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Electrochemical cleaning of microporous metallic filters fouled with bovine serum albumin and phosphate under low cross-flow velocities

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Abstract

A three-electrode electrochemical cell has been designed to test the cleaning efficiency of applying potentials or currents to 0.2 μm pore size silver membranes fouled with bovine serum albumin and phosphate under low cross-flow velocities. It was found that with the improved electrochemical efficiency of the three-electrode design (compared to two-electrode cells) only relatively small current densities (about -40 μA cm^{-2}) needed to be applied in order to charge the membranes sufficiently to cause the reduction of water. The best results for electrochemically cleaning fouled membranes were obtained when negative currents were applied to membranes in a moderate strength acid environment. It was found that the interfacial pH changes associated with the reduction of water were important in cleaning the membranes in addition to the agitation action of bubbles of hydrogen gas.

1. Introduction

Membranes are often used during the processing of biological (e.g., dairy) fluids as a size discriminatory method of separating or concentrating individual components in the filter stream. However, due to the complex nature of the fluid medium, the membranes frequently become fouled resulting in a decrease in the flow rate of solution through the membrane (the permeate flux) and a loss of selectivity. Eventually, the flux diminishes to such an extent that the processing cycle must be stopped, resulting in a plant downtime where a cleaning cycle is initiated. Therefore, there is considerable interest from the processing industry in ways of preventing fouling from occurring and improving the cleaning processes to lower the overall downtime and decrease the quantity of cleaning chemicals. It is with these points in mind that we have investigated whether electrochemistry can be used as a method of cleaning membranes fouled with protein and inorganic material (bovine serum albumin (BSA) and potassium orthophosphate) in a cross-flow filtration cell. The cross-flow filtration technique involves the feed stream being pumped at a relatively high velocity parallel to a membrane surface (Figure 1). This helps to reduce the concentration polarization by thinning the boundary layer thickness and by assisting in sweeping away the filter cake or gel layer film (filter cake refers to colloidal particles and gel layer to macromolecules) [1].

In milk, fouling is thought to be initiated by the deposition of organic thermally unstable components such as the denatured whey proteins and caseins and the deposition of inorganic calcium phosphates [2, 3]. To clean the fouled surfaces a two stage procedure is required. The addition of a strong base causes the protein material to swell which is then removed by the application of a shearing force. The residual mineral scale that is left is subsequently removed by an acid cleaning procedure. Single stage cleaners use a complexing agent such as ethylenediaminetetraacetic acid to solvate the inorganic metal ions, thus breaking up the mineral deposits. However, the complexing agents may cause problems by solvating harmful metal ions which may otherwise precipitate out of solution. Most plants use a combination of a two stage cleaning process, although the order of acid and base treatments vary depending on the conditions. For example, scaling with a high mineral content may undergo acid treatment followed by treatment with base, whereas fouling caused by high levels of protein material usually undergoes treatment with base first. In general the faster the fluid velocity and the hotter the cleaning chemicals, the faster the cleaning rate. There is an optimal alkali cleaning level of 0.5% NaOH for minimising the cleaning time for protein based deposits. A low concentration of base

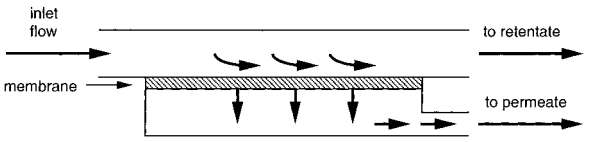

Fig. 1. Schematic diagram of cross-flow filtration technique. The tangential velocity of the solution passing over the membrane aids in preventing concentration polarization (see text).

does not effectively clean the deposits whilst too high a concentration of base causes the protein to gel on the surface. Biofilms also cause fouling of membranes in dairy fluids but will not be discussed further in this paper.

There have been numerous literature reports where electrochemical techniques have been developed to assist membrane processes; in a preventative role by stopping membranes from becoming fouled [4–11], in a restorative role by assisting in cleaning of membranes that are already fouled [12–14], or by enabling the selective separation of species based on charge and size [15–20]. Notably, the most successful applications of applied electric fields in preventing fouling have been in the presence of inorganic feeds, such as TiO_2, and not in complex biological feeds such as milk. Most of the preventative fouling studies [4–10] have used the application of a d.c. field across two electrode plates (although there has also been a report of the use of a.c. fields [11]), with a nonconducting membrane positioned between the plates. An applied electric field is established between the electrodes of the appropriate polarity (usually so that the membrane is in proximity to a negative field since most particles of interest in aqueous solution are negatively charged, particularly for colloidal solutions). It has been found that the application of the electric field in pulses has several advantages over applying an electric field continuously; that is, a lower energy requirement, lower heat production and less time for undesirable chemical changes in the process stream due to electrochemical reactions [12].

Traditionally, membranes were most commonly composed of insulating polymeric materials such as cellulose, polysulphone or polyamide, though ceramic materials are becoming extensively used [1]. The relatively recent development of microporous sintered stainless steels has enabled filtration and electrochemical cleaning studies to be performed with the stainless steel serving as both the membrane and the working electrode with the electrochemical circuit completed with a counter electrode composed of platinised titanium mesh [13, 14]. The application of a sufficiently large potential difference between two electrodes results in bubbles of hydrogen gas being formed at the negative electrode due to the reduction of water whilst at the positive electrode bubbles of oxygen are formed due to the oxidation of water (Equations 1 and 2, respectively).

The formation of hydrogen gas is thought to be important in *in situ* intermittent electrolytic cleaning (IIEMC) [13, 14] due to the agitation action of the bubbles. Localised interfacial changes in pH also occur at the electrodes due to the formation of hydroxide or hydrogen ions which may assist or be detrimental to cleaning. Another significant electrochemical reaction that may occur at negative potentials is the reduction of dissolved molecular oxygen (Equation 3), which produces hydroxide ions [21].

