MANAGEMENT OF EFFLUENTS

FROM FIELD PEA WET MILLING PROCESS

USING ULTRAFILTRATION TECHNOLOGY

By

Alice Kuo

A Thesis
Submitted to the Faculty of Graduate Studies
In Partial Fulfillment of the Requirements
for the Degree of

MASTER OF SCIENCE

Food Science Department
University of Manitoba
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THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES

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LIST OF ABBREVIATIONS

Abbreviation	Definition
BOD	biochemical oxygen demand
BAT	Best Available Technology - U.S.
BPT	Best Practical Technology - U.S.
CEPA	Canadian Environmental Protection Act
COD	Chemical oxygen demand
DO	Dissolved oxygen
EPA	Environmental Protection Agency - U.S.
EPS	Environmental Protection Service - Canada
FWPCA	Federal Water Pollution Control Act Amendments - U.S.
ISO	International Standards Organization
MCLGs	Maximum Contaminant Level Goals
MWCO	molecular weight cut off
NPDES	National Pollutant Discharge Elimination System
POTW	Publically Owned Treatment Works
R	rejection value of membrane
RO	reverse osmosis
SDS-PAGE	sodium dodecyl sulfate - polyacrylamide gel eletrophoresis
SDWA	Save Drinking Water Act - U.S.
SS	suspended solids
TCA	trichloroacetic acid
ThOD	Theoretical oxygen demand
TS	total solids
UF	ultrafiltration
VCR	volume concentration ratio
$(X/M)_{Co}$	capacity per gram (or unit weight) of carbon at the influent concentration

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ABSTRACT

A wet milling process is being used by a process facility in Portage la Prairie, Manitoba, to produce field pea fractions of protein, starch and fiber. The wet milling process requires approximately 700,000 L of fresh water on a daily basis, discharging similar quantities of high strength effluent for municipal treatment. Effluent surcharges based on strength and capacity requirement for municipal treatment are substantial to the plant. Current wet milling process technology results in an estimated loss of protein at the desludger operation of 1434 kg/day due to incomplete precipitation or process inefficiency; a double cost to the company in terms of product revenue loss and effluent surcharge.

The use of an ultrafiltration membrane system was investigated to treat the protein desludger effluent generated in wet milling with the goal of protein recovery. Pretreatment of the desludger effluent by a carbohydrase enzyme Termamyl and use of celite for rapid floc settling was adopted prior to membrane treatment.

The protein desludger effluent was concentrated up to a volume concentration ratio of 20:1 by use of a 30,000 MWCO hollow fiber membrane, or a 30,000 MWCO spiral wound membrane. A 10,000 MWCO spiral wound membrane produced retentates of higher protein content but lower flux during concentration. Process conditions of the desludger effluent, temperature (50°C) and pH (4.5), were shown to be ideal for membrane treatment. Protein was concentrated by a factor of 12.3 to yield 38,160 mg/L. The protein content in the retentate fraction was 72.8% (d.b.). Diafiltration increased the protein content to 88.8% (d.b.). Although flux declined with increasing volume

concentration, membrane fouling was not a major factor in this study. The 30,000 MWCO hollow fiber membrane was able to maintain approximately 50% of its original flux at 20:1 VCR. Chlorinated caustic cleaning solutions successfully restored membrane flux.

The UF concentrated protein could be directly spray dried for improved process economics. Electrophoregram showed certain fractions of protein have been selectively concentrated by UF. The resulting permeate stream contained high levels of organics (10,500 mg/L COD) and color impurities, deterring both discharge and reuse. Activated carbon treatment of the permeate readily removed color impurities and would thus enhance reuse opportunities. For complete decolorization, 2100 mL could be treated per gram of carbon. Activated carbon treatment for organic (COD) reduction would not be economically feasible as high levels of organic and presence of refractory organics would require large amount of carbon for removal.

Chemical costs resulting from the use of enzyme, celite, and activated carbon was estimated at $409 per day. Potential savings to the plant on a daily basis using UF membrane technology and recycle of permeate included recovered protein ($2182) and reduced effluent surcharge ($2132).

I. INTRODUCTION

The processing of yellow field peas (*Pisum sativum* var. Century) into food components has been a segment of Manitoba industry since the 1980s. Woodstone Foods Ltd. developed a wet milling process to fractionate field peas into fiber, starch and protein components. These isolated components have found markets for both their nutritional, and food functional properties, and more recently potential markets are being investigated for their nutraceutical values. Parrheim Foods took over the operation, located in Portage la Prairie, in 1997 and utilizes a similar wet milling process today.

A wet milling process has advantages over traditional air classification technology in that the fractionated components can be isolated in more pure or more concentrated forms, however, large volumes of water are used in the wet process with subsequent effluent discharge creating a potential environmental hazard and costs to the processor for treatment.

In the wet milling process, fresh water serves to wash, extract, separate, transfer, and solubilize field pea components. The unit operations create dissolved and suspended solids which result in an organic loading for discharge referred to as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and suspended solids (SS).

The wet milling operations of initial pea wash, fiber separation, starch separation, and protein separation create a combined plant effluent of the following average characteristics: flow 700,000 L/day, COD 7655 mg/L, BOD 3952 mg/L and SS 8190 mg/L.

The levels of COD and SS are higher than allowed under the municipal by-law established by the city of Portage la Prairie for sewage discharge loading, and the plant is faced with a surcharge that could amount to over $200,000 per annum. The city of Portage la Prairie also in 1994, began negotiating from each industry a fixed cost based on capacity required for secondary treatment assessed on effluent flow, organic and solids loading, and a variable cost assessed as an effluent surcharge. The increased costs were introduced to finance upgraded biological treatment facilities operated by the city.

Woodstone Foods was facing increased cost of water treatment prior to the initiation of the project. Recognizing the cost of wastewater treatment, Woodstone Foods was involved in continuing studies to reduce effluent surcharge, to recover by-products from effluent streams, and to recycle process waters within the plant. In particular, the protein desludger operations, where protein is precipitated at its isoelectric point by pH adjustment, has been identified as producing vast quantities of high strength waste but has potential for by-product recovery to offset treatment costs.

A commercial ultrafiltration and reverse osmosis unit operating on desludger effluent was subject to irreversible fouling when Woodstone Foods started operation and was rendered inactive. Subsequent research supported by Woodstone Foods at the University of Manitoba (Grabowecky, M.Sc. 1988) also cited fouling problems associated with membrane treatment. Further in-house studies by Woodstone Foods to change in operating procedures at the unit operations and the pretreatment of desludger effluent with a carbohydrase enzyme showed promising results such that the company wished to revisit the use of membrane technology.

This study was initiated to examine pretreatment options for protein desludger effluent prior to membrane treatment, to optimize membrane treatment, and to evaluate by-product recovery and recycle opportunities.

The study is based on the following factors:

1. The cost of effluent treatment by municipal government is increasing.
2. The combined effluent from the processing of field peas by the wet milling process is much higher than acceptable levels established by municipal treatment resulting in surcharge to the company.
3. The major contribution to the combined plant effluent is the protein desludger units. Effluent strength at this unit operation largely represents loss of protein material to sewage treatment.
4. Membrane treatment (ultrafiltration) of the protein desludger effluent in-plant can be feasible with appropriate pretreatment to include carbohydrase enzyme addition and rapid removal of the formed floc material.
5. Ultrafiltration allows for recovery of a concentrated protein fraction and a permeate with a lower level of contamination.
6. The potential for membrane treatment is enhanced by the recycle opportunities for the permeate streams. Activated carbon technology can be used to decolorize the amber colored permeate stream if a higher quality permeate is required for recycle.
7. The expenditure in UF technology is offset by the value of protein recovered, and reduced cost of sewage surcharge.

LITERATURE REVIEW

There is a growing interest in the Western world for reduction in animal protein for food use, and increased consumption of vegetable protein for both health and economic reasons. Soy beans are the most important source of vegetable protein in North America, however, protein from other pulse crops such as field peas are finding an important niche in the market place for their nutritional and functional properties.

A. Field peas

1. Commercial status

Field peas (*Pisum sativum L.*) are a major pulse crop in Western Canada. Dry pea production has increased rapidly, especially since 1985 with the opening of the European feed pea market with resulting high prices for peas. In 1997, in Manitoba, 85,000 hectares were harvested producing 6.6 million bushels of peas. This comprised 1.9% of Manitoba's total crop production, 68.1% of Manitoba's special crops average and 10% of Canada's total pea production (Manitoba Agriculture and Food, 1999). Canada has become a world leader in pea exports, with Canadian peas being exported worldwide for both food and feed uses. In 1997, Manitoba exported $37.1 million of peas to the U.S. and European countries. Pea flour has markets in several countries worldwide, while food quality peas are shipped to canning plants in Eastern Canada. The nutritional value of field peas makes them attractive as feed supplements for livestock and poultry. Both nutrition and functional aspects of pea constituents are important in their use in human foods.

The status of vegetable food proteins including those from field peas was reviewed by Lusas et al (1992). Interest has increasingly grown in the utilization of flours or fraction from legumes including field peas (Gujska et al, 1994).

The Canadian pea industry initially was based on the Century pea, a cultivar with large yellow seeds which was registered in 1960, and became the standard for food quality peas. Century variety has largely been replaced by more common pea varieties such as Trapper, Victoria, Titan, Express and Radley. A major disadvantage of Century variety was the excess vine growth which presented problems at harvest. The large increase in pea production since 1985 has resulted in a shift in production from Manitoba to Saskatchewan and Alberta, with an increase in the number of registered cultivars. Value added processing of peas currently is being practiced at Parrheim Foods processing facilities in Saskatoon, and Portage la Prairie.

2. Pea protein - Nutritional/Compositional

Peas, like all pulses, are good sources of protein, fiber, and starch. In addition, peas also contain important nutrients including potassium, niacin, thiamin, pantothenic acid, pyridoine and folic acid. Reichert and MacKenzie (1982) provided detailed compositional data for field peas. Protein varied between 14.5 - 28.5%, starch varied from 49.7 - 59.8% and was negatively correlated with protein content, fiber 3.14 - 4.26%, lipid 2.99 - 4.01% and ash 2.8 - 3.3%.

The protein content of field peas can be highly variable, being influenced by both genetic and environmental factors (Ali-Khan and Youngs, 1973). Amino acid composition

and protein quality of field peas were reported by Holt and Sosulski (1979), who identified the sulfur containing amino acids, especially methionine, as limiting factors. Arginine, aspartic acid and glutamic acid were present in greatest quantities. Leterme et al (1990) provided detailed information on amino acid composition of pea proteins and protein profile of pea flour. Individual amino acid profiles of whole grain, albumins, globulins, insoluble protein and non protein material were presented. In all cases, the amino acid composition was characterized by a high content of lysine with especially low methionine, cystine and tryptophan contents. Reichert and MacKenzie (1982) recommended pea varieties be selected for higher content of methionine and cystine amino acids. Bhatty et al (1973) reported on protein and non protein nitrogen fractions in field peas, while Gueguen and Bardot (1988) provided information on the variability of pea protein composition. Chemical composition and amino aicd profile of field pea as compared to soy bean is shown in Table 1.

Murray et al (1986) suggested that that pulse crops including field pea are important sources of lectins. Recovery of such lectins could yield high value minor components. Although there are no literature references to the nutraceutical potential of field pea, increased research in this field could lead to further value from the processing of field peas.

3. Processing

Currently, three commercial processes are being used in the fractionation of field peas into components of protein, starch and fiber. The processes include air classification, wet milling and membrane treatment.

Table 1. Chemical composition (% dry basis) and amino acid profile of soybean and field pea.

