirlapur, U. (2008), "Some observations on the chemical cleaning of fouled membranes", *Desalination*, **227**(1-3), 132-138.

Field, R.W., Wu, D., Howell, J.A. and Gupta, B.B. (1995), "Critical flux concept for microfiltration fouling", *J. Membr. Sci.*, **100**(3), 259-272.

Hchaichi, H., Siwar, S., Elfil, H. and Hannachi, A. (2014), "Scaling predictions in seawater reverse osmosis desalination", *Membr. Water Treat., Int. J.*, **5**(3), 221-233.

Howell, J., Field, R. and Wu, D. (1996), "Ultrafiltration of high-viscosity solutions: Theoretical developments and experimental findings", *Chem. Eng. Sci.*, **51**(9), 1405-1415.

Hughes, D. and Field, R.W. (2006), "Crossflow filtration of washed and unwashed yeast suspensions at constant shear under nominally sub-critical conditions", *J. Membr. Sci.*, **280**(1-2), 89-98.

Kuzmenko, D., Arkhangelsky, E., Belfer, S., Freger, V. and Gitis, V. (2005), "Chemical cleaning of UF membranes fouled by BSA", *Desalination*, **179**(1-3), 323-333.

Latulippe, D.R., Ghosh, R. and Filipe, C.D.M. (2007), "Pulse injection technique for membrane characterization: Ultrafiltration of dextran solutions", *J. Membr. Sci.*, **289**(1-2), 268-276.

Lim, A.L. and Bai, R. (2003), "Membrane fouling and cleaning in microfiltration of activated sludge waste water", *J. Membr. Sci.*, **216**(1-2), 279-290.

Liu, C., Caothien, S., Hayes, J., Caothuy, T., Otoyo, T. and Ogawa, T. (2006), *Membrane Chemical Cleaning: From Art to Science*, Pall Corporation, USA.

Ogunbiyi, O.O., Miles, N.J. and Hilal, N. (2008), "The effects of performance and cleaning cycles of new tubular ceramic microfiltration membrane fouled with a model yeast suspension", *Desalination*, **220**(1-3), 273-289.

Pearce, G.K. (2011), *UF/MF Membrane Water Treatment: Principles and Design*, Water Treatment Academy, Bangkok, Thailand.

Shi, X., Tal, G., Hankins, N.P. and Gitis, V. (2014), "Fouling and cleaning of ultrafiltration membranes: A review", *J. Water Process Eng.*, **1**, 121-138.

Tomaszewska, M. and Białończyk, L. (2012), "The chemical cleaning of ceramic membrane used in UF", *Polish J. Chem. Technol.*, **14**(3), 105-109.

Vaisanen, P., Bird, M.R. and Nystrom, M. (2002), "Treatment of UF membranes with simple and formulated cleaning agents", *Food Bioprod. Process.*, **80**(2), 98-108.

Vanysacker, L., Bernshtein, R. and Vankelecom, I.F.J. (2014), "Effect of chemical cleaning and membrane aging on membrane biofouling using model organisms with increasing complexity", *J. Membr. Sci.*, **457**, 19-28.

Wu, J.L., Le-Clech, P., Stuetz, R.M., Fane, A.G. and Chen, V. (2008a), "Novel filtration mode for fouling limitation in membrane bioreactorsmembrane bioreactors", *Water Res.*, **42**(14), 3677-3684.

Wu, J.L., Le-Clech, P., Stuetz, R.M., Fane, A.G. and Chen, V. (2008b), "Effects of relaxation and backwashing conditions on fouling in membrane bioreactor", *J. Membr. Sci.*, **324**(1-2), 26-32.

Zator, M., Ferrando, M., Lopez, F. and Guell, C. (2007), "Membrane fouling characterization by confocal microscopy during filtration of BSA/dextran mixtures", *J. Membr. Sci.*, **301**(1-2), 57-66.

Zuriaga-Agustí, E, Alventosa-deLara, E., Barredo-Damas, S., Alcaina-Miranda, M.I., Iborra-Clar, M.I. and Mendoza-Roca, J.A. (2014), "Performance of ceramic ultrafiltration membranes and fouling behavior of a dye-polysaccharide binary system", *Water Res.*, **54**, 199-210.

CC