1. INTRODUCTION

The dairy industry generates a large amount of effluent ranging from 0.2 to 10 L per L of processed milk and cheese (Balannec *et al*., 2005). In dairy plants the process waters generated during the starting, equilibrating, interrupting and rinsing steps contribute to the production of effluents. They correspond to milk products (milk, whey, cream) diluted with water without chemicals (Vourch *et al*., 2005) and also non-accidental losses of milk or dairy products to sewer amount to l-3% of the total milk processed. These significantly contribute to the chemical oxygen demand (COD) of 0.5-6.0 g COD/L end-of-pipe waste-water. The major part of this polluting charge originates from starting, interrupting, and stopping dairy plant procedures, where milk-products are diluted with water and discharged to a purification station or collected to be spread on land (Akoum *et al*., 2004). Within the framework of limited water resources and increasing costs, the food industry need to lower water consumption and to look at process water and effluent treatment for water recycling or reuse.

Whey is a by-product of cheese production which is used mainly as animal feed or released into the wastewater treatment process, although it is rich in valuable components. It contains lactose, minerals (e.g., calcium, magnesium, phosphorus), vitamins, noncasein protein (except glycomacropeptide), and traces of milkfat (German *et al*., 2000; Harper, 2000). Because of its content of organic compounds, whey can not be discharged to receiving environments. It is therefore necessary to process the whey even it may be uneconomic. Also, when its considered that on cheese making about half of the total milk finds its way into the whey, it's more understandable that the processing of whey and in particular its organic constituents is regarded as very important (Kessler, 1981). Therefore recovery of valuable compounds in whey such as protein and lactose received intense attention recently.

Traditional whey treatment processes such as evaporating and drying does not contribute to recovery of valuable products in whey. These methods are used to remove some part of the water in whey to diminish the volume and to enhance the keeping quality. Recent developments in membrane filtration have provided exciting new opportunities for

large-scale protein and lactose fractionation while treating whey to produce cleaner discharge.

The dairy industry has been one of the pioneers in the development of ultrafiltration (UF) equipment and techniques based on the experience gained from its application in the dairy field. UF has two possible applications in the cheese industry: to fractionate the proteins from whey and to make cheese from ultrafiltered milk (Huffman, 1996; DaCosta *et al*., 1993; Mehra and Donnelly, 1993). Whey protein concentrates, which are obtained by whey UF, are available in a great variety concerning the protein content and functional properties. Another aspect which must not be neglected is the utilization of the byproduct resulting from the permeate of UF. In this case new technologies have also been utilized [nanofiltration (NF), reverse osmosis (RO)] for lactose, which can be used in the sweets industry or for fermentation procedures (van der Horst *et al*., 1995; Balint and Okos., 1995; Alkhatim *et al*., 1998). There have been few studies concerning the utilization of nanofiltration and reverse osmosis for whey treatment and protein recovery. Reports NF and RO performances (permeate flux, milk components rejection) of different dairy effluent solutions are present. Studies of material recovery from whey by nanofiltration, comparison of ultrafiltration and nanofiltration for the utilization of whey protein and lactose, and development of complex membrane systems for whey processing were conducted. (Nguyen *et al*., 2003; Atra *et al*., 2003; Rektor and Vatai, 2004; Akoum *et al*., 2003). One-stage and two-stage operations of NF and RO were also investigated for dairy wastewaters (Vourch *et al*., 2004). In this study, NF showed good protein rejection capability but clean effluent was achieved only by employing RO as an additional stage.

Treatment and material recovery of wastewater produced by dairy industry in Turkey is not well established. This study reports on the application of 6 different membranes to recover whey proteins from the cheese whey in its retentate and also to produce cleaner discharge as permeate. White cheese whey, which can be accepted as the utmost consumed cheese product in Turkey, and curd cheese whey were investigated as the feed solutions. One ultrafiltration, two reverse osmosis and three different types of nanofiltration membrane modules were tested under one-stage and cascade operations. The traditional heat treatment followed by reverse osmosis was also investigated for comparison with treatment by membrane processes alone. Efficiencies of each operation were evaluated by

protein rejection and COD removal. The suitability of treated, concentrated whey in the retentate for incorporation into other dairy products such as ice cream and yoghurt or used as animal feed (Kailasapathy *et al*., 1996; Nguyen *et al*., 1997), is discussed.

2. THEORETICAL BACKGROUND

2.1. Dairy Industry

2.1.1. Overview of Turkish Dairy Industry

Reflecting its geographical location, the Turkish dairy industry is just as much a combination of a European familiarity with dairy consumption and Asian dairy chain structures. The majority of the Turkish milk pool is produced in the western half of the country. The Marmara region in the north-west is responsible for 40% of total milk production (Voorbergen, 2004).

Milk production has been on a moderate decline over the last few years. Turkey's estimated 5 million dairy cows on approximately 2.5 million dairy farms produce some 8.5 to 9.5 million tonnes of milk, coming from a level close to 10 million tonnes 5 years ago (Voorbergen, 2004). The dairy efficiency comparison of Turkey with world and the developed countries is represented in Table 2.1. As seen from the tablet hat the dairy efficiency of Turkey is very low with respect to both world and the developed countries (Yavuz *et al.*, 2001).

Table 2.1. The dairy efficiency comparison of Turkey with world and developed countries (per animal) (Yavuz *et al.*, 2001)

Parameters	**Turkey**	**World**	**Developed Countries**
Average carcass weight (kg)	150	210	400
Average milking efficiency (kg/yr)	1,200	3,600	8,000 - 10,000
Animal-breeding/Agricultural production (%)	30	65	-
Average fattening herd (pieces)	5	500	30,000

The allocation of Turkish milk pool to processed products can be seen in Figure 2.1.

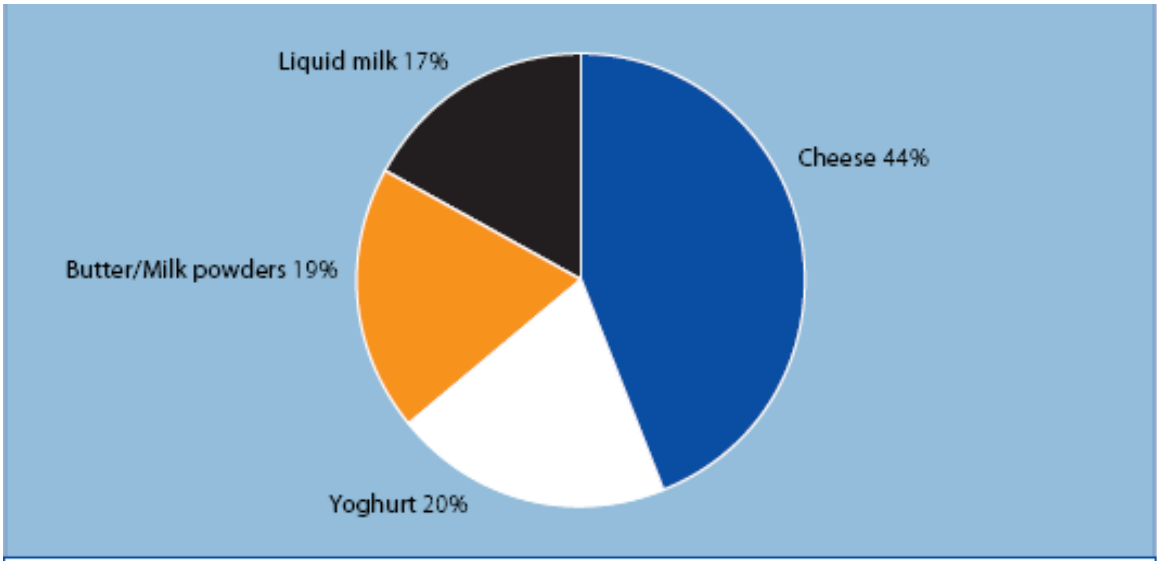

Figure 2.1. Allocation of Turkish milk pool to processed products (Voorbergen, 2004)

As can be seen in Figure 2.1 approximately 44% of the milk pool is processed into cheese. Per capita consumption is around 8.5 kg. Further economic growth will boost cheese consumption closer to European Union levels. Despite the wide variety of cheeses produced, around 85% is white cheese, similar to Feta cheese. The remainder is mainly made up of sheep cheeses (Kashkaval) and goat cheeses (Tulum). Cheese production in Turkey is naturally more labor intensive than other dairy products. Only an estimated 10% of cheese production comes from modern processors.

As can be seen in Figure 2.2, cheese overwhelms the other dairy products from manufacturing point of view. This clearly states that whey production, which is a waste by-product of cheese production, is a major problem since the high COD load of the whey and the consequent loss of beneficial material (such as protein and lactose) in whey.

Considering the aim of this study and the importance of cheese production share in Turkish Market, an overview of cheese and consequent whey production will be covered in the following section.

2.2. Cheese Production

Cheese manufacturing is an art that is more than 5,000 years old. The predominantly rural character of everyday life in the past contributed to the evaluation of thousands of different types of cheese and each village, or even family may have had its own variety, some soft and short lived, some harder and more durable. Modern cheese technology was founded in the 19th century when Joseph Harding perceived a need to adopt strict hygiene and control over method of making cheddar cheese. This represents a step forward in the scientific approach to cheese making (COWL, 2000).

Popular types of natural cheeses include unripened (e. g., cottage cheese, cream cheese), soft (e. g., Brie, Camembert), semi-hard (e. g., Brick, Muenster, Roquefort, Stilton), hard (e. g., Colby, Cheddar), blue veined (e. g., Blue, Gorgonzola), cooked hard cheeses (e. g., Swiss, Parmesan), and pasta filata (stretched curd, e. g., Mozzarella, Provolone). Examples of processed cheeses include American cheese and various cheese spreads, which are made by blending two or more varieties of cheese or blending portions of the same type of cheese that are in different stages of ripeness (EPA, 1997). Production of different types of cheeses contributes to different types of whey from the quantity and the characterization point of view.

2.2.1. Process Description

The modern manufacture of natural cheese consists of four basic steps: coagulating, draining, salting, and ripening. Processed cheese manufacture incorporates extra steps, including cleaning, blending, and melting. No two cheese varieties are produced by the same method. However, manufacturing different cheeses does not require widely different procedures but rather the same steps with variations during each step, the same steps with a variation in their order, special applications, or different ripening practices. This section includes a generic process description; steps specific to a single cheese variety are mentioned but are not discussed in detail.

2.2.1.1. Natural Cheese Manufacture. The following sections describe the steps in the manufacture of natural cheese. Figure 2.2 presents a general process diagram.

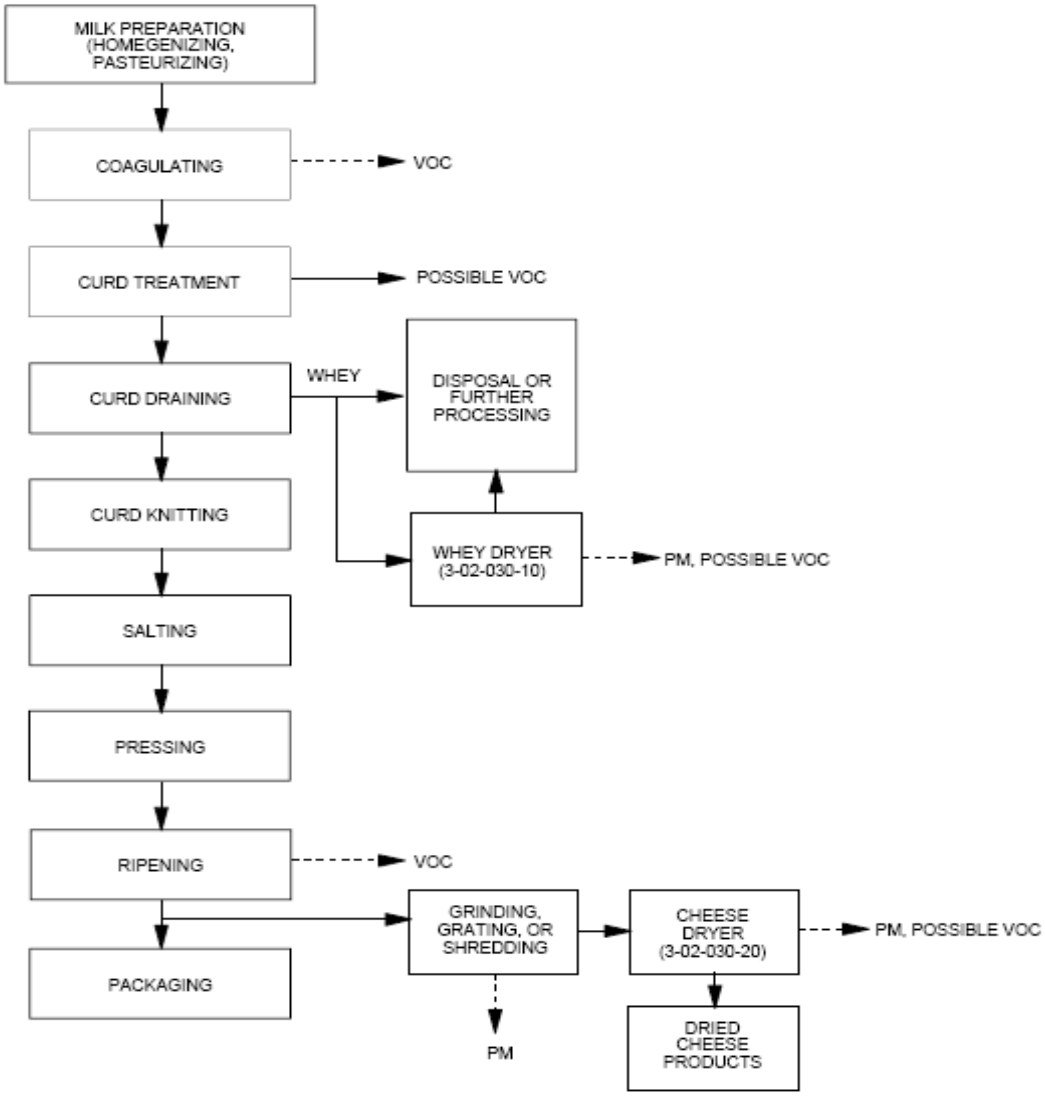

Figure 2.2. Natural Cheese Manufacture (EPA, 1997).

Milk Preparation. Cow's milk is the most widely used milk in cheese processing. First, the milk is homogenized to ensure a constant fat level. A standardizing centrifuge, which skims off the surplus fat as cream, is often used to obtain the fat levels appropriate for different varieties of cheese. Following homogenization, the milk is ready for pasteurization, which is necessary to destroy harmful micro-organisms and bacteria.

Coagulation. Coagulation, or clotting of the milk, is the basis of cheese production. Coagulation is brought about by physical and chemical modifications to the constituents of

milk and leads to the separation of the solid part of milk (the curd) from the liquid part (the whey). To initiate coagulation, milk is mixed with a starter, which is a culture of harmless, active bacteria. The enzyme rennin is also used in coagulation. Most of the fat and protein from the milk are retained in the curd, but nearly all of the lactose and some of the minerals, protein, and vitamins escape into the whey.

Curd Treatment. After the curd is formed, it is cut into small pieces to speed whey expulsion and increase the surface area. The curd particles are cut into various sizes, depending on the variety of cheese being made. Cutting the curd into small cubes reduces the moisture content of the curd, whereas creating larger cubes increases the moisture content. Following the cutting step, the curd is cooked, which contracts the curd particles and acts to remove whey, develop texture, and establish moisture control. The cut curds and whey are heated and agitated.

Curd Drainage. The next step in cheese manufacture, drainage, involves separating the whey from the curd. Drainage can be accelerated by either heat treatment or mechanical treatment, such as cutting, stirring, oscillating, or pressing. After the curd is dry, it is cut into blocks which can then be filled into cheese hoops for further draining and pressing. For some cheeses, special applications and procedures occur immediately before, during, or after the draining stage. For example, internally ripened, or blue veined, cheeses (e. g., Blue, Roquefort) are usually seeded with penicillium powder prior to drainage. Cooked hard cheeses (e. g., Parmesan) are stirred and warmed to accelerate and complete the separation of the whey. The separated whey may be treated and disposed of; shipped offsite in liquid or concentrated form for use as animal feed; used to make whey cheese; dried for lactose, mineral, or protein recovery; or dried for use as a food additive or use in the manufacture of processed cheese.

Curd Knitting. Knitting, or transforming, the curd allows the accumulating lactic acid to chemically change the curd; knitting also includes salting and pressing. This step leads to the characteristic texture of different cheeses. During the curd knitting stage, Provolone and Mozzarella cheeses are pulled and processed (these cheeses are then kneaded, drawn, shaped, and smoothed); a bean gum or some other type of gum is added to cream cheese to stabilize and stiffen it; and a creaming agent (cream and/or milk) is added to cottage

cheese. During this period, specific pH levels are controlled to produce different varieties of cheese

Ripening. During the ripening or curing stage, varieties of cheeses acquire their own unique textures, aromas, appearances, and tastes through complex physical and chemical changes that are controlled as much as possible by adjusting temperature, humidity, and duration of ripening. For all cheeses, the purpose of ripening is to allow beneficial bacteria and enzymes to transform the fresh curd into a cheese of a specific flavor, texture, and appearance. Cottage and cream cheeses are not ripened, and usually have a bland flavor and soft body.

2.2.1.2. Processed Cheese Manufacture. Nearly one-third of all cheese produced in Turkey consists of processed cheese and processed cheese products. There are many different types of final products in processed cheese manufacture. These cheeses are distinguished from one another not only by their composition but by their presentation as individual portions, individual slices, rectangular blocks, or special presentation as cylinders or tubes. Processed cheese is made by pasteurizing, emulsifying, and blending natural cheese. Processed cheese foods, spreads, and cold pack cheeses contain additional ingredients, such as nonfat milk solids and condiments. Several varieties of natural cheeses may be mixed and powdered milk, whey, cream or butter, and water may be added. The following section describes the basic steps necessary for producing pasteurized process cheese, the most common processed cheese.

Pasteurized Process Cheese. Cheeses are selected to be processed from both mild and sharp cheeses. For example, American cheese is made from Cheddar and Colby cheeses. Once selected, the cheeses must be analyzed for their fat and moisture contents to determine the proper amount of emulsifiers and salts to be added. Cheese surfaces are cleaned by scraping and trimming and the rinds are removed. After cleaning, the cheese blocks are ground in massive grinders, combined, and the cheese mixture is heated. At this point, the melted cheese separates into a fat and serum. Emulsifiers are added to disperse the fat, and create a uniform, homogenous mass.

The molten cheese is removed quickly from the cookers and is pumped or dropped into packaging hoppers. The cheese is packaged in the absence of oxygen to inhibit the growth of mold. The cheese is usually wrapped in lacquered aluminum foil or in aluminum foil-lined cardboard or plastic boxes. For sliced processed cheese, the molten cheese is spread uniformly by chilled steel rollers and cut by rotary knives to consumer size.

Processed Cheese Foods. Other processed cheeses that are similar to the above in manufacturing are also commonly produced. For example, to produce pasteurized process cheese food, one or more of the following optional dairy ingredients are added: cream, milk, skim milk, buttermilk, and/or cheese whey. The result is a processed cheese food that is higher in moisture and lower in fat than pasteurized process cheese. After heating, processed cheese intended for spreading undergoes a creaming step, which includes mechanical kneading of the hot cheese and addition of various dairy products and other additives. Other processed cheese products include cold-packed cheese, cold-packed cheese food, and reduced fat cheeses. All processed cheeses may be enhanced with salt, artificial colorings, spices or flavorings, fruits, vegetables, and meats (EPA, 1997).

2.3. Whey

Whey, as discussed previously, is a by-product of cheese manufacturing, containing lactose, minerals (e.g., calcium, magnesium, phosphorus), vitamins, noncasein protein (except glycomacropeptide), and traces of milkfat (German *et al*., 2000; Harper, 2000).

2.3.1. Composition of Whey

Typical composition for different types of whey is given in Table 2.2.

Table 2.2. Typical composition for different types of whey (Milch and Markt, 2005).

Components	Sweet whey (%)	Acid whey (%)	Casein Whey (%)
Solid mass	6.20	5.70	6.10
Lactose	4.80	4.60	4.70
Protein	0.75	0.30	0.50
Fat	0.05	< 0.01	<0.01
Ash	0.60	0.80	4.4

2.3.2. Whey Proteins

Protein is currently the component of whey that produces the greatest value. Not only is the biological value of whey protein superior to most other proteins (Harper, 2000; Bell, 2000), however whey proteins also have proportionately more sulfur-containing amino acids (e.g., cysteine, methionine) (German *et al*., 2000). Sulfur amino acids help maintain levels of antioxidant peptides in the body. Cysteine is a rate-limiting amino acid for the biosynthesis of glutathione, an antioxidant, anticarcinogen, and immune stimulating sulfur-containing tripeptide. Compared to other protein sources, whey proteins have higher concentrations of the branched chain amino acids, L-isoleucine, L-leucine, and L-valine (German *et al*., 2000). Because branched chain amino acids help regulate muscle protein synthesis, their potential use for athletes and others aiming to achieve optimal lean muscle mass is an area of active investigation.

The following individual whey proteins, in order of decreasing concentration in whey, are potential candidates for ingredients in functional foods.

- **Beta-lactoglobulin**. This protein comprises 50 to 60% of total whey protein. Beta-lactoglobulin binds retinol (provitamin A) and has been proposed to be a transport protein for retinol (Harper, 2000). Beta-lactoglobulin is a rich source of the essential amino acid cysteine, which is important for the synthesis of glutathione.
- **Alpha-lactalbumin.** This protein accounts for about 25% of total whey protein. In the mammary gland, alpha-lactalbumin acts as the coenzyme in the biosynthesis of lactose. In some countries, alpha-lactalbumin is used commercially in infant formulas to make

the formula more similar to human milk. In addition, alpha-lactalbumin may enhance immunity and reduce risk of some cancers (German *et al*., 2000, Harper, 2000). Because alpha-lactalbumin is a good source of branched chain amino acids, it may also be used in sports nutrition products (German *et al*., 2000).

- **Immunoglobulins.** The immunoglobulins in bovine whey (and colostrum) include IgA and secretory IgA; IgG1, IgG2, and IgG fragments; IgM; and IgE. This group of whey proteins provides passive immunity for infants and may stimulate immune function in adults (German *et al*., 2000, Harper, 2000).
- **Bovine serum albumin.** Bovine serum albumin binds fatty acids and other small molecules. Because of its high cysteine content, bovine serum albumin may be an important source for the production of glutathione in the liver.
- **Lactoferrin.** This iron-binding whey protein appears to have multiple biological functions. These include iron transport, antibacterial and toxin binding properties, promotion of cell growth, stimulation of the growth of beneficial intestinal bacteria (e.g., Bifidobacteria), antioxidant properties, and immunomodulating and anti-inflammatory effects (German *et al*., 2000, Harper, 2000). Lactoferrin is used in infant formula in some countries to provide a formula similar in protein composition to human milk and to enhance iron absorption without causing constipation. Many of the proposed biological activities of lactoferrin are related to its iron-binding properties, although non-iron-binding activities have also been demonstrated (Schaafsma and Steijns, 2000; German *et al*., 2000; Schupbach *et al*., 1996).
- **Lactoperoxidase**. This milk enzyme is a natural antimicrobial agent with a variety of potential applications including use in dental products such as toothpaste and mouth rinses to inhibit the development of dental caries (German *et al*., 2000, Harper, 2000).
- **Other Peptides**. Whey contains peptides both present in milk and formed by the hydrolysis of various milk constituents, including casein. Glycomacropeptide (GMP), perhaps the most notable, is produced by the action of the enzyme, chymosin, on k-casein (German *et al*., 2000, Harper, 2000). Beneficial biological roles attributed to GMP or peptides derived from it include stimulation of cholecystokinin (a hormone regulating energy and food intake) release from intestinal cells, inhibition of platelet aggregation, and support of beneficial intestinal bacteria (i.e., Bifidobacteria) (German *et al.,* 2000, Harper, 2000). In an in vitro study, GMP prevented adhesion of cariogenic bacteria to tooth surfaces, leading researchers to speculate that GMP may reduce dental

caries (Schupbach *et al*., 1996). Because GMP lacks the amino acid phenylalanine, GMP has potential use as an ingredient in foods for patients with phenylketonuria (PKU). These patients are unable to metabolize phenylalanine and therefore must be provided diets free of phenylalanine (Harper, 2000).Peptides derived from beta-lactoglobulin in whey have antihypertensive activity in spontaneously hypertensive rats (Abubakar *et al*. 1998). Other peptides such as lactoferricin, which is derived from lactoferrin, exhibit antimicrobial activity (Schaafsma and Steijns, 2000).