Component	Soybean	Field pea
Protein (N x 6.25)	33.2 - 45.2	21.2 - 32.9
Total Lipid	21.2	2.9
Dietary fiber	11.9	16.7
Ash	3.3 - 6.4	3.3
Carbohydrate:		
Total	25.4 - 33.5	56.6
Starch	0.2 - 0.9	36.9 - 48.6
Amylose in starch	15.0 - 20.0	23.5 - 38
Soluble sugars:		
Sucrose	6.4	2.3 - 2.4
Raffinose	0.7 - 1.0	0.3 - 0.9
Stachyose	2.2 - 4.2	2.2 - 2.9
Verbascose	0.0 - 0.3	1.7 - 3.2
Amino acid (g/16gN)		
Lysine	6.3	7.2
Threonine	3.9	3.8
Valine	5.1	4.6
Leucine	7.9	6.9
Isoleucine	5.0	7.4
Methionine	1.5	1.0
Tryptophan	1.3	0.8
Phenylalanine	5.1	4.6
Arginine	8.1	9.5
Histidine	2.7	2.3
Glycine	4.4	4.4
Alanine	4.3	4.3
Serine	5.1	4.8
Tyrosine	3.6	3.1
Proline	5.9	4.0
Cystine	1.7	1.7
Aspartic acid	11.8	11.5
Glutamic acid	18.0	17.1

Source: Parrheim Foods (1999).

a. Air classification

Air classification is a unit process operation whereby particles differing in density and mass are separated in a stream of air. Mechanical dehulling, and pin mill processes usually proceed air classification in order to produce a flour. However, the processes do not completely separate protein from the starch fraction (Vose et al, 1976).

Air classification has found use for both cereal (Vose, 1978) and legume (Tyler et al, 1981; Reichert, 1982) processing to produce a protein rich fraction.

Air classification has advantages over the wet milling procedures where protein isolates are prepared with associated effluent disposal problems, and additional chemical and drying costs (Wright et al, 1984). Characterization of air-classified fractions of field peas has been reported (Tyler et al, 1981: Sosulski et al, 1987).

Air classification can result in protein concentrates from field peas containing approximately 50% protein content (Wright et al, 1984). Higher protein content concentrates could be produced but with yield loss. Another limiting factor of air classification is the tendency of lipid to fractionate with the protein, resulting in a concentration of lipid in the pea protein concentrate which could affect both storage and functional properties (Wright et al, 1984).

Reichert (1982) reported that protein concentrates ranging from 33.6 - 60.2% could be produced from field peas using air classification. A major limitation to product quality and uniform composition was the variability of protein in the field pea (14.5 - 28.5%) which affected the protein content of the concentrate. Efforts to increase the protein separation efficiency have been reported (Tyler et al, 1981; Tyler et al, 1984; Sosulski et

al, 1987). Parrheim Foods Saskatoon plant has been processing pea protein, starch and fiber by air classification since 1989.

b. Wet milling

Wet milling is a second process used in the preparation of protein fractions from field peas. This process is designed to produce a protein isolate by aqueous extraction (either acid or alkaline), followed by precipitation at the isoelectric point. Starch and fiber fractions are separated by using slurry screens prior to protein extraction. The protein precipitate is washed, centrifuged and spray dried. The procedure is described by Sumner et al (1981), and Sosulski and McCurdy (1987). These procedures describe the alkali extraction of the protein at pH 9.

Woodstone Foods, Portage la Prairie, used a patented process (Nickel, 1981) to produce protein isolate from field peas incorporating solubilization of the protein in acid (pH 2.5-3.0), prior to isoelectric precipitation. Marketed as Woodstone Gold, the protein isolate contained 83-85% protein (Duxbury, 1992).

Parrheim Foods acquired the processing facility at Portage la Prairie, and using similar technology produces a concentrated natural protein fraction (82% protein) of yellow peas known as Pro-Flo. Typical composition is shown in Table 2.

Although producing a superior protein fraction compared to air classification, the wet milling method requires large volumes of water in processing, with subsequent discharge of high concentration, high volume effluents (Grabowecky, 1988). Czuchajowska and Pomeranz (1994) developed a method of legume fractionation reported

Table 2. **Composition of concentrated protein fraction of field pea.**

Typical Analysis:		**(DWB)**
Chemical:		
Moisture	(16 hrs at 100 deg +/- 5 deg C)	<6.0%
Protein	(Kjeldahl-Nx6.25)	82% +/-2%
Fat	(AOAC 7.060, 14th Ed)	<3.0%
Ash	(AOAC 14.006, 14th Ed)	<4.0%
pH	(10% solution)	Neutral
Lipase	(Fluorescene Method)	very low (u/g)
Microbiological:		
Standard Plate Count	(AOAC 46.015, 14th Ed)	<10,000/g
E. Coli	(AOAC 46.016, 14th Ed)	Negative
Salmonella	(AOAC, 14th Ed)	Negative
Yeasts and Molds	(AACC 42-50, 8th Ed)	<100/g

Minerals:	
Sodium	6,000 ppm
Potassium	1,000 ppm
Calcium	300 ppm
Phosphorus	8500 ppm
Iron	150 ppm
Zinc	32 ppm
Mercury	<10 ppb
Lead	<10 ppm
Cadium	1 ppm
Arsenic	<10 ppm

Physical Data:	
Flavor	Bland
Color	Light Cream
Particle Size:	
Through 80 mesh Tyler	>95%
Microns	180

Source: **Parrheim Foods (1999).**

to be superior to current methods. This technology for separation of starch and protein fractions is a combination of both dry and wet milling procedures. The patented method reduces water usage in the washing steps and recycles within the wash stages and eliminates chemicals. Otto et al (1997) used the patented technology for fractionation of pea flours producing isolated fractions of high yield and purity, with less water usage.

c. Membrane processing

Protein isolates from plant sources can also be produced from processes involving membrane technology. Lawhon et al (1977) initially reported on a process using ultrafiltration and reverse osmosis to produce protein isolates and concentrates from oilseed flour extracts. Cheryan (1998) reviewed further advances in the use of membrane technology in the separation of protein from various plant sources. A company in Denmark is reported to be using ultrafiltration technology in the manufacture of pea protein isolate (van Dongen, 1999).

4. Protein isolate

The composition of field pea protein isolate as produced by Parrheim Foods is characterized in Table 2. Field peas have been evaluated as a high protein crop for use in food products such as bread, tortillas, pasta, meat, dairy, health foods and snack bars (Parrheim Foods, 1999). The functionality of pea protein fractions and isolates was reviewed by Sosulski and McCurdy (1987), Megha and Grant (1986), and Sumner et al (1981). The protein fractions exhibited excellent whipping properties, foam stability,oil

absorption and water holding capacities which were similar to soy protein. Pea protein concentrate would require supplementation with methionine to improve its protein quality for use in certain food applications (Keith et al, 1977). The preparation of pea protein curd similar to tofu was reported by Gebre-Egziabher and Sumner (1983). Delaquis (1983) used pea protein isolates as extenders in pork sausage. Duxbury (1992) indicated it was possible to use pea protein for fortification of foods. Lusas et al (1992) reviewed the development of vegetable food proteins including field pea.

B. Membrane applications in processing of plant material

1. Membrane technology

Cross flow membrane technology had its beginning with the development of reverse osmosis by Sourirajan in 1959 (Paulson et al, 1984). The first commercial applications of this pressure driven technology was initiated in the late 1960s for both ultrafiltration and reverse osmosis following the development of anisotropic polymeric membranes by Loeb and Sourirajan (Cheryan, 1998). Since that time, there have been several commercial developments in membrane science. Cellulose acetate, the first generation membrane, had limitations in food process applications due to temperature tolerance ($<50°C$), pH conditions (pH 3-8) and low tolerance for chlorine. These conditions impose restrictions on cleaning and sanitizing. Second generation membranes such as polysulfones and polyethersulfone have wider tolerance to temperature ($<80°C$) and pH (pH 0.5-13), and are widely used in food applications. Inorganic or mineral membranes developed in the

1980s have high temperature tolerances (400°C) with no pH restrictions (Cheryan, 1998). Materials such as sintered stainless steel, zirconia, alumina and titania make these membranes extremely versatile, and despite their relatively high initial cost, these membrane provide benefits in long membrane life, higher flux, and wider ranges of operating parameters.

Membrane equipment is similar for all crossflow technology. The equipment for these pressure driven processes include plate and frame, tubular, hollow fiber and spiral wound membrane. The permeability of the membrane differentiates microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Jelen, 1991). Cheryan (1998) provides detailed description of membrane equipment.

Ultrafiltration is a fractionation process based on size exclusion whereby the membrane retains large molecules while smaller solutes and water pass through the membrane. Ultrafiltration membranes have typical molecular weight cut-off (MWCO) values in the range of 10,000-15,000 Daltons, and operate with a pressure range of 70-690 kPa. Ultrafiltration technology has applications in the separation, fractionation, and purification of proteins and other components, and offers the industry advantages in reduced energy and operating costs, increased product yield, improved product quality, creation of new products, recycle opportunities and reduced waste.

2. Operating parameters

The amount of fluid passing through the membrane is defined as flux (in terms of volume per unit membrane area per unit time). It is characterized as liters/m^2/hour (LMH) (Cheryan, 1998). Four major operating parameters can affect the flux of a membrane: (1) pressure, (2) feed concentration, (3) temperature and (4) turbulence in the feed channel. Cheryan (1998) provided an in-depth review of these factors. There have been attempts to model flux as a function of operating parameters and physical properties, but no one model has proven wholly satisfactory (Cheryan, 1998). One widely used theory for modeling flux is the film theory, which states that flux decreases exponentially with increasing feed concentration. It is ideal to operate a membrane system at the highest temperature consistent with limits of the feed and membrane, as higher temperatures lead to a higher flux. In addition, higher temperatures reduce feed viscosity, lowering pumping energy, and high temperature (>55°C) can minimize microbial growth (Cheryan, 1998). Turbulence in the feed chanel is usually obtained by increasing cross-flow velocity and can improve flux.

3. Soy processing

The use of membrane technology has found application in the processing of vegetables such as soybean to:

a) remove undesirable oligosaccharides implicated with gastrointestinal stress;

b) reduce lipid-lipoxygenase interactions for improved nutrition;

c) remove phytic acid, and/or trypsin inhibitors for improved nutrition.

This results in a purified protein stream with superior functional properties (Cheryan, 1998). Another virtue of ultrafiltration is its mild operating conditions adding to the improved functionality of the soy isolates. The production of soy protein isolates (90% protein) and soy protein concentrate (70% protein) from defatted soy flour using ultrafiltration technology was reported by Nichols and Cheryan (1981). Production of protein products from full-fat soy extracts was reviewed by Cheryan (1998).

An economic advantage of UF in the manufacture of soy products is the inclusion of whey proteins normally lost in conventional manufacturing methods. Similar to whey proteins from milk, soy whey proteins are soluble at the isoelectric point and are lost into the whey during processing. UF technology thus results in an increased protein recovery for isolate manufacture. A sequence of ultrafiltration, diafiltration and ultrafiltration is recommended.

Deeslie and Cheryan (1991) used ultrafiltration to separate peptides of differing molecular weight following the enzymatic hydrolysis of soy protein isolate. The functional properties of the molecular weight distributions were noted to be quite different. With newer ultrafiltration membranes of narrow pore size distribution, ultrafiltration technology could be a useful technique in producing protein fractions with unique functional properties.

4. Processing of other plant material

Membrane processing has been reported in the literature as being used to fractionate and concentrate proteins from potato processing wastewaters (Cheryan, 1998). Cited advantages included low energy consumption and low cost for water removal, and the coagulation of the potato protein was more efficient after ultrafiltration.

