Influence of solute–membrane–particle interaction on permeate quality during cross flow ultrafiltration of whey suspensions using tubular ceramic membranes

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การกรองสารละลายหางนมด้วยระบบเมมเบรนอุลตราฟิลเตรชันที่มีการไหลแบบแนวขนานโดยใช้เมมเบรนเชิงประกอบชนิดท่อ โดยศึกษาผลของค่าความเป็นกรดด่างหรือค่าพีเอช สารรวมตะกอนอลูมิเนียมซัลเฟต และสารลดแรงตึงผิว 2 ชนิดได้แก่ โซเดียมโอเคซิลซัลเฟตและซิติลไตรเมทิลแอมโมเนียมโบรไมด์ที่มีต่อคุณภาพของสารเพอมิเอทหรือสารที่กรองผ่านเมมเบรน โดยประเมินจากค่าความขุ่นและสารอินทรีย์คาร์บอนทั้งหมด ขณะที่เมมเบรนและหางนมจะศึกษาคุณสมบัติด้านไคเนติกส์ทางไฟฟ้าโดยการวัดค่า ζ-potential ผลการทดลองชี้ให้เห็นว่าค่า ζ-potentials ของสารละลายหางนมและเมมเบรนต่างขึ้นอยู่กับค่าพีเอช โดยค่า ζ-potential จะมีค่าเป็นบวก เมื่อค่าพีเอชต่ำกว่า 3.5 และจะมีค่าเป็นลบมากขึ้นเมื่อค่าพีเอชสูงขึ้น ผลการทดลองส่วนใหญ่พบว่า ค่าความขุ่นและค่าสารอินทรีย์คาร์บอนลดลงอย่างน้อย 97% และ 22-28% ตามลำดับ ในขณะที่ฟลักซ์จะแปรผันอยู่ระหว่าง 13.2 ถึง 21.5 (x 10^{-6}) ม^3 ม$^{-2}$ วินาที$^{-1}$ ผลการทดลองที่แตกต่างกันขึ้นอยู่กับผลของค่าพีเอช ความเข้มข้นของอลูมิเนียมซัลเฟตและสารลดแรงตึงผิว ค่าฟลักซ์เมมเบรนที่ดีที่สุดพบที่ค่าพีเอช 6.2 เมื่อทั้งหางนมและเมมเบรนมีค่า ζ-potential เป็นลบในทางตรงข้ามค่าอินทรีย์คาร์บอนจะลดลงเมื่อค่า ζ-potential ของเมมเบรนและหางนมเป็นบวกและมีค่าเข้าใกล้ศูนย์ ซึ่งแสดงให้เห็นอย่างเด่นชัดว่าสภาวะของสารละลายและคุณสมบัติไคเนติกส์ทางไฟฟ้ามีบทบาทสำคัญในระบบเมมเบรนอุลตราฟิลเตรชัน

Abstract

The tangential flow ultrafiltration of whey suspensions using tubular composite membranes and the effects of pH, coagulant of aluminium sulphate, $Al_2(SO_4)_3$, and surfactants of sodium dodecyl sulphate (SDS) and cetrytrimethyl ammonium bromide (CTAB) on permeate quality, are investigated. The permeate quality was assessed in terms of turbidity and the total organic carbon (TOC). The membranes and particulates were characterised using an electrokinetic property named the ζ-potential. The results indicate that the ζ-potentials of whey suspensions and membranes depend on the pH being positive at lower pH 3.5 and more negative at higher pH. In most cases the permeate turbidity and the TOC were reduced at least 97% and by about 22.1-

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28.1 %, respectively. Permeate fluxes varied between 13.2 to 21.5 (x 10^{-6}) $m^3m^{-2}s^{-1}$. The results were found to depend on the combination of pH, $Al_2(SO_4)_3$ and surfactant concentrations. The best permeate flux was found at pH 6.2 when both particles and membrane had significant, negative ζ-potentials. In contrast the best reduction in TOC was observed when the ζ-potential of both membranes and particles were positive, but very close to zero. It is clear that the electrolyte conditions and electrokinetics play an important role in this ultrafiltration.

Keywords: Cross-flow ultrafiltration, Whey suspensions, Ceramic membranes

Introduction

Recently, tangential or cross flow ultrafiltration (UF) has become increasingly important in commercial enterprises such as the food, beverage, dairy and biotechnology industries. The acceptance of cross flow UF in the treatment of whey suspensions has been relatively commercial, however as decrease in the permeate flux through the membrane during filtration is considered to be a problem that is caused by membrane fouling, and this leads to the need for membrane cleaning (Carić et al., 2000). During the past few decades, much research has been undertaken concerning various aspects of whey especially in relation to its use in food products and various investigators have studied either its behaviour in terms of aggregation and adsorption or treatment of whey effluents from dairy industries using membrane filtration (Hanemaaijer, 1985; Alkhatim et al., 1998; Moritz et al., 2001; Martín et al., 2003; Lee and Moon, 2004).