Different whey proteins, when solely obtained, can be of great interest for re-use. Fractionation of above mentioned whey proteins, especially beta-lactoglobulin and alpha-lactalbumin can be achieved by membrane processes in high purity to be specifically used in different industries such as pharmaceutical industry.

2.3.3. Treatment of Whey

Because of its content of organic compound such as protein and lactose, whey can not be discharged to receiving environments. It is therefore necessary to process the whey even it may be uneconomic. Also, when its considered that on cheese making about half of the total milk finds its way into the whey, its more understandable that the processing of whey and in particular its organic constituents is regarded as very important (Kessler, 1981).

Whey processing can be conducted in various ways. Whey powder has been produced by the evaporation of whey followed by roller or spray drying. Whey proteins can be obtained by ultrafiltration and by heat-acid precipitation. The main constituent, lactose can be crystallized out, converted into a single cell protein by growing yeast in whey, fermented to produce an alcoholic beverage or hydrolyzed to glucose and galactose.

The dried whey can be used as animal feed, in the manufacture of processed milk, for baked goods, for confectionery, for the production of alcohol and yeasts as an addition to batch preparations etc. (Kessler, 1981).

Proteins dissolved in whey can be gathered in various ways. Ultrafiltration of whey is a much applied method. It results in separation as well as concentration. Diafiltration (i. e., adding water during the process) gives a purer protein. The spray-dried preparation is

called whey protein concentrate. Gel filtration has the drawback that it does not lead to concentration and, moreover, is expensive. Accordingly, it is rarely applied. Protein separation by ion exchange yields a protein that often mainly comprises beta-lactoglobulin and alpha-lactalbumin. The product obtained, called whey protein isolate, can be very pure, especially if it is also ultrafiltered to concentrate the protein and to remove dissolved constituents. Evaporating whey to crystallize lactose; then the crystals are removed and the concentrate is desalted. Desalting is mostly done by electrodialysis. Removing the last amounts of salt requires much energy and, alternatively, ion exchange is therefore applied. Most whey proteins can be precipitated at low pH by carboxymethylcellulose or with hexametaphosphate. The protein then is partly electropositive and the precipitating agent negative, so that these two compounds associate. The whey protein complexes formed have poor solubility at low pH (pH < 5) and of course they contain the precipitating agent. The complexes can also be formed at neutral pH by ferric ions plus polyphosphates; such products have poor solubility and very high ash content. Reverse osmosis, evaporation, and drying are also applied for concentrating whey. There may be several combinations of process steps, depending on the practical possibility, the effect on product properties, the potential to convert various waste products, and the processing costs. Spray-dried whey protein concentrates can be highly soluble (Walstra, 1999).

Recovery of beneficial material in whey can be accomplished in various different techniques (some of which are named above). These techniques, as a whole, can be considered as “concentration techniques” since the process is mainly reducing the water content of the whey thus concentrating the solid content. The most commonly used concentration processes, with intensity on membrane processes, are discussed in detail in the following section.

2.4. Concentration Processes

2.4.1. General Aspects

Milk, skim milk, whey, and other milk products can be concentrated, i.e., part of the water can be removed. This is applied to diminish the volume and to enhance the keeping quality. Water can be removed from milk by evaporation. In addition to water, volatile substances, especially dissolved gases, are removed as well. Evaporation is usually done under reduced pressure — hence, decreased temperature— to prevent damage caused by heating. Water can also be removed by reverse osmosis and nanofiltration, i.e., high pressure is applied to pass milk through a suitable membrane. Water as well as part (some 1% to 20%, depending on conditions) of some low molar mass substances passes the membrane. A different way of concentrating is by freezing. The more ice crystals are formed, the higher the dry matter content in the remaining liquid. Removal of water to such a low level that the product becomes solid-like is called drying. Drying is achieved by evaporation of water, usually from concentrated milk.

A particular fraction of the dry matter can, of course, be concentrated as well. Examples are cream and syneresed curd. In ultrafiltration, besides water most dissolved components are removed, whereas fat globules, casein micelles, serum proteins, leukocytes, bacteria, and so forth are concentrated. Solutes of a higher molar mass (e. g., citrate) are also concentrated to some extent (Walstra, 1999). There are various techniques for concentration of whey which are covered as follows:

2.4.2. Evaporating

Evaporation of products like milk, skim milk, and whey is applied:

a. To make such concentrated products as evaporated milk, sweetened condensed milk, and concentrated yogurt
b. As a process step in the manufacture of dry milk products, considering that the removal of water by evaporation requires far less energy than by drying (see Table 2.3)
c. To produce lactose (lactose hydrate) from whey by means of crystallization

Table 2.3. Energy requirements for different processes (Walstra, 1999).

Heat of evaporation of water at 100°C	2,255 kJ
Heat of evaporation of water at 40°C	2,405 kJ
Sorption heat of evaporation of water from skim milk up to about 60 % dry matter	~ 5 kJ
Evaporation, 3 stages	~ 800[a] kJ
Evaporation, 6 stages, with thermal vapor compression	~ 230[a] kJ
Evaporation, 1 stage, with mechanical vapor compression	~ 115 kJ
Roller drying	~ 2,500[a] kJ
Spray drying	~ 4,500[a] kJ
Reverse osmosis	20 – 35 kJ

[a] Excluding mechanical energy (pumps, etc.).

Evaporation is always done under reduced pressure, primarily to allow boiling at a lower temperature and thus prevent damage due to heating. Moreover, evaporation under vacuum facilitates evaporation in several stages, which results in a considerable saving in energy and in cooling water for the condenser.

When manufacturing whey powder, the amount of water removed in the evaporating process should be as large as possible. The limit is set by the high viscosity of the concentrate. The viscosity of the concentrate thus is an important parameter in the evaporating process (as it is in the spray drying process, where it affects the droplet size in the spray). Several factors affect the viscosity. The viscosity increases more than proportionally with the dry matter content.

The degree of concentration is usually checked by means of the density or the refractive index. These parameters can be determined continuously in the concentrate flow. This enables automatic control of the evaporating process by adjusting the steam or the milk supply. This is far from easy, given the prolonged holdup time and the great number of process steps.

Different products allow different degrees of evaporation and that the same concentration factor affects the concentration of dissolved constituents differently. Lactose will not crystallize in highly concentrated milk, whereas it may do so readily in highly concentrated skim milk. Concentrated whey may show considerable fouling of the evaporator equipment, due to supersaturated salts precipitating on the heating surface. This drawback can largely be overcome by keeping the partly evaporated whey outside the equipment for some time (say, 2 hours) before it is further concentrated (Figure 2.3.). The salts then are allowed to crystallize in the bulk and lactose crystallizes at the same time.

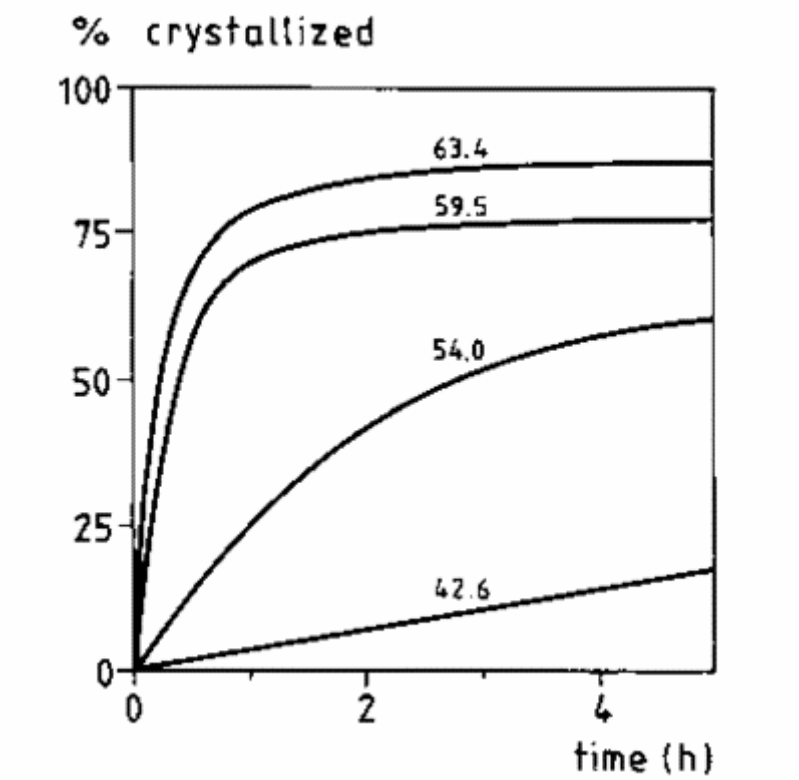

Figure 2.3. Crystallization of lactose in concentrated whey (parameter is % dry matter) as a function of the time after cooling to 20° C. (Walstra, 1999).

In the range of 15–40° C, the crystallization rate depends little on the temperature.

2.4.3. Drying

2.4.3.1. Objectives. Drying is usually applied to make a durable product that is easy to handle and, after reconstitution with water, is very similar in properties to the original

material. Drying is applied to products like milk, skim milk, whey, cream, ice cream mix, protein concentrates, infant foods, all of which have high water content. Removal of water is expensive, especially with respect to energy. Furthermore, driers are expensive. Therefore, the material is often concentrated to fairly low water content by evaporation or by membrane processes.

The main technological problem is to prevent the drying product from undergoing undesirable changes. The rate of many reactions greatly depends on the water content. It mainly concerns reactions that render protein insoluble, since these strongly depend on temperature. At 80° C, about half of the protein present in concentrated skim milk with 13% water becomes insoluble. Thus it is advantageous to pass the interval from, say, 20% to 8% water rapidly and at a moderate temperature. However, the effective diffusion coefficient of water and, consequently, the drying rate significantly decrease with decreasing water content and with decreasing temperature.

2.4.3.2. Drying Methods. There are several methods for drying liquids. The dairy manufacturer uses only a few of them.

Drum Drying. A thin film of milk, whey, etc., is dried on a large rotary metal cylinder or drum that is steam-heated internally. Often, two drums are set up side by side. The water evaporates within a few seconds. The dried film is scraped off from the drum by means of a steel knife, collected, and ground. Considerable product damage due to heating occurs, mainly because scraping off is always imperfect and, accordingly, a part of the milk is repeatedly wetted and dried. The quality of the powder can be improved by using a vacuum roller drier, in which the milk is dried at a lower temperature; but this method is expensive. Nowadays the roller drying process is little used.

Foam Drying. Under pressure, air or nitrogen is injected into the concentrate, and the mixture obtained is heated in a vacuum. Many gas cells are formed in the concentrate, which soon turns into a spongy mass that can subsequently be dried fairly quickly. The process can be carried out batchwise (concentrate in shallow trays) or continuously on a conveyer belt. The dried cake is ground to a voluminous, easily soluble powder. The powder quality can be excellent due to the low drying temperature applied. The process is

expensive and is only applied for some composite products like infant formulas. An advantage of the method is that it can be applied to inhomogeneous products.

Freeze Drying. A thin layer of the liquid is frozen, whereupon the ice is sublimated under a high vacuum. A voluminous cake is left (the space of the ice crystals is now occupied by holes) and is subsequently ground. A batch processing or a continuous operation in a high-vacuum belt drier can be applied. The method is expensive. Damage due to heating does not occur, but that also holds for spray drying if skillfully performed. The drawback is that nearly all of the fat globules coalesce, which causes freeze-dried whole milk powder to show segregation after its reconstitution. Freeze drying is suitable for processing in small quantities and is applied in the drying of lactic starters, etc.

Spray Drying. This is the common method. There are several variants, but the following are essential process steps that are always involved (Figure 2.4).

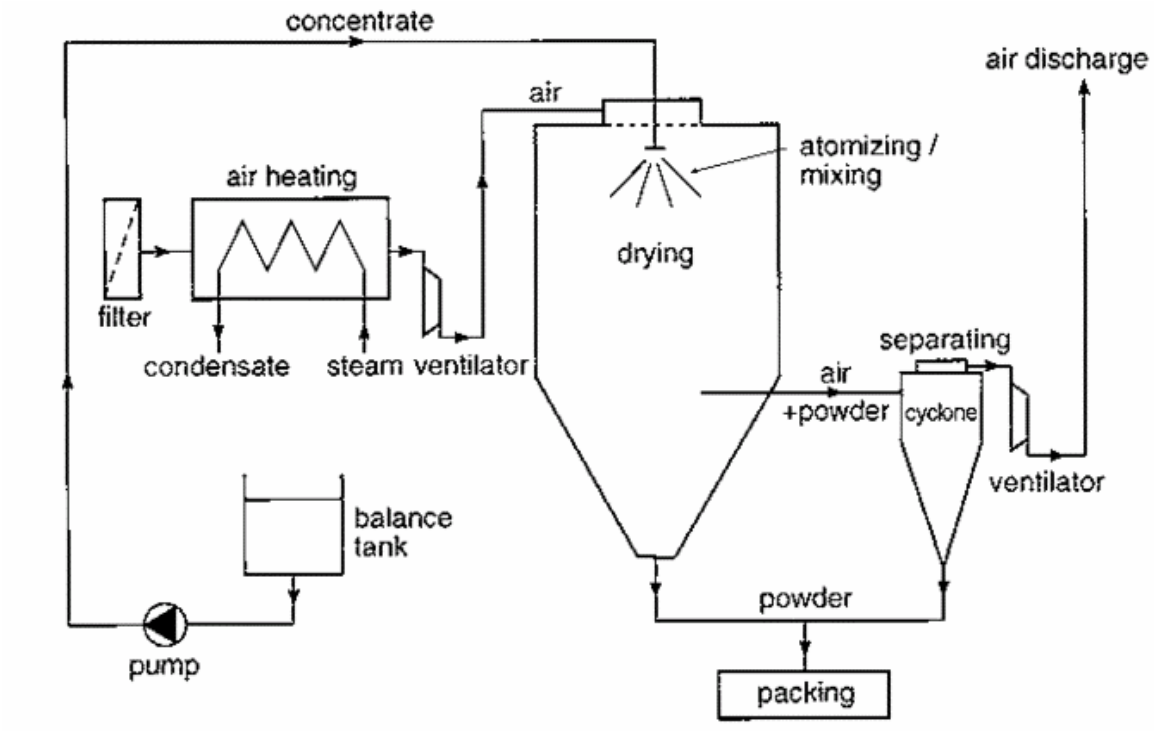

Figure 2.4. Simplified diagram of an example of the spray drying process.

a. Air heating. To achieve this, the air is passed around bundles of steam pipes (steam pressure is 9 atm to reach air temperatures up to 175° C) or the air passes a wall heated by gas jets to reach at most 260° C. Nowadays, the latter is the common method. A more economic use of heat is made by direct combustion of gas in the drying air, but this process releases nitrogen oxides that would contaminate the powder. The air leaving the drier at, 100° C is sometimes used to warm up the fresh air in a heat exchanger (Walstra, 1999).

b. Atomizing the concentrate in the air to such small droplets as to dry very quickly, with either a spinning disk or a pressure nozzle. Often, the liquid is first heated to a suitable temperature.

c. Mixing hot air and atomized liquid. Drying occurs correspondingly. Air and liquid usually enter the drying chamber co-currently and are mixed so intensely that the air cools very rapidly. Consequently, the larger part of the drying process occurs at temperatures not much over the outlet temperature. In other words, something close to perfect mixing occurs. The shape of the drying chamber is of great importance: the larger the chamber (at a given capacity), the more expensive; the smaller, the greater the risk of incompletely dried droplets touching the wall and fouling it. Furthermore, too intense heating of part of the drying droplets should be prevented. Obviously, the mixing should comply with strict requirements. However, drying chambers generally are designed on the basis of experience and the mixing is not quite as desired.

d. Separating powder and consumed drying air. Cyclones are commonly used; essentially, the chamber itself also acts as a cyclone. On the one hand, the aim is to accumulate the powder in such a way that it can readily be packed; often, it is necessary to cool a little, e. g., by adding cold air. On the other hand, the amount of powder in the outlet air should be small because it implies loss of yield as well as air pollution. A complicated system of cyclones is often applied. For example, the air released from a powder-separating cyclone is purified in a second cyclone or by means of filters. Sometimes the finest powder is returned to the chamber. Alternatively, the outlet air passes a wet washer, in which it collides with a water film that takes up the residual powder.

Final Drying. In the drying of a liquid several stages can be distinguished, e. g., a stage in which the liquid turns into a more or less solid mass and a stage in which the solid mass obtained decreases further in water content (‘‘final’’ drying). In milk products, a solid material is obtained at a water content near 8% (the product obtained is no longer sticky and appears to be dry), whereas a powder with, say, 3% water is desired. Traditionally, one process step included both drying stages, though in freeze drying the temperature must be raised during the final drying to complete it within a reasonable time. In spray drying, advantage is often taken of separating the final drying from the main process (Walstra, 1999).

The processes covered above are relatively cheap and somewhat effective processes but the main disadvantage is that heat is employed in these techniques and high temperatures can result in undesirable changes in the dried product. Generally, it is only after the powder has been dissolved again that the changes involved are noted. In actual practice, the outlet temperature of the drying air in particular determines the damage due to heating, though the inlet temperature may also have an effect. The followings are possible effects of high drying temperatures:

a. Inactivation of enzymes. Often inactivation is considerably slowed down at low water contents. The drying conditions may be adjusted in such a way that any heat inactivation is virtually avoided.
b. Killing of microorganisms. (It should be realized that the drying itself, even if carried out at a very low temperature, may reduce the number of living organisms. Such reduction closely depends on the bacterial species present and varies from, say, 10% to 99%). Generally, heat-labile microorganisms will not survive the drying. On the other hand, it is generally not possible to effectively kill all undesirable bacteria by drying.
c. Denaturation of serum proteins may be restricted by selecting moderate drying conditions.
d. Insolubilization of the powder. A fraction of the protein may be rendered insoluble if the drying temperature is too high at a somewhat low, though not very low, water content.
e. Hair cracks in the powder particles. A consequence of cracks is that a considerable amount of fat in the powder can be extracted by organic solvents such as petroleum ether and chloroform. Often, the result of the extraction is called ‘‘free fat’’ content, a

designation that makes little sense, because by far most of the extracted fat originates from fat globules that are in contact with cracks, vacuoles, or the particle surface and can thereby be removed by the solvent.

As described before this study explores new opportunities in concentrating whey thus obtaining valuable products such as protein, lactose and producing cleaner discharge. A general overview of membrane processes used in dairy industry and previous studies are discussed in the following section.

2.5. Membrane Processes in Dairy Industry

2.5.1. Fundamentals of Separation

Before detailing the membrane processes dairy industry, fundamentals of separation are discussed. In the application of a membrane separation process, a solution is enclosed in a system confined by a semipermeable membrane.

2.5.1.1. Roles of Separation Processes in Industry. Separation processes play critical roles in industry, including the removal of impurities from raw materials, purification of products, separation of recycle streams, and removal of contaminants from air and water effluents. Overall, separation processes account for 40-70% of both capital and operating costs in industry and their proper application can significantly reduce costs and increase profits.

2.5.1.2. Separating Agents. The heart of the separation process is the *separating agent* which can take the form of energy or mass (King, 1980). Some examples of separation processes and their separating agents are given in Table 2.4.

Table 2.4. Examples of Separation Processes and Separating Agents

Process	**Separating Agent(s)**	**Application(s)**
Absorption	Solvent	Removal of CO_2 and H_2S from natural gas with amine solvents
Adsorption and Ion Exchange	Adsorbent Resin	Separation of meta- and paraxylene, air separation, water demineralization
Chromatography	Adsorbent	Separation of sugars
Crystallization	Heat Removal	Production of beverages such as "ice" beer
Distillation	Heat	Propylene/propane separation, production of gasoline from crude oil, air separation
Drying	Heat	Drying of ceramics, plastics, and foods
Electrodialysis	Membrane	Water desalination
Evaporation	Heat	Water desalination, sugar manufacture
Extraction	Solvent	Recovery of benxene/toluene/xylenes from gasoline reformate, removal of caffeine from coffee
Stripping	Stripping Gas	Removal of benzene from wastewaters
Membranes	Membrane	Separation of hydrogen from hydrocarbons, concentration of fruit juices, water desalination

In this study, recovery of beneficial materials from wastewater and producing clean effluents with membrane processes, as addition to the applications in Table 2.4, will be discussed.

2.5.1.3. Efficiency versus Capacity. The two key design and operating parameters in any separation process are *efficiency* and *capacity*. Efficiency is related to the mass transfer and product purity. Capacity, on the other hand, is related to the hydraulics and the rate of material which can be processed without a loss in efficiency.

Efficiency and capacity are interdependent. In any separation process, it is often necessary to compromise factors which promote efficiency (and product purity) versus factors which enhance capacity (and product rate). For example, in membrane processes

capacity (flux) can be increased by increasing the size of the membrane pores, allowing molecular species to pass more quickly. However, increased pore sizes allow a broader range of molecular species to pass, thereby reducing efficiency. In the practical world, the relationship between efficiency and capacity is often a "give and take" situation.

2.5.2. Membrane and Membrane Process Definition

There are a number of definitions of the word "membrane", which can vary considerably in comprehensiveness and clarity. For the purposes of this study about using membrane technology in material recovery and treatment of whey, former Director of the School of Water Sciences, Cranfield, Prof. George Solt's, definition: "A material through which one type of substance can pass more readily than others, thus presenting the basis of a separation process" (Judd and Jefferson, 2003) is the most suitable.

2.5.3. Membrane Structure

Although membrane materials vary vastly according to chemical composition and process type, the principal objectives in membrane manufacture are always the same. An ideal material will:

- Have reasonable mechanical strength,
- Maintain a high throughput,
- Be selective for the desired permeate constituent.

These last two parameters are mutually counteractive, since a high degree of selectivity is normally only achievable using a membrane having small pores and thus an inherently high hydraulic resistance (or low permeability). The permeability also increases with increasing density of pores, and the overall membrane resistance is directly proportional to its thickness (in accordance with Darcy's Law). Finally, selectivity will be compromised by a broad pore size distribution. An optimum physical structure for any membrane material is thus:

- A thin layer of material,
- A narrow range of pore size
- A high porosity.

Membrane materials can be categorized as either *dense* or *porous,* and by the mechanism by which separation is actually achieved. Separation by dense membranes relies to some extent on physicochemical interactions between the permeating components and the membrane material, and relate to separation process having the highest selectivity. Porous membranes, on the other hand, achieve separation mechanically by size exclusion (i.e. sieving), where the rejected material may be either dissolved or suspended depending on its size relative to that of the pore. Since some membranes exhibit properties that can be associated with more than one process type, the boundaries between the adjacent membrane processes are somewhat nebulous. For example, International Union of Pure and Applied Chemistry (IUPAC) (Judd and Jefferson, 2003) states that the upper and lower boundary limits for mesopores, as are characteristic of a UF membrane, are 2 and 50 nm. According to Kesting (1996), however, these boundaries are at 1 and 20 nm, respectively.

2.5.4. Membrane Materials and Their Manufacture

Membrane manufacture concerns the production of a permeable material at a reasonable cost. The membrane cost is dependent not only on the raw material but also on the ease with which pores of the desired size or size distribution can be introduced. This can vary considerably from one material to the next according to the method used and the corresponding precision of the pore size distribution (or degree of isoporosity).

The range of available membrane materials employed in dairy waste treatment is not very broad. Polysulfone and polyethersulfone are widely used membrane materials especially in treatment of wastewaters produced by dairy industry.

2.5.5. Pressure Driven Membranes

Since the membrane processes used in dairy industry (generally for purpose of material recovery) are pressure-driven processes, attention will be given to these types of processes in this study.