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \quad (1)$$

$$6\,H_2O \rightarrow O_2 + 4\,H_3O^+ + 4\,e^- \quad (2)$$

$$2\,O_2 + 2\,e^- + H_2O \rightarrow O_2 + HO_2^- + OH^- \quad (3)$$

Several studies have reported obtaining improved flux during the filtration of BSA solutions [9, 10, 12] using polymeric membranes (pore size $> 0.1\ \mu$m) suspended in electric fields. One study [12] reported that good results were obtained by the pulsed electrophoretic filter-cake release in dead-end membrane filtration of BSA. Another study reported [10] that in high conductivity solutions, at a constant applied potential of 100 V, degradation of the protein occurs which results in almost total loss of permeate flux. The reason for the degradation was assigned to localised heating of the membrane surface, but it can also equally be envisioned that pH changes associated with Equations 1–3 also occur which could result in either precipitation or denaturing of the protein. BSA is more soluble above and below its isoelectric point of 4.6 but at high and low pH values can denature [22, 23]. A recent ellipsometry study [24] has reported that adsorption of BSA on solid electrodes (stainless steel and gold) always occurs with applied potentials (positive and negative). It has also been reported that the application of positive or negative potentials to stainless steel surfaces in contact with solutions containing milk proteins and inorganic material often makes fouling much worse [25].

Studies on microfiltration of proteins have shown that considerable deposition of material occurs within the pores of the membrane and very little on the surface as a gel [26, 27] (this is in contrast to ultrafiltration where gel layers invariably form due to the small pore size relative to the size of the macromolecule), and the decrease in permeability occurs at a faster rate at higher pressures. The conclusion that there was little concentration polarization in the microfiltration of BSA came from the observation that stirring the solutions during filtration had little effect on the permeation rate [26] and that the decrease in permeation rate could be quantified based on the decrease in pore volume due to deposition of protein on the walls of the pores. In this paper, data obtained from electrochemical cleaning experiments using 0.2 μm pore size silver membranes as the working electrode are discussed. As far as we are aware, the other electrochemical cleaning studies where the membrane is also the electrode have been restricted to more porous membranes (pore size $> 1\ \mu$m) [13, 14].

2. Experimental details

2.1. *Design of electrochemical cross-flow filtration cell*

All of the reported literature on cross-flow microfiltration cells that use applied currents to clean membranes are based on a two-electrode cell design (working and counter electrodes). In order to improve the electrochemical efficiency of the cross-flow electrofiltration cell and to obtain better potential control, we have designed a three-electrode (working, auxiliary [28, 29] and reference) electrochemical cross-flow filtration cell where the applied potential/current is controlled through a potentiostat/galvanostat.

A cross-section through the electrochemical cross-flow cell is given in Figure 2. The solution flowed into the cell in the direction given in Figure 2, passing over the membrane surface and either exiting the cell at the opposite end to the entrance to be recirculated into the feed stream (retentate), or to pass through the membrane where it was collected as the permeate. The inlet tube on the cell was connected via polymer tubing to a peristaltic pump. Two 250 kPa pressure gauges were attached to the tubing lines, one just before the solution entered the cell and the other on the retentate outlet side (Figure 3). A Hoffman clamp (Figure 3) was used to increase the pressure difference across the membrane.

The cell was constructed of an acrylic that was resistant to moderate strength acids and bases and designed to hold a rectangular membrane of 24 mm$\times$ 6 mm that was supported on a perforated Teflon sheet. A sheet of platinum foil served as the auxiliary electrode and a 0.2 μm pore size silver membrane served as both the working electrode and the filter separating the retentate and permeate solutions. The distance between the membrane and the platinum foil auxiliary electrode was 4 mm. In order for the cell to remain water tight,

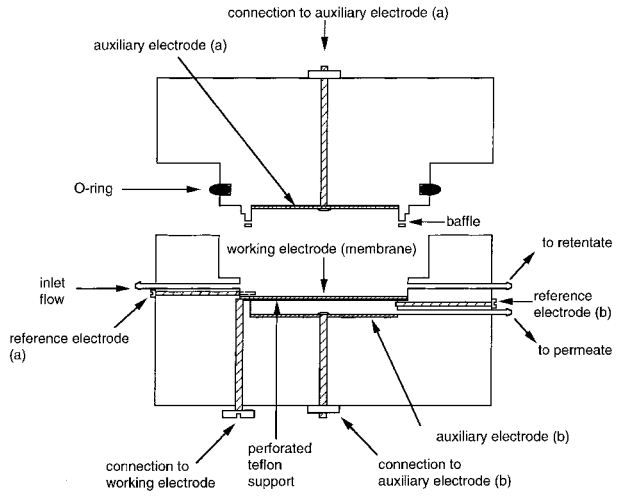

Fig. 2. Cross section through the electrochemical cross-flow filtration cell showing position of the working (membrane), auxiliary and reference electrodes. Reference electrodes (a) and (b) were used in conjunction with auxiliary electrodes (a) and (b), respectively.

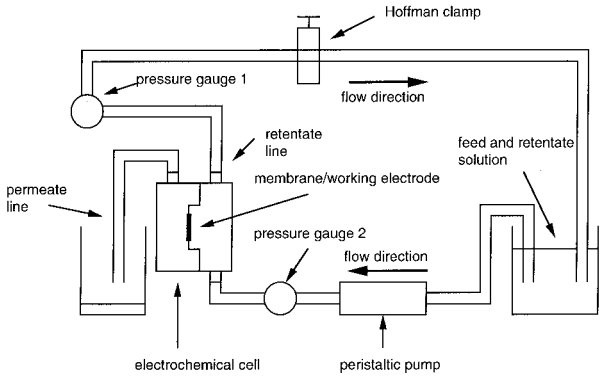

Fig. 3. Schematic diagram of system used for cross-flow filtration experiments.

the reference electrode simply consisted of a stainless steel screw that was threaded into the acrylic. Although stainless steel is not traditionally used as a reference electrode material, even for pseudo reference electrodes, it was found that it functioned adequately for the purpose of lowering the potential drop (Equation 4) between the working and auxiliary electrodes.