Mixtures of whey and water are highly turbid and form biological suspensions containing both materials which settle and colloidal materials. Coagulation and flocculation are very important as a pre-treatment process for filtration and an essential requirement for efficient separation. It is known that the rate of coagulation depends mainly on the stability of the colloid particles and that the salt concentration and pH are two important parameters affecting colloid stability (Lee and Moon, 2004; Kaewkannetra et al., 2009). Another way of assessing the changes in the colloidal stability of suspensions is to consider changes in their turbidity. It should be remembered that although turbidity measurement is an indirect technique, it provides an easy method of appraising the performance of a flocculation process. The turbidity of a suspension can reflect the amount of colloidal material present and thus the effectiveness of a flocculation process can be readily established in term of the residual turbidity of the suspensions following physico-chemical treatment and subsequent setting or coagulation (Lee and Moon, 2004). If inorganic coagulants are used then the changes in the electrokinetic properties of the suspensions can sometimes be related to the residual turbidity.

UF membranes are usually used to separate colloidal solids often from aqueous dispersion and because the pore sizes will also be of colloidal dimensions, colloidal interactions between the membrane material and the particulate phase become important. One way of characterising solute-membrane-particle interactions is to gather knowledge of the zeta potentials (hereafter called the ζ-potential) of both particle and membrane (Martín et al., 2003). This electrostatic characterisation of membranes is a

useful way to predict and interpret the performance of filtration processes. The interaction of colloidal particles with membrane surface in aqueous solution is dependent on, among other variables, the ζ-potential of the membrane surface and suspended particles. These, in turn, are controlled by the surface chemistry of the membranes and colloidal particles, as well as by the chemistry of the solution (Elimelech et al., 1994; Bowen and Cao, 1998; Moritz et al., 2001). In membrane filtration, interactions can occur between the particles in suspension and between the suspended particles and the membrane material. Therefore the stability of the particles and that of the particle-membrane system could affect the filtration process. Thus if the particles and the membrane pores are of colloidal dimensions, knowledge of the electrokinetic properties of both particles and membranes is fundamental to the better understanding of the membrane separation process. Normally, the ζ-potential is related to the electrokinetic mobility potential through the Helmholtz-Smoluchowski equation (Bowen and Cao, 1998; Kaewkannetra et al., 2009):

$$\zeta = \frac{\mu_{el}\eta}{\varepsilon_r \varepsilon_o} = \frac{\eta \nu}{\varepsilon_r \varepsilon_o E} \qquad (1)$$

where μ_{el}, ν, E, η, ε_r, ε_o are the electrokinetic mobility of the aggregates (ν / E), the velocity of the particles, the electric field, the viscosity of the solution, the dielectric constant of the liquid and the permittivity of free space respectively. The ζ-potential of colloid suspensions reflects their surface chemical properties, the chemical composition of the water and the way in which particles interact with each other (Moritz et al., 2001; Lee and Moon, 2004). Knowledge of the interaction forces between whey in suspension is essential for interpreting the stability of these suspensions and also the adhesive behaviour of the particles.

The use of coagulation process in conjunction with the UF process has been studied in wastewater applications as part of the precipitation chemistry necessary to remove insoluble materials. However the nature of coagulant species formed is influenced by coagulant doses, the solution pH and its ionic strength (Moritz et al., 2001) together with the concentration of organic compounds in water being treated (Senée et al., 2001). Therefore, an inorganic salt, $Al_2(SO_4)_3$ together with surface active agents, CTAB and SDS, were used in experiments designed over a range of pH to assess the filtration process (Kim et al., 2001). This approach has also been evaluated as a means of enhancing the permeate flux in addition to the reduction of turbidity and colour in water (Kim et al., 2001; Guigui et al., 2002).

The main objective of this work is to investigate ways in which the ζ-potential of particles and membranes affects the quality of permeate from UF ceramic membranes in order to better understand the mechanisms that could affect membrane performance. In addition to the primary aim, the secondary aim is to evaluate the efficiency of cross flow UF of whey suspensions using tubular composite membranes in terms of permeate flux and quality.