The pressure-driven membrane processes are:

- Reverse osmosis
- Nanofiltration
- Ultrafiltration
- Microfiltration

In these processes, pressurized feed water enters one or more pressure vessels containing membranes, called membrane modules. Membranes are permeable to water but not to substances that are recovered or removed. All membrane processes separate feed water into two streams. The permeate (for RO, NF, or UF) or filtrate (for MF) stream passes through the membrane barrier. The concentrate (or retentate) stream contains the substances removed from the feed water after being rejected by the membrane barrier. Pressure-driven membrane processes can be designed for cross-flow or dead-end operating mode. In the cross-flow mode, the feed steam flows across the membrane surface and permeate (or filtrate) passes through the membrane tangential to the membrane surface. Cross-flow operation results in a continuously flowing waste stream. Sometimes a cross-flow system is designed with a concentrate recycle with a reject stream (feed-and-bleed mode). Many MF and some UF systems treating relatively low-turbidity waters are designed to operate in a dead-end flow pattern where the waste retentate stream is produced by an intermittent backwash. Cross-flow operation is vastly chosen in treating dairy products, especially whey, since there exists a high fouling potential of whey due to its high protein and lactose content.

2.5.6. Membrane Configurations

A membrane is only useful if it takes a form which allows water or pollutants to pass through it. The configuration of the membrane, i.e. its geometry and the way it is mounted and oriented in relation to the flow of water, is crucial in determining the overall process performance. Other practical considerations concern the way in which the membrane elements, i.e. the individual discrete membrane units themselves, are housed to produce modules, the complete vessels through which water flows. The optimum membrane configuration is one that has the following characteristics:

a) A high membrane area to module bulk volume ratio
b) A high degree of turbulence for mass transfer promotion on the feed side
c) A low energy expenditure per unit product water volume
d) A low cost per unit membrane area
e) A design that facilitates cleaning
f) A design that permits modularization

All membrane module designs, by definition, permit modularization (f), and this presents one of the attractive features of the membrane processes. However, some of the remaining characteristics are mutually exclusive. For example, promoting turbulence (b) results in an increase in the energy expenditure (c). Direct mechanical cleaning of the membrane (e) is only possible on comparatively low area:volume units (a) where the membrane is accessible. Such module designs inevitably increase the total cost per unit membrane area (d). Finally, it is not possible to produce a high membrane area to module bulk volume ratio without producing a unit having narrow feed channels, which will then adversely affect turbulence promotion.

There are five principal configurations currently employed in membrane processes, which all have various practical benefits and limitations (Table 2.5). The configurations are based on either planar or cylindrical geometry and comprise:

- Pleated filter cartridge
- Plate-and-frame

- Spiral Wound
- Tubular
- Hollow fibre

Table 2.5. General Data on Membrane Configurations (Judd and Jefferson, 2003).

Configuration	**Area/vol. ratio(m^2/m^3)**	**Cost**	**Turbulance Promotion**	**Backflushing**	**Application**
Pleated Cartridge	500-1500	Very Low	Very Poor	No	DEMF[b], low TSS waters
Plate-and-frame	100-300	High	Fair	No	**ED**,UF,RO
Spiral Wound	800-1200	Low	Poor	No	**RO**,NF,UF
Tubular	150-300	Very High	Very Good	No	CFMF[c], high TSS waters
Capillary Tube[a]	1500-5000	Low	Good	Yes	UF
Hollow fibre	10000-20000	Very Low	Very Poor	Yes	**MF**,RO

[a] Capillary tube used in UF: water flows from inside to outside the tubes

[b] DEMF: Dead-end microfiltration

[c] CFMF: Cross-flow microfiltration

2.5.7. The Process Fundamentals

2.5.7.1. Process Performance Definitions.

Flux. The key elements of any membrane process are the influence of the following parameters on the overall permeate flux:

- The membrane resistance
- The operational driving force per unit membrane area
- The hydrodynamic conditions at the membrane-liquid interface

- The fouling and subsequent cleaning of the membrane surface

The flux is the quantity of material passing through a unit area of membrane per unit time. This means that it takes SI units of m^3 m^{-2} s^{-1}, or simply ms^{-1}, and is occasionally referred to as the permeate velocity or the cross-flow velocity. Other non-SI units used are l m^{-2} h^{-1} and m^3 per day, which tend to give more accessible numbers. The flux relates directly to the driving force and the total resistance offered by the membrane and the internal region adjacent to it.

Conversion. In membrane processes there are three possible streams: a feed, a retentate and a permeate stream. The retentate stream is unpermeated product. If there is no retentate stream the operation is termed dead-end or full-flow (Figure 2.5.). Such operation is normally restricted to either low-solids water, as for cartridge filtration of boiler feedwater or ultrafiltration for apyrogenic pure water production, or cyclic operation with frequent backwashing, such for most microfiltration and ultrafiltration membrane plant for municipal water treatment. For waters having a significant solids loading and/or membranes of limited permeability (dense membranes), it is not desirable to try and convert all of the feed to permeate product in a single passage through a module. In such case, cross-flow operation is employed (Figure 2.5) whereby some of the feedwater is collected as concentrate (or retentate) stream. This expedites the removal of accumulated materials from the membrane-solution interfacial region provided by the scouring action of the retentate flowing over the membrane surface.

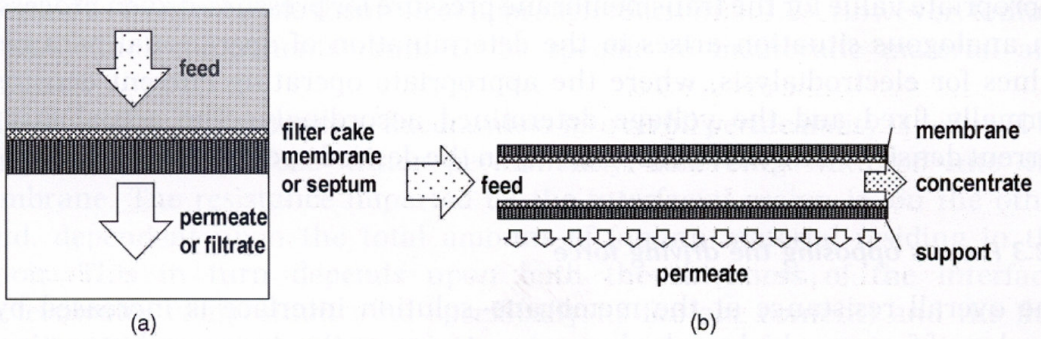

Figure 2.5. (a) Dead-end filtration and (b) cross-flow filtration (Judd and Jefferson, 2003).

The combination of the flux and the total membrane area determine the conversion of the recovery process. The conversion, normally expressed as a percentage Θ, is the amount of the feed that is recovered as permeate. Thus, for a concentration C and flow Q in feed, retentate and permeate (Figure 2.6), a simple mass balance dictates that:

$$Q = Q_P + Q_R \tag{2.1}$$

$$QC = Q_P C_P + Q_R C_R \tag{2.2}$$

where % recovery or conversion is given by:

$$\Theta = Q_P / Q \tag{2.3}$$

and the subscripts P and R refers to permeate and retentate, respectively.

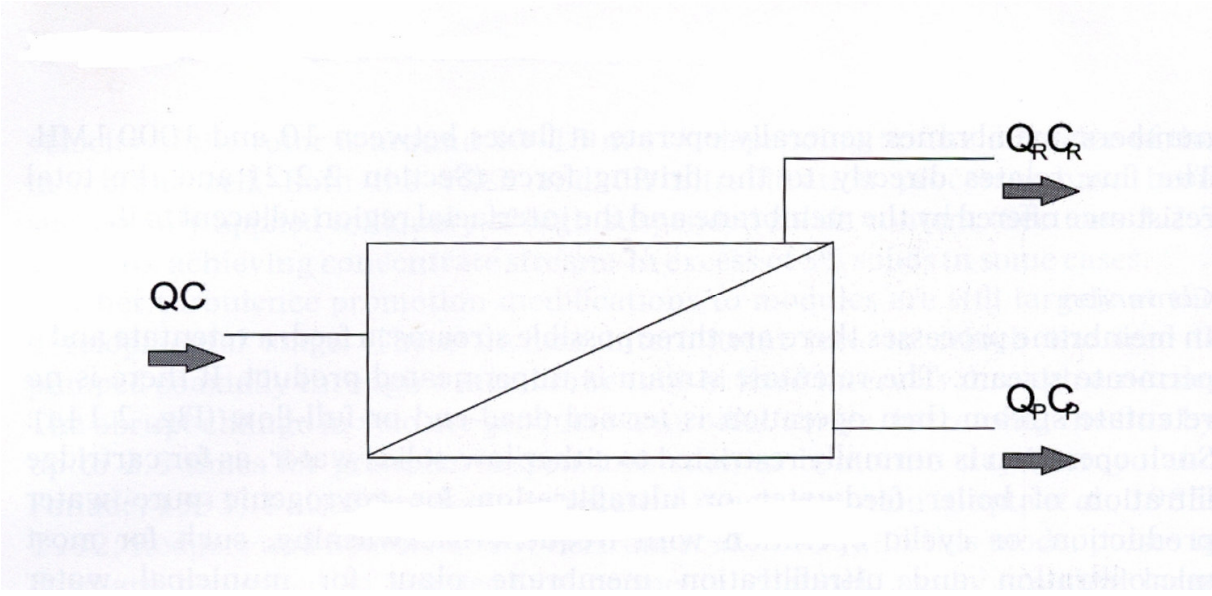

Figure 2.6. Membrane module mass balance (Judd and Jefferson, 2003).

Rejection. The permselective property of the membrane is normally quantified as the rejection where:

$$R = 100\ \% \ (1 - C_P / C) \qquad (2.4)$$

It is possible to have negative rejection values if the membrane is selective for specific contaminants, as would be the case for an extractive membrane system.

The Driving Force. The driving force for the process may be a transmembrane pressure (TMP) gradient, as with filtration and reverse osmosis, a concentration gradient as with dialysis, or electromotive as with electrodialysis. In almost all pressure-driven membrane processes applied to water treatment the desired permeate is water, such that the retained or rejected material (the retentate) is concentrated. In extractive and electrodialytic operations the permeate is the dissolved solute and the retentate is the product water. For extractive systems the driving force is a concentration gradient, whereas for electrodialysis an applied potential difference is employed to move dissolved ions through electromigration.

Since the flux and driving force are interrelated, either one can be fixed for design purposes. It is usual to fix the value of the flux and then determine the appropriate value for the TMP for pressure-driven processes.

Factors Opposing the Driving Force. The overall resistance at the membrane-solution interface is increased by a number of factors which each place a constraint on the design and the operation of membrane process plant:

- The concentration of rejected solute, as in RO and UF, or permeated ions, as in ED, near the membrane surface
- The depletion of ions near the membrane surface, as with ED
- The precipitation of sparingly soluble macromolecular species (gel layer formation, as in UF) or salts (scaling, as in RO) at the membrane surface
- The accumulation of retained solids on the membrane (cake layer formation, as in MF)

All of the above contribute to membrane fouling. Fouling can take place through a number of physicochemical and biological mechanisms which all relate to increased deposition of solid material onto the membrane surface (also referred as blinding) and

within the membrane structure (pore restriction or pore plugging/occlusion). This is to be distinguished from clogging, which is the filling of the membrane channels with solids due to poor hydrodynamic performance. Fouling may be both temporary (removed by washing) and permanent (removed only by use of chemicals).

Concentration Polarization. Concentration polarization (CP) is the term used to describe the tendency of the solute to accumulate at the membrane-solution interface within a concentration boundary, or liquid film (Figure 2.7).

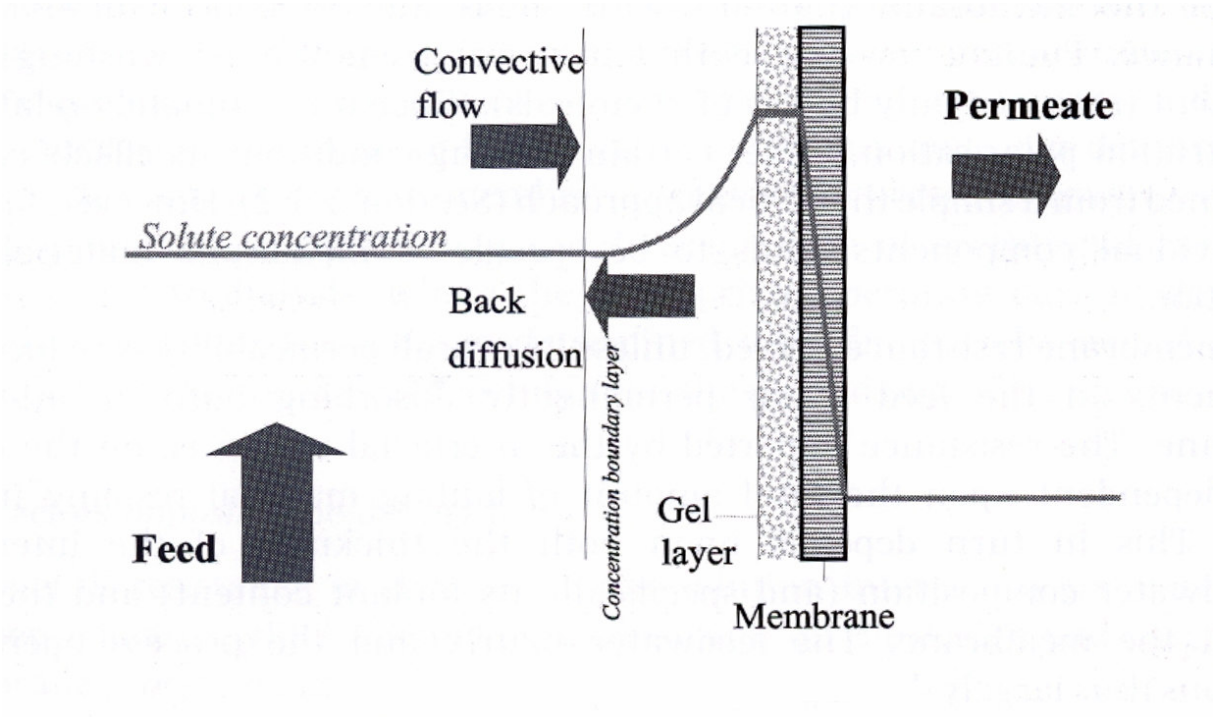

Figure 2.7. Concentration polarization (Judd and Jefferson, 2003).

For pressure-driven processes, the greater the flux, the greater the build-up of the solute at the interface; the greater the solute build-up, the higher the concentration gradient; the steeper the concentration gradient, the faster the diffusion. Under normal steady-state operating conditions there is a balance between those forces transporting the water and constituents within it towards, through and away from the membrane. This balance is determined by CP. CP also raises the effect of osmotic pressure at the membrane-solution interface, increasing the required TMP for operation. It is thus always desirable to suppress

CP by promoting turbulence and/or operating at a flux below that at which CP starts to be significant.

CP effects on specific processes are summarized in Table 2.6**.** All membrane processes are subject to CP, but it is only in specific cases where certain CP phenomena become significant.

Table 2.6. Concentration Polarization Effects (Judd and Jefferson, 2003).

Process	**Osmotic Pressure Elevation**	**Electrical Resistance Elevation**	**Scaling**	**Gel Layer Formation**	**Selectivity Change**
RO	X	-	X	X	(X)[a]
NF	(X)[a]	-	X	X	(X)[a]
ED	-	X[2]	(X)[a]	-	(X)[b]
UF	-	-	-	X	-
MF	-	-	-	-	-

[a] More marginal effect

[b] Depletion polarization

The relationship between driving force and polarization in pressure-driven membrane separation processes can be summarized as follows:

- The flow through a given type of membrane varies as the membrane area and the net applied force; and the power consumption is proportional to the driving force, and inversely proportional to the membrane area installed. This is analogous to electrical conduction, where current varies with the cross-sectional area of copper in the cable and with the applied voltage, and the power loss in the cable varies with the voltage loss inversely with the area.
- The selective nature of the process means that rejected material remains on the membrane surface. Cross-flow operation affords some limitation to the extent to which rejected material accumulates in the interfacial region.

These two factors are interlinked: a high driving force yields high flux and high rate of rejected material collecting on the membrane surface, which then needs to be dispersed rapidly if the process is not to grind to a halt. In extractive and dialytic processes, CP tends to deplete the permeating species at the membrane, which in electrodialysis has the effect of increasing electrical resistance and decreasing permselectivity.

Critical Flux. The critical flux concept was originally presented by Field *et al*. (1995), these authors stated that: "The critical flux hypothesis for microfiltration is that on start-up there exists a flux below which a decline of flux with time does not occur; above it, fouling is observed". Two distinct forms of the concept have been defined. In the strong form, the flux obtained during sub-critical flux is equated to the clean water flux obtained under the same conditions. However, clean water fluxes are rarely attained for most real feed waters due to irreversible adsorption of some solutes. In the alternative weak form, the sub-critical flux is the flux rapidly established and maintained during the start-up of the filtration, but does not necessarily equate to the clean water flux. Alternatively, stable filtration operation, i.e. stable permeability for an extended period of time, has been defined as sub-critical operation even when preceded by an initial decline in flux (Howell, 1995). Such conditions would be expected to lead to lower critical flux values than those obtained for absolutely constant permeability operation (i.e. from t=0), however, since an initial permeability decline implies foulant deposition (Judd and Jefferson, 2003).

2.5.8. Membrane Processes as Concentration Processes for Whey

As implied previously, whey is a very problematic by-product of dairy industry containing high concentrations of lactose and proteins. Membrane processes are used to concentrate these components. Some components of the whey solution can pass the membrane; some cannot. The driving force may be a pressure difference over the membrane or a difference in electrical potential. The latter method refers to electrodialysis. In dialysis the driving force is a concentration difference or, more precisely, an activity difference. In microfiltration and ultrafiltration a relatively small pressure difference of, e.g. 1 bar is involved; in reverse osmosis a far higher pressure difference is applied. Microfiltration is intermediate between common filtration and ultrafiltration. The pores in

the membrane are fairly wide, i.e., 0.1 µm, and the pressure difference is small. The method may be used to remove small particles and microorganisms from cheese brine or wastewater, and is in principle also suitable to remove bacteria from skim milk. Microfiltration may especially be used if the amount of ‘‘retentate’’ is relatively small. Ultrafiltration effectively separates macromolecules (e.g., proteins) and particles (casein micelles, fat globules, cells, bacteria, etc.) from the solution. The common aim is to accumulate protein. The process is often applied to whey and to skim milk. In principle, it can cause appreciable change in the composition of milk products, and it thus allows preparation of unconventional products. Alternatively, the milk may be concentrated to an extent as to approach the composition of curd (or quarg) and be clotted subsequently. Ultrafiltration is an almost unique process, though gel filtration can provide comparable results. However, industrial application of gel filtration incurs many problems and is costly. Nanofiltration (Figure 2.8) is used on an industrial scale to separate mixtures of proteins and peptides on a molecular size basis. Moreover, some nanofiltration membranes can be used for desalting, when high pressures are applied; this is an alternative to electrodialysis. Reverse osmosis is applied to remove water, and it thus is an alternative to evaporation because it consumes far less energy. Its capital expenditure and maintenance costs are usually higher; hence, its profitability depends on conditions. The process is applied to whey, skim milk, and highly polluted wastewater, and has the advantage of operating at low temperature and of retaining a great deal of volatile substances. Disadvantages may be that milk cannot be highly concentrated and that the permeate is by no means pure water. Electrodialysis is aimed at removing ions, e. g., in the preparation of dietary products, or as a step during the manufacture of a purified protein concentrate. The process is applied to partially demineralize whey. Passing milk over ion exchange columns with suitable resins also removes ions, but that method has several drawbacks, e. g., because the resin must be regenerated frequently (Walstra, 1999).

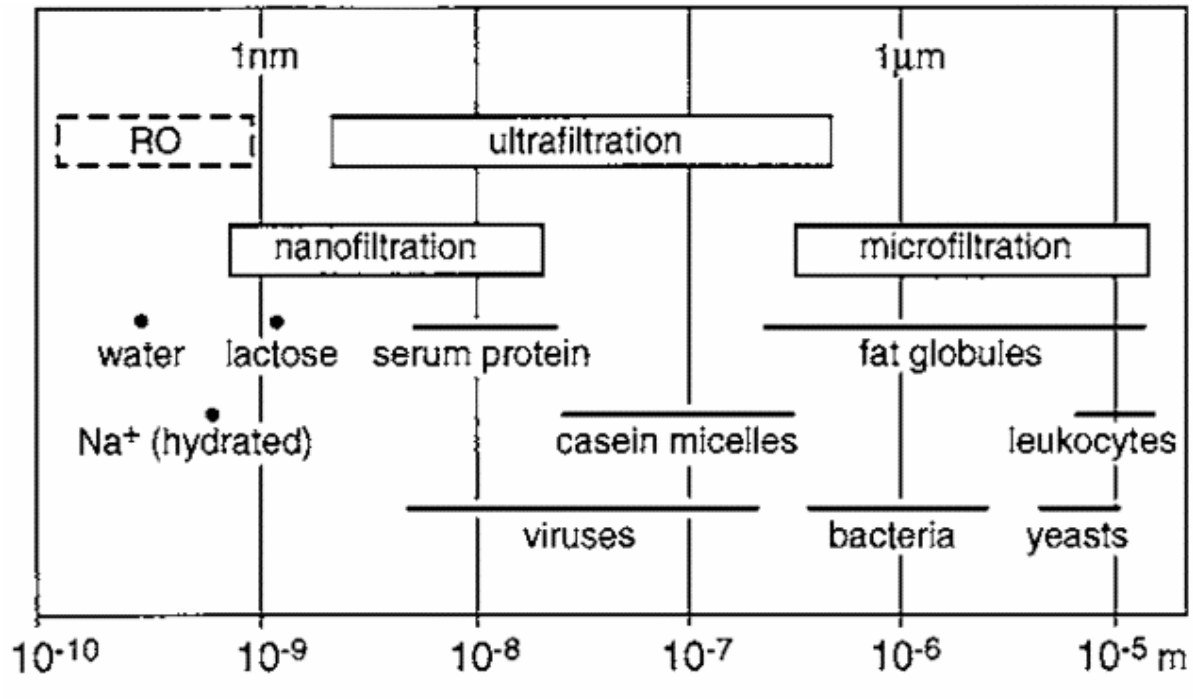

Figure 2.8. Approximate particle sizes for which separation by means of micro-, ultra-, and nanofiltration can be applied (Walstra, 1999).

2.5.8.1. Ultrafiltration.

Composition of the Retentate. An ultrafiltration membrane is a filter with very narrow pores (mostly a good 1 nm in width) through which most molecules and ions can pass, whereas macromolecules and particles are retained. In principle, water activity, ionic strength, and pH are equal on either side of the membrane. In the retentate, protein accumulates and its properties, including conformation, remain essentially unaltered. The ratio between, for instance, protein and sugar in the retentate changes considerably. Consequently, a retentate of skim milk has a composition completely different from that of evaporated skim milk and, as a result, has different properties: it is much more heat-stable at an identical protein content, and has a higher viscosity at identical dry matter content can conveniently be expressed in kg per kg of water; Cw, the concentration of water, then equals 1 (Walstra, 1999).

The rejection concept (R) was described previously. Ideally, R = 0 for small molecules and R = 1 for protein. R is a function of molecular size, and that function

depends on the type of membrane involved. R changes gradually with molar mass, partly because of a spread in pore width in a membrane, and differences in spread explain the differences in the slope of the curves. Even for identical pore widths, however, R will gradually change with molar mass. This is because the pores in the membrane exert a mechanical sieve action on the movement of even small molecules. The nearer the molecular size is to the pore width in the membrane, the greater the resistance. If the pores cause the same resistance to the solute as to the water molecules, R = 0. R not only depends on the type of membrane, but for small molecules it also increases to some extent with the pressure difference Δp over the membrane. Often, R also depends on the presence and thickness of a gel layer. At high concentrations the difference may be considerable, partly because a relatively large proportion of the water is not available as a solvent. In the ultrafiltration of skim milk and whey, low molar mass proteins or peptides are not fully retained. Usually, for lactose R = 0.02 – 0.15, for citrate R = 0.01 –0.10, and for smaller ions R is negligible (Walstra, 1999). Anions in milk serum are on average larger than cations. The ensuing difference in flux has to be counterbalanced by a flux of hydroxyl ions, which causes the pH of the permeate to be 0.04 – 0.10 higher than that of the original liquid. Figure 2.9 illustrates some of the aspects mentioned. Calculated curves are drawn for R = 1 and R = 0. The curve for R = 0 is not horizontal. This is because at a constant and equal ratio of solute to water on either side of the membrane, the solute concentration in the total volume (C in Figure 2.9) decreases during concentration, since the water content of the retentate decreases.