Protein concentrate from chickpeas was obtained by ultrafiltration (Ulloa et al, 1988) yielding a concentrate in which some of the undesirable factors such as flatulence producing compounds (raffinose and stachyose) and goitrogenic agents (oligopeptides) were separated from the protein. The concentrate had potential use in infant formula.

Ultrafiltration is a major unit operation in the preparation of rapeseed protein isolate. Rapeseed is available in large quantities, and the excellent nutritional quality of the protein suggests that it should play an important role in supplying protein to the world's food supply. Tzeng et al (1988) reported on a process including UF to produce a protein isolate free of glucosinolates, low in phytates and fibre, bland in taste, with good potential for use as a food ingredient.

Numerous membrane applications have been developed for corn refining including for separation of corn proteins (Cheryan 1998). Corn proteins have a lower demand for food uses because of their relatively poor functional properties. Corn protein concentrates and isolates have been produced as well as individual protein fractions of glutelin and zein. Mannheim and Cheryan (1993) used a combination of enzyme modification and ultrafiltration to increase the functional properties of the zein proteins. Attempts to extract protein from stillage of dry milling ethanol plants using UF was reported by Wu et al, 1985. Wu (1988) concluded that the treatment of corn light steep-water by UF followed by RO could improve the economics of corn wet milling by producing a high protein concentrate, and a permeate suitable for reuse or safe disposal.

The application of ultrafiltration in several other vegetable protein systems including alfalfa, cottonseed, faba beans, navy beans, peas and sunflower seeds were referenced by Cheryan (1998).

5. Application to other food industries

The applications of membrane ultrafiltration to food processing was initially reviewed by Porter and Michaels (1970). Other review articles include Paulson et al (1984), Hedrick (1984), Swientek (1986), and Dziezak (1990). Mans (1991) questioned why membrane technology with its benefits and advantages has not achieved more recognition in the food industry. Koseoglu (1998) reported that all industry applications of membranes in 1994 was 490,000 m^2 with the dairy industry being the major user (180,000 m^2). The use of membrane technology in the dairy industry is continually growing (van der Horst, 1995). Emerging technologies which could benefit from membrane processing include the extraction and fractionation of high value components and nutraceuticals (Kutowy, 1998).

6. Wastewater applications

A major application of membrane technology is in the processing of cheese whey. Its disposal is a major problem for the dairy industry based on its low solids content, lactose:protein ratio, and high biological oxygen demand (32,000 - 60,000 mg/L). It is estimated that nearly 50% of the whey produced annually is, however, still disposed of by sewage treatment (Cheryan, 1998). Both ultrafiltration and reverse osmosis are well

established technologies in fractionation, purification, and concentration of whey components.

The recovery of brine solutions for cheese types is an important application of UF. UF removes contaminants such as fat, protein, turbidity, foam and bacteria with a yield of clean brine of 99.5% (Membrane Systems Specialists, 1992). The brine is reused, eliminating a disposal problem, and favorably affecting economics.

Balbuena et al, 1988, reported on the use of UF to regenerate brines from Spanish green olives. Membrane treatment allowed for recycling of the brine with no adverse effect on product quality. Ultrafiltration, combined with activated carbon technology, was used as a treatment system in renovating and reusing fishery refrigeration brine (Welsh and Zall, 1984).

Chiang and Pan (1986) reported on the use of UF in the treatment of sweet potato process water. UF reduced the BOD of the effluent by two-thirds at a volume concentration ratio of 5, mainly due to retention of protein and macromolecules. A combination of UF/RO resulted in 99% removal of BOD with the permeate cited as being used for fresh water make-up within the plant.

Lawhon et al (1981) used UF, termed the membrane isolation process, to recover protein from oil peanut extracts avoiding generation of wheys resulting from acid-precipitation procedures. The membrane isolation process was also used to produce a protein concentrate from cottonseed flour (Lawhon et al, 1980) and oil seed flours (Lawhon et al, 1977) with similar favorable environmental effects.

7. Fouling

Cheryan (1998) suggests that fouling problems were the primary reason for the relatively slow acceptance of membranes for commercial applications. Considerable progress has been made in understanding the mechanism of fouling and regimes to overcome these problems (International Dairy Federation, 1995).

When a membrane is fouled, only cleaning will restore flux. Fouling is defined as a decline in flux with time during operation. Membrane fouling is due to deposition and accumulation of feed components either on the membrane surface, or within the pores of the membrane. Virtually all components in the feed will foul a membrane to a certain extent. Process factors including cross-flow velocity, pressure, and temperature can also affect fouling. The basis of evaluation of fouling is the clean water flux of a membrane as described by membrane suppliers. The consequences of fouling include higher capital costs due to the lower average flux, higher expenses related to cleaning, and rejection and yields may be affected (Cheryan, 1998).

In dairy operations, proteins have been widely studied because of the numerous applications of ultrafiltration. Proteins are considered a major foulant in membrane processing (Marshall and Daufin, 1995). Protein functional groups play an important role in allowing protein to interact not only with other feed components, but also with the membrane. The nature of the resulting fouling is affected by environmental factors such as pH, ionic strength, shear, and temperature. Membrane fouling results from gel formation, adsorption or deposition of solutes on the membrane (Daufin and Merin, 1995).

Many studies related to the fouling of membranes by dairy components have been reported since the 1970s (International Dairy Federation,1995). The studies have involved identification of the foulants, pretreatment options to minimize fouling, and investigation of preprocessing steps to result in flux increase (Pouliot and Jelen, 1995). Studies have involved model solutions of varying concentrations of dairy components, and the use of electron microscopy to identify the nature of the fouling.

Pretreatment options include pH and temperature adjustments, clarification and/or fat removal, demineralization, addition of sequestering agents, and treatment with proteolytic enzymes.

As reported by Cheryan (1998) there have been several attempts to concentrate proteins from potato process effluents, however potato effluent, like cheese whey, is described as having a great tendency to foul membranes. Chiang and Pan (1986) reported on the use of ultrafiltration and reverse osmosis in the production of sweet potato starch. Fouling of the hollow fiber UF membrane was moderate, and RO of the UF permeate stream proved effective. If primary process water was used directly as RO feed, excessive fouling resulted. The possible foulants were thought to be protein, inorganic salts, and a pectin-like substance. These components, although retained by UF, did not contribute to excessive fouling of the UF membrane. Chiang et al (1986) also reported that UF pretreatment was required to prevent excessive fouling of RO membranes in the treatment of mushroom blanch water.

The production of soy protein isolates by membrane filtration has not resulted in the severe membrane fouling as with cheese whey. Research conducted by Lawhon et al

(1977, 1978, 1979) reported on the use of UF followed by RO to produce protein isolates and concentrates from oilseed flour and soy flour with high permeation rates reported and little reference to fouling problems. One commercial membrane system achieved acceptable protein recovery and product quality while generating a mean flux greater than three times that achieved in commercial UF of cheese whey (Lawhon et al, 1978).

When using UF to process soybean water extracts, Omosaiye and Cheryan (1979) reported that at concentration levels greater than 5 volume concentration ratio (VCR), severe fouling problems resulted. With diafiltration and re-ultrafiltration, the desired purification and concentration was achieved.

Nichols and Cheryan (1981) also reported on the production of soy isolates from defatted soy flour water extracts. Solute-solute interactions, and solute-membrane interactions resulted in some loss of expected protein yield. These interactions did not seem to contribute to fouling problems.

Membrane flux is affected by both concentration polarization and fouling which have limited the development of membrane technology in several possible applications. Concentration polarization results when macromolecules such as proteins are rejected by the membrane, but tend to form a layer on the membrane surface (Cheryan, 1998). Concentration polarization is a further resistance to permeate flow. Concentration polarization is assumed to be dynamic, and changes in operating procedures such as decreasing transmembrane pressure, lowering feed concentration, or increasing turbulence could increase the flux.

8. Membrane cleaning

Both cleaning and frequency of cleaning are key economic factors in membrane technology. Cheryan (1998) suggests productivity defined as the volume of permeate between cleanings, is more important than flux per second. Chemical companies and membrane manufacturers both sell chemical cleaning compounds and recommend cleaning conditions specific for a membrane type. Choice of cleaning agent, either alkali, acid or enzyme and their sequence of use may also depend on the type of fouling. Addition of chlorine, and polymers such as polyethylene oxide (Tzeng and Zall, 1990) to alkali detergents can greatly improve cleaning efficiency. Advances in the understanding of fouling and cleaning phenomena in pressure driven membrane processes was recently reviewed (International Dairy Federation, 1995). Krack (1995) suggests that given the wide knowledge base and specialized products available, a compatible cleaning regime for any membrane process operation can be guaranteed.

C. Environmental protection and regulations in relation to the food processing industry

1. Water pollution: Food processing

The relative impact of food processing industries on water pollution must take into account that although highly diverse, most effluents are biodegradable, and that plants generally discharge to land treatment systems, or to municipal treatment systems. The food industry represents a significant group of point source dischargers.

The United States Environmental Protection Agency (Environmental Protection Agency, 1979) conducted a review of the major sources of water pollution, air pollution and solids wastes from food processing industries. Wastewater volume, biological oxygen demand (BOD) and suspended solids (SS) loads for all major industries were tabulated. The food industry ranked 5 (scale 1 to 11) based on total wastewater volume, ranked 3 in terms of BOD_5, and ranked 1 in terms of SS loading. A more recent report by the Council for Agriculture Science and Technology (1995) described the wastes generated by the food processing industry. Processes reviewed included grain processing for oils, fruit and vegetable, dairy and meat and poultry processing. The report concluded that the food process industry still contributes significant pollution loads to the environment.

2. Environmental protection laws and regulations - U.S.

Countries worldwide have recognized the danger of environmental pollution and have enacted legislation to protect the environment. In the United States, since the 1970s several legislative acts have been passed to protect air, water and land. These laws have had far reaching effects including into Canada. The U.S. Environmental Protection Agency (EPA) was established in 1970 with an overall mission of enhancement and maintenance of environmental quality, and to administer the laws and regulations (Green and Kramer, 1979).

a. Clean Water Act (1972) and Amendment (1976)

A comprehensive program in the United States, the Federal Water Pollution Control Act Amendments of 1972 (FWPCA) or Public Law 92-500 commonly known as the "Clean

Water Act" was enacted to prevent, reduce and eliminate water pollution. The original intent of FWPCA was:

i. By 1983 to achieve a goal of water quality clean enough for the production and propagation of fish, shellfish and wildlife.

ii The elimination of discharges of pollutants into all waters by 1985 (Zero discharge).

To realize zero discharge, the Act established quidelines so that industries discharging into surface water supplies (rivers, lakes and streams) were to apply Best Practical Technology currently available (BPT) by 1977 and to apply Best Available Technology economically achievable (BAT) by 1983 to meet interim standards.

The Clean Water Act was amended in 1977 to establish additional control over toxic pollutants (PL95-217). EPA established an original list of 129 priority pollutants including metals, asbestos, cyanides, pesticides, purgeable, acid and alkaline extracted organics. Provision was made for inclusion of other toxic pollutants on a regular basis.

b. Safe Drinking Water Act (1974) and Amendment (1986)

The Safe Drinking Water Act (SDWA) of 1974 (PL-93-523) in the U.S. was enacted to provide increased safety of drinking water supplies. The act was significantly amended in 1986 to establish new drinking water quality and treatment regulations according to specific timetables. Maximum contaminant levels (MCL) and goals were developed for priority pollutants with provisions for adding additional contaminants.