$$E = IR_s \tag{4}$$

(R_s is the solution resistance, I is the current and E is the potential drop). Accurately maintaining a known stable thermodynamic potential to the nearest millivolt was of lesser importance to this study since in most instances all that was necessary was that the potential or current was sufficiently negative to form bubbles of hydrogen gas during the reduction of water. The auxiliary electrode could be positioned in one of two positions (Figure 2, auxiliary electrode (a) or (b)) on either side of the silver membrane and, depending on the chosen position of the auxiliary electrode, the reference electrode could also be positioned either side of the silver membrane working electrode (Figure 2, reference electrode (a) or (b)). Theoretically, the lowest potential drop between the working and auxiliary electrodes should occur when the reference electrode is positioned on the same side of the membrane as the auxiliary electrode [30], that is, reference electrodes (a) and (b) were used in conjunction with auxiliary electrodes (a) and (b), respectively. The electrical contacts to the working and auxiliary electrodes were made through stainless steel screws.

2.2. *Experimental method*

The general procedure involved circulating a solution through the cross-flow cell while controlling the pressure through the membrane with the use of the Hoffman clamp (Figure 3). The pressures at gauges 1 and 2 were adjusted to 10 kPa and 20 kPa, respectively, and during the course of the experiments the Hoffman clamp was adjusted to keep the pressure constant at these set values. The crossflow rate was 1×10^{-2} m s^{-1} and the permeate flow was calculated by measuring the weight

or volume of fluid exiting the permeate line as a function of time. The solution compositions were changed by flushing the entire system to a waste reservoir with the new solution for 2–3 min before allowing the solution to return to the retentate for recycling.

2.3. *Chemicals and equipment*

The potential or current were controlled using a PAR (model 273) potentiostat/galvanostat interfaced to an IBM compatible computer using the PAR software, SoftCorr. 0.2 μm pore size silver membranes (50 μm thickness) were obtained from Osmonics, Poretics Products, Livermore, CA, USA (the manufacturing procedure yields high precision pore size and uniformity). BSA (>99%) was obtained from Sigma chemicals and all other chemicals were analytical grade. Distilled water was used for all experiments. 0.1% BSA solutions were prefiltered through a 0.2 μm filter to remove particulate material before cross-flow filtration experiments were commenced. Scanning electron microscopy (SEM) micrographs were obtained on a Cambridge Stereoscan 250 Mk 2. Solutions used were; 0.1 M $NaClO_4$ (pH 6.5), 0.1% BSA (pH 6.5), 0.05 M K_2HPO_4 (pH 9.4), 0.1% BSA and 0.05 M K_2HPO_4 (pH 8.8), 0.5% NaOH (pH 12.5) 0.1% BSA and 0.1 M Na_2SO_4 (pH 6.3) and 0.01 M HCl (pH 2.1).

3. Results and discussion

3.1. *Electrochemical performance of cross-flow microfiltration cell*

Figure 4 shows voltammetric potential sweep data obtained at several permeate fluxes at the silver membrane working electrode with the auxiliary and reference electrodes in position (a) in the diagram shown in Figure 2. The data in Figure 4 illustrate that as the potential is increased from about 0 to -1.2 V (vs. stainless steel) an increase in negative current is observed up to an almost plateaux region around -1 V. The increase in current can be attributed to the reduction of dissolved molecular oxygen (Equation 3). As the flow rate in the cell increases, the limiting current also increases which suggests that the current associated with the reduction process is controlled by the transfer of O_2 to the electrode surface via a convective–diffusive mechanism. The sigmoidal shaped voltammogram shown in Figure 4 is analogous to the voltammetry observed under other hydrodynamic conditions such as at rotating disk or channel flow cell electrodes [31, 32], albeit somewhat more drawn out than would be expected for a simple electron transfer process. Applying potentials more negative than -1.2 V resulted in a sharp increase in negative current due to the reduction of water, indicating that the potential control in the cell is similar to what would be expected from a normal three electrode electrochemical cell and showing that only relatively small overpotentials need to be applied to obtain the desired electrochemical result (i.e., the reduction of water).

3.2. *Chemical cleaning of membranes fouled with BSA and phosphate*

Several 'chemical only' cleaning experiments were performed as a basis with which to compare data obtained from electrochemical/chemical cleaning experiments. Figure 5(a) shows typical permeate flux against time data for solutions of (○) 0.1% BSA, (▽) 0.05 M K_2HPO_4 and (△) 0.1% BSA with 0.05 M K_2HPO_4. The BSA solution was chosen as a representative protein component of milk and the K_2HPO_4 as an inorganic phosphate. BSA itself has a size of $\sim$17 nm $\times$ 3.4 nm (assuming a prolate ellipsoid) [22–24] and so should readily pass through the membrane. The reason for the decreasing permeate flux with time for the solution of BSA shown in Figure 5(a) is likely due to a process involving deposition within the membrane rather than

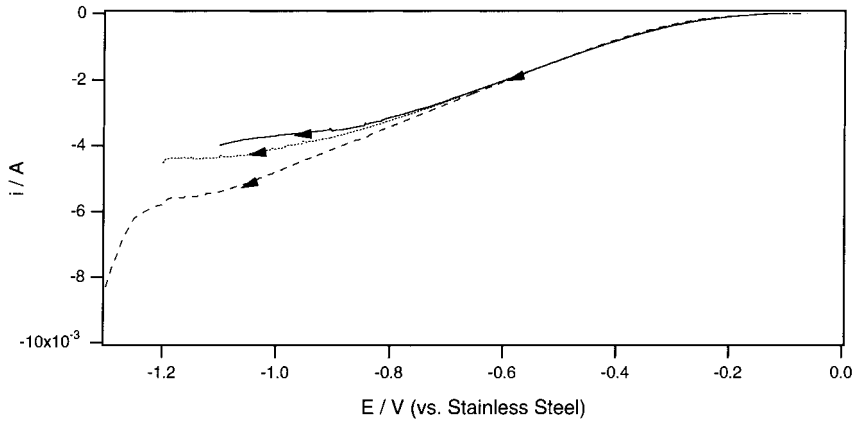

Fig. 4. Linear sweep voltammogram showing the reduction of molecular oxygen, obtained at a scan rate of 2 mV s^{-1} at a 0.2 μm pore size silver membrane in water (0.1 M $NaClO_4$) at several permeate fluxes. Reference and auxiliary electrodes in position (a) (refer to Figure 2). Permeate flux: (——) 0.24, (·····) 0.31 and (- - - -) 0.42 L s^{-1} m^{-2}.

