Removal of lactic acid from acid whey using electrodialysis

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ABSTRACT

The processing of acid whey, a by-product of cream cheese making, casein production and strained yogurt manufacture, has been a challenge in the dairy industry. The high lactic acid concentration causes operational problems in downstream spray drying operations due to increased powder stickiness. In this work, electrodialysis, a well proven demineralisation technology is used to remove the lactate ions from acid whey. If the ratio of lactic acid to lactose is to be reduced to the same level found in sweet whey, 80% of the lactate ions must be removed. For both laboratory prepared solutions and acid whey samples, the lactate ions were removed at a slower rate compared to other anions present in the system. Increasing the pH (from pH 4.6 to pH 6) of the feed solution led to a small enhancement in the rate of lactate ions removal at 5 °C. No impact was observed, however, at 30 and 45 °C where membrane resistance and solution viscosity is lower. To achieve the same level of lactate ion removal, the processing time in a batch process was three times shorter at 45 °C, compared to that at 5 °C. This means that significantly less membrane area is required in a continuous industrial electrodialysis operation. The energy consumption (~0.014 kW h/kg whey processed) for achieving 90% demineralization of the acid whey was comparable to the energy requirement reported for sweet whey demineralization in a typical commercial electrodialysis unit, illustrating the feasibility of this approach.

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1. Introduction

Acid whey is a by-product of cream cheese and strained yoghurt manufacture and is also produced from chemical acidification of milk in casein production. This whey stream contains about 20% of the protein (~1%m/v) and most of the lactose (LT) (~4.4%m/v) from the original input milk [1]. Sweet whey is generated from rennet cheese manufacture, and while similar in composition, acid whey can contain up to 16 times the concentration of lactic acid (LA) to that in sweet whey [1]. Traditionally, sweet whey is further processed to make whey powder, lactose, whey protein concentrate and demineralised whey powder. One of the essential steps for manufacturing these products is the use of spray dryers. The presence of lactic acid in acid whey prevents a similar process as the acid whey makes the resulting whey powder more susceptible to moisture absorption [2–4], due to the hygroscopic nature of the lactate ions [5,6] and this leads to the formation of powder agglomerates and sticky deposits within the dryer that cannot be tolerated in normal operation. Consequently, acid whey is often used as a stockfeed to neighbouring farms or discharged as effluent, rather than providing a valuable source of protein for human diet consumption.

The formation of these sticky deposits is a function of the proportion of lactose that is present in a crystalline rather than an amorphous phase, which in turn depends upon the glass transition temperature of the powder, relative to the dryer operating temperature. In turn, this glass transition temperature is related to the level of lactic acid present in the feed [5]. For example, the temperature of sticking increases from ~70 °C to ~95 °C, when the mass ratio of lactic acid to lactose decreases from ~0.2 g LA/g LT in acid whey to ~0.04 g LA/g LT in sweet whey powder [5].

The effect of lactic acid in the crystallisation process of lactose/protein powders has previously been studied by Saffari and Langrish [7] and Shrestha et al. [2] who used laboratory scale spray drying units. The ratio of LA to LT was found to correlate well with a decline in spray dryer powder recovery and the glass transition temperature of the recovered powder. Typically, by increasing the concentration of lactic acid from ~2 g/l (in sweet whey) to ~6 g/l (in acid whey), the yield of the sprayed dried powder decreased by ~20% [7]. At the same time, the glass transition temperature decreased significantly. Similar trends were reported by Shrestha et al. [2], who observed that a free flowing powder could be produced only if the lactose solutions contained less than 4.2 g

of lactic acid per 100 g lactose. This is equivalent to the ratio of LA/LT in sweet whey.

Therefore, a reduction in lactic acid concentration is necessary before acid whey can be efficiently processed by downstream spray drying unit operations. The neutralization of the lactic acid has been studied as a potential approach to resolve this issue [2,3] but this approach results in bitter and astringent flavours. Alternatively, electrodialysis has been successfully demonstrated to recover lactic acid from fermentation broths [8,9], as well as to demineralise sweet whey prior to whey powder production [10,11]. This unit operation relies on the transfer of charged species from the diluate (feed) stream to a concentrate stream, through a series of cation and anion selective membranes under a constantly applied electrical potential.

While lactose molecules are uncharged, lactic acid is a weak acid that can dissociate into its conjugate base (a lactate ion, CH_3-$CH(OH)COO^-$) and protons (Eq. (1)). It is expected that lactose will be retained in the diluate stream while lactate and other charged ions will be transferred to the concentrate, effectively demineralising the acid whey.