The act has several provisions which affect the food industry's use of land for wastewater disposal and discharge of effluent to a receiving body of water or to Publically

Owned Treatment Works (POTW). SDWA was designed to protect both surface and ground sources of drinking water from initial contamination wherever possible. The identification of drinking water contaminants that may be harmful to humans and establishing Maximum Contaminant Level Goals (MCLGs) were the driving forces behind the SDWA.

c. National Pollutant Discharge Elimination System (NPDES)

The mechanism for reducing the discharge of pollutants to a receiving body of water is known as the National Pollutant Discharge Elimination System (NPDES) which sets forth the limitations of discharge. Permits are required by industry (point source) and compliance is legally enforceable.

Industry discharging waste effluents to a municipal sewer, commonly referred to as Publically Owned Treatment Works (POTW) do not require a NPDES permit. However, the POTW would require such a permit for discharge. The POTW has its own discharge limitations imposed by regulatory bodies, and if exceeded, the POTW can be fined or required to upgrade with costs passed onto the dischargers.

As discharge limitations are becoming more stringent, the food industry is faced with ever increasing charges as POTW facilities are upgraded, and the POTW has the right to refuse or require pretreatment standards for industrial effluents. The food industry may be forced to make an economic choice between treatment on site or contracting to the POTW facility. Government mandates that all POTW users pay their fair share of all costs.

3. Environmental protection laws and regulation - Canada

The Clean Water Act of 1972 in the U.S. and its imposed deadlines leading to zero discharge by 1985 had immediate effects on regulations for discharge in Canada.

In Canada, in response to the growing awareness of environmental issues, the Federal Government established the Department of Environment in 1971. The Environmental Protection Service (EPS) was specifically responsible for environmental protection. First generation environmental statutes included the Clean Air Act, the Canada Water Act, the Fisheries Act Pollution Amendments and Industry Regulation. A comparison of effluent and water quality requirements of Canada, U.S. and Japan is shown in Table 3.

The approach of EPS was to adopt a strategy of containment at source by means of BPT, similar to EPA regulations. The philosophy of Environment Canada was to encourage industry to adopt in-plant controls and physical-chemical treatments leading to recycle and reuse systems instead of biological treatment outside the plant (Anon, 1977).

Effluent regulations and guidelines by the Environment Protection Service (1977) were established for several food processing industries including potato, meat and poultry and fish. The Fisheries Act is the legislation under which water pollution control regulations are promulgated. The Fisheries Act of 1868 was amended in 1971 to permit the establishment of regulations limiting the discharge of substances similar to the 1982 Federal Water Pollution Control Act in the U.S.. The aim of the regulations and guidelines was to insure that all processing plants in Canada apply BPT to effluent control.

Table 3: Effluent and water quality requirements.

Parameter	Wastewater effluent	Stream quality
	Canadian Objectives (Ontario)[1]	
BOD_5	15 mg/L max.	4 mg/L max.
SS	15 mg/L max.	—
DO	2 mg/L min.	4 mg/L min.
Total Coliforms	—	5,000/100 mL max. (water supply)
		1,000/100 mL max. (swimming area)
Fecal Coliforms	200/100 mL max.	500/100 mL max. (water supply)
	United States Standards (Typical)	
BOD_5	30 mg/L max.	4 mg/L max.
SS	30 mg/L max.	—
DO	—	4 mg/L min.
Total Coliforms	—	5,000/100 mL max. (water supply)
		1,000/100 mL max. (swimming area)
Fecal Coliforms	200/100 mL max.	500/100 mL max. (water supply)
	Japanese Standards[2]	
BOD_5	20 mg/L max.	2 mg/L max.
SS	70 mg/L max.	25 mg/L max.
DO	—	7.5 mg/L min.
Total Coliforms	—	5,000/100 mL max. (water supply)
		1,000/100 mL max. (swimming area)
Fecal Coliforms	30/100 mL max.	

[1] Ontario Ministry of the Environment (1978).

[2] Hayashi, T., "Water Pollution Control in Japan." *Journal of the Water Pollution Control Federation* 52 (1980): 855; Tamaki, T., "Wastewater Treatment Works in Japan." *Journal of the Water Pollution Control Federation* 52 (1980): 864.

Source: Henry and Heinke, 1989.

Environment Canada initially defined BPT based on a reasonable level of plant operation and secondary (biological) treatment. In pursuit of its philosophy for plants to adopt recycle and re-use systems, a project was sponsored by EPS in 1979 to provide a comprehensive review of physical, physical-chemical and other advanced treatment technologies applicable to waste treatment of the Canadian food processing industry (Environment Canada, 1979).

Other significant Canadian laws include the Canadian Environmental Protection Act (CEPA) 1988, which is similar to the U.S. Clean Water Amendment 1986, dealing with toxic control. The Manitoba Environment Act, 1988, was enacted to allow provincial regulation of environmental issues in the province.

a. Regulatory review - Canada

Environment Canada initiated a regulatory review in 1992 following concerns that regulations impede Canada's competitiveness by imposing needless costs on companies and consumers and that the cost to tax payers to maintain many regulations now in place is no longer affordable. An underlying principle of sustainable development is to achieve environmental objectives without imposing unnecessary economic barriers.

The review concluded that in the food processing sector, potato processing plant liquid effluent regulations and meat and poultry products plant liquid effluent regulations should be replaced with a national code of practice (Table 4). The reasoning was that the majority of effluents from food processing plants are discharged to municipal treatment or treated off-site prior to discharge to the environment.

Table 4: Regulatory review on Meat and Poultry Products Plant Liquid Effluent Regulations and Potato Processing Plant Liquid Effluent Regulations.

Regulations	Comments Received	Recommendations	Action Plan
MEAT AND POULTRY PRODUCTS PLANT LIQUID EFFLUENT REGULATIONS (FA) These regulations limit the discharge of specified deleterious substances in the effluent of these plants.	- There is concern over duplication, i.e., that federal standards are superimposed upon provincial and municipal standards. - Sampling and testing protocols are onerous for small businesses. - There is confusion over the scope of regulatory applicability. Comments on the findings - supported revoking the regulations and replacing them with a national code of practice; - revealed that the Province of Newfoundland and Labrador does not have similar regulations; it wants an appropriate system in place before repeal.	- Repeal the regulations after the inventory information is updated and after extensive consultation with the provinces and territories.	- Plans to revoke the regulations will be added to the 1995 Federal Regulatory Plan. - Consultations and studies will take place in 1995-96 to develop a national code of practice. contact: Mr. H. Cook (819) 997-3714
POTATO PROCESSING PLANT LIQUID EFFLUENT REGULATIONS (FA) These regulations limit the discharge of specified deleterious substances in the effluent of these plants.	- There is concern over duplication, i.e., that federal standards are superimposed upon provincial and municipal standards. - Sampling and testing protocols are onerous for small businesses. - There is confusion over the scope of regulatory applicability. Comments on the findings - supported revoking the regulations and replacing them with a national code of practice; - revealed that the Province of Newfoundland and Labrador does not have similar regulations; it wants an appropriate system in place before repeal.	- Repeal the regulations after the inventory information is updated and after extensive consultation with the provinces and territories.	- Plans to revoke the regulations will be added to the 1995 Federal Regulatory Plan. - Consultations and studies will take place in 1995-96 to develop a national code of practice. contact: Mr. H. Cook (819) 997-3714

Source: Environment Canada, 1994.

Agriculture Canada (1994) issued a report dealing with water quality and competitiveness in dairy processing. This is especially important in that policy changes to the dairy industry, a supply-managed industry, are imminent. There already exists large differences between Canadian and world prices for dairy products. The report concluded that effluent regulations do not provide a competitive advantage or disadvantage to dairy producers compared to other countries. The review also concluded that there should be a federal and provincial environmental bodies to provide a simplified approach to environmental protection.

4. ISO 14000 - New standards for environmental management

In 1987, the International Standards Organization (ISO) developed a series of quality standards referred to as ISO 9000 to rate quality management and assurance. These standards are increasingly being recognized in Canada.

In 1993, the ISO initiated new standards on environmental management known as ISO 14000. It is suggested that environmentally conscious consumers may become the biggest proponent of ISO 14000, demanding that companies comply with the global environmental standard established (Swientek, 1995).

5. Waste water management

Mans (1993) suggested that the ideal approach to wastewater problems is for the industry to develop a waste/water management program to reduce water usage and reduce the amount of food product being discharged as effluent. The steps to a wastewater program for an individual company are:

i. To obtain management approval and backing.

ii Appoint a wastewater management supervisor. Duties:

1. Perform plant survey - water lines, sewer lines.
2. Determine amount of water used.
3. Determine amounts and strengths of waste generated.
4. Evaluate plant critically.
5. Formulate a plan to correct problems.
6. Institute a water/waste education program.

Mans in his article used the dairy industry as an example; however, this approach is applicable to all food processing plants.

6. Research - Environmental issues

The food processing industry is faced with considerable costs and liabilities when complying with environmental laws and regulations. In the U.S., food industry expenditures for pollution abatement increased by more than 40% between 1985 and 1989.

Cooper (1993) described research needs required on air pollution, water pollution and solid waste, suggesting there is still inadequate information on source, types and

quantities of wastes being disposed of by industry. Additional research is required in processing unit operations to minimize waste generation and to improve treatment technologies.

Reuse and recycle technologies are the most ideal solutions to reducing the quantity of water used and solids generated. Research is required to demonstrate the safety of recycling and should include the evaluation of technologies such as membranes which could provide safety factors. The development of rapid analytical methods for detection of constituents of regulatory significance is also important.

The need for wastewater treatment at the plant site is increasing as municipalities are running out of treatment capacities for industrial users, and regulatory constraints of discharge to land or bodies of water is increasing. In the U.S., amendments to the Clean Water Act provides levels of regulations that are in some cases lower than the standards for drinking water. By regulation, water exiting a food processing plant may be required to be cleaner than water used for processing (Bowers, 1993).

III. MATERIALS AND METHODS

A. Sampling

1. Sampling sites : effluent characterization

Effluent samples were collected from seven unit operations within the Woodstone Foods pea processing plant and a composite sample from all plant process waters discharged. The sites included pea wash station, fiber and starch separators, primary protein desludgers #1 and #2, secondary protein desludgers #1 and #2, and a composite sample from an outside effluent equalization tank. Effluents generated by the wet milling process are illustrated in Fig 1.

2. Sampling period : effluent characterization

Plant personnel were responsible for sample collection at the sampling sites. Samples (2L) were taken every 4 hours during the 16 hour processing day by a grab sampling technique and stored under refrigeration (4-6°C). A composite sample of 4L size for each site from the sampling periods was delivered under refrigeration (4-6°C) to the Food Science Department for analysis. Two separate sampling periods consisted of sampling 1 day each week for six consecutive weeks, and also 1 day each week for 12 consecutive weeks.