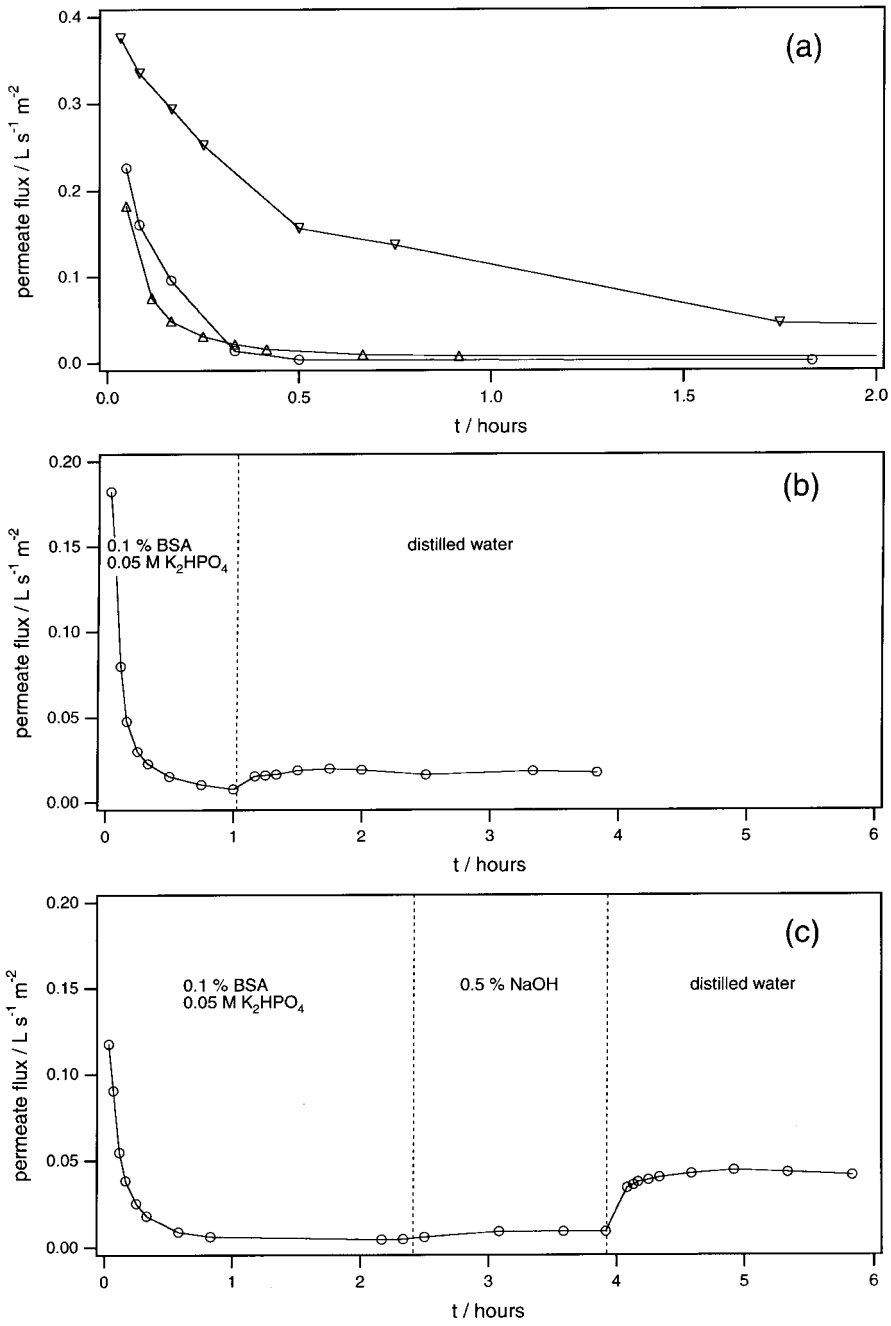

Fig. 5. Plot of permeate flux through a silver membrane as a function of time for, (a) (○) 0.1% BSA, (▽) 0.05 M K_2HPO_4 and (△) 0.1% BSA with 0.05 M K_2HPO_4, (b) a membrane fouled with BSA/K_2HPO_4 and cleaned with distilled water, and (c) a membrane fouled with BSA/K_2HPO_4 and cleaned with 0.5% NaOH then distilled water.

gel/cake film formation on the membrane surface. SEM micrographs (Figure 6(a) and (b)) of the surface of the membranes and energy dispersive X-ray (EDX) analysis failed to detect any difference between the surfaces of the fouled and clean (unused) membranes, which is supportive of the decrease in flux being due to adsorption occurring within the membrane and is in agreement with previous reports on the microfiltration of BSA solutions [26, 27]. The flux decline observed in K_2HPO_4 solutions (Figure 5(a)) implies that very small ions can also cause blockage of the membranes. Furthermore, it was observed that filtration of dilute solutions (~1 mM) of small water soluble organic molecules such as ascorbic acid decreased the permeate flux indicating that adsorption processes can occur within the 0.2 μm pore size membranes in addition to the aggregation (and possible denaturing) of protein macromolecules.