Figure 2.9 shows that there is no total reflection for protein. The reflection for total N is still smaller because it comprises non-protein nitrogen (NPN), for which R mostly approximates zero and NPN constitutes about 25% of the nitrogen in whey. Obviously, any component that closely associates with protein, such as Cu, is retained in the retentate, though to a lesser extent the same holds true for the counterions of the negatively charged protein, in this case cations. Figure 2.9 also shows that Ca^{2+} is present in a relatively higher concentration as a counterion in the diffuse double layer than Na^{+}, which is fully in line with theory.

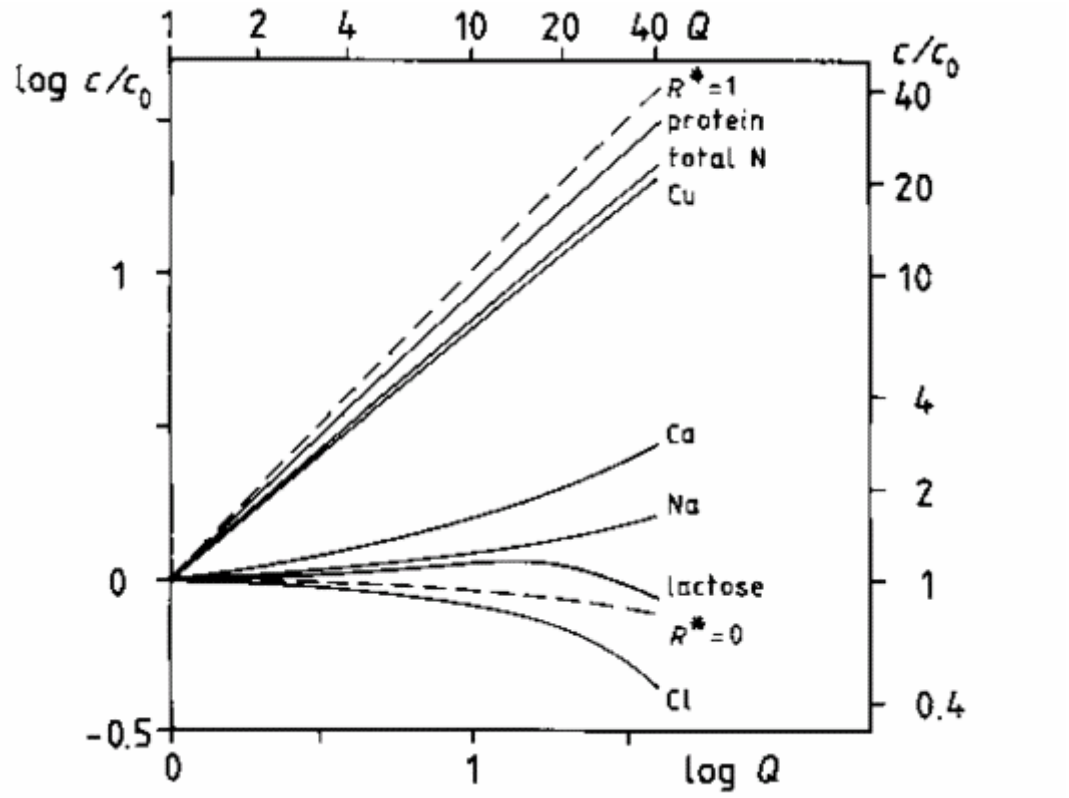

Figure 2.9. The ratio of the concentration, c, of some components in the retentate of ultrafiltered sweet whey to their original concentration (Co) as a function of the concentration factor Q (original volume/ retentate volume). (Hiddink *et al.,* 1978)

The retention changes even stronger by applying diafiltration. In diafiltration, water is added to the retentate after a certain Q has been reached, and ultrafiltration is continued. In this way, the ratio between protein and solutes in the retentate can be increased. Of course, this holds to a far lesser extent for the ratio of protein to counterions, and to components bound to protein. If a protein concentrate of low 'ash content' is to be made by using ultrafiltration, it is advisable to lower the pH appreciably before ultrafiltration. Table 2.7 gives examples of the composition of retentates obtained from whey. The composition of the permeate also depends on other conditions. The main variable in ultrafiltration usually is the membrane because that primarily determines the reflection for various constituents.

Table 2.7. Composition of the dry matter obtained by ultrafiltration of whey (Walstra, 1999).

Q	1	5	10	20	35	35[a]	20
Dry Matter (%)	6.6	10	14	20	25	22	17
pH during Ultrafiltration	-	6.6	6.6	6.6	6.6	6.6	3.2
Protein / Dry Matter (%)	12	34	45	58	70	82	59
Lactose / Dry Matter (%)	74	51	39	27	17	7	27
Ash / Dry Matter (%)	8	6	5	4	3.5	2.5	2.7
Citrate / Dry Matter (%)	2.5	1.8	1.7	1.6	1.4	-	-
Fat / Dry Matter (%)	1	2	3	4	5	6	4

[a] Followed by diafiltration, i.e., water is added to increase the volume by a factor of 3, and the mixture is ultrafiltered again.

The flux achieved during ultrafiltration of whey or skim milk is many times lower than that during ultrafiltration of water. The following are possible causes (Walstra, 1999).

a. The viscosity of the permeating liquid is higher than that of water, e. g., by 20%.
b. Protein molecules immediately adsorb onto the membrane, also in the pores, and thereby reduce the effective pore width. The effect is hard to determine precisely, but presumably it is considerable. Obviously, the narrowing of the pores increases the selectivity.
c. Part of the solutes is retained. Any retention of solute causes a difference in osmotic pressure on either side of the membrane, resulting in a somewhat lower effective pressure difference. The decrease is small, e.g. 10%.
d. A concentration gradient is formed because liquid passes the membrane and part of the material in that liquid cannot pass. The gradient is counteracted by the mixing effect of the liquid moving along the membrane, but a certain gradient or a liquid layer with increased dry matter content will be formed anyway.
e. The concentration gradient can, however, affect the permeate flux much more strongly if it increases near the membrane to such an extent that the concentration of some constituents, especially proteins, exceeds their solubility. A layer of precipitated material then is formed on the membrane. This ‘‘gel layer’’ causes a further reduction of the flux, the more so the thicker the layer and the higher the pressure, because a higher pressure

compresses the gel layer thereby narrowing its pores. Usually, a gel layer also improves the reflection of many constituents; in other words, it enhances the membrane selectivity.

The above-mentioned facts may explain the effects of some process and product variables on the ultrafiltration flux, at least qualitatively. The composition of the liquid at the pressurized side is paramount because that determines whether a gel layer can be formed or not. The pH strongly affects the solubility of the protein.

2.5.8.2. Reverse Osmosis. Reverse osmosis differs from ultrafiltration in the application of much higher pressures (3 –10 MPa). It removes water against an osmotic pressure. The osmotic pressure is considerable. For nonconcentrated milk or whey, 0.7 MPa, and it increases during concentration by removal of water according to Q*, where Q* is the relative increase of the dry matter content in proportion to water. Clearly, the membrane is semipermeable. It does not act as a filter with narrow pores but rather as a layer of material in which water can dissolve and through which it can pass, while most of the other (mainly hydrophobic) components cannot do so or can barely do so. Transport of a component occurs by diffusion through the membrane or, essentially, through the thin layer of the membrane, which is semipermeable, and the porous remainder of the membrane is merely a support. The rate of transportation is proportional to the solubility of the component in the membrane and to its effective diffusivity. The diffusion coefficient in the membrane decreases considerably with increasing molar mass of the diffusing component. Obviously, the retentate obtained by reverse osmosis differs somewhat from the concentrate after evaporation, and the permeate is by no means pure water. The rejection coefficient R of small molecules is 0.75 - 0.99, greatly varying with the composition of the membrane. Urea can pass to some extent, and even lactose and low molar mass peptides may do so. Accordingly, bacteria can grow in the permeate. Volatile flavor substances are satisfactorily retained (Walstra, 1999).

Applying reverse osmosis to whey or skim milk results in a lower flux than when pure water is used. This is comparable to conditions during ultrafiltration; however, the first two will hardly have an effect because the viscosity of the permeate is and remains similar to that of water and there are no pores that can foul. The increase of the osmotic pressure, on the other hand, is of paramount importance.

Reverse osmosis is usually not applied to milk. First, the fat globules increase the viscosity and, second, the globules are easily homogenized when the retentate flows out of the equipment through the pressure release valve. Such homogenization causes considerable lipolysis if raw milk is involved. Gradual release of pressure via discharge of the concentrate through a long capillary tube can prevent the homogenizing effect. Furthermore, high concentration of the milk causes crystallization of lactose and subsequent blockage of the equipment, at least at low temperature. If the membrane does not endure high temperatures, a concentration greater than about 22 g lactose/ 100 g water cannot be achieved. If applied to whey, a dry matter content of about 24% can be reached (Walstra, 1999). Reverse osmosis is technically carried out in much the same way as ultrafiltration. The higher pressures applied necessitate several adaptations, e. g., to the pumps and to the membrane support. The flux increases with the temperature, almost as strongly as the viscosity of water decreases with temperature**.**

2.5.8.3. Electrodialysis. Electrodialysis can be carried out in various ways, but membranes that let pass cations only or anions only are generally used. It thus is an open system; a salt solution flows along the electrodes and also serves to remove the formed gas. The number of parallel membranes is large, and their mutual distance is about 1 mm. During electrodialysis, concentration polarization occurs and a gel layer forms (e. g., from calcium phosphates and small peptides) but constant flushing of the equipment may maintain an acceptable capacity. In demineralizing whey, the ash content is reduced by, e.g. 80%. Any further reduction requires excessive electrical energy. Different salts are removed at widely differing rates. Figure 2.10 gives examples. Obviously, the removal of a salt depends primarily on its ionization and therefore on the pH. That explains why at low pH lactate can hardly be removed. Furthermore, co-ions will be more readily removed than cations, which preferably occur as counterions of the proteins. Moreover, the mobility of the various ions in a potential field varies. The greater the mobility, the better the removal. Finally, the permeability of the membrane for various ions can vary. Accordingly, the selectivity of electrodialysis markedly depends on conditions.

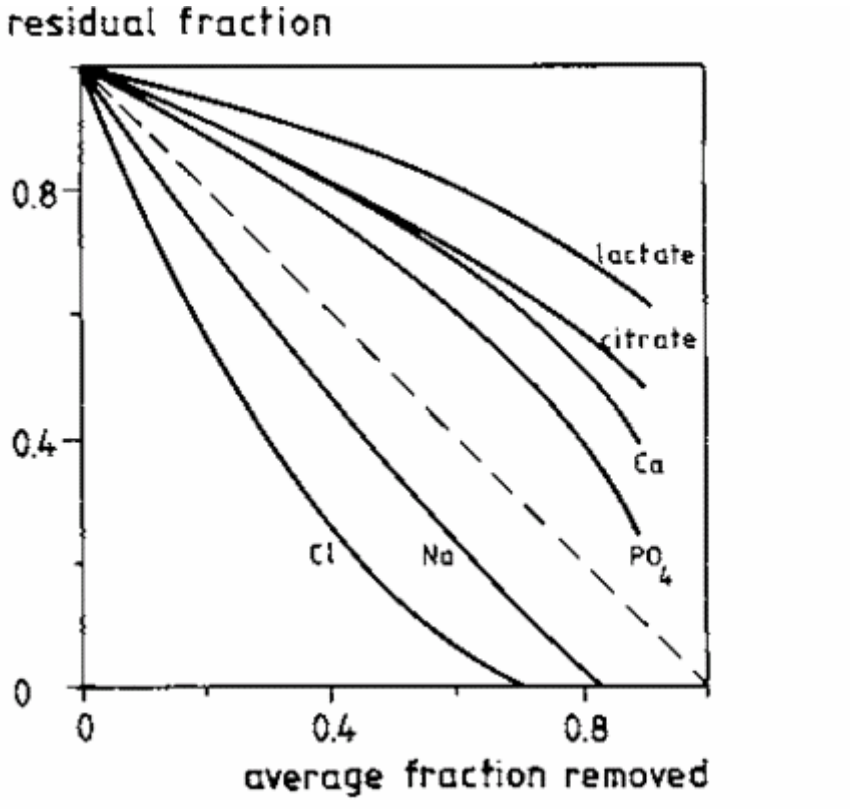

Figure 2.10. Example of demineralization of acid whey (pH = 5.2) by electrodialysis as a function of the quantity removed (Walstra, 1999).

2.5.9. Membrane System Components and Design Considerations

Some of the more important considerations in membrane system design are the system components, feed water characteristics, and pretreatment that may be required.

Once treatment objectives have been identified, design criteria can be developed for the membrane process. The design considerations can be grouped for:

- RO and NF units
- UF and MF units
- ED and EDR units

These groups are identified as to the process fundamentals, rejection characteristics and process variables. Regarding the focus of this study, RO and NF unit design will be covered.

2.5.9.1. Reverse Osmosis and Nanofiltration Unit Design. Because of the high solute rejection of RO and NF membranes, which concentrate inorganic ions among other constituents, there are many special considerations in the treatment unit design.

The basic behavior of permselective (semi-permeable) membranes can be described by the following two diffusion model equations. Permeate flow through the membrane can be expressed as:

$$F_w = A * (P_{tm} - \pi_{tm}) \quad (2.5)$$

Where F_w = water flux (g/cm^2-s)

A = water permeability coefficient (g/cm^2-s-atm)

P_{tm} = hydraulic pressure difference applied across membrane (atm)

π_{tm} = osmotic pressure difference across membrane (atm)

The solute flux through the membrane can be expressed as:

$$F_s = B * (C_1 - C_2) \quad (2.6)$$

Where F_s = solute flux (g/cm^2-s)

B = solute permeability coefficient (cm/s)

$C_1 - C_2$ = concentration gradient across membrane (g/cm^3)

Water and solute permeability coefficients are characteristic of the particular membrane type. Water flux depends on applied pressure, but solute flux does not. As pressure of membrane feed water increases, water flow through the membrane (water flux) increases, while solute flow remains essentially unchanged. Permeate quantity increases with increased applied pressure, as does the quality (decreased solute concentration). Water flux decreases as the salinity of the feed increases because of increased osmotic

pressure differential resulting from increased salinity. As increasing amounts of water pass through the membrane system, the salinity of the remaining feed water (concentrate) increases. Concentrate osmotic pressure increases, resulting in a lower water flux with increasing overall percent water recovery.

Finally, because salinity of the feed-concentrate stream increases with increasing permeate production from a given volume of feed, and the membrane rejects a fixed percentage of solute, product water quality decreases (higher concentration) with increasing recovery.

2.5.9.2. Recovery Considerations. As recovery increases, the following factors must be considered in designing an RO or NF system.

Scaling. The concentration factor and potential for scaling increase as recovery increases. The source feed water composition must be evaluated to estimate maximum operating recovery and the necessary pretreatment requirements (for example, pH adjustment or scale inhibitor addition).

Hydraulics. Optimal performance requires adhering to minimum concentrate and maximum feed flow conditions for membranes. Feed flow to the first element in a pressure vessel and concentrate flow from the last element in a pressure vessel must satisfy the manufacturer's stated requirements. System design must provide adequate membrane concentrate flow. Concentrate staging of membranes and pressure vessels is typically used for recoveries greater than 50% to 60%. Two stages are commonly used for recoveries between 50% and 60% and between 75% and 85%; three stages are used for higher recoveries (up to about 90%). Some small systems are designed with concentrate recycle to produce flows above the minimum specified by the membrane manufacturer.

Source Water Use. The required volume of source feed water necessary to produce the same volume of permeate decreases as the recovery rate increases. Maximizing recovery rates minimizes both the source water requirement and the volume of concentrate generated.

Permeate Water Quality. Feed-concentrate average salinity increases as recovery increases. Because the flow of solutes through the membrane is a direct function of their concentration in the feed-concentrate stream, permeate quality decreases as recovery increases (American Society of Civil Engineers Staff, 1997).

2.6. Previous Studies on Whey Treatment by Membrane Processes

Although whey processing represents one of the first fields of application of membrane processes in the dairy industry (Zadow, 1987; Maubois, 1991), recently there have been a great need for optimized processes, better membrane material, structure and configuration for treatment of dairy products, especially whey since the characteristics of whey changes from process to process and also recovery and re-use for material in whey achieved great importance. Consequently, there have been approaches to seek solutions for problems associated with whey treatment and material recovery with membrane processes. The studies, which will be summarized below, basically concentrated on identifying the optimal membrane material, optimal membrane configuration, optimal process parameters for membrane treatment of different whey types. Ultrafiltration and reverse osmosis are well established pressure-driven membrane processes that are widely used in the dairy and other food industries throughout the world. Recent developments in the membrane technology have expanded the range of applicability of these traditional processes offering the processing industry new alternatives to the more traditional technological approaches. Usage of nanofiltration for whey treatment is one of those recent developments and this process is currently being investigated for efficiency in by-product recovery in dairy industry. So nanofiltration can be accepted as an alternative for the concentration and demineralization of whey for the previously mentioned processes. Zydney *et al.* (1998) proposed membrane separations as new opportunities in whey fractionation. The article focuses on previous usage of membrane operations, namely, microfiltration for lipid removal prior to ultrafiltration for retention of whey proteins. Nanofiltration and its applications were to be investigated further.

There is not much study on nanofiltration for whey treatment. Alkhatim *et al.* (1998) was focused on improving the demineralization rate achieved by commercial nanofiltration

membranes by using laboratory-manufactured membranes. Model solutions of whey were applied as well as model solutions for each salt (single-salt solutions), allowing them in this way to study the performance and transport of salts when each salt is treated alone and when all are together (whey salts) in the feed solution. They investigated the membrane performances from the points of pressure, pH and temperature effects on permeability and flux. The most suitable membrane is selected for its best (the highest) flux as well as optimum rejection of salts. It was interesting that one of the commercial membranes used (NF-90) resembled RO characteristics more than a NF membrane. Results obtained by NF-45 and ACE-3-93-TY were satisfactory and prove the suitability of nanofiltration process in whey demineralization. Best fluxes were obtained at pH < 4 but permeability was not as good as when pH > 4.5 was applied. Thus the best pH interval for this application should be in the range of 4.5 to 5.2. ACE-3-93-TY membrane showed good results at pH 4.5 and pressure of 10 bar. Pressure as shown in results affects selectivity considerably.

Balannec *et al*. (2002), reports NF and RO performances (permeate flux, milk components rejection) of an effluent model solution (diluted skimmed milk). Whey is not used in this study but it is worth mentioning since it compares performances of eight NF and RO membranes were compared by dead-end filtration. The performances of dairy process waters treatment with membranes for recovery of milk constituents and water were analysed in terms of COD and ion rejection. Different types of membranes were compared in cross-flow and dead-end filtration modes. Cross-flow experiments with NF and RO spiral-wound membranes confirmed the results obtained by dead-end filtration. The results showed that one single membrane operation allowed the milk constituents to be concentrated in the retentate but reusable water of composition complying with the standard of purified water from process water was not reached. A finishing step (RO membrane, other) is needed for the production of reusable water.

Study of material recovery from whey by nanofiltration was conducted by Nguyen *et al*. (2002). An investigation into the required pretreatment was also carried out to remove curd fines and to stop the growth of cheese starters. The pretreatments required for the whey samples were decanting, heating to 65 °C and filtering through a cheese bag (5 μm) in order to remove casein fines. The samples were then heated again to 65 °C and held for 60 min for pasteurization and calcium precipitation, subsequently passed through filtering

pads (4.0 μm) and cooled to the processing temperature. The final concentrated samples from the nanofiltration trials were pasteurized at 75 °C for 15 s before storage at 5 °C. The trials were made in three steps with 2, 2.7 and 3.4 MPa TMP. And the flux was observed to decrease from 35 to 7 L/m/h at the end of the runs. The cottage cheese whey was successfully concentrated up to 24% total solids level using nanofiltration technique with major reduction of sodium content in the final concentrate. The final concentrate contained significant amounts of fat, protein and lactose and is considered to be suitable for use in dairy products such as ice cream and yoghurt. Alternatively, it can be converted into sweet syrup for use in other products. The study also investigated the economics of the process and showed that, based on a 30 m^3 per day of whey; the cost of a nanofiltration system can be recovered in less than 10 months. According to this study it can be concluded that there is definitely the potential to use nanofiltration on other by-product streams to concentrate fat, protein and lactose and this will help to reduce the pollution treatment cost and recover more dairy solids from the original raw materials as part of Cleaner Production.

Atra *et al.* (2003) compared ultrafiltration and nanofiltration for the utilization of whey protein and lactose. The performance of ultra- and nanofiltration membranes were characterized in terms of permeate flux, membrane retention and yield, which parameters are determined by pressure, recycle flow rate and temperature. The influence of these parameters on milk- and whey protein and lactose concentration was measured. The experiments were carried out using laboratory scale ultra- and nanofiltration units. The permeate flux, protein and lactose content in the permeate and in the concentrate fractions were measured during the experimental runs. From the experiments it can be concluded that the concentration of the light milk, concentration and incorporation of the whey protein by ultrafiltration, and also the concentration and utilization the ultrafiltration permeates by nanofiltration can be successfully achieved by the investigated membranes (FS10, SP015 and RA55) with a high efficiency by means of high protein rejection values (92-98 %) for ultrafiltration membranes with reasonable flux (30 $L/m^2/h$) and low lactose concentration in the NF permeate (0.1 – 0.3 %).

Rektor and Vatai (2004) aimed to develop a complex membrane filtration technology for whey processing using all membrane filtration methods to find the potential applications of membrane systems for whey recycling and utilization. Whey was first pre-

filtered with microfiltration for the removal of bacteria and lipid molecules, the permeate was treated with ultrafiltration for whey protein retention and the permeate of ultrafiltration is treated with both nanofiltration and reverse osmosis. The permeate of microfiltration is also treated with nanofiltration and RO alone for comparison. After the experiments the author proposed three different alternatives for whey recycling namely MF + NF, MF + UF + NF and MF + RO. These three different lines were concluded to be suitable for different sized industries and, of course, to produce effluents with different characteristics such as the line with RO would produce low COD water. The attention must be given to the conclusion that small sized membranes would be applied to nearly raw-whey, without damaging or fouling the membranes.

Akoum *et al.* (2003) proposed a different operation of membrane processes for dairy wastewaters. The permeate flux and chemical oxygen demand (COD) reduction were investigated in dairy process waters using a vibratory shear-enhanced filtration system (VSEP) and various nanofiltration (NF) and reverse osmosis (RO) membranes. The VSEP system, as has been recognized by Nuortila-Jokinen et al. (Nuortila-Jokinen and Nyström, 1996; Nuortila-Jokinen *et al.,* 1998; Nuortila-Jokinen and Nyström, 2000), is simply used to create oscillations throughout the membrane surface for break-up of the deposited gel layer thus increasing the permeate flux. In NF the highest permeate flux (270 l/m^2/h) at 4MPa, 45 ˚C and initial concentration) was obtained with a Filmtec membrane which yielded also the highest permeate COD (94 mg O_2/L). The best compromise was obtained with a Desal 5 DK membrane which yielded a COD of 36 O_2/L and a flux of 240 L/m^2/h under same conditions. In concentration tests, the permeate flux decreased with increasing volume reduction ratio (VRR) to reach 25 L/m^2/h for the 5 DK membrane at VRR = 7 while permeate COD soared to 1050 mg O_2/L. A comparison with published data collected using a spiral module and same test fluid at 25 ˚C and 1.9MPa showed a definite advantage for the VSEP equipped with the same 5 DL membrane and operated at same pressure and temperature. The VSEP yielded a permeate COD of 24 mg O_2/L versus 128 mg O_2/L for the spiral module together with a higher flux 71 L/m^2/h versus 24 L/m^2/h. The better performance of the VSEP can be attributed to its higher membrane shear rate which reduces lactose concentration at membrane and its transmission. Permeate COD was further reduced to less than 22 mg O_2/L at a VRR of 5.6 by using an RO membrane.