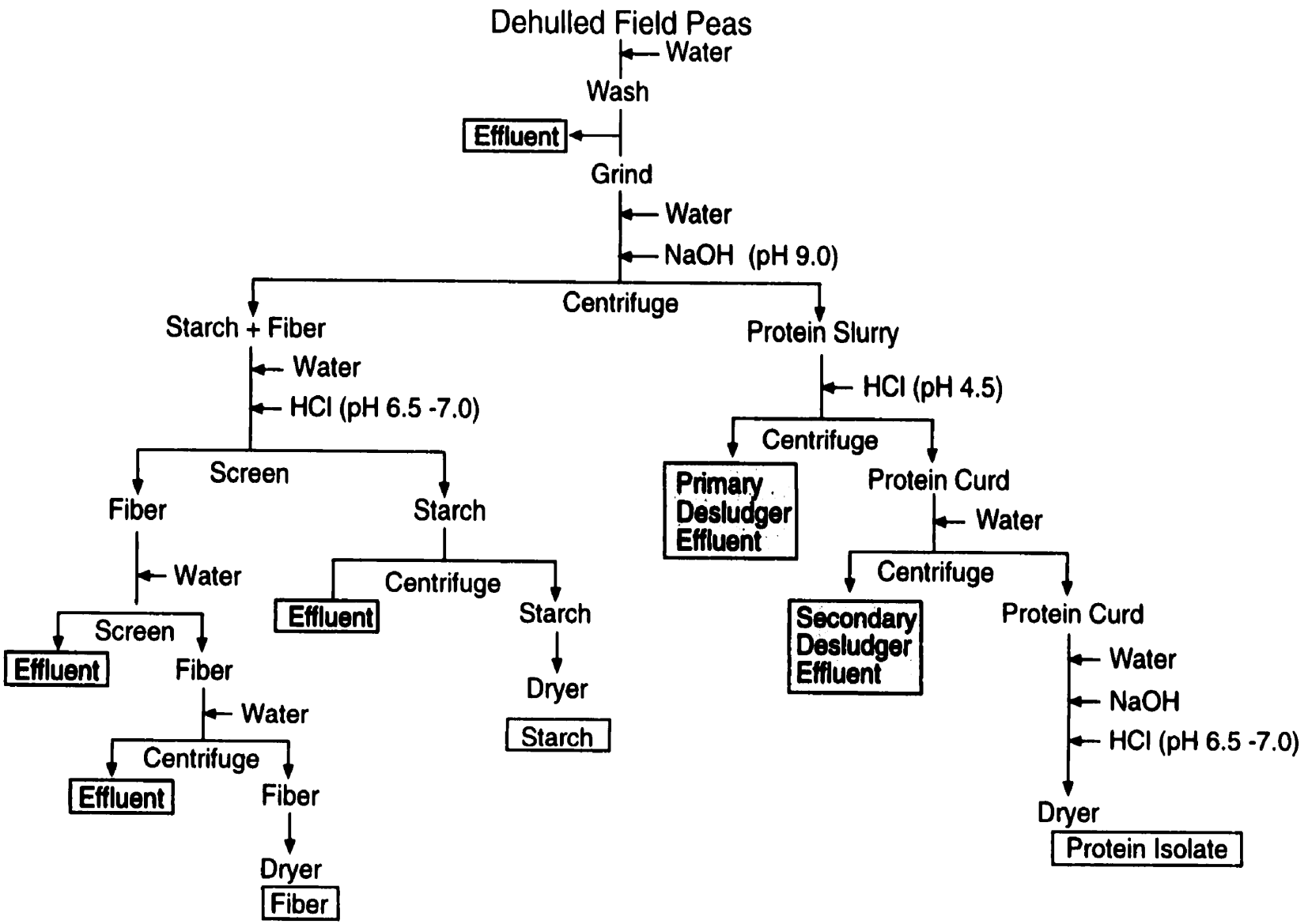

Figure 1. Production of Field Pea Protein, Starch and Fiber (Parrheim Foods).

3. Protein desludger sites : membrane studies

Protein desludger effluents were selected for subsequent membrane studies due to their high protein and solids content and rate of discharge. Three sets of samples were taken for examining compositional variation of the protein desludger effluents by drawing samples every 2 hours for 24 hours. Subsequent membrane studies utilized composite effluent samples drawn from both primary and secondary protein desludgers every two hours for eight hours. Samples were immediately transported to the Food Science Department under refrigeration (4 - 6°C) for analysis and membrane treatment.

B. Effluent characterization

Effluent samples were subjected to the following analysis: biological oxygen demand (BOD), chemical oxygen demand (COD), carbohydrate, protein, TCA precipitable nitrogen, ash, total solids, suspended solids, pH and temperature.

1. Biochemical oxygen demand (5-day BOD)

Biochemical oxygen demand (BOD) analysis is an empirical test which measures the amount of oxygen utilized for both the biochemical degradation of organic material and the oxidation of some inorganic material during a specified incubation period, and thereby providing an estimate of the waste loading of wastewaters and effluents. In this study, the 5-day BOD (BOD_5) test was used according to method 5210 B, Standard Methods for the Examination of Water and Wastewater (APHA, 1989). It has been found that a reasonably large percentage of the total BOD is exerted in 5 days, and consequently, the test has been

developed on the basis of a 5-day incubation period. The seeding for the test was obtained from the City of Winnipeg South-end Water Pollution Control Centre. The BOD_5 test has been widely used throughout the world for water and wastewater and data has been accumulated and correlated with other characteristics of existing wastewaters (Green and Kramer, 1979).

2. Chemical oxygen demand

Chemical oxygen demand (COD) for the determination of organic matter was by the closed reflux, colorimetric method (5220 D) in Standard Methods for the Examination of Water and Wastewater (APHA, 1989).

COD measures the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant under acidic conditions. The test is useful for monitoring organic loading, and can be related empirically to the BOD test (APHA, 1989). In comparison to BOD, COD is rapid, relatively inexpensive and reproducible. Due to these advantages, COD is the most widely used test for the estimation of organic strength.

3. BOD:COD ratio

The calculated BOD:COD ratio for individual food plants or process effluents is an important quality aspect since COD data can provide more immediate information (approximately 3 hours). Regulatory agencies will accept COD data once a ratio has been established (Green and Kramer, 1979). Comparison of BOD, COD and theoretical oxygen

demand (ThOD) results has been tabulated by Ramalho (1983). Standard COD values vary from 80 - 100% of ThOD, depending on the composition of the effluent, while BOD values vary from 58 - 65% of ThOD. Each wastewater, however, will have its own correlation factor. The correlation factor for the BOD:COD ratio for pea processing effluents was determined by relating the analytical test results in this study.

4. pH

The pH values for process effluents was measured using an Accumet pH meter model #910 (Fisher Scientific Company, Fairlawn, New Jersey).

5. Total solids

Total solids were determined for the effluent samples as described in section 2540 B in Standard Methods for the Examination of Water and Wastewater (APHA, 1989).

6. Suspended solids

Suspended solids were measured according to procedure 2540 D outlined in Standard Methods for the Examination of Water and Wastewater (APHA, 1989). A glass fiber filter disk (Whatman GF/C glass microfibre filters, 2.1 cm diameter) was used in the test.

7. Settleable solids

Settleable solids were measured according to procedure 2540 F outlined in Standard Methods for the Examination of Water and Wastewater (APHA, 1989).

8. Nitrogen determination

The protein content of the effluent was estimated by a micro-Kjeldahl technique (AACC method 46-13, 1983). To convert total nitrogen to protein content the factor 6.25 was used. Trichloroacetic acid (TCA) precipitation to determine non-protein nitrogen followed the method outlined by Bhatty et al (1973). A 12% TCA solution was used.

9. Carbohydrate

Carbohydrate was determined according to a colorimetric method using phenol and sulfuric acid (Benefield and Randall, 1976). The samples were first filtered through Whatman GF/C glass microfibre filter paper to remove suspended solids. A LKB Blochrom ultrospec II Spectrophotometer (Cambridge, England) was used to measure the absorbance of the test samples for carbohydrate at 490 nm.

10. Ash content

Ash content of samples was determined according to method 2540 E in Standard Methods for the Examination of Water and Wastewater (APHA, 1989).

11. Temperature determination

Temperature measurements were performed using a digital platinum thermometer (ET-5, BCR Industries Inc.).

12. Flow rate

Flow measurements were taken by using a 10L graduated container and a stop watch. The time taken to fill the container was recorded. The sampling sites were as listed in section A.1. Flow measurements were performed during sample collection (in Section A.2.).

13. Viscosity

Viscosity measurement was performed using a capillary flow viscometer. A Ubbelohde viscometer (Cannon Instrument Co. State College, PA), size 1B was used. The time (efflux time) for the test liquid to fall through the capillary tube between set markings was recorded. The viscosity of the sample was calculated by multiplying the efflux time by the viscometer constant. The viscosity experiment was run at 50°C using a constant temperature water bath.

14. Color

Color was determined using a Hellige Aqua Tester (Hellige Inc. NY). Sample color was determined by comparison with a permanent color disk and recorded as Hellige color units.

15. Electrophoresis

Pea protein flour (Parrheim Foods) and UF concentrated protein were analyzed by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) with and without the reducing agent 2-mercaptoethanol according to the method of Ng et al (1988). The stacking gel acrylamide concentration was 3%, and the separating gel was 12%. A dual cooled vertical slab gel electrophoresis unit (SE600-15-1.0, Hoefer Sceientific Instruments, San Fernando, CA) was used. Ten tooth slot formers and a 1.5 mm spacer were utilized. A constant amount of protein was loaded in each lane, and electrophoresis was carried out at 25mA for 3-4 h. Marker proteins (Sigma SDS-PAGE standards) of known molecular weight including egg albumin (45,000) and bovine serum albumin (66,000) were run with SDS-PAGE gels as reference standards.

16. Gel filtration

The UF concentrated protein was analyzed for molecular weight distribution using a K26/100 column packed with Sephacryl S-300 HR (Pharmacia Biotech AB, Uppsala, Sweden). The eluted samples in a buffer of 0.2 M Na acetate (pH 7.5) were collected with a LKB 2212-010 HeliRac collector (LKB-Produkter AB, Bromma, Sweden). The eluted fractions (2.8 ml) were collected and analyzed for protein by recording absorbance at 280 nm. The resulting elution profile diagram was analyzed using a standard curve of marker proteins (Biorad Gel Filtration Standards #1511901) to determine the pea protein molecular weights. Marker proteins included thyroglobulin (670,000), gamma globulin (158,000), ovalbumin (44,000), myoglobin (17,000) and vitamin B-12 (1,350).

C. Membrane Study

1. Pre-treatment of desludger effluent

a. Enzyme pre-treatment. The enzymes used in this study included Termamyl Novozym, Viscozyme, Celuclast, and Pectinex (Novo Nordisk Biochem, Franklinton, NC). These enzymes were selected based on having activity at 45-50°C and at a pH close to 4.5, both characteristics of the protein desludger effluent. Effluent was heated to 50°C in a tilting steam kettle prior to addition of enzyme or combination of enzymes. Termamyl was evaluated alone, or was used in combination with the other enzymes. The enzymes were evaluated using a concentration ranging from 0.002% to 0.2% based on product information from Novo Nordisk Biochem (Franklinton, NC).

The effectiveness of enzyme treatments was based on the time required for a floc formation, negative starch test, and viscosity measurement at 50°C. The qualitative test for starch was according to the iodine test (Novo Nordisk Biochem, Franklinton, NC). Iodine reacts with starch to give a blue-colored complex. Viscosity measurement was made according to the method outlined in Section B.13.

b. Celite pre-treatment. Successful enzyme pre-treatment was based on the formation of a fine floc. Once the floc formed, celite was added as a filter aid for more effective and rapid settling of floc that developed. Celite was added at a predetermined concentration of 0.02% (Berger, 1995).

c. Decantation

Decanted effluent was used as the feed to the membrane in some studies. The

enzyme and celite treated effluent was held under quiescent conditions for up to 30 min, then decanted by pouring the clarified effluent through a 100 mesh screen to a receiving vessel.

d. Centrifugation. The pre-treated effluent was centrifuged using a Sorvall RC-3 centrifuge at average G force of 900 for 5 min. The supernatant represented the feed to the membrane in some studies using the Amicon CH2 laboratory unit.