Figure 5(b) shows the effect on permeate flux on cleaning a membrane fouled with BSA/phosphate with distilled water. A small increase in flux was observed upon changing the BSA/phosphate (pH ~9) solution to distilled water (pH ~5–6 depending on concentration of dissolved CO_2). Figure 5(c) shows the flux results when a membrane fouled with BSA/phosphate was cleaned first with NaOH, then with distilled water. Only a small increase in flux was observed when 0.5% NaOH

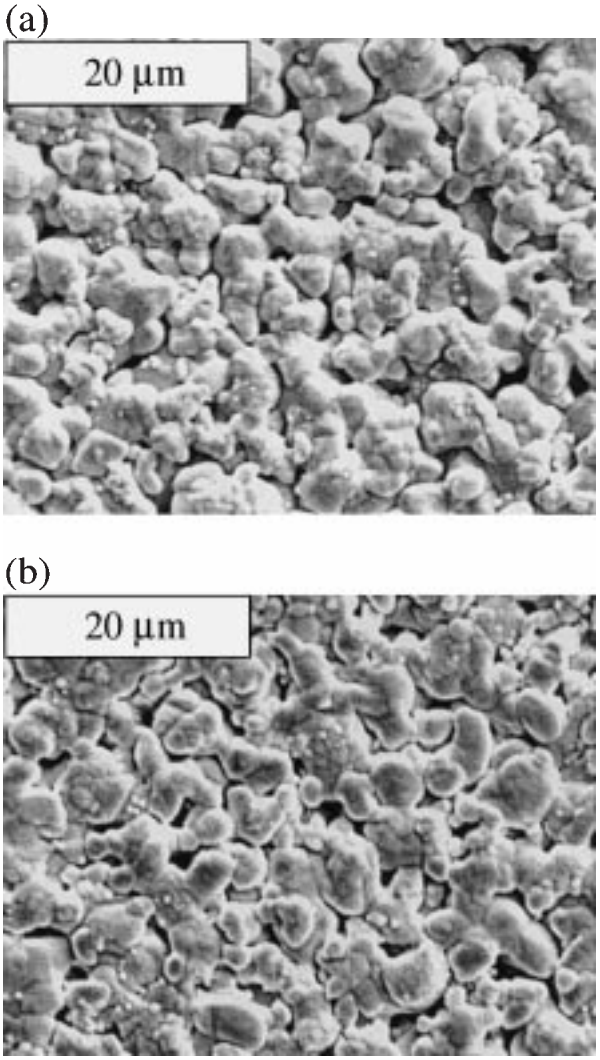

Fig. 6. Scanning electron microscopy micrographs of 0.2 μm pore size silver membranes, (a) clean and unused and (b) fouled with 0.1% BSA in the cross-flow filtration cell followed by a distilled water rinse for 3 min.

(pH ~12.5) was passed through the membrane. However, when the NaOH cleaning was followed by distilled water a greater increase in flux was observed than when the membrane was cleaned with only distilled water (compare 'distilled water' region in Figure 5(b) and (c)).

The data in Figure 5(b) and (c) show that cleaning a membrane fouled with BSA/K_2HPO_4 with 0.5% NaOH then distilled water resulted in a better flux recovery than cleaning the membrane with either NaOH or distilled water alone. An explanation for this phenomenon can be deduced by assuming that the deposits fouling the membrane are composed of intercalated protein and phosphates. This is a reasonable assumption since the data in Figure 5(a) show that both BSA and K_2HPO_4 foul the membrane. Distilled water has a pH of ~5–6 and it is unlikely that cleaning with pure water will assist in removing the BSA as generally more basic conditions are used to swell proteins to assist in their removal. However, any adsorbed phosphates are likely to be more soluble in the slightly acidic environment of distilled water than the strongly basic 0.5% NaOH solution. Therefore, it is possible that the addition of NaOH causes the protein layers to swell enabling the distilled water to dissolve the intercalated inorganic deposits further enabling breakdown of the fouled layers and leading to an increase in flux.

3.3. In situ *electrochemical cleaning of membranes fouled with BSA or phosphate*

It was found that applying small positive (not enough to cause the oxidation of silver) and negative potentials (not enough to create bubbles of H_2) made no detectable difference to the flux, suggesting that small applied fields were not influencing the gross fouling processes within the membrane (data not shown). With an electrolyte concentration of 0.05–0.1 M, the application of −10 to −25 mA was sufficient to cause the visible appearance of bubbles of hydrogen gas according to Equation 1. Applying current pulses greater than −25 mA did not notably increase the flux recovery. The value of −25 mA is not significant when comparing results with other workers because the applied current necessary to form bubbles of hydrogen gas will vary depending on the electrolyte concentration, the cell design and the electrode area. The current density is difficult to accurately determine as the exact surface area of the membrane is not known. A simplified calculation based on the pore size and volume porosity of the membrane allowed the active area of the membrane to be estimated to be 600 cm^2 [33]. Therefore, for an applied current of −25 mA, the average current density is −40 μA cm^{-2}. However, it is likely that the current density will vary through the membrane with the portions of the membrane closest to the auxiliary electrode carrying the highest charge.

Figure 7 shows how the potential at the membrane typically changed with time as −25 mA was applied for 60 s intervals at a 0.01 m s^{-1} cross-flow for a solution of BSA and Na_2SO_4. The solid and dashed lines in Figure 7 are the first and second current pulses respectively. For the first current pulse, the potential began at a relatively low value and increased to more negative potentials, especially in the first 15 s. The change in potential can be rationalised by considering an adsorption process where the adsorption of nonconducting or poorly conducting material forces the potential to shift to more negative potentials in order to achieve the desired current. With the second current pulse the steady state potential is reached at a faster rate, possibly because most of the metal–surface based adsorption has already occurred in the first few seconds of the first current pulse. This is in agreement with the ellipsometry study by Beaglehole et al. [24] who found adsorption always occurred when a potential was applied to a surface of gold or stainless steel (see also Introduction). However, the occurrence of a potential dependant adsorption process suggested by the electrochemical data (Figure 7) is unlikely to be as problematic to