Many membrane operations have been described for the treatment of dairy effluents in other previous studies namely: one- step operations based on UF, NF (Koyuncu *et al*., 2000), RO (Delbeke, 1981) or two-stage operations such as UF+RO (Argellier and Pannuzzo, 1999), NF +NF (Mavrov, et al., 2001) or RO + RO (Koyuncu *et al*., 2000). It has been shown that NF and RO are convenient operations for the production of water for reuse in dairy plants from low contaminated process water (Chmiel *et al*., 2000).

Vourch *et al*. (2004) again investigated different cascade operations of NF and RO for dairy wastewaters. The study reports one-stage and two-stage (NF + RO and RO + RO) spiral-wound membrane treatments with five model process waters representative of the main composition variations observed in dairies. Performances (permeate flux, milk components rejection, purified water characteristics) of the different operations were compared. Five model process waters, representative of the main composition variations of 10 industrial dairy plants process waters, were treated by one stage and two-stage membrane operations. It was shown that, except with aged process water (process water naturally acidified due to 24-h storage at 25°C), the treatment of the four different model process waters gave similar performances: permeate fluxes were almost similar, composition of permeates and retentates, just as rejection of the different components, were nearly identical. In the range of this study, heat treatment, fat content and whey/milk ratio of the process waters did not have a significant effect on the performance of the treatments. A drawback was also shown: process water must be treated within a few hours before degradation of milk components occurs because membrane operations afford moderate quality permeates. After a single RO or NF+RO operations, the water could be reused in replacement for cleaning, heating or cooling purposes and for boiler feed water. With a RO+RO treatment, highly purified water complying with TOC drinking water regulation was obtained and could be reused, with specific and special permission, for applications where unexpected contact with products may occur (risk of leakage) in order to prevent possible contamination.

Balannec *et al.* (2004) compared nanofiltration and reverse osmosis applications for dairy effluent treatment. The study was focused on selection of NF and RO membranes during a concentration mode by dead-end filtration. For a high loaded skimmed milk used as process water, both rejections of lactose, COD and multivalent ions with most NF and

RO membranes were >94% during a concentration step by dead-end filtration. COD, involving lactose, was a valuable criterion for selection of NF and RO membranes. Rejections of divalent cations using NF membranes were unexpectedly high (>90%) for counter-ions in accordance with negative rejection of chloride (co-ion) only observed at VRR 3, balanced with monovalent cations. The negatively charged proteins at pH 6.6, acting as a dynamic membrane, were likely entrapped in a soft gel which was observed at the end of the run of dead-end filtrations. This gel was reversibly removed by a flush with tap water under pressure. Dead-end filtration appeared as a useful tool to show the relative content of permeate and the occurrence of a limiting flux upon concentration involving a gel formation. However, at end of run (VRR 3), COD concentrations in permeate (mainly due to lactose) were many times higher than the limiting value for human consumption water because of the high initial load of the effluent (COD ≈ 36 g/L). Water quality, close to vapor condensates issued from milk and whey drying steps, is needed for reuse in boiler feed; it should be likely reached with an RO + RO cascade or possibly with a single RO with a low charged feed.

3. MATERIALS AND METHODS

3.1. Materials

In this study, experiments were conducted by using two types of whey as feed for membrane modules and heating. These are white cheese whey and curd cheese whey. As explained in the previous section, whey, which is the byproduct of cheese manufacturing process, is produced in the coagulation process. Coagulation is brought about by physical and chemical modifications to the constituents of milk and leads to the separation of the solid part of milk (the curd) from the liquid part (the whey). To initiate coagulation, milk is mixed with a starter, which is a culture of harmless, active bacteria. The enzyme rennin is also used in coagulation. Most of the fat and protein from the milk are retained in the curd, but nearly all of the lactose and some of the minerals, protein, and vitamins escape into the whey.

The white cheese whey used in the experiments, obtained from Sutaş A.Ş. Karacabey, is the byproduct of white cheese with high fat content. 74,700 liters of white cheese whey is produced for 100,000 liters of milk used for every period of white cheese manufacture.

The curd cheese whey is produced after another heating step. Whey produced by manufacturing of kashkaval cheese undergoes a heating step up to 95^{o}C, in order to precipitate the protein content to be used as curd cheese. The wastewater remaining from this heat step is called the curd cheese whey. 90,900 liters of curd cheese whey is produced for 100,000 liters of milk used for every period of kashkaval cheese manufacture. After heating stage, 3,272 kg of curd is collected to be used as curd cheese and the remaining 92,148 kg is wastewater. The heating step is not applied for white cheese whey since it contains small amounts of protein, namely not worthy to recover. Characteristics of white cheese whey and curd cheese whey are presented in Table 3.1.

Table 3.1. Characteristics of curd cheese whey and white cheese whey.

	Curd Cheese Whey	**White Cheese Whey**
Fat Content (%)	0	0.2
COD (mg/L)	Approx. 100.000	Approx. 110.000
Protein (mg/L)	0.002	0.003
Lactose (mg/L)	0.047	0.048
Minerals (mg/L)	0.007	0.008

3.2 Methods

3.2.1 Membrane Processes

Membrane processes namely ultrafiltration, nanofiltration, and reverse osmosis were carried out with both curd cheese whey and white cheese whey samples. The schematic diagram of the membrane treatment system is shown in Figure 3.1. The system consists of a 200 L plastic feed tank, stainless-steel membrane housing (which is replaced by another in different applications), feed and recycling pumps, pressure indicators, and flow meters.

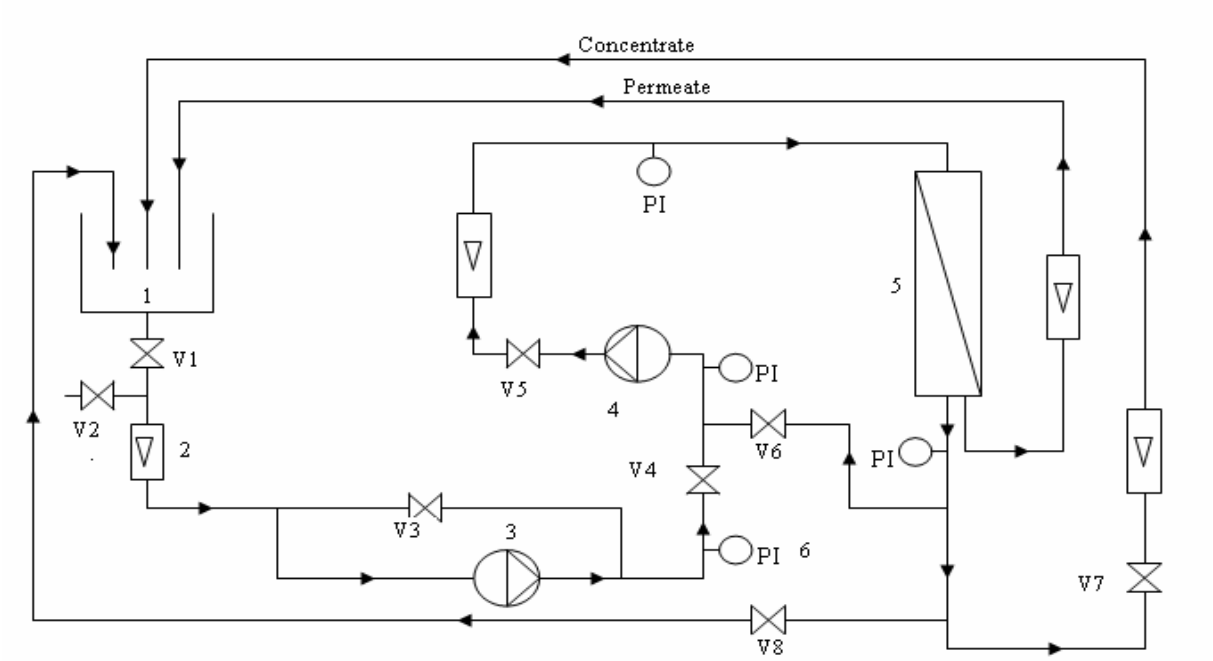

Figure 3.1. Schematic diagram of the experimental apparatus. 1 feed tank, 2 flowmeter, 3 feed pump, 4 recirculation pump, 5 membrane module, 6 manometer (Çaloğlu, 2003).

For each type of membrane application the membrane housing and the membrane module inside the housing is replaced and the experiment is conducted. The feed was pumped to membrane module by means of feed pump (3), which was the main pump that provides a high pressure to the system (WILO). V2 was an emergency valve to discharge the water in the tank. V3 and V4 were used to adjust the pressure of the feed pump (3). V3 was used for rough and V4 was used for fine adjustment of the inlet pressure. Pressure for feed pump was observed via pressure indicator (PI 1). V6 adjusted the inlet pressure of recirculation pump (4) and it was measured by pressure indicator (PI 2). Function of the recirculation pump was to create sufficient cross-flow velocity through the membrane surface for good permeation of the whey sample and to remove the deposited particles on the membrane to prevent fouling. Membrane inlet pressure was regulated by flow meter (F2). Membrane outlet pressure was set by V7 and monitored from pressure indicator (PI 4). The permeate was steadily removed and collected separately but the concentrate stream was recycled back to the feed tank in order to ensure maximum solute concentration. The fluxes of permeate and concentrate were measured with F3 and F4 flow meters. The transmembrane pressure is the driving force for permeate flux in the pressure-controlled region. The transmembrane pressure was adjusted by throttling the valve V7. Two pressure

gauges (PI 3 and PI 4) fitted at the inlet and outlet of membrane module were used to monitor system transmembrane pressure. The transmembrane pressure was calculated by the average value of inlet and outlet membrane pressure. The permeate flux was calculated by dividing the permeate volume by the product of effective membrane area and time.

The pure water fluxes of each membrane module were determined before experiments in order to have a reference value for flux. The deviation of pure water flux after the experiment gives a clear indication of membrane fouling and need for chemical cleaning. Simple sieving was applied for both white cheese whey and curd cheese whey before membrane treatment in order to remove coarse protein particles that would cause severe membrane fouling.

3.2.1.1. Membrane Modules. Three different nanofiltration modules, one ultrafiltration module, and two reverse osmosis modules were used during the experiments. The specifications of each module are given in Table 3.2., Table 3.3., and Table 3.4.

Table 3.2. Specifications for nanofiltration membrane modules.

	MODULE A	**MODULE B**	**MODULE C**
Membrane Type	NF	NF	NF
Manufacturer	NADIR Gmbh	NADIR Gmbh	Trisep Corp.
Commercial Name	SPIRA-CEL SS-NF-PES10 4233C	SPIRA-CEL SS-NF 30F 4233C	4040-XN45-TSF
Configuration	Spiral-Wound	Spiral-Wound	Spiral-Wound
Material	Polyethersulfone	Polyethersulfone	Polyamide-Urea
Membrane Area	5.5 m^2	5.5 m^2	7.5 m^2
Maximum Inlet Pressure	40 bar	40 bar	41 bar
Operating pH Range	2 – 11	2 – 11	3 – 11
Operating Temp. Range	5 – 55 ^{0}C	5 – 55 ^{0}C	2 – 45 ^{0}C
Module, Outer Diameter	108.5 mm	108.5 mm	102 mm
Module, Length	838 mm	838 mm	1,016 mm
Permeate Tube, Inner Diameter	21.05 mm	21.05 mm	19.1 mm

Table 3.3. Specifications for ultrafiltration membrane module.

	MODULE D
Membrane Type	UF
Manufacturer	NADIR Gmbh
Commercial Name	SPIRA-CEL DX-P020F-6338C
Configuration	Spiral-Wound
Material	Polyethersulfone
Membrane Area	14.4 m^2
Maximum Inlet Pressure	40 bar
Operating pH Range	3 – 14
Operating Temp. Range	5 – 80 ^{0}C
Module, Outer Diameter	161.5 mm
Module, Length	965 mm
Permeate Tube, Inner Diameter	28.9 mm

Table 3.4. Specifications for reverse osmosis membrane modules.

	MODULE E	**MODULE F**
Membrane Type	RO	RO
Manufacturer	TRISEP Corp.	TRISEP Corp.
Commercial Name	4040-ACM2-TSF	4040-X201-TSF
Configuration	Spiral-Wound	Spiral-Wound
Material	Polyamide-Urea	Polyamide-Urea
Membrane Area	7.5 m^2	7.5 m^2
Maximum Inlet Pressure	41 bar	41 bar
Operating pH Range	4 – 11	4 – 11
Operating Temp. Range	2 – 45 ^{0}C	2 – 45 ^{0}C
Module, Outer Diameter	102 mm	102 mm
Module, Length	1,016 mm	1,016 mm
Permeate Tube, Inner Diameter	19.1 mm	19.1 mm

3.2.1.2. Cleaning Procedure of Membrane Modules. Membranes were reused after each experiment with ensuring no fouling remained in the module and the module would act as a virgin membrane in each experiment. The generally proposed clean in place (CIP) step-by-step procedure for recovery of proteins in whey is used:

- The whole filtration system is drained immediately after the experiment by draining with tap water.

- The system is flushed with 30 – 50 ^{o}C tap water. The permeate and the concentrate is discharged until the concentrate stream is clear. Then the filtration system is drained again.
- Acidic cleaning was applied. 0.5 % of acidic cleaning chemical, Ultrasil 75 (manufactured by Henkel Corp.), is circulated in the system for 30 minutes at 40 – 55 ^{o}C.
- The system was drained and flushed with tap water for 10 minutes at 30 – 50 ^{o}C then drained again.
- Strong alkali cleaning was applied. 1 % of alkali cleaning chemical, Ultrasil 110 (manufactured by Henkel Corp.), is circulated in the system for 30 minutes at 40 – 55 ^{o}C.
- The system was drained and flushed with tap water for 10 minutes at 30 – 50 ^{o}C then drained again.
- Oxidizing cleaning (disinfection) was applied. 0.5 % of oxidizing chemical, Ultrasil 25 (manufactured by Henkel Corp., contains free chlorine), is circulated in the system for 30 minutes at 40 – 55 ^{o}C.
- The system was drained and flushed with tap water for 10 minutes at 30 – 50 ^{o}C then drained again.

The above procedure was applied for all membrane modules used in this study. The pure water fluxes of each module were measured after the cleaning procedure for comparison purpose.

3.2.2. Analytical Procedure

The effectiveness of all membrane processes were determined by measuring the permeate flux during the experiments, calculating the protein rejection and the COD removal of each membrane module.

The protein rejection of each module is calculated from the equation 2.4:

$$R = 100\ \% \ (1 - C_P / C)$$

where C and C_P are protein concentrations in the feed and permeate respectively.

3.2.2.1. COD Measurements. COD measurements were conducted closed reflux method (spectrofotometric) in accordance with Standard Methods of Water and Wastewater Analysis (APHA/AWWA/WPCF, 1994).

3.2.2.2. Protein Determination. Protein measurements were conducted by Kjeldahl Method in accordance with Standard Methods of Water and Wastewater Analysis. The total kjeldahl nitrogen of the samples were calculated by the formula:

$$TKN\ (mg/L) = [(A - B) * 280] / ml\ of\ sample \quad (3.1)$$

Where A is the ml of sulfuric acid used for titration and B is the ml of sulfuric acid used for blank.

Kjeldahl nitrogen value was than multiplied by coefficient (0.6) in order to calculate the protein fraction of total kjeldahl nitrogen (Kırdar, 2001).

3.2.2.3. Total Solids Determination. Total solid content were determined by gravimetric method, evaporating at 105^{o}C (APHA/AWWA/WPCF, 1994).

4. RESULTS AND DISCUSSION

4.1. One Stage Concentration Operations

As implied before, this study focuses on the feasibility of different membrane processes for treatment of dairy industry waste, whey, with special interest on COD removal and protein recovery for different possible uses. One stage operations, namely ultrafiltration, nanofiltration, and reverse osmosis are investigated in this section. Curd cheese whey and white cheese whey are treated by one type of ultrafiltration membrane module, three types of nanofiltration modules and two types of reverse osmosis module. The performance of each module is evaluated via the permeate flux ($L/m^2/h$), COD removal efficiency per cent and protein rejection per cent.

4.1.1. One Stage Concentration of Curd Cheese Whey and White Cheese Whey by Nanofiltration Module A

90 liters of pretreated curd cheese whey and white cheese whey was treated with the membrane module A separately as one stage operations. The operating TMP pressure for both experiments was 5 bar. This is a low operating pressure considering the maximum allowable pressure that this module can withstand (40 bar). The aim of applying low pressure is to see how this relatively open pore sized nanofiltration membrane behaved under low pressure operations and also achieving good results with low pressures is desirable from the economics point of view since high pressures requires high pump energy thus increased costs.

The recycle flow rate that creates the cross-flow of the whey through the membrane surface was 2,000 L/h. This parameter was always kept around this value in order to create sufficient cross-flow velocities thus retarding the deposition of protein and lactose on membrane surface, also the manufacturer recommends at least 2,000 L/h recirculation flow rate. As cross-flow velocity increases, concentration polarization decreases, hence the point of pressure independence advances to higher pressures (Kessler, 2002).

The experimental procedure was the same in all operations; the retentate stream was continuously fed back into the feed tank in order to achieve full concentration of proteins in curd cheese whey. Samples from permeate and retentate streams were taken at the end of each experiment. Changes in permeate flux and volume reduction ratio (VRR) with respect to time were investigated and presented in Figures 4.1 and 4.2. Permeate Flux ($L/m^2/h$)

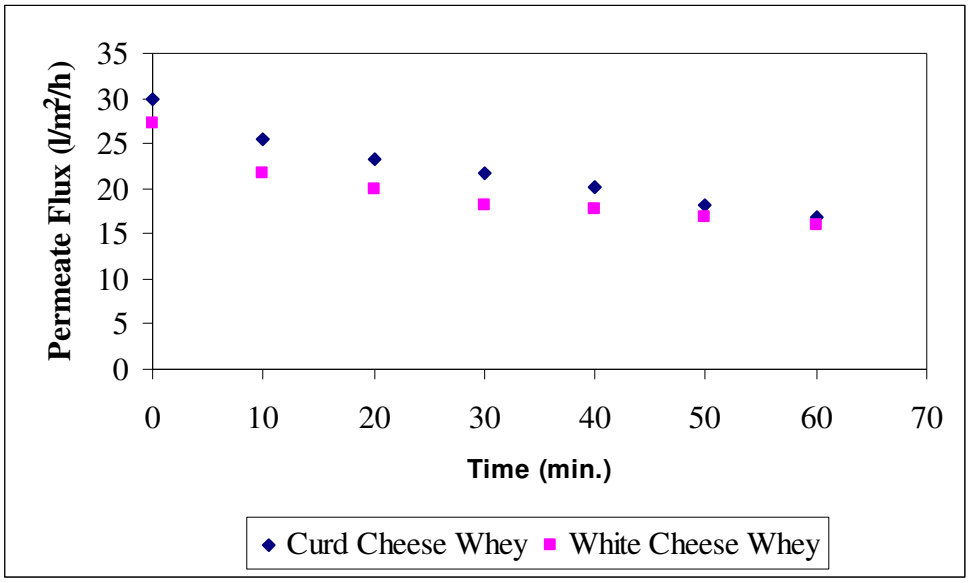

Figure 4.1. Permeate flux vs. time graph for nanofiltration module A. Feed = Curd and White cheese whey, TMP = 5 bar, recycle flow rate = 2,000 L/h.

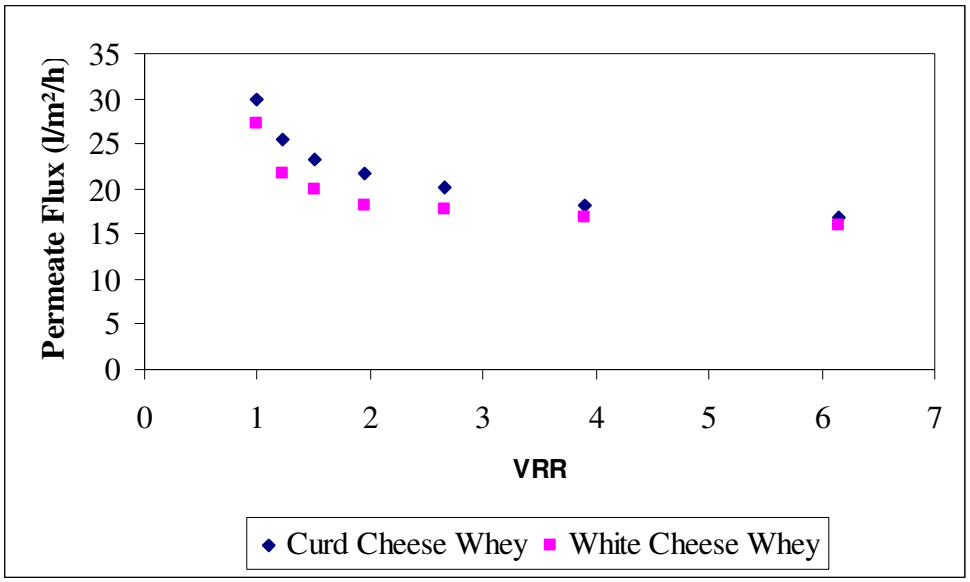

Figure 4.2. Permeate flux vs. VRR graph for nanofiltration module A. Feed = Curd and White cheese whey, TMP = 5 bar, recycle flow rate = 2,000 L/h.

As can be seen in Figure 4.1 the initial permeate flux for curd cheese whey was 30 L/m^2/h. The permeate flux dropped to 17 L/m^2/h with a mild decline. This decline in the permeate flux is well expected due to the gel layer formation on the membrane surface as the feed concentration increase and deposition occurs. For pressure-driven processes, the greater the flux, the greater the build-up of the solute at the interface; the greater the solute build-up, the higher the concentration gradient; the steeper the concentration gradient, the faster the diffusion. Under normal steady-state operating conditions there is a balance between those forces transporting the water and constituents within it towards, through and away from the membrane. This balance is determined by concentration polarization. CP also raises the effect of osmotic pressure at the membrane-solution interface, increasing the required transmembrane pressure for operation. It is thus always desirable to suppress CP by promoting turbulence and/or operating at a flux below that at which CP starts to be significant (Judd and Jefferson, 2003).

The limiting flux could not be reached since the 90 liters sample of curd cheese whey was finished however it is expected to be around 17 L/m^2/h due the slope of the curve seen in Figure 4.1. In the experiment conducted using the feed stream as the white cheese whey, the module showed the same reaction when examining the permeate flux values except that the starting permeate flux was a little bit lower (27 L/m^2/h) than that of the experiment

conducted with curd cheese whey. This is due to higher fat content in white cheese whey than in curd cheese whey. The decline in the flux was similar to that of curd cheese whey. The last data collected for permeate flux was 16 $L/m^2/h$. It is clearly seen in Figure 4.1 that the flux values approached the same value both for white cheese whey and curd cheese whey.

Figure 4.2 provides useful data for optimum operating conditions for module A with respect to VRR. In both experiments, the VRR of 6.2 was reached in a very short time (40 minutes) without any indication of membrane fouling, namely a critical drop in permeate flux. The permeate flux values shows a steep decline while concentrating whey 2 times of its original concentration. Further concentration of whey did not affect the permeate flux as much. This parameter could be chosen due to the desired protein and lactose content in the final retentate.