Materials and methods

1. Membranes

Tubular ceramic membranes, (Schumasiv® single channel TI 01070, produced by USF Schumacher, Germany) were assembled in the membrane rig. These are constructed so that the inorganic oxide particles comprising the inner surface layer of the circular tube determine the pore size of the membrane. This surface layer is supported by a more porous ceramic tube which can be made from

the same or an alternative metal oxide. Membranes have 0.05 μm nominal pore sizes and an active inner surface made of a layer of zirconium dioxide which is deposited on a porous alumina support having a nominal pore diameter of 1.2 μm. The overall dimensions for the membranes are: 6.67 mm I.D., 10 mm O.D. and 131 mm in length and the permeate area for each tubular membrane tube is approximately 2.75 x 10^{-3} m^2.

2. Materials

All suspensions were prepared using spray dried whey (2000 mgL^{-1}) from bovine milk (SIGMA® , USA) in a flocculation rig fitted with a variable speed impellor (Flocculator SW1, Stuart Science, UK). The manufacturer's analysis of the main constituents are lactose (65%), protein (13%), lactose (8%), ash (2%) and the rest of these are 12 % total solids that can be separated to be fatty and non-fatty acid solids. Sodium hydroxide (0.1 M) and nitric acid (0.1 M) were used to change the pH of solutions. The ionic strength was maintained by using sodium chloride (0, 0.01, 0.001 M) as a background electrolyte and aluminium sulphate, $Al_2(SO_4)_3$, (0-10 mgL^{-1}) was used as an inorganic coagulant and SDS and CTAB (1-6 mgL^{-1}) were used as the surface active agents to destabilise the colloid suspensions. All chemicals were analytical grade (Sigma®-Aldrich, UK), and were prepared with ultra pure water (ELGASTAT® , USF Memcor, England).

3. Membranes and whey particles characterisation

Small pieces (2-3 mm in length) of membrane and granular dried whey (2-3 beads) were examined to determine their size, shape and surfaces using a scanning electron microscope (SEM) (FEI QUANTA 200, Purge, Czech Republic) operated at an accelerating voltage of 30 kV. The particles size distributions and the ζ-potentials were measured using a laser scattering instrument (Mastersizer 2000, Malvern Instruments, UK) and an optical technique (Zetasizer 3000HS Advance, Malvern Instruments, UK), respectively. The ζ-potentials reported here were calculated from the average of at least five separate injections per sample. Measurements were obtained over the desired pH range and at different ionic strengths. All experiments were carried out at a temperature 25 ^{o}C.

4. Filtration experiments

Figure 1. shows a schematic diagram of the UF rig used in this study. Whey suspensions were pumped to the membrane from the storage tank with a variable speed peristaltic pump. The transmembrane pressure (TMP) was maintained at 250 kPa and was monitored by two pressure gauges and controlled by a valve to generate the necessary back pressure. The permeate was weighed as it was collected on a balance to determine its flux and the turbidity and TOC were monitored (WPA TU1100, Cambridge, U.K. and Shimadzu TOC analyzer, Japan, respectively).

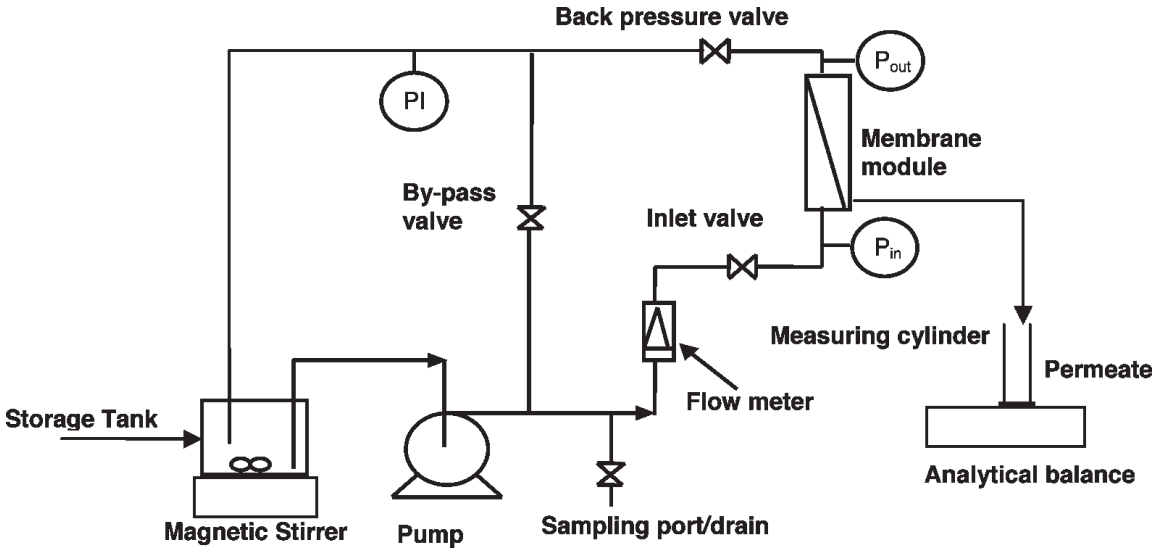

Figure 1. A schematic diagram of membrane ultrafiltration rig (Kaewkannetra et al., 2009)