2. Ultrafiltration

Two different ultrafiltration systems were examined for concentration of pea desludger effluents as follows:

(1) Amicon MPD-100 laboratory unit (Fig. 2). The membrane cartridge was a hollow fiber type H5P30-43. The membrane was constructed from polysulfone, had a nominal molecular weight cut-off (MWCO) of 30,000 Daltons, and a surface area of 0.45 m^2. The ultrafiltration unit was operated at an inlet pressure of 140 kPa and an outlet pressure of 35 kPa. The feed solution was kept at 45-50°C during concentration.

(2) Amicon CH2 laboratory unit (Fig. 3). The membrane cartridges employed were of two types: SIY30 (30,000 Daltons), and an SIY10 (10,000 Daltons) spiral-wound cartridges. The membranes were regenerated cellulose-based. The membrane area was (0.09m^2). The ultrafiltration unit was operated at a pressure of 140 kPa. The feed solution was kept at 45 - 50°C during concentration.

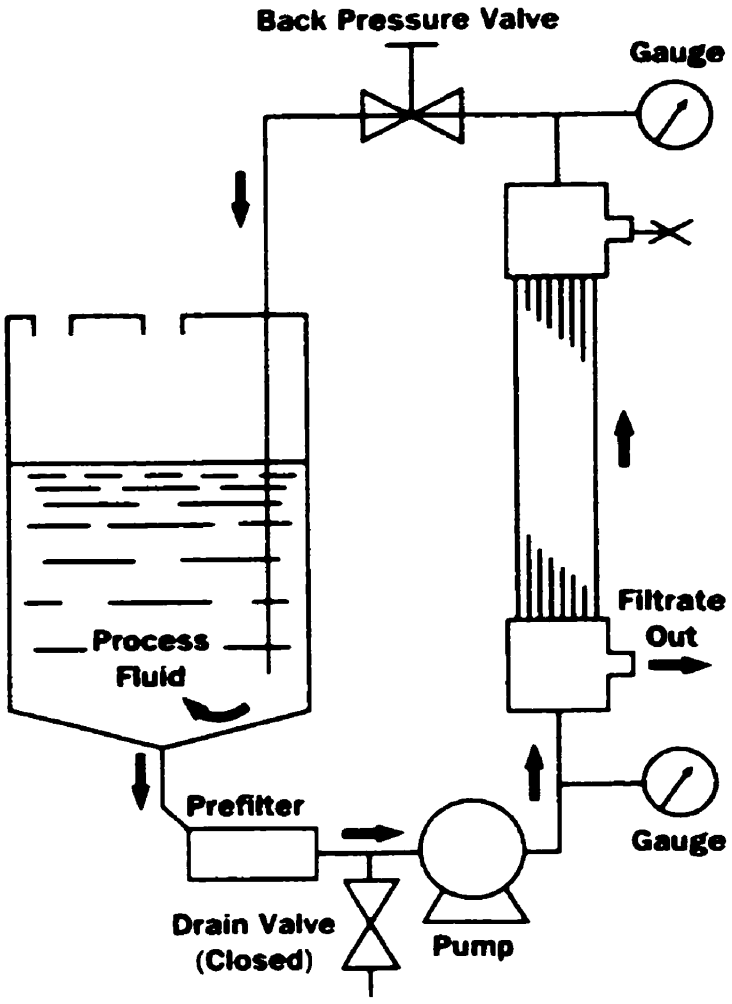

Figure 2. **Batch mode concentration with hollow fiber system.** (Amicon, 1995)

Membrane cartridge: H5P30-43 (30,000 MWCO)
Membrane material: Polysulfone
Membrane area: 0.45 m^2

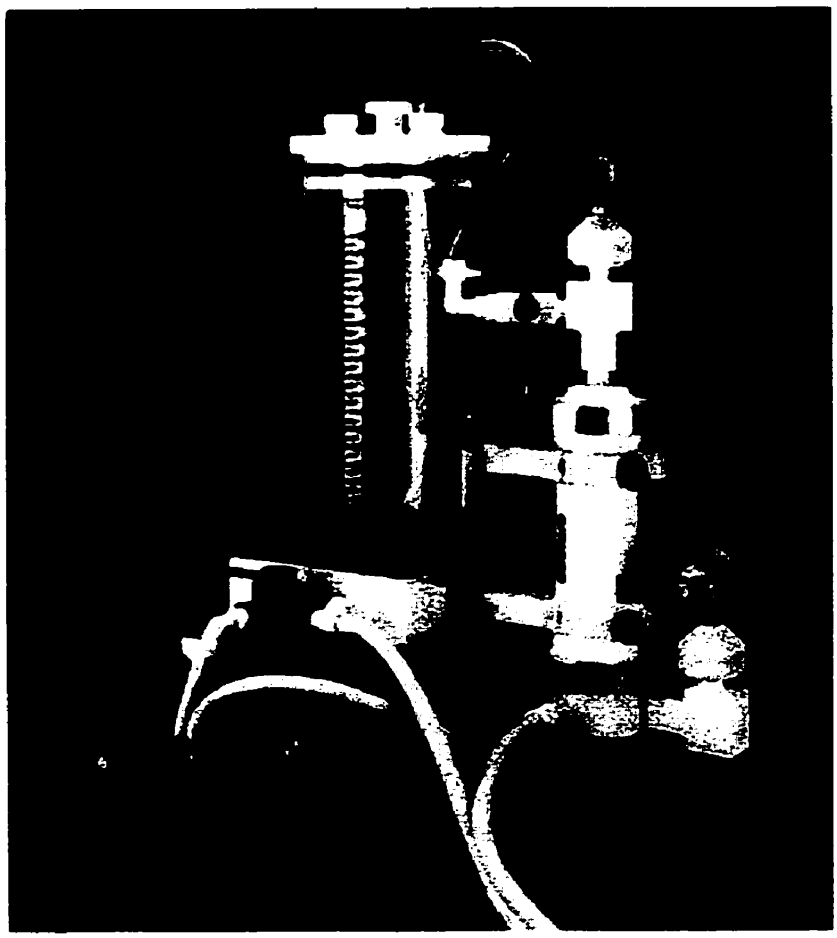

Figure 3. **Batch mode concentration with spiral wound cartridge.** (Amicon, 1995)

Membrane cartridges:	SIY30 (30,000 MWCO) SIY10 (10,000 MWCO)
Membrane material:	Cellulose
Membrane area:	0.09 m^2

Both hollow fiber and spiral wound membrane systems were used in this study to compare the effect of operating parameters, and resulting UF fraction compositions. The membrane systems and membranes used were based on availability at the Food Science Department. The Amicon CH2 laboratory unit was used especially for concentration studies at 20:1 VCR, convenient in effluent handling and concentrate recovery.

a. Concentration

The effluents were concentrated up to 20:1 volume concentration ratio. Other volumetric concentration ratio samples were obtained by dilution of final retentate with appropriate volumes of permeate. Retentates were stored at refrigeration temperature (4-6°C) for subsequent testing.

b. Diafiltration

Diafiltration was carried out using a discontinuous diafiltration mode by concentrating to a determined concentration volume, followed by adding an equal volume of water to the retentate (50°C) and reconcentrating to the determined concentration volume.

3. UF operating parameters

a. Flow rate (mL/min)

The permeate flow rate was monitored at start time and at determined intervals by collecting permeate in a graduate cylinder for a period of one minute. The clean water flow rate was used to evaluate membrane integrity and the effectiveness of the cleaning operations.

b. Flux (LMH)

The volumetric rate of flow of the permeate through the membrane in terms of volume per unit membrane area per unit time (liters/m^2/hour) was calculated from flow rate and membrane surface area data.

c. Volume concentration ratio (VCR)

The volume concentration ratio was determined by recording the initial feed volume, and volume of permeate generated or retentate volume.

VCR = Initial feed volume (V_o) / Retentate volume (V_R)

d. Rejection (R)

Rejection measures of how well a membrane retains or allows passage of a solute. The higher the rejection value, the more a solute will be retained in the retentate. Rejection (R) is defined as: $R = 1 - C_p/C_R$

where: C_P = the solute concentration in the permeate

C_R = the solute concentration in the retentate

4. Membrane cleaning

a. H5P30-43 cartridge

The following procedure was used to evaluate cleaning of the hollow fiber membrane:

i. Membrane was flushed with RO water (University of Manitoba supplied) at 50°C for 10 minutes.

ii. Alkaline cleaning solutions were evaluated using a) 0.1N NaOH, b) 0.1N NaOH with 200 mg/L NaHOCl, and c) commercial alkaline chlorinated

solution (Monarch Filtra Pure 140 powder) adjusted to 200 mg/L NaHOCl, by circulation at 50°C for 15 - 60 minutes. Permeate was directed back to feed tank during washing.

iii. Membrane was flushed with RO water (50°C) for 10 minutes or until pH of clean water was established.

iv. Membrane was subsequently washed with acid (0.1N HCl) for 30 minutes at 40°C if flow rate was not restored to membrane specifications, and flushed with RO water.

v. Membrane was stored in soak solution (Divos Soak, Diversey) at refrigeration temperature (4-6°C).

b. SIY10 and SIY30 membranes

For the spiral wound membranes, the following cleaning procedures were evaluated:

i. Membrane was flushed with RO water (University of Manitoba supplied) at 50°C for 10 minutes.

ii. Alkaline cleaning solutions were evaluated using a) 0.1N NaOH at 50°C for 15 - 60 min and b) 0.1N NaOH with 75 mg/L NaHOCl at 20°C for 15 - 60 minutes.

iii. Membrane was flush RO water at 50°C for 10 minutes.

iv. Membrane was subsequently wash with acid (0.05 N HNO_3) if flow rate was not restored to membrane specifications, and flushed with RO water.

v. Membrane was stored in 0.2% sodium azide solution.

D. Activated carbon treatment

1. Test liquid

Permeate from the membrane treatment of pea protein desludger effluent was treated with activated carbon to determine the effect of carbon on color and COD removal.

2. Activated carbon type

The activated carbon adsorbent used in this study was Darco powdered activated carbon grade S51. The choice of carbon was based on personel communication with Mr. L. Carvalho (STC laboratories, Winnipeg). STC laboratories is a major user of activated carbon in Winnipeg.

3. Adsorption isotherm procedure

Determination of adsorption isotherms experimentally was according to (Hassler, 1974). Different amounts of carbon were weighed into 250 ml Erlenmeyer flasks, the test liquid (100 ml) was added, and the samples and carbon were shaken on a rotary shaker (Fermentation Design Inc., Allentown, PA.) at 300 rpm for 1 hour. A control (no added carbon) was also carried through the test procedure. The samples were filtered free of carbon by using a Buchner funnel fitted with Whatman filter paper No.5. The filtrate was analyzed for color and organics (COD).

4. Adsorption isotherm evaluation - The Freundlich adsorption isotherm

The Freundlich equation for adsorption isotherms (Hassler, 1974) was used to determine the adsorption capacity of the activated carbon. The Freundlich equation is a mathematical expression relating the amount of substance adsorbed and the unadsorbed quantity that is left in solution. The equation is written:

$$x/m = kc\ 1/n$$

Where: x = units of impurity adsorbed
c = equilibrium concentration of impurity remaining in solution after adsorption
m = carbon weight
x/m = concentration of impurity in adsorbed state
k, n = constants

The isotherm is generated by plotting log x/m versus log c which theoretically yields a straight line.

$$\log x/m = \log k + 1/n \log c$$

1/n = slope of the straight line plot
k = intercept of the line at c = 1

The adsorption isotherm plot indicates the degree of purity that can be obtained with activated carbon treatment. By extrapolation of the isotherm plot to intersect the horizontal straight line drawn from the influent concentration (C_o), the adsorption capacity of the activated carbon can be determined. The value $(x/m)C_o$ obtained from the isotherm plot represents the amount of impurity adsorbed per unit weight of carbon.