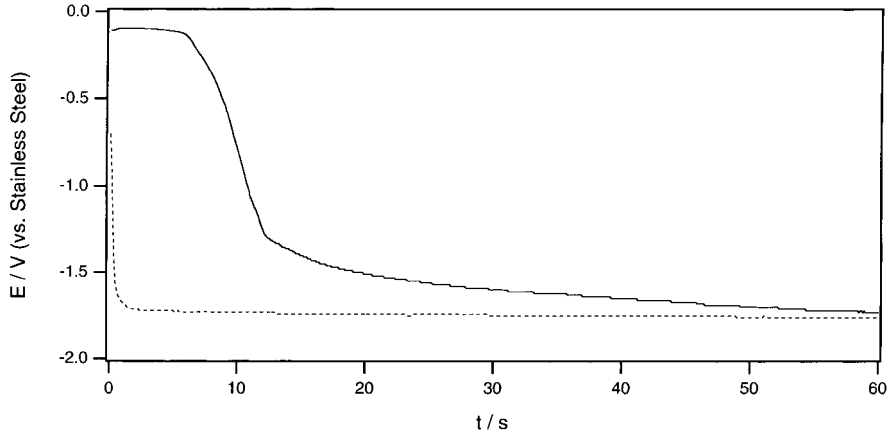

Fig. 7. Change in potential against time when −25 mA was applied to a silver membrane in the presence of 0.1% BSA and 0.1 M Na_2SO_4 at a cross-flow of 0.01 m s^{-1}, (——) first current pulse, (- - - - -) second current pulse.

fouling as the protein deposition within the pores of the membrane which takes place over longer periods of time (see Figure 5 and references [26, 27]).

Figure 8(a) shows data obtained from experiments conducted to determine the effect of *in situ* electrochemical cleaning membranes in the presence of BSA. (In the following discussion the term *in situ* refers to the situation where the protein/electrolyte solution is the same as the cleaning solution. The term *ex situ* refers to the situation where the protein/inorganic solution has been replaced with a cleaning solution (usually, acid, base or water) for the purpose of cleaning the membrane. Both *in situ* and *ex situ* experiments involve operation of the membrane within the cross-flow filtration cell).

The first experiments were conducted by replacing K_2HPO_4 with the less basic electrolyte, 0.1 M Na_2SO_4. It was found that the best results (larger increases in flux

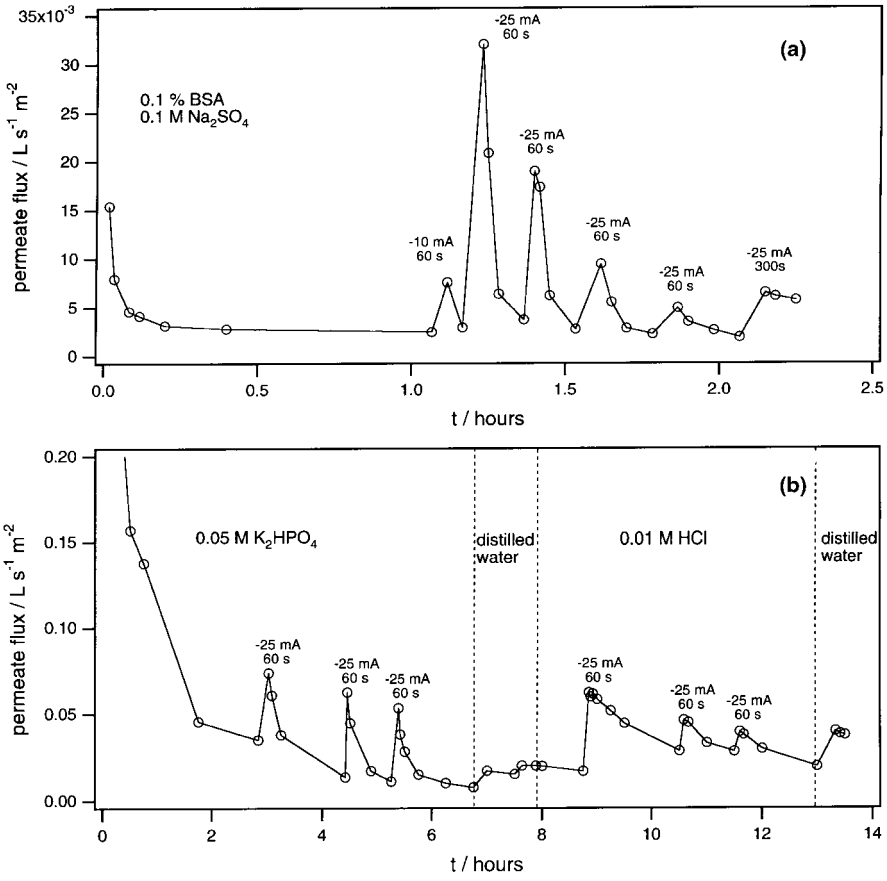

Fig. 8. (a) Plot of permeate flux through a silver membrane as a function of time for (a) a membrane fouled with BSA/Na_2SO_4 and cleaned with electrochemical pulses of −10 and −25 mA, (b) a membrane fouled with K_2HPO_4 and cleaned with distilled water then electrochemical pulses of −25 mA with HCl as the electrolyte.

upon applied potential) were obtained by having the auxiliary and reference electrode on the retentate side of the membrane (Figure 2, auxiliary and reference electrode (a)) rather than on the permeate side. The data in Figure 8(a) show that providing a sufficiently negative current is applied (i.e., −10 mA), an increase in flux is observed on application of the current. However, the flux recovery is only temporary and the flow rate returns to its initial value in several minutes. Repeatedly applying negative current pulses resulted in an increase in flux, but by a diminishing amount each time, for example, Figure 8(a) shows that by the time the fourth consecutive current pulse of −25 mA was applied, the flux recovery had decreased to approximately 15% of its initial value.