Results and Discussion

1. Scanning Electronic Microscopy

The SEM micrographs show that whey particles are approximately spherical in shape and the surface whey texture is loosely agglomerated and the powders are readily disaggregated when dispersed in water. (See Figure 2.). Previous studies (Hanemaaijer 1985; Alkhatim et al., 1998; Carić et al., 2000) have shown a range of whey sizes from 0.3 μm to 10 μm. This seems to depend on the source of the whey particles. Figure 3. also shows typical SEM image of used zirconia membranes. The active inner surfaces show that, after washing, no whey particles were retained on the clean membrane surface. Because of the efficiency of the chemical method used to clean the membranes (Narong and James, 2006) the permeate flow was restored after washing and consequently the results showed good reproducibility. Each experiment was repeated a minimum of three times for each test condition and the reported results are the average taken over the number of repetitions. The nominal pore size of the membranes was smaller than most of the particles in whey suspensions.

Figure 2. SEM image of whey powder at high resolution showing the loose aggregation of the primary whey particles (Magnification = x1200)

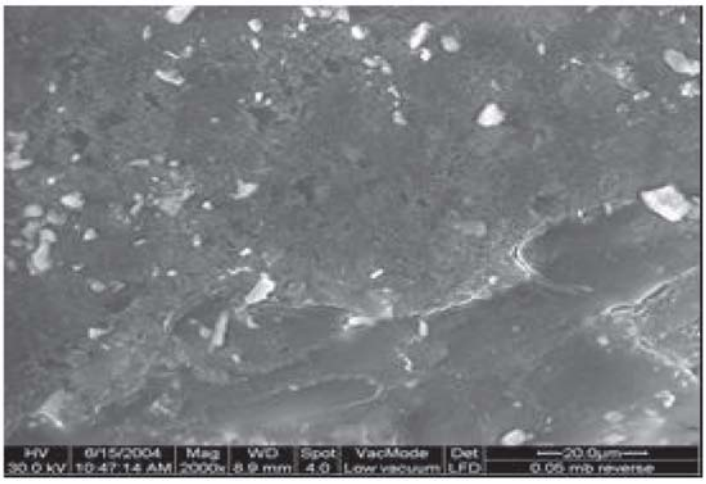

Figure 3. SEM image of an inner surface of zirconia UF membranes (Magnification = x2000)

2. Particle size distribution

It is important to know the size distribution of the whey particles in these prepared samples. Evidently, there can be a wide spread of particle sizes present, depending on the relative proportions of the main constituents in the whey. A previous study measured the particle size of whey protein stabilized emulsions and found an average diameter of 0.53 μm (Kulmyrzaev and Schubert, 2000). It has been found that casein micelles from whey have a maximum diameter of 0.3 μm (Al Akoum et al., 2002). Elsewhere, it is reported that non-sieved dry colloidal whey has an average particle size around 10 μm (Ricq et al., 1996; Hudson and Daubert, 2001). In Figure 4. the average particle size (5.3 μm) of the whey suspension at pH 7 with no ionic strength is shown and consequently, the high quality of permeate flux (shown by low turbidity) is a direct result of the small pore size of the membranes (0.05 μm) and most of the whey particles remain in the retentate flow.