IV. RESULTS AND DISCUSSION

A. Plant Effluent Characterization

The field pea processing plant uses a wet milling process (Fig. 1) for the separation of field pea components. Water is used to wash the peas, transport pea slurry for separation of starch and fiber, solubilize (with pH adjustment) protein, separate protein by isoelectric precipitation and centrifugal action, and to transfer components within the plant including to final spray drying operations. The processing facility has a requirement for approximately 700,000 L of fresh water on a daily basis.

As illustrated in Fig. 1, effluents are generated at the various unit operations, drained to a central outside tank, and discharged by pump for municipal treatment. The plant currently employs a once-through water use with no recycle/reuse.

The effluent characterization study was set up to characterize the effluents generated at each process site and total plant effluent at discharge. Previous information was reported by Grabowecky (1989), however process improvements were made at the plant in the interim and current information was required by the plant. The results of this study would be beneficial to the plant in determination of:

1. Capacity required by company at Publically Owned Treatment Works (POTW) - fixed cost.

   In 1995, the City of Portage la Prairie was upgrading its secondary treatment facility and was requiring industry to submit a capacity requirement for the facility. This % capacity would determine the fixed cost of charge to the company for treatment at the facility. Fixed cost is defined as % of actual cost of the secondary system. Capacity is based on flow, BOD, COD, SS, and Total Kjeldahl Nitrogen (TKN) loading.

2. Effluent surcharge - variable cost.

   The effluent surcharge is based on above average domestic sewage defined by the City of Portage la Prairie as 300 mg/L BOD, 450 mg/L COD and 350 mg/L SS.

3. Process efficiency at unit operation sites.

4. Potential for protein recovery from desludger effluents by membrane treatment.

5. Recycle potential of the generated effluents.

Three separate studies were designed to characterize the field pea process effluents.

1. Effluent characterization at each unit operation.

2. Total plant effluent discharge characterization.

3. Detailed protein desludger discharge characterization.

1. Unit process operations

The characterization of field pea process effluents generated at separate unit operations is illustrated in Table 5. The results are based on 6 sampling dates over a 3 month period. Samples were taken periodically (four times daily) by plant personal during the day shift and a composite sample was used for analyses. Effluents are generated at seven major unit operations in the plant as illustrated in Figure 1 and are discharged for municipal treatment.

The discharge loading of the plant to municipal treatment was considerably higher than the domestic level established at 450 mg/L COD, 300 mg/L SS. An average organic loading of 7655 mg/L COD and 8190 mg/L SS were discharged to the municipal sewage system. These high levels would result in both a high fixed and variable cost to the company for sewage treatment.

The major sites contributing to the organic loading were the primary protein desludgers. The COD values for the primary desludger #1 and desludger #2 effluents were 15,520 mg/L and 13,810 mg/L, respectively, while SS values were 1640 mg/L and 1525 mg/L. These high values also are indicative of potential product loss through inefficient desludger operation. At the desludgers, proteins are isoelectrically precipitated and removed from the slurry by centrifugal force. Optimum conditions of pH 4.5, temperature 50°C, and residence time (not established) for precipitation and separation as established by the company are requirements for process efficiency (Berger, 1995). The protein values of the effluent were measured as 5465 mg/L and 4830 mg/L at the primary desludgers representing product loss to the company. Soluble whey proteins, and

Table 5. Composition of field pea process effluents[a].

Source	COD (mg/L)	Carbohydrate (mg/L)	Protein (mg/L)	Total Solids (mg/L)	Suspended Solids (mg/L)	pH
Wash	6240 ± 1225	3300 ± 664	1250 ± 433	6645 ± 1092	3425 ± 1222	6.10 ± 0.80
Fiber separator	1410 ± 356	390 ± 140	115 ± 38	1540 ± 414	980 ± 155	6.30 ± 0.80
Starch separator	6445 ± 1610	1950 ± 690	330 ± 117	6600 ± 1741	2100 ± 619	6.40 ± 0.45
Primary desludger #1	15520 ± 1616	6630 ± 595	5465 ± 1125	16380 ± 1730	1640 ± 554	4.76 ± 0.31
Primary desludger #2	13810 ± 1743	5990 ± 652	4830 ± 993	14440 ± 1806	1525 ± 372	4.74 ± 0.46
Secondary desludger #1	4140 ± 842	1925 ± 475	1335 ± 305	4200 ± 975	119 ± 55	4.85 ± 0.22
Secondary desludger #2	4085 ± 1110	2040 ± 394	1460 ± 377	4190 ± 853	132 ± 45	4.82 ± 0.28
Discharge tank	7655 ± 3028	1845 ± 798	2385 ± 976	8190 ± 2240	3630 ± 558	6.40 ± 1.90

[a] Average of six sampling days; one day from each week for six consecutive weeks at Woodstone Foods. Based on composite analysis of grab samples taken four times daily.

non-protein nitrogen fractions may also contribute to these values. Carbohydrate also contributes significantly to the primary desludger effluent values at 6630 mg/L and 5990 mg/L for desludger #1 and desludger #2, respectively. The secondary desludgers, used to wash the precipitated protein for improved separation and purity, were considerably lower in loading at 4140 mg/L and 4085 mg/L for COD, and 1335 mg/L and 1460 mg/L for protein. The values are, however, indicative of further product loss at this operation.

The fiber separation unit operation contributed least to the organic loading analyzed at a mean value of 1410 mg/L COD. The purpose of water at this unit operation is to effect a physical separation, not dissolution of solute components from the field pea. Water is used for a similar physical purpose at the starch separator operation. However, average COD values measured 6445 mg/L and contributed significantly to the organic loading of the discharge effluent. Similar organic loading was found at the initial pea grinding and wash stage where protein contributed significantly to the organic composition (1250 mg/L).

Total solids values obtained for the pea process effluents at the unit operations sampled were similar in value to the COD results (Table 5). This finding could provide the company with an inexpensive, routine test to monitor for organic matter in-house. The relationship between total solids and COD at the unit operations is illustrated in Table 6.

Solids monitoring also included suspended solids and settleable solids, constituents of importance in primary and secondary treatment of effluents. The suspended solids discharge to municipal treatment averaged 3630 mg/L. This value again is considerably higher than the maximum limit for domestic sewage (350 mg/L). The pea wash water was

Table 6. Field pea process effluents[a] COD/total solids ratio.

Effluent source	COD (mg/L)	Total Solids (mg/L)	COD/Total Solids
Wash	6240	6645	0.94
Fiber separator	1410	1540	0.92
Starch separator	6445	6600	0.98
Primary desludger #1	15520	16380	0.95
Primary desludger #2	13810	14440	0.96
Secondary desludger #1	4140	4200	0.99
Secondary desludger #2	4085	4190	0.97
Discharge tank	7655	8190	0.93

[a] Average of 6 sampling days; one day from each week for six consecutive weeks at Woodstone Foods.
Based on grab samples taken four times daily.

the major contributor to suspended solids, averaging 3425 mg/L. Pea hulls, foreign matter, and insoluble pea fragments would be major contributors to the suspended matter. Starch separation contributed a value of 2100 mg/L SS, which could result from incomplete starch separation, and the SS value for the primary desludgers (1640 mg/L and 1525 mg/L) could indicate precipitated protein that was not removed upon centrifugation. The presence of SS in the effluents at the unit operations represents a loss to the company in terms of revenue from pea fractions, and is a surcharge cost to the plant on discharge.

The solids content of the discharge tank was futher characterized as to its settleable solids component. The mean value obtained was 3194 mg/L, approximately 88% of the suspended solids mean value (3631 mg/L). Settleable solids are relatively easy to remove, through primary treatment by the use of filters, screens, centrifugal force and gravity separation. The high value of suspended solids that would settle could warrant the company to investigate a removal system for reduction of the suspended solids, lowering the municipal surcharge for handling. The recovered solids could find use in local hog feeding operations, an option which was being considered by the company.

The mean pH value of the plant discharge was 6.4, and was within the guidelines for effluent discharge. Of importance to the company was the pH value for the primary protein desludgers. The company tries to maintain a pH of 4.5 for optimum precipitation of protein. Deviation from this pH could result in a less efficient operation, reduced protein precipitation, and a higher organic loading in the desludger effluents. The average pH value for the primary desludgers was 4.70, with a range of 4.58 - 4.81. The combined discharge of the protein desludger effluents with other plant effluents raised the pH to a discharge value of 6.4.

The composition data is also reported in terms of sewage loading in kg/day (Table 7). COD (5362 kg/day) and SS (2541 kg/day) loadings are important in evaluating sewage surcharge and capacity costs. The desludger operations discharge 1434 kg/day of protein, a significant level when considering membrane treatment for recovery of effluent components.

2. Establishment of BOD:COD ratio

The sewage by-laws for the City of Portage la Prairie established a limit of discharge of organic matter at 300 mg/L BOD. Later in this study, in 1997, the by-laws were amended establishing levels of 300 mg/L BOD and 450 mg/L COD. Both BOD and COD are approved methods for the measurement of organic matter.

While BOD is well established as the legal reporting measurement of organic matter, the COD test is often used as a quick, convenient test procedure. The COD analyses is then correlated to the BOD value. In this study, the BOD/COD ratio was established at 0.52 (Table 8) for the total plant discharge flow. The protein desludger ratio was 0.51, starch separator ratio 0.57, and fiber separator ratio 0.38. These values for BOD:COD ratio at the plant differed from the city of Portage la Prairie by-law regulations which established a ratio of 0.67 in determining sewage surcharge. The COD test was used in this study for the measurement of organic matter.

Table 7. Waste water loading of field pea process effluents[a].

Source	COD (kg/day)	Carbohydrate (kg/day)	Protein (kg/day)	Total solids (kg/day)	Suspended solids (kg/day)
Wash	306	162	61	325	168
Fiber separator	178	49	14	194	133
Starch separator	767	232	39	785	250
Desludger operations	4105	724	1434	4295	420
Discharge tank	5362	1292	1670	5733	2541

[a] Average of 6 sampling days; one day from each week for six consecutive weeks at Woodstone Foods. Based on composite analysis of grab samples taken four times daily.

Table 8. Field pea process effluents[a] BOD_5 /COD ratio.

Effluent source	BOD_5 (mg/L)	COD (mg/L)	BOD_5 /COD
Fiber separation	536	1410	0.38
Starch separation	2449	6445	0.57
Protein desludgers	7522	14750	0.51
Plant discharge	3952	7655	0.52

[a] Average of six sampling days; one day from each week for six consecutive weeks at Woodstone Foods.
Based on measurement of grab samples taken four times daily.

3. Total plant effluent discharge

In consultation with the company, an expanded sampling plan was established to obtain additional information on characterization of total plant effluent. The study was conducted to monitor the plant discharge on a weekly basis for 12 consecutive weeks. The data provided further information on 1) plant operating conditions, 2) potential capacity requirement for secondary municipal treatment, and 3) effluent surcharge costs. The results are illustrated in Fig. 4 - 6.

The analyses confirmed the high strength and variability of plant discharge loadings. During the 12 week sampling period, the plant discharge flow ranged from 0.318 X 10^6 L / day to 0.791 X 10^6 L / day. Organic discharge varied from a low of 6970 mg/L COD to a high value of 14,250 mg/L, while SS ranged from 3000 mg/L to 9140 mg/L, and pH varied from 4.0 - 8.6. The plant consistently discharged effluent over the maximum limits of COD and SS established by the city. The large variation in effuent strength and pH could reflect plant processing difficulties and additional cost in determining secondary treatment capacity.