Figure 8(b) shows data obtained for the electrochemical cleaning of a solution of potassium orthophosphate. Because K_2HPO_4 is itself an electrolyte, Na_2SO_4 was not needed for these experiments. Similar results were obtained upon application of applied current as for the BSA/Na_2SO_4 solution, that is, an increase in flux was observed that diminished with repetitive pulsing. (Note that there is a sixfold difference in flux and time-scale, between the data in Figures 8(a) and 8(b)). Changing the solution composition to water and then 0.01 M HCl (pH ~2) and applying short current pulses did not notably improve the flux recovery.

The data in Figure 8(a) and (b) show that applying electrochemical pulses of −25 mA is partially effective in increasing the flux through membranes fouled with BSA and K_2HPO_4. A possible reason for the stepwise decrease in flux recovery as the number of pulses increases is that the pH change associated with the formation of —OH may also result in the denaturing of the protein or cause the deposition of some insoluble material, thus partially blocking the membrane. The current pulsing technique appears to be more effective at increasing the flux for a solution of K_2HPO_4 than for 0.1% BSA with 0.1 M Na_2SO_4 (compare the flux axis scales in Figure 8(a) and (b)). Due to the diminishing flux recovery with multiple pulses it appears that the *in situ* electrochemical cleaning technique will be unsuccessful in completely unblocking the membrane to allow reasonable permeate fluxes.

3.4. Ex situ *electrochemical cleaning of membranes fouled with BSA/phosphate in the presence of acid or base*

Figure 9(a) shows data that were obtained by first fouling a membrane with a solution of BSA and K_2HPO_4, rinsing the membrane with water then NaOH and finally electrochemically cleaning the membrane in the presence of 0.5% NaOH. The data are generally very

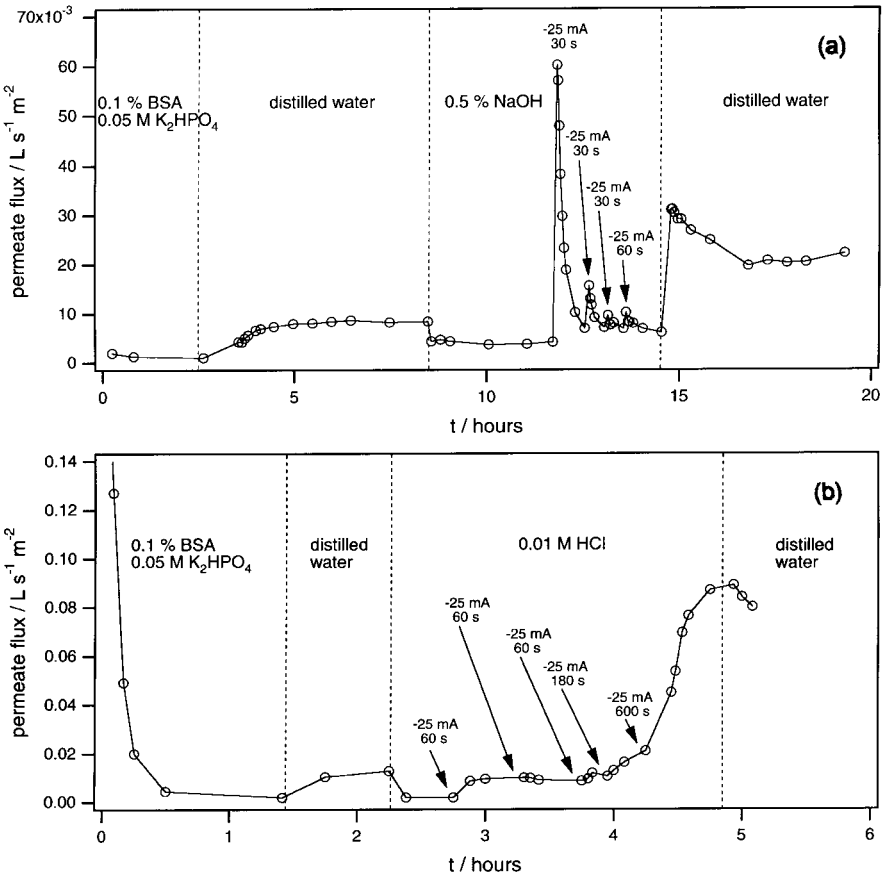

Fig. 9. Plot of permeate flux through a silver membrane as a function of time for a membrane fouled with BSA/K_2HPO_4 and cleaned with electrochemical pulses of −25 mA with (a) NaOH and (b) HCl as the electrolyte.

similar to that obtained when electrochemically cleaning a membrane fouled with BSA with Na_2SO_4 as the electrolyte (Figure 8(a)). A large increase in flux was observed when a current pulse was applied for the first time, however, the increase in flux decreased rapidly (within a few minutes) and the flux rate could not be sustained with multiple pulses (Figure 9(a)). Applying an extended current in the range -25 to -50 mA for several minutes did not improve the flux (data not shown). Rinsing the membrane with distilled water at the completion of the electrochemical cleaning did increase the flux through the membrane (Figure 9(a)).

Figure 9(b) shows data obtained by cleaning a membrane fouled with BSA/K_2HPO_4 with current pulses applied under acidic conditions (pH $\sim$2). The data in Figure 9(b) differs in two major ways from the data in Figure 9(a). First, the initial application of -25 mA for 30 s had very little effect on the permeate flux under acidic conditions (Figure 9(b)) compared to under basic conditions (Figure 9(a)). Second, the application of several constant current pulses under acidic conditions resulted in a sustained improvement in the permeate flux. The longer the constant current was applied under acidic conditions the better the flux recovery.

Electrochemical cleaning with an acid as an electrolyte (Figure 9(b)), when the current was applied for at least several minutes, resulted in a sustained increase in flux. The reason for the increase in flux when electrochemical cleaning is performed in the presence of acid is possibly due to the fact that the applied current causes hydroxide ions to form (according to Equation 1). Therefore, the application of a negative current in the presence of an acid results in a combined acid/base cleaning regime (providing the acid is not so concentrated to neutralize all of the base). This mimics traditional cleaning techniques where a base treatment is used to cause the proteins to swell and be more easily removed by the cross-flow, while the acid cleaning is used to dissolve inorganic material.