The dissociation of lactic acid is given by the Henderson–Hasselbalch equation:

$$pH = pK_a + \log \frac{[CH_3CHOHCOO^-]}{[CH_3CHOHCOOH]} \qquad (1)$$

where the pK_a of lactic acid at 25 °C is 3.86 [12]. The association constant at a different temperature can then be estimated by the following correlation [13]:

$$-d(pK_a)/dT = (pK_a - 0.9)/T \pm 0.004 \qquad (2)$$

Williams and Kline [14] patented an electrodialysis approach that used a three compartment stack to reduce the acidity of acid whey for use in ice cream, by neutralisation with caustic solution. Bipolar membranes allow a salt to be split into the corresponding alkali and acid during electrodialysis and this approach has also been used to split salts such as ammonium lactate, formed during fermentation of whey permeate, into lactic acid and ammonium hydroxide [15]. The focus of this prior work with electrodialysis has either been to neutralise the acidity of a whey solution by removing protons, or to provide high purity lactic acid as a product from a high concentration fermentation broth. Conversely, the focus of the present work is the removal of lactate anions at relatively low concentration from a whey solution. The reduction in the concentration of lactate potentially allows for the processing of acid whey in a similar manner as sweet whey, allowing the proteins and lactose to be recovered for sale.

2. Experimental

2.1. Materials

Raw acid whey samples were obtained from a dairy processing company in Victoria, Australia. The acid whey was treated in a pilot plant at Dairy Innovation Australia Ltd (Werribee, Victoria Australia) using a centrifugal separator (GEA Westfalia Separator, Model SC 6-01-576) to remove the whey cream and most of the casein fines. This stream is referred to as the skimmed acid whey. Part of the skimmed acid whey was further filtered in the laboratory through a 10 kDa ultrafiltration membrane (Koch) so that the residual fat and protein are removed. This stream is referred to as the acid whey UF permeate sample. This standardises the acid whey samples and reduces the possibility of microorganism growth [16] and protein fouling in the electrodialysis stack [17,18]. All acid whey samples were refrigerated at 2–4 °C. The

skimmed acid whey samples were used within two weeks while the ultrafiltered permeate samples were used within four weeks.

The composition of acid whey was found to be consistent with that reported in the literature, as shown in Table 1. Fats were expected to be removed completely by the ultrafiltration process. Protein was also not detected in the ultrafiltration permeate. The concentrations of lactose and lactate ions decreased slightly after ultrafiltration, while all other ions passed through the membrane. In a typical dairy processing facility, ultrafiltration is employed after the whey cream is separated from the raw whey by a centrifugal separator, in order to recover the protein for the manufacture of whey protein concentrate and whey protein isolate, similar to the process applied here. The skimmed acid whey and the ultrafiltered acid whey samples were both used in this work, to understand the impact of the residual fats and protein on the performance of the electrodialysis unit.

Purified water (13.2 MΩ cm, Millipore) was used for preparing all solutions used in this work. Model solutions, described as LA + LT + NaCl, were prepared by mixing lactic acid (85%, Ajax Finechem) with lactose ($\geqslant$99.8%, Ajax Finechem) to mimic the concentration of lactate ions and lactose in acid whey. In addition, sodium chloride (NaCl, >99.5%, Merck) was added to mimic the conductivity of acid whey (i.e. 7.8 mS/cm). The pH of these artificial solutions was also adjusted to 4.6 or 6 using an appropriate amount of 10 M NaOH. The composition and general characteristics of the model artificial solution are also shown in Table 1. Solutions of sodium sulphate (Na$_2$SO$_4$ Ajax Finechem) (20 g/L) and NaCl (5.5 g/L) were prepared as the electrode rinse solutions and the concentrate solutions respectively.

The cation exchange membranes (Neosepta CMB) and anion exchange membranes (Neosepta AHA) were purchased from Astom (Japan). These membranes were selected because of their wide pH tolerance and temperature stability (Table 2). The relatively high electrical resistance means that the energy consumption and separation performance can be assessed in a conservative manner. All membranes were preconditioned by soaking the membranes in a 3 wt% NaCl solution overnight to allow for membrane hydration and expansion.

2.2. Electrodialysis

The electrodialysis experiments were conducted using an FT-ED-40 module manufactured by FuMA-Tech GmbH (Germany). The ED module consists of two titanium–iridium plasma coated stainless steel electrodes. The module was set with two pairs of cation and anion exchange membranes with alternating diluate and concentrate spacers. In order to prevent migration of anions to the electrode compartment, a third cation exchange membrane was employed at the cathode [26]. The effective area per ion exchange membrane is 36 cm^2. The potential difference was generated by a DC power supply (Agilent DC Modular Power System N6764A) with an output voltage range of 0–60 V and output current range of 0–20 A. The electrodialysis unit was operated with a constant voltage of 7 V across the ED stack. At this voltage, the current density declined from 130–300 A/m^2 to 10–50 A/m^2, depending on the operating temperature and the degree of salt removal. Operating at constant voltage is preferred in batch operation since it reduces the possibility of operating the stack beyond the limiting current density of the system [27]. This in term reduces water splitting which may occur when the conductivity of the solution changes over time in a batch process, or along the flow path of the stack during a large scale continuous operation. Water splitting is known to decrease current efficiency and result in a dramatic shift in pH, making the electrodialysis process uneconomical [28].