Protein rejection of this membrane module for curd cheese whey was 87 % and for white cheese whey was 83 % at VRR = 6.2. However the COD removal efficiency of the module was far from satisfactory which is only 58 % for curd cheese whey producing a permeate stream with COD value of 43,568 mg O_2/L. For white cheese whey the COD removal efficiency was even lower (53 %) producing a permeate stream with COD value of 13,568 mg O_2/L. These are unexpected results regarding the typical COD values of nanofiltration permeate which is generally 3,000-4,000 mg O_2/L. The COD values of the permeate stream of nanofiltration module A are typical ultrafiltration permeate values which generally have a biological oxygen demand (BOD) of 30,000–45,000 mg O_2/L (Qureshi and Manderson, 1995). The high COD value of the permeate stream can be attributed to the high lactose content in it (the yellowish color of the permeate is another evidence of high lactose concentration.). From this point of view nanofiltration module A rather behaved as an ultrafiltration module treating both curd cheese whey and white cheese whey under the above mentioned operating conditions.

4.1.2. One Stage Concentration of Curd Cheese Whey and White Cheese Whey by Nanofiltration Module B

65 litres of pretreated curd cheese whey and white cheese whey is treated with the nanofiltration membrane module B. The operating transmembrane pressure was 8 bar. This is again a low operating pressure considering the maximum allowable pressure that this module can withstand (40 bar) but as can be seen in the specifications of both modules A and B this membrane has smaller pore size thus higher rejection. In this manner, lower permeate fluxes would be expected with the same influent whey. Higher operation transmembrane pressure is chosen to compensate this effect and to investigate the effect of higher pressure on whey concentration.

The recycle flow rate that creates the cross-flow of the whey through the membrane surface was again adjusted to a higher level namely 2,500 L/h.

The retentate stream was continuously fed back into the feed tank in order to achieve full concentration of proteins in curd cheese whey. Samples from permeate and retentate streams were taken at the end of each experiment. Variation of permeate flux and volume reduction ratio with respect to time can be seen in Figures 4.3 and 4.4.

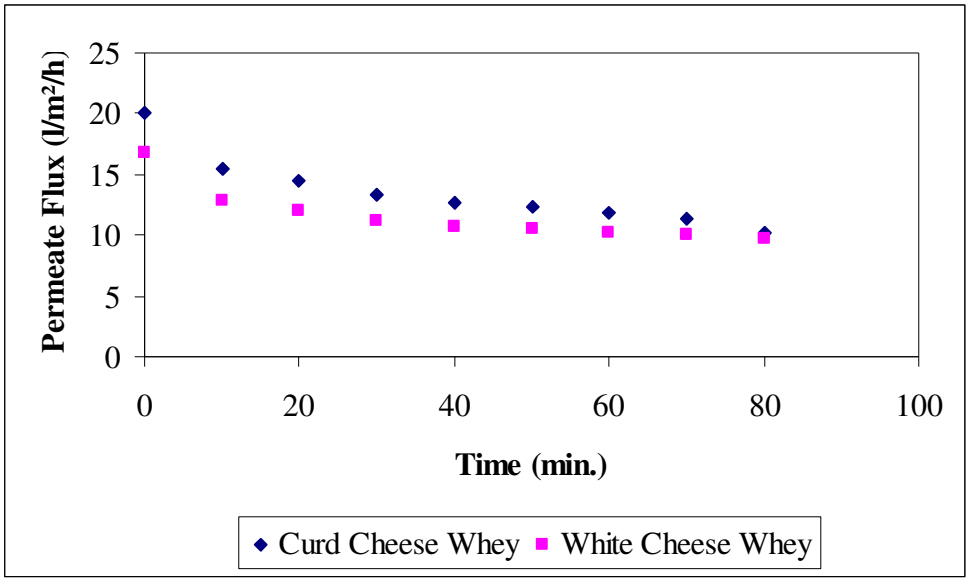

Figure 4.3. Permeate flux vs. time graph for nanofiltration module B. Feed = Curd cheese whey and white cheese whey, TMP = 8 bar, recycle flow rate = 2,500 L/h.

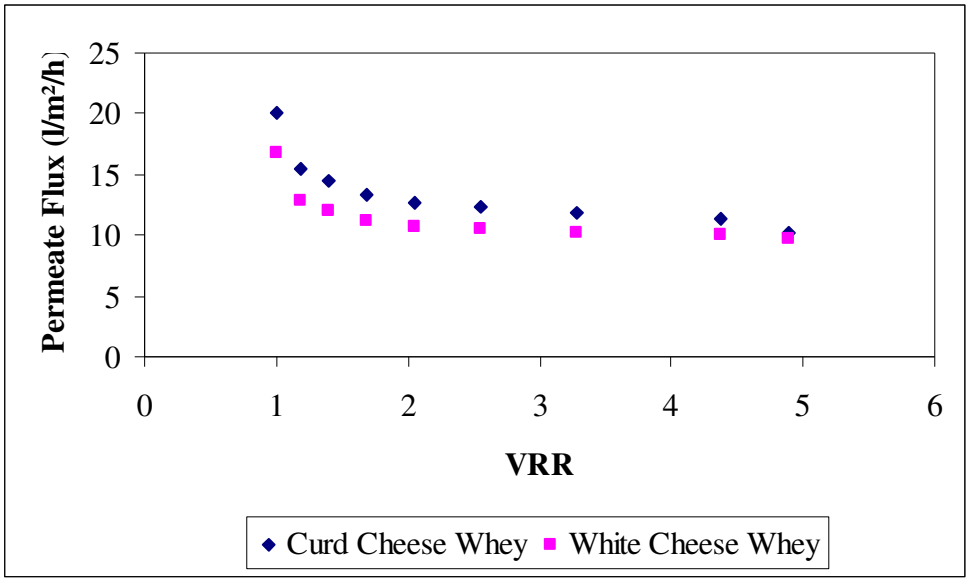

Figure 4.4. Permeate flux vs. VRR graph for nanofiltration module B. Feed = Curd cheese whey and white cheese whey, TMP = 8 bar, recycle flow rate = 2,500 L/h.

As can be seen in Figure 4.3 the initial permeate flux was 20 L/m^2/h which is very low when compared to that of nanofiltration module A although a higher transmembrane pressure was applied. This is due to the smaller pore size of module B. The permeate flux dropped to 10.12 L/m^2/h with a mild decline. In the case when the feed was white cheese whey, the initial permeate flux was 16.7 L/m^2/h which then dropped to 9.75 L/m^2/h. The same outcome was observed again such as the difference between the permeate flux values at the beginning of the experiments were decreased at the end of the experiments conducted with two different whey types. The limiting flux could not be reached again since the 65 liters sample of whey was finished. In the 80th minute of the experiment, the permeate flux showed a steeper decline when compared to previous data. This is an indication of a thicker gel layer on the membrane surface retarding the flow through the membrane. Water flux decreases as the salinity of the feed increases because of increased osmotic pressure differential resulting from increased salinity. As increasing amounts of water pass through the membrane system, the salinity of the remaining feed water (concentrate) increases. Concentrate osmotic pressure increases, resulting in a lower water flux with increasing overall percent water recovery. Finally, because salinity of the feed-concentrate stream increases with increasing permeate production from a given volume of feed, and the membrane rejects a fixed percentage of solute, product water quality

decreases (higher concentration) with increasing recovery (Judd and Jefferson, 2003). From this point on the recycle-flow rate should be increased to achieve better scouring of deposited particles on the membrane surface.

As can be seen in Figure 4.4 a lower VRR (4.8) was reached in a long time (80 minutes) in both experiments with curd cheese whey and white cheese whey, when compared to module A. The permeate flux values shows a steep decline before concentrating whey 1.5 times of its original concentration.

Due to its relatively low permeate flux and high fouling potential observed during the experiment, nanofiltration module B was expected to create higher protein rejection and COD removal efficiency however the results were not so. In the experiment with curd cheese whey as the feed, protein rejection of this membrane module was 83 % at VRR = 4.8. The COD removal efficiency of the module was just a little better from that of module A, 62 % producing a permeate stream with COD value of 37,648 mg O_2/L. In the experiment with white cheese whey as the feed, the protein rejection was nearly the same, 81 % at VRR 4.8. The COD removal efficiency was again lower (%54) producing a permeate stream with COD value of 14,628 mg O_2/L.

The high COD value of the permeate stream can be attributed to the high lactose content in it (the observed yellowish color of the permeate is another evidence of high lactose concentration.). As a result module B again behaved as an ultrafiltration membrane with disadvantages when compared to nanofiltration module A.

4.1.3. One Stage Concentration of Curd Cheese Whey and White Cheese Whey by Nanofiltration Module C

As described in the materials and methods section, nanofiltration module C is manufactured by TRISEP Corp. Unlike modules A an B which are manufactured by NADIR Gmbh. and specifically suggested for dairy applications, module C is offered for a wide variety of applications. The membrane material in this module is polyamide-urea which shows less fouling characteristics. In this manner one stage operation with module C

would provide useful information about the behavior of different membrane materials, namely polyamide-urea and polyethersulfone, when treating two different types of whey.

55 litres of pretreated curd cheese whey and white cheese whey is treated with the nanofiltration membrane module C. The operating transmembrane pressure was 8 bar. The recycle flow rate that creates the cross-flow of was 2,000 L/h.

The experimental procedure was the same as previous one stage operations. Figures 4.5 and 4.6 shows the changes in operational parameters during the experiments conducted with curd cheese whey and white cheese whey.

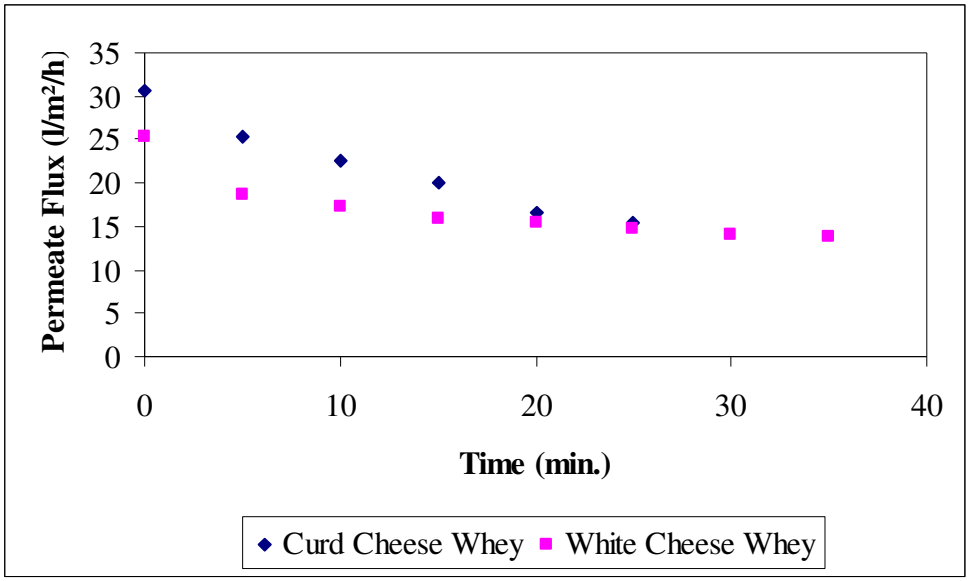

Figure 4.5. Permeate flux vs. time graph for nanofiltration module C. Feed = Curd cheese whey and white cheese whey, TMP = 8 bar, recycle flow rate = 2,000 L/h.

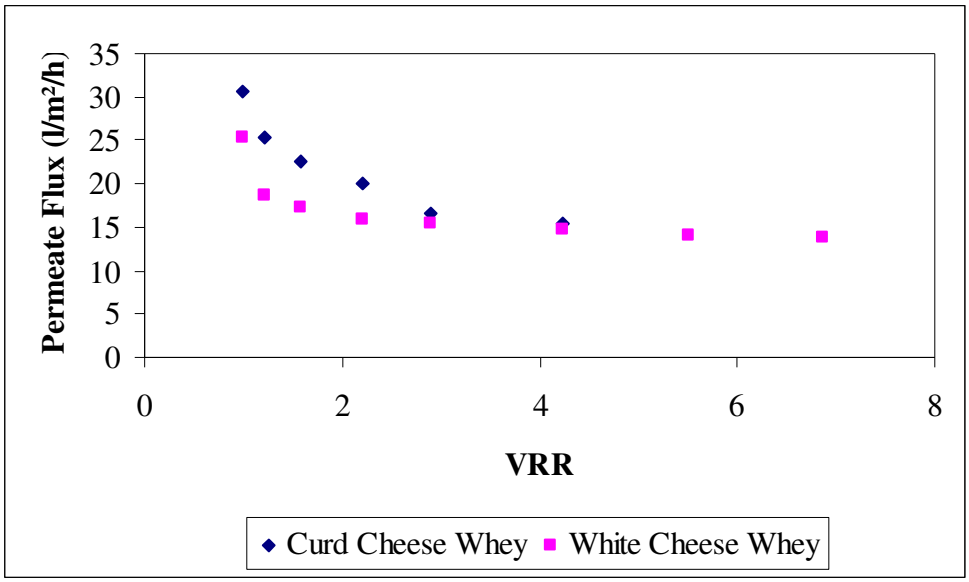

Figure 4.6. Permeate flux vs. VRR graph for nanofiltration module C. Feed = Curd cheese whey and white cheese whey, TMP = 8 bar, recycle flow rate = 2,000 L/h.

As can be seen in Figure 4.5, the same permeate flux values are obtained with nanofiltration module C when compared to the experiments conducted with nanofiltration module B. This comparison can only be made with module B since the experiment conditions were the same. The initial permeate flux when treating curd cheese whey was 30.8 L/m^2/h. The permeate flux values, as observed in the experiments with modules A and B, were lower when treating white cheese whey. The initial value was 25.6 L/m^2/h. The last permeate flux values were 15 L/m^2/h for both experiments.

Higher volume reduction ratios within a shorter time period were achieved with this module in comparison with modules A and B. The VRR at the end of both experiments with curd cheese whey and white cheese whey were 6.8. Both experiments took 35 minutes for completion.

The COD removal efficiencies were again low. The experiment with curd cheese whey produced a permeate stream with COD value of 23,502 mg O_2/L with removal efficiency of 77 %. These parameters were 35,965 mg O_2/L and 65 % respectively when the feed was white cheese whey. Even low, nanofiltration module C produced better results than modules A and B in terms of COD removal. The protein rejection of module C was

slightly higher with 88 % in both experiments with white cheese whey and curd cheese whey.

4.1.4. Concentration of Curd Cheese Whey by Ultrafiltration Module D

Ultrafiltration of whey mainly aims the concentration of the protein content in whey. Previous experiments in this study mainly focused on protein and lactose rejection with applying nanofiltration to curd and white cheese whey thus producing cleaner effluent. However, as implied in previous sections, all three nanofiltration modules failed to reject lactose and produced permeate streams with high COD value that can not be discharged to receiving environments without further treatment.

In this experiment an ultrafiltration module (module D) is used for comparison with the performances of modules A, B, and C. Module D is manufactured by NADIR Gmbh., the manufacturer of modules A and B. The membrane material is permanently hydrophilic Polyethersulfone with a nominal MWCO (molecular weight cut-off) of 20 kDa. The product specifications imply that protein rejection of this membrane module should be bigger than 97 %. This value is set regarding a test of the membrane with a feed solution containing 0.05 % β - Lactoglobulin, a whey protein with molecular weight of 36,560 Da. The TMP value was 3 bar in the test. The ultrafiltration module D has larger membrane are (14.4 m^2) when compared to modules A, B, and C which have 5.5 m^2 of membrane area.

In the experiment 55 litres of pretreated curd cheese was treated with the ultrafiltration membrane module D. The operating transmembrane pressure was 3 bar. This value was set lower than that of the experiments conducted with nanofiltration modules. This was made in order to achieve comparison with the test conditions implied by the manufacturer. The general operating TMP values for ultrafiltration for various applications are given as 140-520 kPa (1.4-5.2 bar) (Judd and Jefferson, 2003). The recycle flow rate was set to the value of 2,000 L/h. This parameter was not kept low as done with the TMP value in order to ensure good scouring of the protein molecules deposited on membrane surface.

The retentate stream was continuously fed back into the feed tank in order to achieve full concentration of proteins in whey. Samples from permeate and retentate streams were taken at the end of each experiment. Changes in permeate flux and volume reduction ratio with respect to time were investigated and presented in Figures 4.7 and 4.8.

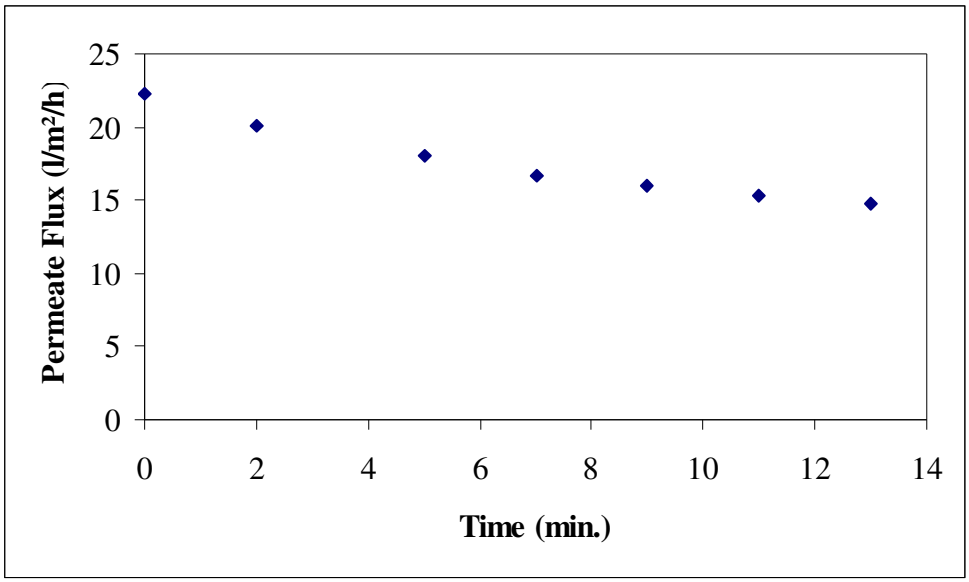

Figure 4.7. Permeate flux vs. time graph for ultrafiltraion module D. Feed = Curd cheese whey, TMP = 3 bar, recycle flow rate = 2,000 L/h.

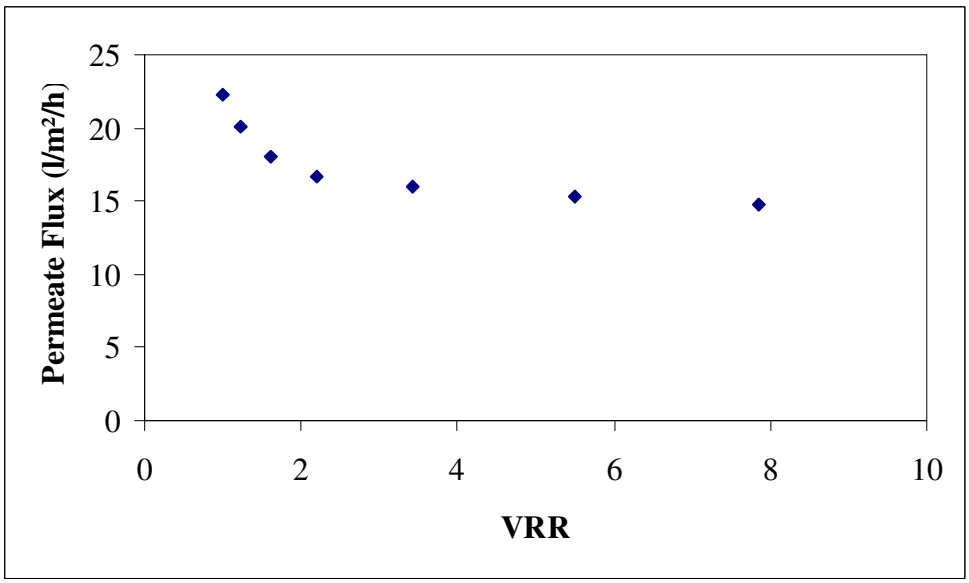

Figure 4.8. Permeate flux vs. VRR graph for ultrafiltraion module D. Feed = Curd cheese whey, TMP = 3 bar, recycle flow rate = 2,000 L/h.

The experiment with module D produced very high overall permeate flux values due to its larger membrane area. (320 L/h initial permeate flux). But this permeate flux values, when calculated per unit area of the membrane, were smaller compared to nanofiltration modules. As can be seen in Figure 4.7 the initial permeate flux value appears to be 22.2 $L/m^2/h$. This can be attributed to the lower operating TMP value. However this is not the indication of low performance of module D since it produces large volumes of permeates due to its larger area and capacity. 55 liters of curd whey was finished immediately in 13 minutes with no signs of protein fouling (the last recorded value of permeate flux at the end of the experiment was 14.7 $L/m^2/h$). The difference between the initial and the final permeate flux values is low and there is a mild decline throughout the experiment as seen in Figure 4.7. No limiting flux was reached.

The same conclusion can be reached by examining Figure 4.8. No critical drop of permeate flux between VRR values of 1 and 2 is observed. A high VRR value of 7.8 is reached in a very short period of time namely 13 minutes.

The COD removal efficiency of the ultrafiltration module D was low as expected. The module produced a permeate stream with COD value of 54,331 mg O_2/L with removal efficiency of 42 %. The protein rejection of this module appeared to be 78 %. This value is slightly smaller when compared to the rejections of nanofiltration modules A, B, and C since pore size of module D is higher than the nanofiltration modules.

4.1.5. Concentration of Curd Cheese Whey by Reverse Osmosis Module E

As the main scope of this study is to investigate the concentration of whey by one-stage and cascade operations of mainly nanofiltration and other processes like ultrafiltration and reverse osmosis, one-stage operation of reverse osmosis is carried out to have an idea about the behavior of the reverse osmosis membrane module when a high concentrated wastewater such as whey, without any intensive pre-treatment, is the influent. RO is usually employed as a polishing step after UF or NF to further remove COD in order to produce high quality water that can be reused (Balannec *et al*., 2005).

90 litres of pretreated curd cheese whey is treated with the reverse osmosis membrane module E. The operating transmembrane pressure was 12 bar. This value is especially adjusted since RO modules require high pressures due to their very small pore sizes but 12 bar is a low operating pressure considering the maximum allowable pressure that this module can withstand (40 bar). Low pressure is applied since, when treating problematic (highly concentrated) wastewaters such as whey, the gel layer that is responsible for concentration polarization is highly concentrated consequently and when the inlet pressure is high this layer get even denser thus quickly fouling the membrane (Judd and Jefferson, 2003). Considering the module being a reverse osmosis module, fouling would be expected to occur most quickly and severely. Also as mentioned in the previous sections, achieving good results with low pressures is desirable from the economics point of view since high pressures requires high pump energy thus increased costs.

The recycle flow rate that creates the cross-flow of the whey through the membrane surface was 3,000 L/h. This parameter was kept high to efficiently scour particles through the membrane surface. Variation of permeate flux and volume reduction ratio with respect to time can be seen in Figures 4.9 and 4.10.

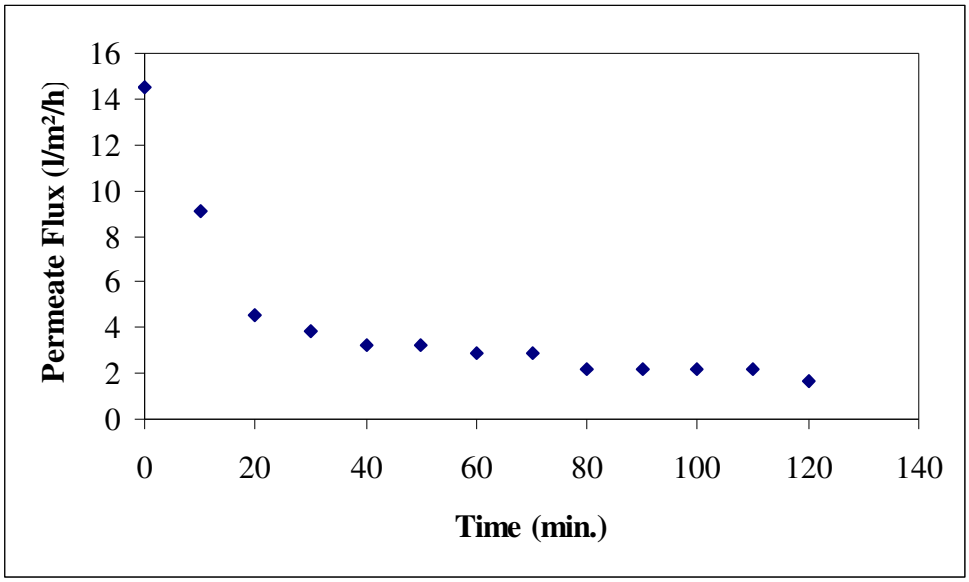

Figure 4.9. Permeate flux vs. time graph for reverse osmosis module E. Feed = Curd cheese whey, TMP = 12 bar, recycle flow rate = 3,000 L/h.