4. Conclusions

The flux through 0.2 μm pore size silver membranes decreases continually in the presence of solutions of both BSA and K_2HPO_4 which is indicative of adsorption–deposition processes occurring within the membrane pores. The adsorption occurs more rapidly for solutions of BSA than for solutions of K_2HPO_4. *In situ* electrochemical cleaning where the protein/electrolyte solution is the same as the cleaning solution is relatively ineffectual at cleaning membranes. Applying negative current pulses to the membrane does produce a transitory increase in flux, but the flux recovery diminishes with repeated current pulses. *Ex situ* electrochemically cleaning membranes where the protein/phosphate solution was replaced with an acid or base resulted in an improved flux. Prolonged negative current pulses with an acid as the electrolyte are particularly effective at cleaning membranes fouled with BSA/K_2HPO_4. A likely explanation for this phenomenon is that the application of a negative potential in the presence of an acid results in a combined acid/base cleaning regime (providing the acid is not so concentrated to neutralise all of the base that is formed electrochemically). SEM and electrochemical evidence suggest that in solutions of BSA/phosphate much of the fouling occurs within the membranes rather than on the surface as a gel layer (at least for the particular membrane and cell design used in this study).

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References

1. W.R. Bowen, *in* R.A. Williams (ed.), 'Colloid and Surface Engineering' (Butterworth, London, 1992), pp. 215–247.
2. G. Daufin and U. Merin, 'Fouling and Cleaning in Pressure Driven Membrane Processes', IDF Special Issue 9504 (Brussels, 1995).
3. G. Bylund, 'Dairy Processing Handbook', Tetra Pak Processing Systems AB, S-221 86 (Lund, Sweden, 1995).
4. J.D. Henry Jr, L.F. Lawler and C.H. Alex Kuo, *AIChE J.* **23** (1977) 851.
5. J.M. Radovich and R.E. Sparks, *in* A.R. Cooper (ed.), 'Ultrafiltration Membranes and Applications' (Plenum Press, New York, 1979), pp. 249–267.
6. H. Yukawa, K. Shimura, A. Suda and A. Maniwa, *J. Chem. Eng. Japan* **16** (1983) 305.
7. R.J. Wakeman and E.S. Tarleton, *Chem. Eng. Sci.* **42** (1987) 829.
8. C. Visvanathan and R. Ben Aim, *Sep. Sci. Technol.* **24** (1989) 383.
9. A.K. Turkson, J.A. Mikhlin and M.E. Weber, *Sep. Sci. Technol.* **24** (1989) 1261.
10. R.J. Wakeman, *Trans I Chem E* **76** (1998) 53.
11. P.V. Zumbusch, W. Kulcke and G. Brunner, *J. Membrane Sci.* **142** (1998) 75.
12. W.R. Bowen and A. Latif Ahmad, *AIChE J.* **43** (1997) 959.
13. W.R. Bowen, R.S. Kingdon and H.A.M. Sabuni, *J. Membrane Sci.* **40** (1989) 219.
14. W.R. Bowen and H.A.M. Sabuni, *Ind. Eng. Chem. Res.* **30** (1991) 1573.
15. T. Tsuru, S-I. Nakao and S. Kimura, *J. Chem. Eng. Japan* **23** (1990) 604.
16. S. Saksena and A.L. Zydney, *Biotechnol. Bioeng.* **43** (1994) 960.
17. A. Garem, G. Daufin, J.L. Maubois and J. Léonil, *Biotechnol. Bioeng.* **54** (1997) 291.
18. S. Lentsch, P. Aimar and J. Luis Orozco, *J. Membrane Sci.* **80** (1993) 221.
19. L. Pupunat, G.M. Rios, R. Joulié, M. Persin and G. Pourcelly, *Sep. Sci. Technol.* **33** (1998) 67.
20. M. Nishizawa, V.P. Menon and C.R. Martin, *Science* **268** (1995) 700.
21. D.T. Sawyer and J.S. Valentine, *Acc. Chem. Res.* **14** (1981) 393.
22. D.C. Carter and J.X. Ho, *Adv. Protein Chem.* **45** (1994) 153.
23. F. Vojdani, *in* G.M. Hall (ed.), 'Methods of Testing Protein Functionality' (Blackie Academic and Professional, London, 1996), p. 15.
24. D. Beaglehole, B. Webster and S. Werner, *J. Colloid Interface Sci.* **202** (1998) 541.
25. G. Daufin, F.L. Kerherve and A. Quemerais, 2nd International Conference on Fouling and Cleaning in Food Processing, Depart-

ment of Food Science, University of Wisconsin, Madison (14–17 July, 1985), p 263.
26. W.R. Bowen and Q. Gan, *Biotechnol. Bioeng.* **38** (1991) 688.
27. C. Herrero, P. Prádanos, J.I. Calvo, F. Tejerina and A. Hernández, *J. Colloid Interface Sci.* **187** (1997) 344.
28. Usually counter electrode is a term used in connection with two-electrode experiments and auxiliary electrode is used in descriptions of three-electrode systems.
29. P.T. Kissinger, *in* P.T. Kissinger and W.R. Heineman (Eds), 'Laboratory Techniques in Electroanalytical Chemistry' (Dekker, New York, 1984), p. 167.
30. A.M. Bond, 'Modern Polarographic Methods in Analytical Chemistry' (Marcel Dekker, New York, 1980).
31. C.M.A. Brett and A.M.O. Brett, 'Electrochemistry: Principles, Methods and Applications' (Oxford University Press, Oxford, 1993).
32. J.A. Cooper and R.G. Compton, *Electroanalysis* **10** (1998) 141.
33. The calculation of the area of the membrane was based on a 30.8% volume porosity stated by the manufacturer and by assuming 0.2 μm diameter spherical pores.