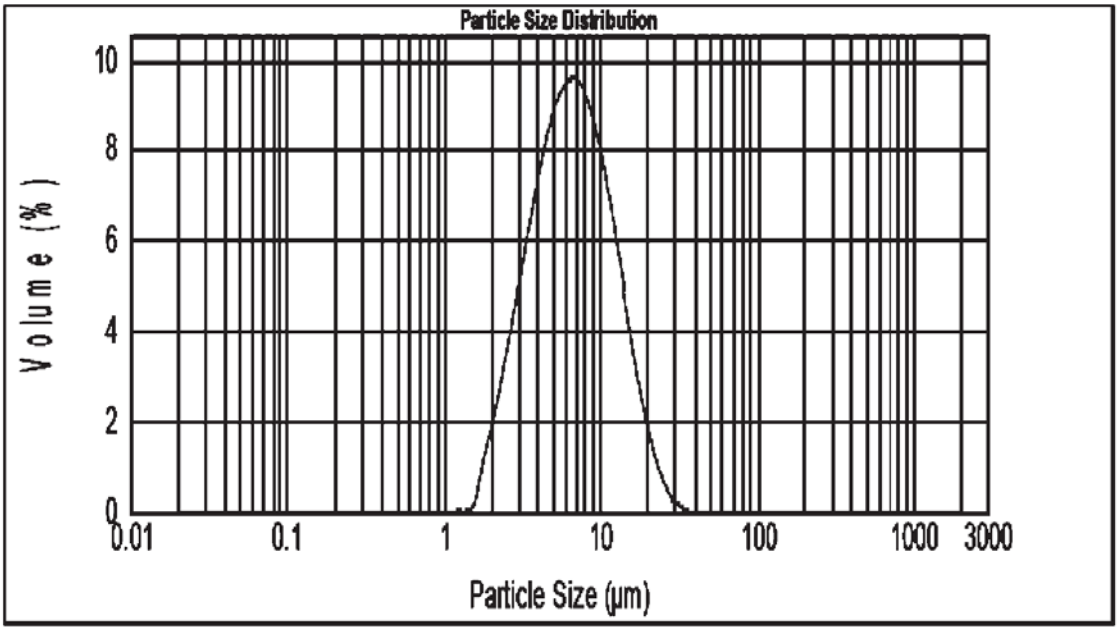

Figure 4. The particle size distribution of a whey suspension at pH 7 and 0 M NaCl.

3. The ζ-potentials of whey and membranes

Figure 5. shows the ζ-potentials of whey suspensions as functions of pH in the presence of NaCl as background electrolyte at three different concentrations (0 M, 0.001 M and 0.01 M NaCl). The results show clearly that the ζ-potential has a maximum positive charge for all conditions only at pH 3 being 9.7 mV, 4.4 mV and 3.4 mV, respectively. As the pH increases the ζ-potentials decrease and become negative and reach their lowest ζ-potentials (-30.1 mV, -24.4 mV and -21.9 mV) at pH 10 for the samples containing NaCl of 0 M, 0.001 M and 0.01 M, respectively. Furthermore, each curve passes through an isoelectric point (i.e.p) at around pH 3.4, implying that the whey should be the least stable at this pH (Senée et al., 2001). In previous studies (Silvestre et al., 1999; Senée et al., 2001 Al Akoum et al., 2002) the i.e.p. of whey suspensions is reported in the range pH 4.5 to pH 5.5, but these results seem to depend on differently constituted whey suspended in different types and concentrations of electrolyte (0-20 µM CaCl2, 0-100 µM $CuCl_2$ and 0-100 mM KCl).