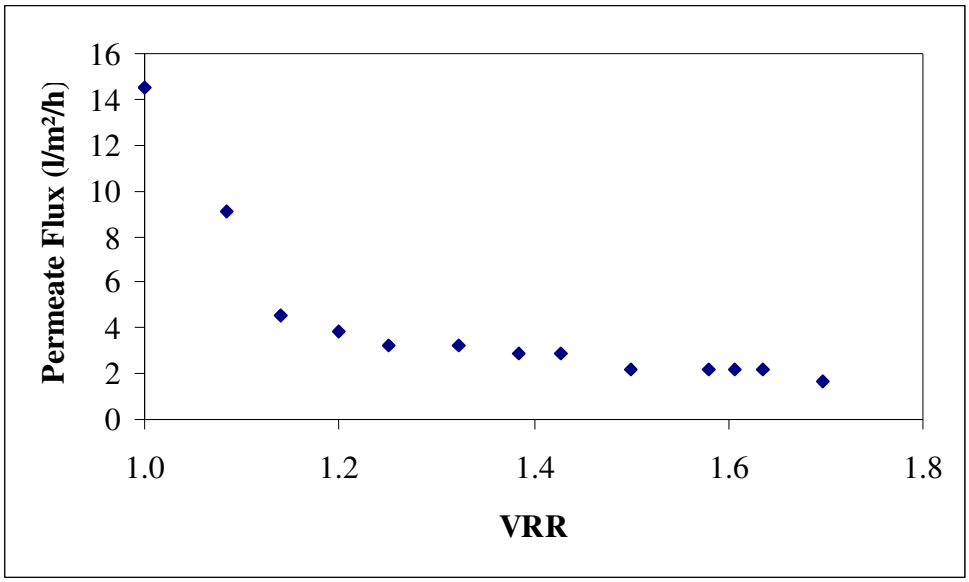

Figure 4.10. Permeate flux vs. VRR graph for reverse osmosis module E. Feed = Curd cheese whey, TMP = 12 bar, recycle flow rate = 3,000 L/h.

As can be seen in Figure 4.9 the initial permeate flux was 14 L/m^2/h which is a very low value. The permeate flux dropped to 1.6 L/m^2/h with a very sharp decline in the first 20 minutes. From this point on the permeate flux began to decrease very slowly. This phenomenon shows that the membrane is quickly fouled in the first 20 minutes and due to the gel layer formed during this time, the permeate flux decreased from 14 L/m^2/h to 4.55 L/m^2/h. The drop from 4.55 L/m^2/h to 1.6 L/m^2/h took 100 minutes and no significant effect of VRR has been observed on the permeate flux. This tells that the limiting flux of the membrane was reached where no effect of VRR of transmembrane pressure exists on the permeate flux due to the stiff layer formed on the membrane surface (Field *et al*., 1995).

VRR reached by reverse osmosis module E was very poor (1.7). Even two folds of volume reduction could not be reached. As can be seen in Figure 4.10 VRR of 1.7 was reached in a long time (120 minutes) because of severe membrane fouling. The permeate flux values shows a steep decline while concentrating whey 1.2 times of its original concentration. Further concentration of whey did not affect the permeate flux as much.

Protein rejection of this membrane module was very good, 94 % at VRR = 1.7, as expected. The COD removal efficiency of the module was again very good. The COD

removal efficiency achieved with reverse osmosis module E was 92 % producing a permeate stream with COD value of 3,847 mg O_2/L. This COD value does not comply with usual RO effluent values. Typical COD values of reverse osmosis permeate is generally 500-1,000 mg O_2/L (Qureshi and Manderson, 1995). The permeate stream was clear without any indication of lactose content.

Regarding the protein rejection and COD removal efficiency, reverse osmosis module E seems best fit among other modules tested with curd cheese whey. But operation parameters such as permeate flux and volume reduction ratio were very low so this module is not suitable for full scale applications. No more one-stage operations were conducted with module E.

4.2. Cascade Concentration Operations

According to the results of one stage operation experiments presented in the previous chapter, it is clear that one stage operations of membrane processes for full scale whey concentration does not fulfill the objectives such as sufficient permeate flux and COD removal efficiency together. In this section cascade operations are investigated. Permeate streams of any stage is subjected to another membrane operation to increase the COD removal efficiency and protein recovery. The most suitable sequence of operations for full scale application is investigated. The results are presented in the following sections.

4.2.1. NF + RO Treatment of Curd Cheese Whey

In this two stage operation, nanofiltration membrane module A is chosen as the first stage. As can be seen in the one stage operation, this module behaved as an ultrafiltration module rather than nanofiltration. As ultrafiltration is one of the well accepted processes for protein recovery and pretreatment for cleaner discharge (Brans *et al*., 2004) module A is selected as the first step before reverse osmosis. The permeate stream of module A is subjected to reverse osmosis module E. Since the permeate stream of module A would have very low protein content thus reduced organic load, performance of module E was expected to be higher namely, permeate flux would be higher while producing a permeate

stream very low in COD content. Recovery by module E was also investigated since the permeate stream of module A still included a small fraction of protein content.

One stage operation of nanofiltration module A produced 65 liters of permeate (see section 4.1.1.). The experiment with reverse osmosis module E was conducted with this permeate as the feed water. The operating transmembrane pressure (8 bar) and the recycle flow rate (2,000 l/h) were kept low compared to the one stage operation with the same module since influent water is much less loaded so low pump energy would create a more economically feasible situation. The results are presented in Figure 4.11 and Figure 4.12.

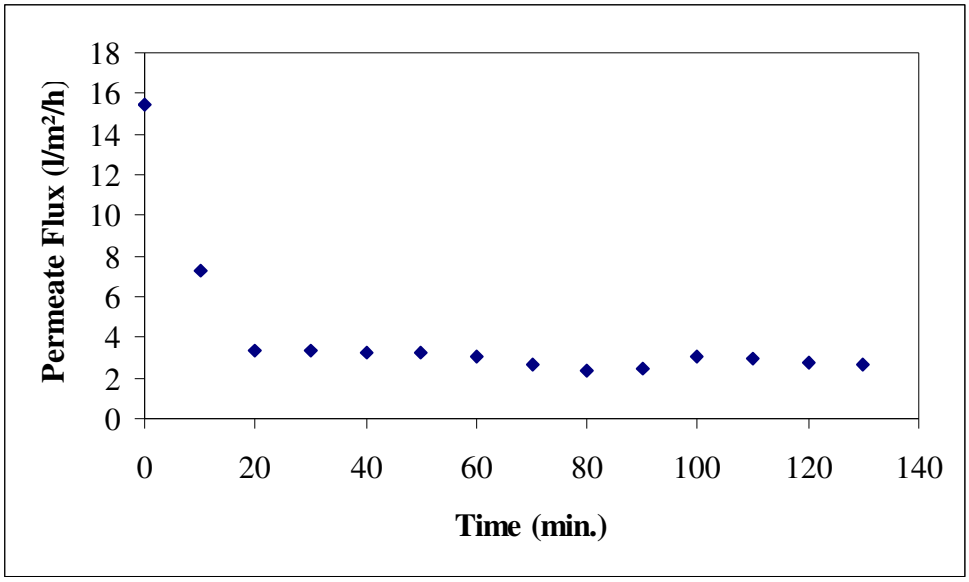

Figure 4.11. Permeate flux vs. time graph for reverse osmosis module E. Feed = Permeate Stream of nanofiltration module A, TMP = 8 bar, recycle flow rate = 2,000 L/h.

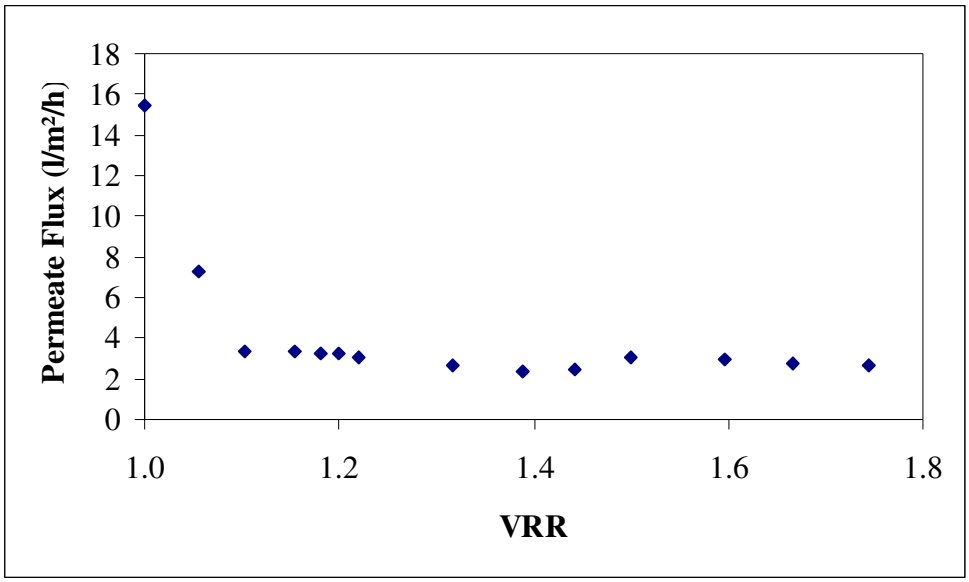

Figure 4.12. Permeate flux vs. VRR graph for reverse osmosis module E. Feed = Permeate Stream of nanofiltration module A, TMP = 8 bar, recycle flow rate = 2,000 L/h.

As can be seen in Figure 4.11, the initial permeate flux is 15.45 L/m^2/h which is nearly the same as that of the one stage operation with the same module. The permeate flux shows a steep decline in first 20 minutes however, the values does not change at all until the end of the experiment. The last permeate flux value recorded was 2.69 L/m^2/h which can be accepted as the limiting flux for this experiment since no significant flux change has occurred. The reverse osmosis module E produced nearly the same results as in the one stage operation experiment. This can be attributed to high lactose concentration in the influent stream since no other significant solute concentration was present. Adjusting the operating parameters such as TMP and recycle flow rate would not be the remedy of this situation since higher TMP would cause the gel layer formed by lactose to be more concentrated on the membrane surface (Field *et al.*, 1995). Recycle flow rate should be adjusted to a very high level to overcome this situation however this would cause increased energy consumption that would make this operation economically unfeasible. It is clear that the influent stream of reverse osmosis module E should be low in both protein and lactose content and must be employed only for further COD removal, not concentration purposes.

Again a very poor VRR ratio was reached at the end of the experiment (1.75). This is another indication of the ineffectiveness of this module as the following of one stage nanofiltration. The experiment took a very long time reaching this low VRR value.

The COD removal efficiency of module E was high, 94%, as expected. The COD value of the permeate of this second stage was 2,450 mg O_2/L.

4.2.2. NF + NF + RO Treatment of White Cheese Whey

In this experiment, relatively high loaded influent white cheese whey is treated with a three stage operation. Nanofiltration module A is chosen as the first stage again since this module has the most open pores among the other nanofiltration membranes. Second stage that received the permeate stream of module A was nanofiltration module B. Module B, like module A, behaved as an ultrafiltration module in one stage operations however due to the results in experiments conducted with this module and its specifications, it has smaller pores that would further clean the permeate of module A. Also conditions where a cleaner feed stream is fed to module B were investigated. The permeate stream of module B was subjected to further treatment by reverse osmosis module E to see how module E acts when treating a stream that has undergone two stages of ultrafiltration.

One stage operation of nanofiltration module A with white cheese whey produced 65 liters of permeate. The second stage experiment with nanofiltration module B was conducted with this permeate as the feed water. The operating TMP (8 bar) and the recycle flow rate (2,000 L/h) were kept the same compared to the one stage operation to see how the module reacts to these conditions with a cleaner feed stream. The results are presented in Figure 4.13 and Figure 4.14.

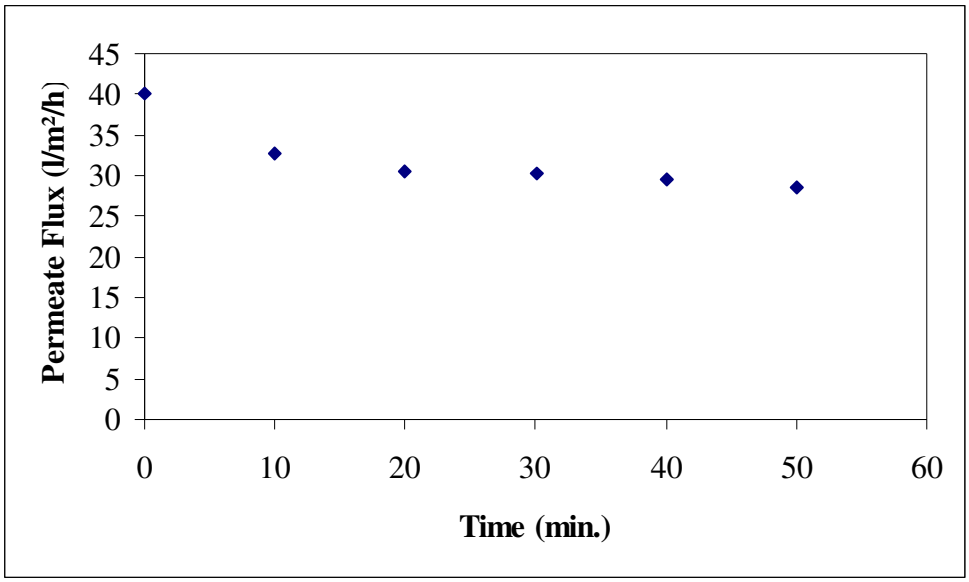

Figure 4.13. Permeate flux vs. time graph for nanofiltration module B. Feed = Permeate Stream of nanofiltration module A, TMP = 8 bar, recycle flow rate = 2,000 L/h.

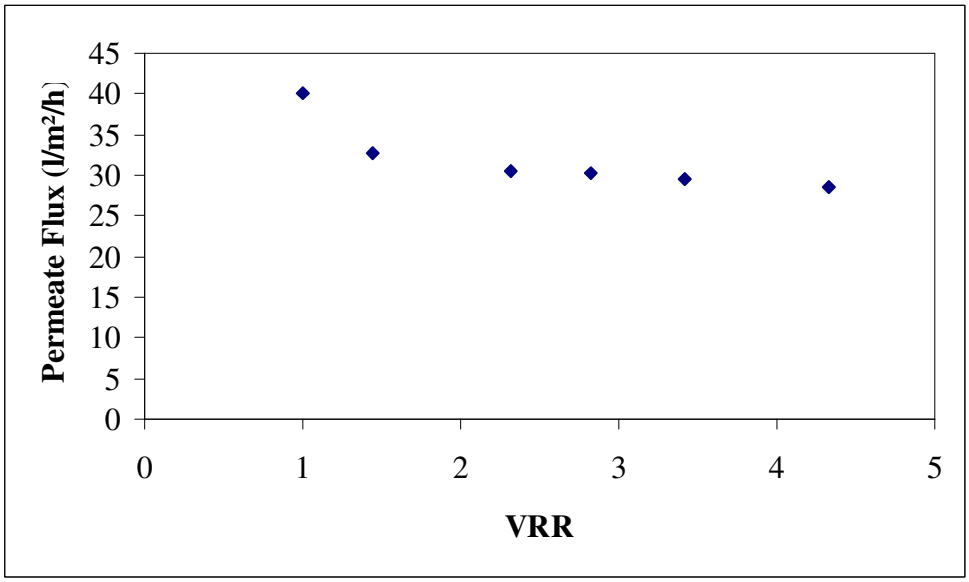

Figure 4.14. Permeate flux vs. VRR graph for nanofiltration module B. Feed = Permeate Stream of nanofiltration module A, TMP = 8 bar, recycle flow rate = 2,000 L/h.

As can be seen in Figure 4.13, the initial permeate flux for module B is 40 L/m^2/h which is a significantly higher value when compared to the value obtained in the one stage

experiment with same module treating white cheese way. This is a very reasonable increase since most of the protein content in the white cheese whey is removed by nanofiltration module A in the first stage. The problematic fat content of the white cheese whey is also removed by module A, producing a clean permeate for a second stage ultrafiltration. When the feed water is finished, the permeate flux was dropped to 28.55 $L/m^2/h$. This small decline is the indication of a thin gel layer of lactose and a small portion of protein formed on the membrane surface that does not retard the water flow cross the membrane.

Figure 4.14 gives good information from VRR point of view. No sharp decline in permeate flux is observed from VRR 1 to 2. That means no sign of fouling occurred on the membrane surface of module B.

The operating parameters of this stage were very promising for an economical full scale application regarding the previous studies (Atra *et al*., 1995; Balannec *et al*., 2005) however the important parameters for this second stage of nanofiltration are COD removal efficiency and rejection of remaining protein and lactose from the first stage. The COD removal efficiency for this second stage of nanofiltration was only 30 % and the protein rejection was 31 %. These values mean that only the remaining protein content from the first stage was held by module B and a significant portion of lactose again passed to the permeate stream. The COD value of the permeate stream of this second stage was 9.400 mg O_2/L.

The permeate stream of this second stage is then treated with reverse osmosis module E. The operating transmembrane pressure (8 bar) and the recycle flow rate (2,000 L/h) were kept the same compared to the two stage NF + RO operation to see how the module reacts to these conditions with a cleaner feed stream which have undergone two stages of nanofiltration. The results are presented in Figure 4.15 and Figure 4.16.

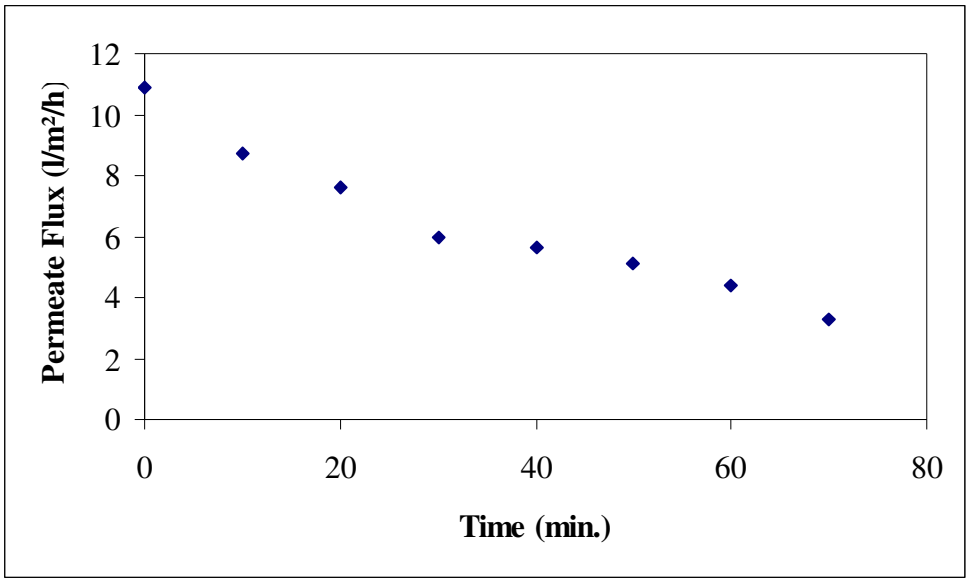

Figure 4.15. Permeate flux vs. time graph for reverse osmosis module E. Feed = Permeate Stream of nanofiltration module B, TMP = 8 bar, recycle flow rate = 2,000 L/h.

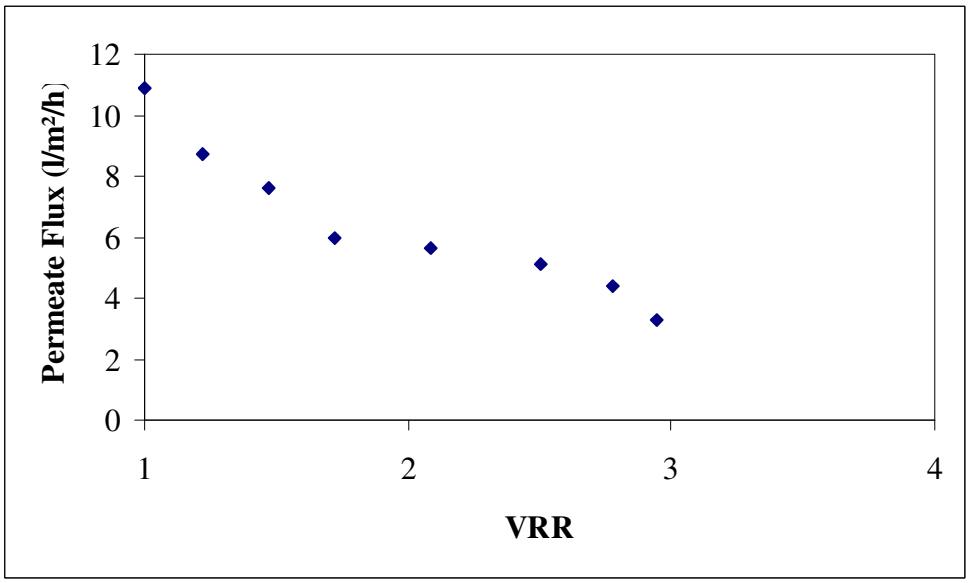

Figure 4.16. Permeate flux vs. VRR graph for reverse osmosis module E. Feed = Permeate Stream of nanofiltration module B, TMP = 8 bar, recycle flow rate = 2,000 L/h.

In the beginning of the experiment, the module produced a lower permeate flux (10.9 $L/m^2/h$) than that of the flux produced by the same module in the two stage operation (15.4 $L/m^2/h$). This is an unexpected value since the feed stream is cleaner in this experiment.

This result can be attributed to some fouling due to lactose has occurred in the reverse osmosis module E and the higher fat content of the white cheese whey. As can be seen in Figure 4.15 the behavior of the permeate flux throughout the experiment is quite different when compared to the two stage operation. The flux decline is not sharp; instead, it shows a mild decline. The module has not fouled in the beginning of the experiment and the permeate flux dropped to 2.94 L/m^2/h at the end of the experiment.

The same outcome can be observed in Figure 4.16. A higher VRR value of 2.9 is reached in a relatively short time (70 minutes) compared to the results produced by the same module in the two stage operations. Again no sharp decline in permeate flux between VRR 1 and 2 is observed. These results show that the two stages of nanofiltration before treatment with reverse osmosis module E created a feed stream easier to be handled by module E. The operating parameters were more satisfactory compared to the two stage operation.

As described in the second nanofiltration stage, the influent COD was 9,400 mg O_2/L. This parameter was dropped to 3,323 mg O_2/L by this third stage of reverse osmosis module E with COD removal of 64 %. So this stream can be easily treated with conventional biological treatment.

4.3.3. UF + NF Treatment of White Cheese Whey

In this two stage operation, ultrafiltration membrane module D is chosen as the first stage. Ultrafiltration for the purpose of protein recovery followed by nanofiltration or reverse osmosis for COD removal is one of the well accepted cascade operations for whey treatment (Brans *et al*., 2004). UF + NF operation is investigated from the point of protein recovery efficiency and COD removal with ultrafiltration module D followed by nanofiltration module C. The permeate stream of module D is subjected to module C.

One stage operation of ultrafiltration module D produced 50 liters of permeate. The experiment with nanofiltration module C was conducted with this permeate as the feed water. The operating transmembrane pressure (8 bar) and the recycle flow rate (2,000 L/h) were kept the same compared to the one stage operation with the same module since

influent water is the UF permeate which is less loaded in terms of protein content but it still contains some amount of protein and high COD load (54,331 mg O_2/L). The results are presented in Figure 4.17 and Figure 4.18.