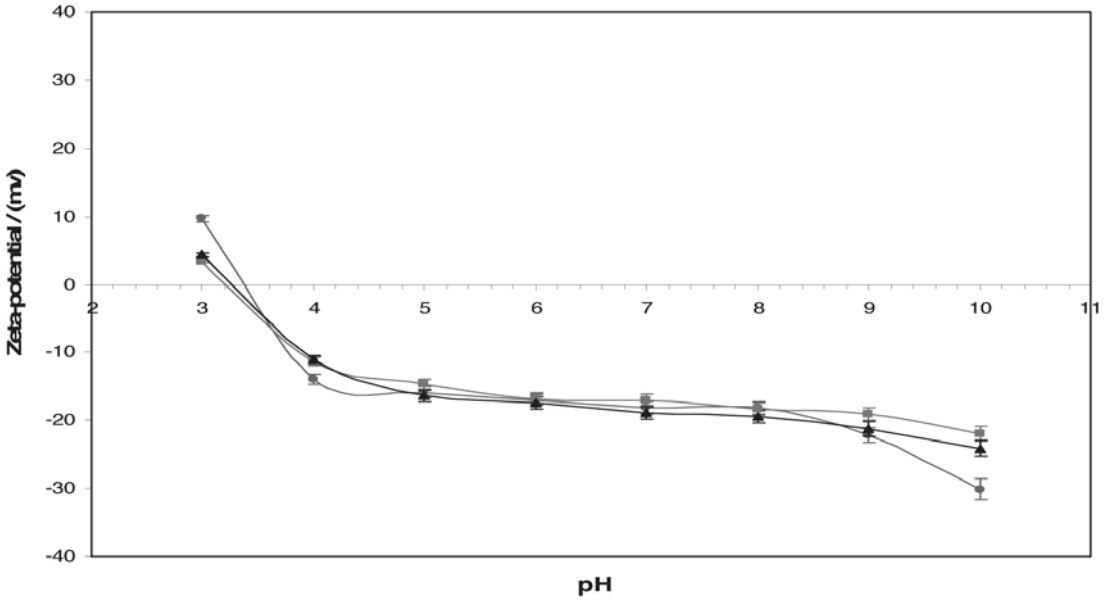

Figure 5. The ζ-potentials of whey suspensions as a function of pH dispersed in various concentrations of NaCl (—●— 0 M NaCl, —▲— 0.001 M NaCl, —■— 0.01 M NaCl).

The zirconia dioxide (ZrO_2) UF membrane was also characterised using ζ-potentials. The electrophoretic mobility of powdered membrane was determined and ζ was calculated using the Helmholtz-Smoluchowski equation (see Eq.1). Figure 6. shows the ζ-potential as a function of pH (pH 3 and pH 10) for membrane particles dispersed in NaCl solution at ionic strengths of 0 M, 0.01 M and 0.001 M, respectively. It is seen that ZrO_2 has a positive ζ-potential around pH 3 but this becomes increasingly negative as the pH increases. The i.e.p. was found at pH 3.8 in all concentrations of NaCl solution and in the same way, the positive charge was found at pH 3, being ζ = 22 mV, 14.3 mV and 11 mV and having the highest negative charge of ζ = -26 mV, -22 mV and -16 mV at pH 10 for the samples containing 0 M, 0.001 M and 0.01 M of NaCl, respectively. In a previous study (Senée, et al., 2001), it is reported that the i.e.p. of ZrO_2 UF membranes is close to pH 3.5 which is in good agreement with the present results. This is noteworthy since in the other study the ζ-potential was found from streaming potential measurements rather than by microelectrophoresis (Elimelech et al., 1994; Silvestre et al., 1999)

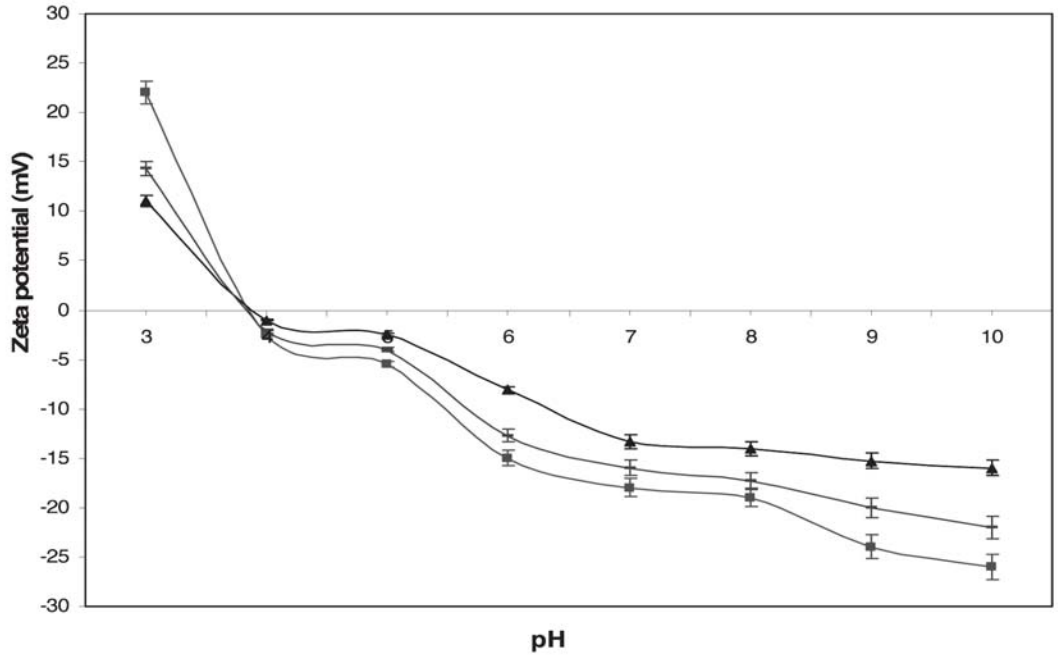

Figure 6. The ζ-potential of zirconia membrane suspensions as a function of pH in the presence of NaCl (—■— 0 M NaCl, —— 0.001 M NaCl, —▲— 0.01 M NaCl).

Following the results obtained from whey suspensions, prepared in the flocculation rig, only the results obtained with 3 mgL^{-1} of $Al_2(SO_4)_3$ are shown in Figure 7., which indicates the relationship between the turbidity and the ζ-potential of whey suspensions. The results show that the turbidity is lowest (140 NTU) while the ζ-potential is positive (3.4 mV) at about pH 3. As pH increases the ζ-potential decreases and charge reversal is observed. The lowest negative ζ-potential is reached at pH 10 (-21.9 mV) at pH 10. Meanwhile, as pH increases from 4 to 10 the highest turbidity was registered at pH 4 around 215 NTU, and after that it was slightly decreased until pH 10. The ζ-potential measurements clearly indicate that whey particles remain negatively charged even though it was expected that the addition of $Al_2(SO_4)_3$ would change the sign of ζ. However, it is seen that both pH and $Al_2(SO_4)_3$ concentration influence the ζ-potential.

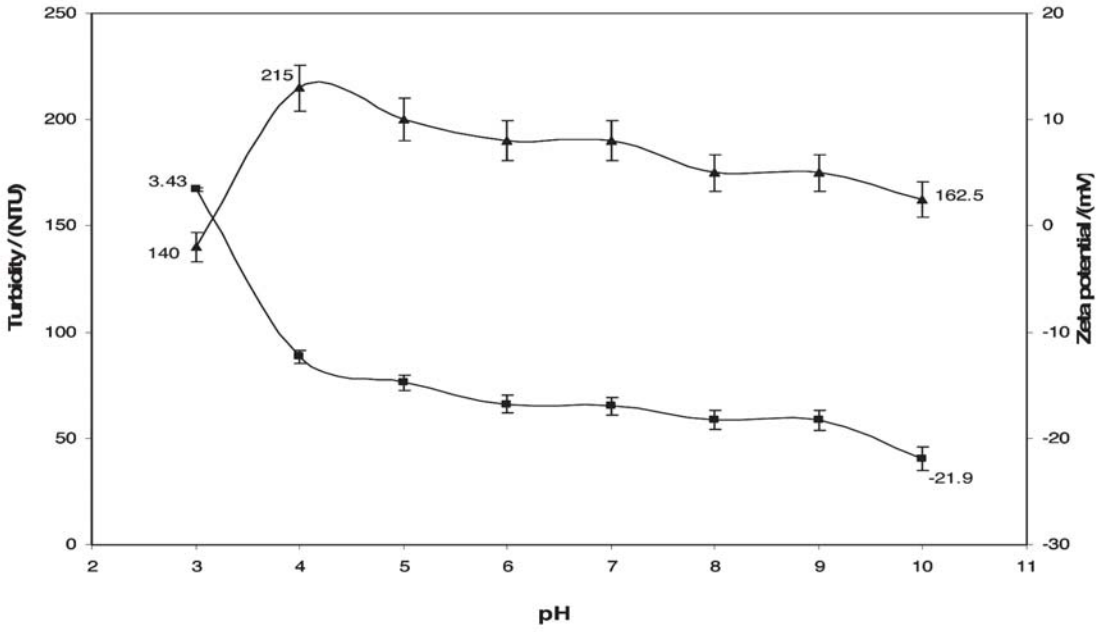

Figure 7. Turbidity and zeta potentials in whey suspensions as a function of pH in the presence of 3 mg L^{-1} aluminium sulphate ($Al_2(SO_4)_3$. (—▲— turbidity —■— zeta potential).

3.4. Performances of whey suspensions using membrane ultrafiltration

The UF of whey suspensions, using 0.05 μm zirconia tubular ceramic membranes, is investigated in various conditions with a constant TMP of 250 kPa and are shown as permeate qualities in term of TOC and the turbidity reduction in Figures. 8-9.

From TOC reduction obtained in a range of 22.1% -28.1%, in situations when the initial pH at 6.2, the best TOC reduction of 28.1%, obtained in the condition containing $Al_2(SO_4)_3$ and CTAB, was better than that for the controlled pH (pH 3) (see Figure 8). Meanwhile, residual turbidity found under seven various planned conditions are in the range from 97.2 % to 98 %. The turbidity of the feed solution was found between 156-190 NTU and the least effluent was obtained at about 4.2 NTU (see Figure 9). In addition, it is also clear that good results can be obtained using various combinations of electrolyte. The best results would be achieved under conditions where the initial pH was not controlled (pH 6.2), the best permeate flux of 21.5 x 10^{-6} m^3 m^{-2} s^{-1} in the sample presenting both $Al_2(SO_4)_3$ and SDS (Kaewkannetra et al., 2009). The former results are in agreement with previous study (Carić et al., 2000) that explained this phenomenon in terms of whey adsorption. These results correspond to two different sets of particle and membrane ζ-potentials. When the flux is highest the ζ-potentials of the whey particles and membrane are fairly high and give rise to repulsive electrostatic forces that restrict fouling and when the TOC removal is the best they are close to zero and positive and allow fouling and possibly adsorption to occur. Note that the important factor is that the ζ-potentials are close to zero which suggests that the electrostatic repulsive forces are almost zero.