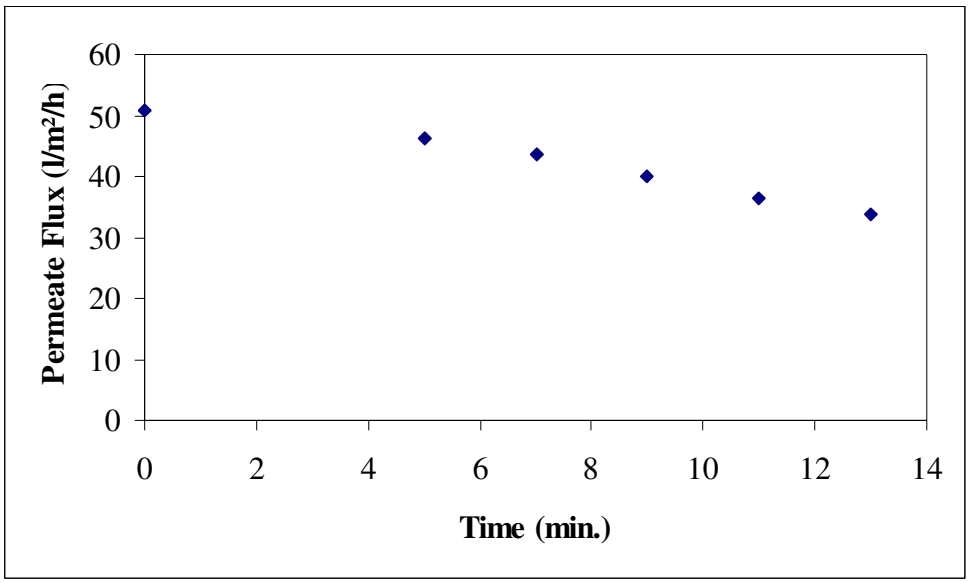

Figure 4.17. Permeate flux vs. time graph for nanofiltration module C. Feed = Permeate Stream of ultrafiltration module D, TMP = 8 bar, recycle flow rate = 2,000 L/h.

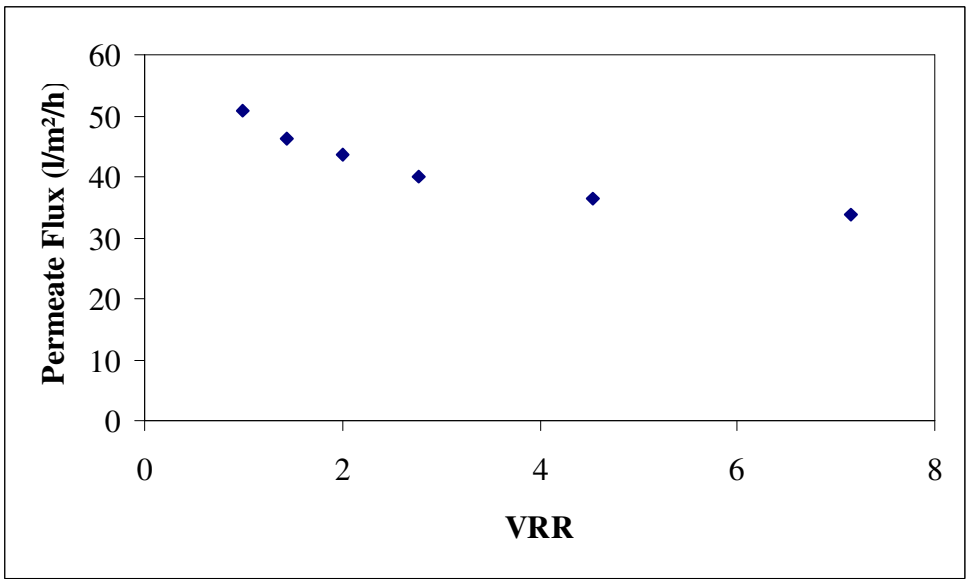

Figure 4.18. Permeate flux vs. VRR graph for nanofiltration module C. Feed = Permeate Stream of ultrafiltration module D, TMP = 8 bar, recycle flow rate = 2,000 L/h.

The initial value of permeate flux (51 L/m^2/h) was significantly higher than that of the one stage operation with the same module (34.5 L/m^2/h) due to the influent characteristics of the operation. The feed water is finished very quickly with no fouling as expected. A high VRR ratio (7.14) is reached at the end of the experiment.

The first step UF operation , as expected, eased the operation of nanofiltration module C in terms of higher permeate fluxes at higher volume reduction ratios. But no improvement in COD removal was observed again. Nanofiltration module C, when treating the permeate stream of ultrafiltration module D, produced a permeate stream with COD load of 27,438 mg O_2/L. This value is achieved with a COD removal efficiency of only 49 %.

4.3.4. Heating + RO Treatment of Curd Cheese Whey

As described in the materials and methods section, the production of curd cheese whey involves heating the product up to 90^{o}C and collecting the precipitate as the curd cheese. The remaining is called the curd cheese whey which is also rich in protein content.

In this two stage operation, heating the curd cheese whey up to 100^{o}C in order to precipitate the protein portion was applied as the first stage. The supernatant was than used as the feed stream of reverse osmosis module F.

The curd cheese whey, after heating up to 100^{o}C, is cooled and the de-solubilized protein molecules were left to be settled. The protein denaturation is of importance in this first stage. Denaturation can be defined as any modification of secondary, tertiary, or quaternary structure of the protein molecule, excluding breakage of covalent bonds. Denaturation is therefore a process by which hydrogen bonds, hydrophobic interactions and salt linkages are broken and the protein is unfolded.

When a protein solution is gradually heated above a critical temperature, it undergoes a sharp transition from the native state to the denatured state. The temperature at the transition midpoint, where the concentration ratio of native and denatured states is 1, is

known either as the melting temperature (Tm), or the denaturation temperature (Td) (Scopes, 1994). Figure 4.19 shows the schematic illustration of the denaturation of a protein molecule.

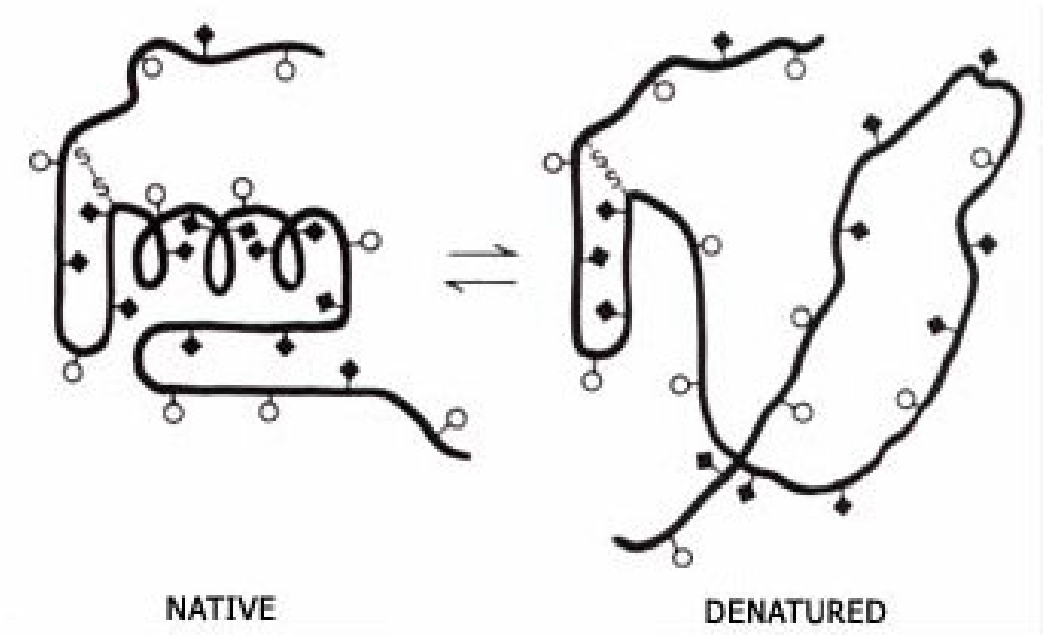

Figure 4.19. Schematic illustration of the denaturation of a protein molecule (Fennema, 1976).

The mechanism of temperature-induced denaturation is highly complex and involves primarily destabilization of the major noncovalent interactions. Hydrogen bonding, electrostatic, and van der Waals interactions are exothermic in nature. Therefore, they are destabilized at high temperatures and stabilized at low temperatures.

The theoretical curve for the amount of a protein denatured at a given temperature in 10 min is shown in Figure 4.20. Note that at only 5^{o}C above the 50% denaturation temperature, barely 1 % remains, but at 5^{o}C below, as much as 8% is lost (Scopes, 1994).

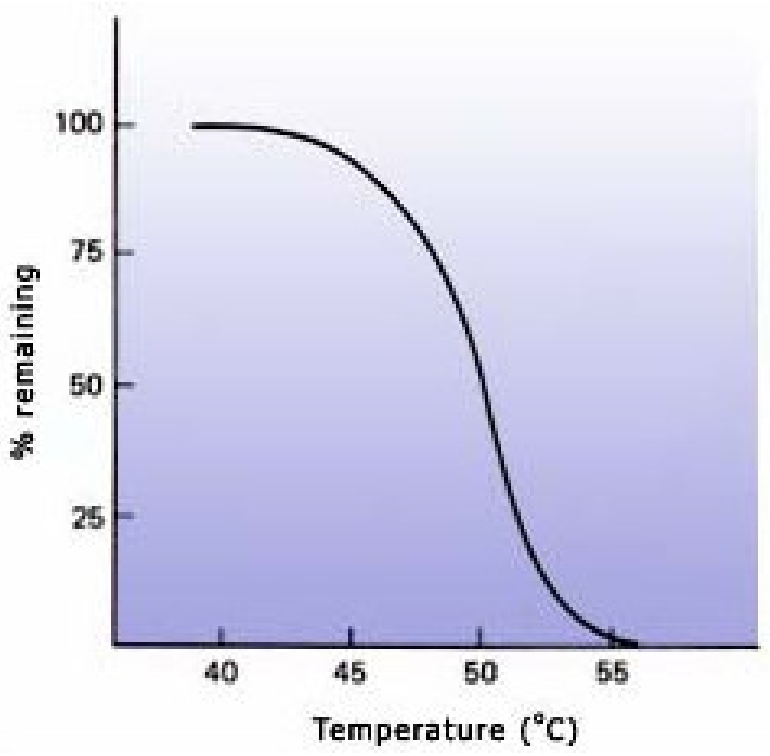

Figure 4.20. Theoretical diagram showing the percent of protein remaining undenatured after 10 min incubation (Scopes, 1994).

Since the temperature applied in the first stage operation exceeded the denaturating temperature of proteins, the proteins in the curd cheese whey were de-solubilized losing their structure leaving a clear supernatant. However the nutritional value of the precipitated product remains the same so it can be used further for animal feed or raw material.

50 litres of curd cheese whey, after heating, produced 3 liters of precipitate, with a protein concentration of 315 mg/L. The total solid content of the precipitate was 116 g/L.

By precipitating the proteins, the organic load of the curd cheese whey was decreased. The COD removal efficiency of the first stage heating operation was 34 % producing a supernatant with COD value of 68,760 mg O_2/L.

This supernatant was then treated with reverse osmosis module F. This module, manufactured by TRISEP Corp. is known by its low-fouling characteristics due to its

polyamide-urea material which posses a combination of properties inherent in it structure that are uniquely advantageous in significantly resisting colloidal particulate fouling and befouling (Kremen and Knappe, 2005).

The experiment with reverse osmosis module F was conducted with this 45 liters of supernatant as the feed water. The operating transmembrane pressure was 10 bar and the recycle flow rate was 2,500 L/h. The results are presented in Figure 4.21 and Figure 4.22.

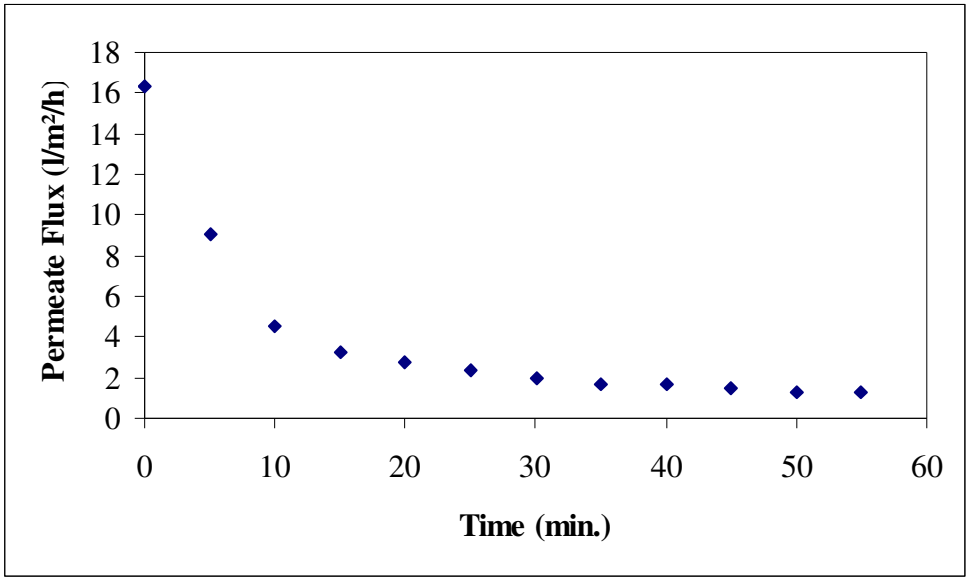

Figure 4.21. Permeate flux vs. time graph for reverse osmosis module F. Feed = Supernatant of the heating stage, TMP = 10 bar, recycle flow rate = 2,500 L/h.

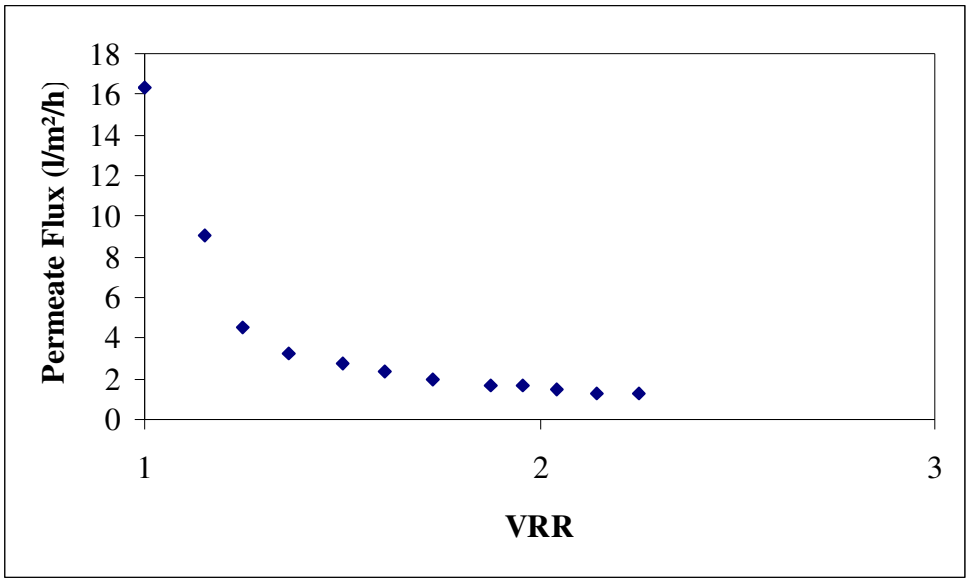

Figure 4.22. Permeate flux vs. VRR graph for reverse osmosis module F. Feed = Supernatant of the heating stage, TMP = 10 bar, recycle flow rate = 2,500 L/h.

As can be seen in Figure 4.21 reverse osmosis module F shows somewhat better permeate flux values when compared to the other reverse osmosis module E treating NF permeate. The initial permeate flux value was 16.4 $L/m^2/h$. This can be attributed to the TMP difference between two experiments (the operating TMP for reverse osmosis module E was 8 bar). However it should be noted that the influent stream of module F was organically more loaded, including some protein portion hasn't been precipitated in the heating stage. The 45 liter feed water is finished in a relatively short time (55 minutes) and the permeate flux value at the end of the experiment was 1.3 $L/m^2/h$. The limiting flux was reached at the 50^{th} minute.

The COD removal efficiency was lower when compared to that of reverse osmosis module E namely 89 % while producing a permeate stream with a COD value of 7,040 mg O_2/L.

5. CONCLUSION

Six different membrane modules, (1 ultrafiltration module, 3 nanofiltration modules, and 2 reverse osmosis modules) were investigated in treatment of a very problematic by-product of cheese production: whey. Two different whey types, namely white cheese whey and curd cheese whey were treated in one stage and cascade operations. The performance of these operations were evaluated via ease of operation (permeate flux), protein recovery and COD removal efficiency.

Each module was tested as one stage operations at the beginning. Only nanofiltration modules were tested with both white and curd cheese whey since ultrafiltration is the well accepted operation for protein recovery from whey and sufficient data exist for about the performance of ultrafiltration as one stage operation. Reverse osmosis as one stage operation for curd cheese whey treatment produced ineffective results. No further one stage treatment experiment of white cheese whey with reverse osmosis was conducted.

The permeate flux values obtained by one stage nanofiltration operations with curd cheese whey as the feed were 30 $L/m^2/h$, 20 $L/m^2/h$, and 30.8 $L/m^2/h$ for modules A, B, and C respectively. The same modules produced lower permeate flux values when treating white cheese whey (27 $L/m^2/h$, 16.7 $L/m^2/h$, and 25.6 $L/m^2/h$ respectively). These values represent a good performance from the operation point of view especially when compared to the previous studies conducted by different nanofiltration modules treating dairy products (Rektor and Vatai, 2004; Balannec et al., 2005). In these previous studies, highest permeate flux obtained was 22.19 $L/m^2/h$ even when microfiltration was applied as pretreatment of whey, even lower flux values were achieved (3.5 – 5 $L/m^2/h$) when NF is applied without any pretreatment. The higher fluxes obtained in this study can be attributed to the characterization of membrane modules used. The above discussed permeate flux values were obtained for volume reduction ratio of 1. In other words when no concentration of whey proteins occurs.

By employing modules with different membrane areas, treatment capacities were tested. The experiment with nanofiltration module A was conducted with TMP of 5 bar

and with modules B and C it was 8 bar. The one stage operation of ultrafiltration module D produced 22.2 L/m^2/h permeate flux under an operating TMP of 3 bar. This is low when compared to that of the nanofiltration modules however the reason for this is the larger membrane area of module D. The results obtained by reverse osmosis module E were very low (14 L/m^2/h) that this module as one stage can not be utilized for whey treatment.

Since the aim of this study is to efficiently concentrate and recover the whey proteins, permeate flux values in higher volume reduction ratios are of importance too. Modules A, B, C, and D operated efficiently while reducing the volume of the whey thus producing concentrated proteins. Module A reached a VRR of 6.5 in 40 minutes while module B reached 4.8 in 80 minutes, module C reached 6.8 in 35 minutes for both white cheese whey and curd cheese whey. The greatest VRR (7.8) was reached by ultrafiltration module D in only 13 minutes for curd cheese whey. This is due to the relatively larger pore size of ultrafiltration module when compared to nanofiltration and reverse osmosis. Obtaining higher permeate fluxes for different VRR values are of more importance than reaching higher ultimate VRR value. In this study, modules A, B, C, and D all produced good permeate flux values in different VRR values when compared to previous studies where NF, together with MF as pretreatment, produced 21.32 L/m^2/h of permeate flux at VRR = 2 (Rektor and Vatai, 2004).

The obtained permeate flux values for curd cheese whey was higher than the values obtained when treating white cheese whey. This is due to the higher fat content of white cheese whey. However, the flux values were the same at the end of each experiments and also the VRR values reached were the same. This is because the protein content of both white and curd cheese whey were nearly the same and the build up of protein layer on the surface of the membranes that cause the flux decline were the same.

The protein rejection performances for nanofiltration modules and the ultrafiltration module were also very promising. The best results were obtained by nanofiltration module C with protein rejection of 88 % for both white and curd cheese whey.

However the COD removal efficiencies for modules A, B, C, and D were very low. The best results were again achieved with nanofiltration module C. The experiment with

module C while treating curd cheese whey produced a permeate stream with COD value of 23.502 mg O_2/L with removal efficiency of 77 %. These parameters were 35.965 mg O_2/L and 65 % respectively when the feed was white cheese whey. In this manner, all three nanofiltration modules behaved like ultrafiltration modules, failing to recover the lactose. The high COD value of the permeate streams are due to the high lactose content. One stage operation of reverse osmosis with curd cheese whey produced a permeate stream with COD value of 3.847 mg O_2/L (92 % removal efficiency) but since the operating performance of this module is not sufficient, it is not regarded to be employed as one stage alone.

Evaluating the overall performances of modules A, B, C, and D, they are quite effective in terms of permeate flux and protein rejection. The recommended modules are nanofiltration module C due to its high protein rejection and ultrafiltration module D due to its high treatment capacity. The curd and white cheese whey was successfully concentrated up to 24% total solids level using nanofiltration module C. The final concentrate contains significant amounts of protein and is considered to be suitable for use in dairy products such as ice cream and yoghurt. Alternatively, it can be converted into sweet syrup for use in other products.

However, none of the modules (except the reverse osmosis module E) that were tested for one stage operations succeeded in terms of COD removal. Thus it can be concluded that one stage operation with available modules for this study is not suitable for both protein recovery and COD removal. An additional stage is needed to further purify the one stage effluent for direct discharge or conventional treatment.

Three cascade operations with membrane modules, namely NF + RO, NF + NF + RO, and UF + NF, were investigated. An alternative cascade treatment method, Heating + RO, was also investigated. In cascade operations involving only membrane solutions, it was clear that an additional stage of reverse osmosis is required for achieving effluents low in COD value since UF + NF treatment produced an effluent stream with COD value of 27.438 mg O_2/L, which can not be discharged to receiving environments while it can still be considered highly loaded for conventional wastewater treatment. The COD value for effluent produced by NF + RO treatment was 2.448 mg O_2/L and it was 3.323 mg O_2/L for

NF + NF + RO effluent. Regarding these values, NF + RO treatment is the best choice with available modules. It also has the advantage from the economics point of view since two stages are employed instead of three.

The problem with cascade operations with RO as the last stage was the performance of RO in terms of permeate flux, although the decreased influent load caused by the first NF stage, did not improve when compared to one stage operation of the same module. The permeate stream produced by the first stage NF had the COD load of 43.568 mg O_2/L vastly due to lactose since proteins were recovered. The permeate flux achieved by second stage RO module E with this influent was only 15.45 L/m^2/h. This value dropped to 2.69 L/m^2/h after 130 minutes of operation which is a very low value. The reason for this is that the maximum TMP that the experimental set up can withstand was just over 10 bar and the TMP for the experiment was 8 bar. 8 bar of driving pressure for RO module while treating high loaded influents would not be enough to exceed the osmotic pressure that the influent solution creates across the membrane. High TMP such as 30 – 40 bars should be applied in order to achieve better results in terms of permeate flux.

Another benefit of using NF + RO cascade treatment with available modules appeared as recovery of protein and lactose separately. As discussed above, the first stage NF behaved more like an UF module, concentrating only the protein portion and leaving the high lactose content in the permeate. With this permeate stream treated by second RO stage, lactose was recovered separately producing a clean effluent.

Lastly, another cascade treatment, Heating + RO, was applied in order to compare the performance with cascade operations involving only membrane solutions. First stage heating up to 100^{o}C was applied in order to precipitate the protein content thus producing cleaner influent for RO. 50 litres of curd cheese whey, after heating, produced 3 liters of precipitate, with a protein concentration of 315 mg/L. The total solid content of the precipitate was 116 grams/liter. This is a product that also can be used as ingredient dairy industry or animal feed. The supernatant that was treated with second stage RO had the COD load of 68,760 mg O_2/L. In this case, as expected, heating produced worse results when compared to first stage NF. The second stage RO, conducted with another module (module F) showed slightly better results when compared to that of reverse osmosis

module E. The initial flux was 16.4 $L/m^2/h$, which again is not suitable for full scale applications because of the low TMP (10 bar) that can be employed.

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