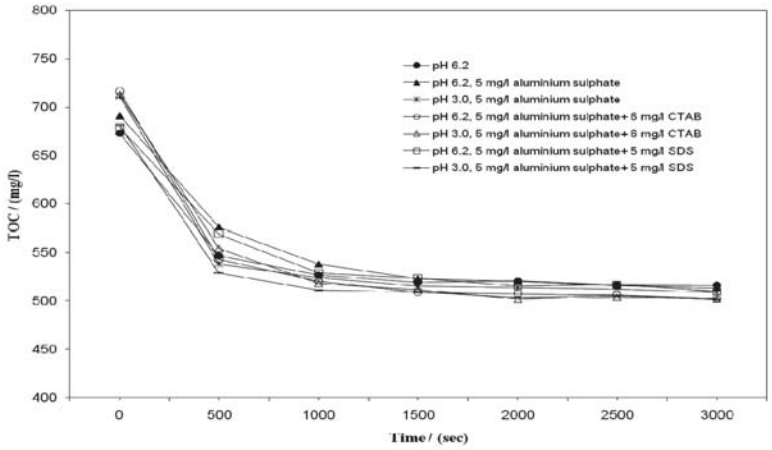

Figure 8. TOC reductions of whey suspensions as a function of time at TMP = 250 kPa (Note that at t = 0 the TOC value refers to that found in the feed).

Conclusions

SEM images show that whey particles are approximately spherical and granulometric analysis suggests that in suspension whey particles have an average size of 5.3 μm. The ζ-potentials of whey particles and membranes are usually negatively charged and the addition of $Al_2(SO_4)_3$ does not change the sign of the ζ-potential. The permeate turbidity is very low (up to 98 % reduction over feed turbidity) and the TOC of the permeate was reduced by up to 28.1%, however, the best turbidity did not correspond to the reduction in TOC. Using 5 mgL^{-1} $Al_2(SO_4)_3$ and 5 mgL^{-1} SDS the best permeate flux is found at pH 6.2 while using 5 mgL^{-1} $Al_2(SO_4)_3$ and 6 mgL^{-1} CTAB, the TOC reduction is achieved at pH 6.2. The best permeate flux occurs when the ζ-potentials of the membranes and particles are high while the best TOC reduction occurs when they are low. Electrokinetic characterisation of particles and membranes is an important step in achieving the best filtration performance.

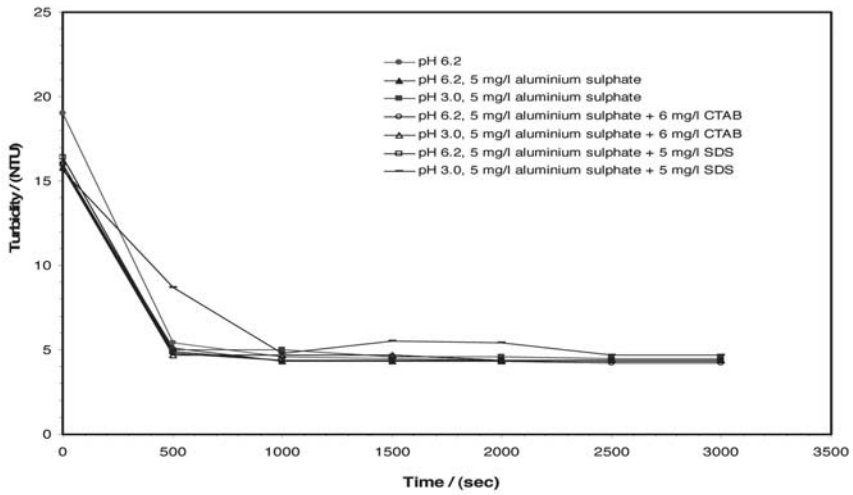

Figure 9. The residual turbidity reduction of whey suspension as a function of time at TMP = 250 kPa (t = 0 the turbidity value refers to that found in the feed x10 NTU).

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