4. Water usage at unit operations

The major unit operations in field pea processing were characterized as to their contribution to effluent discharge in terms of flow as shown in Table 9. The protein desludger operation (primary and secondary) had a combined discharge of 47% of the total. The fiber separation and starch separation accounted for 17% and 18%, respectively. The initial pea wash and slurry discharged 7% of the total effluent. Other sources of discharge such as cleaning operations accounted for 11%.

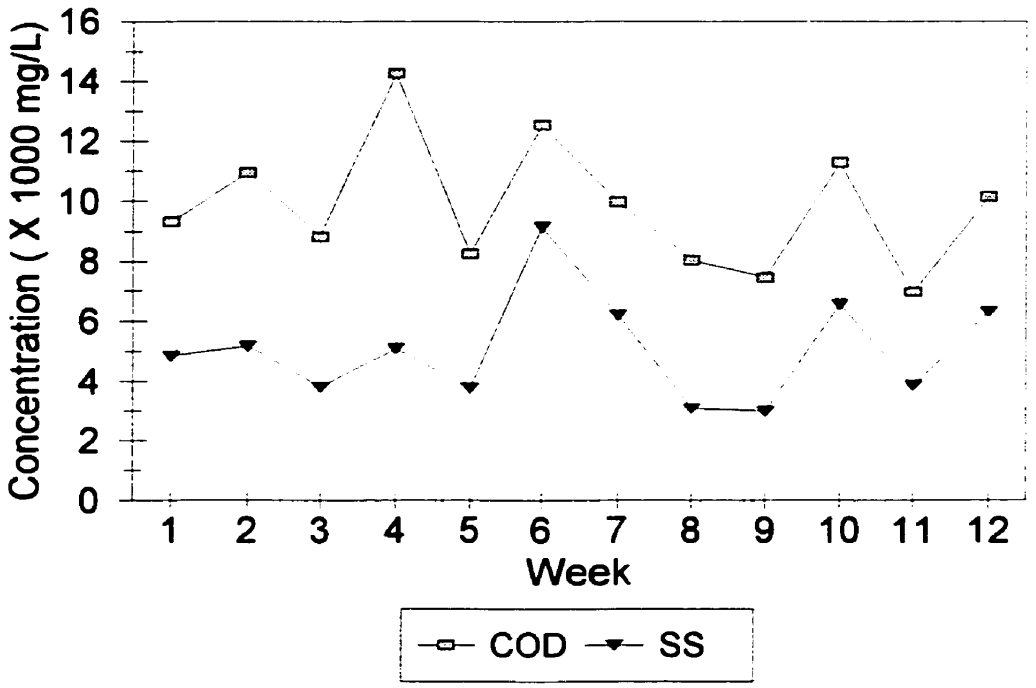

Figure 4. **Total plant effluent strength.**
Composite sample collected 1 day each week for 12 consecutive weeks in June, July and August of 1995.

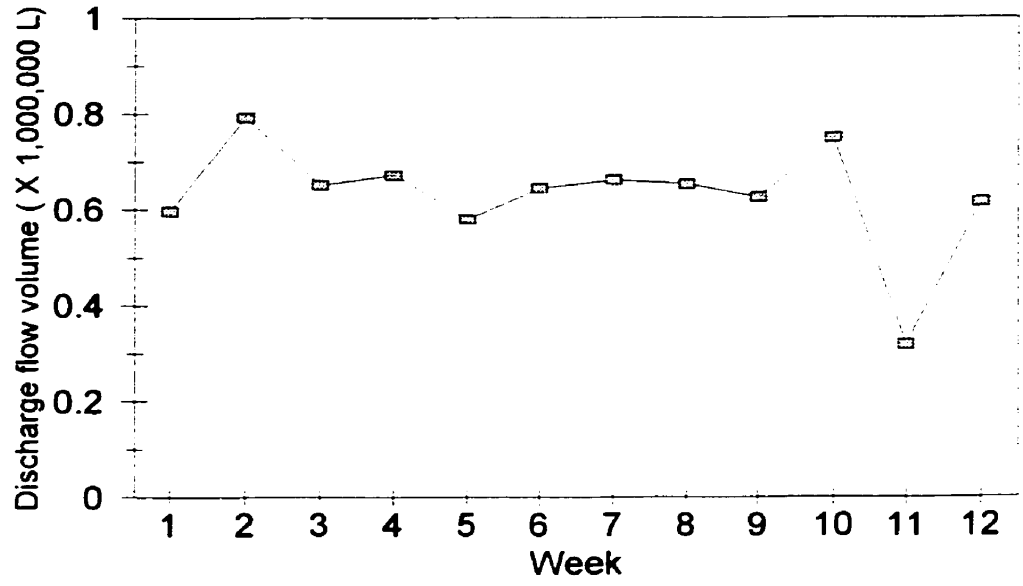

Figure 5. **Discharge flow volume of total plant effluent .**
Average daily flow rate for samples collected 1 day each week for 12 consecutive weeks in June, July and August of 1995.

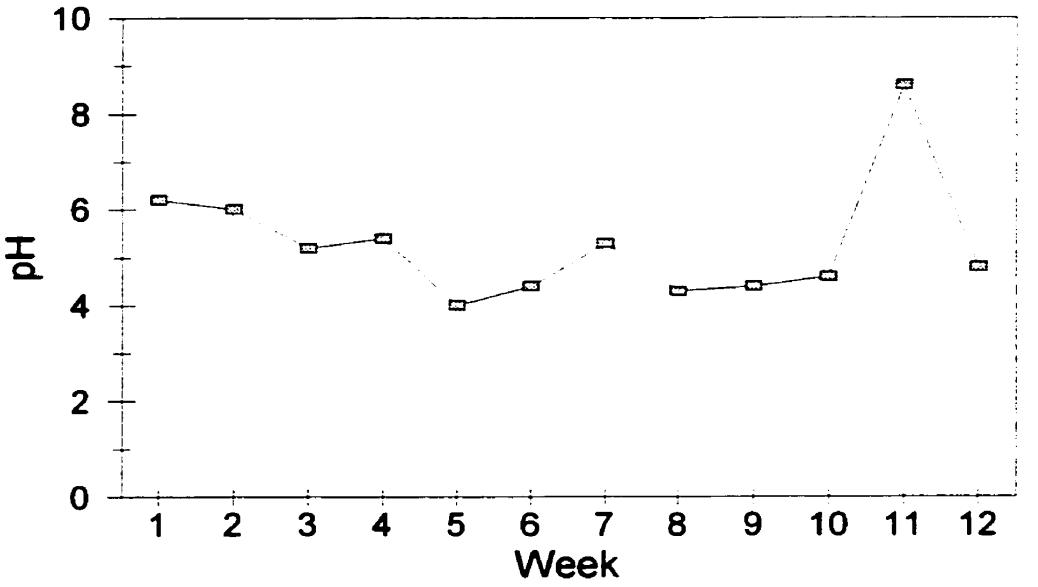

Figure 6. **pH value of total plant effluent .**
Composite sample collected 1 day each week for 12 consecutive weeks in June, July and August of 1995.

Table 9. Field pea process effluents[a] generated at wet milling operations.

Unit operation	Flow (L/day)	% Total
Pea wash	49,000	7
Fiber separation	126,000	18
Starch separation	119,000	17
Desludger operations[b]	329,000	47
Other[c]	77,000	11
Total	700,000	100

[a] Average of six sampling days; one day from each week for six consecutive weeks at Woodstone Foods.
Based on measurement of grab samples taken four times daily.
[b] Primary desludger effluent: 260,000 L/day
secondary desludger effluent: 69,000 L/day
[c] Other include wash up operations and spills.

The water use values at each operation are important to the plant in establishing process efficiency, and possible recycle/reuse opportunities. A wet milling operation typically has a high demand for water. Although criteria have not been established for water quality at each unit operation, recycle opportunities are possible given the quantity of discharge and the functions of water at each stage, some of which are mainly physical. At the desludger operation, recycling of disludger effluent may reduce the acid requirement for precipitation of protein since the pH of the desludger effluents is at the isoelectric point of the pea protein.

5. Protein desludger effluents

Protein desludgers are the major source of discharge from the unit operations in pea fractionation in terms of organic loading (Table 10). To maximize process efficiency at the desludger operation and minimize effluent loading, pH, temperature and residence time are factors that must be optimized. To determine the efficiency of operation of the protein desludgers on a continuous basis, samples were collected every two hours during the operating day. Three operating days over a 3 month period were sampled. The results are shown in Figs. 7 - 9. Whey proteins may also be soluble at the isoelectric point chosen for pea protein precipitation (pH 4.5), contributing to a soluble organic loading. Characterization of protein desludger effluents indicates that carbohydrate is a major contaminant of the protein effluent. The non-protein nitrogen fraction (fraction remaining after TCA precipitation) was shown to represent approximately 52% of the protein value. Non-protein nitrogen is composed of amino acids, peptides, and other non-protein nitrogen compounds.

Table 10. Characterization of field pea protein primary desludger effluent[a]

Desludger sample	Component (mg/L)				
	Protein[b]	NPN[c]	Carbohydrate	Total solids	COD
Average	4250	2210	6700	16340	14750
Maximum	5900	3068	6900	20300	20500
Minimum	3056	1589	4950	12600	10125

[a] Protein desludger effluent - daily average over 3 month period; 4 samples per day.
[b] Kjeldahl nitrogen x 6.25.
[c] Non protein nitrogen after TCA precipitation.

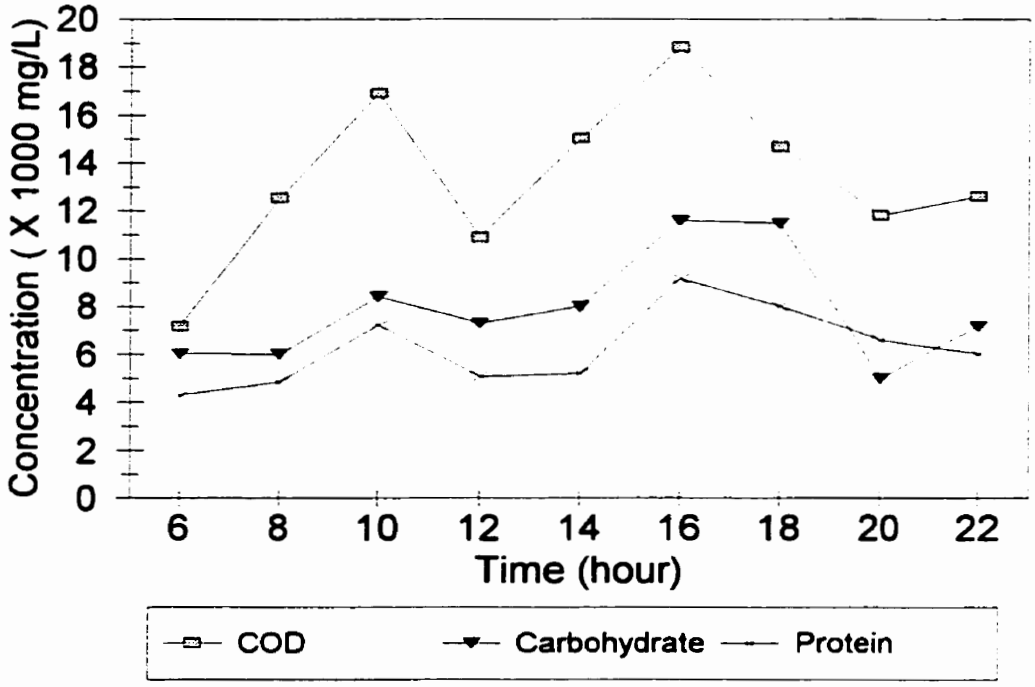

Figure 7. **Hourly protein desludger effluent strength.**
Effluents collected every 2 hours on September 4, 1995.

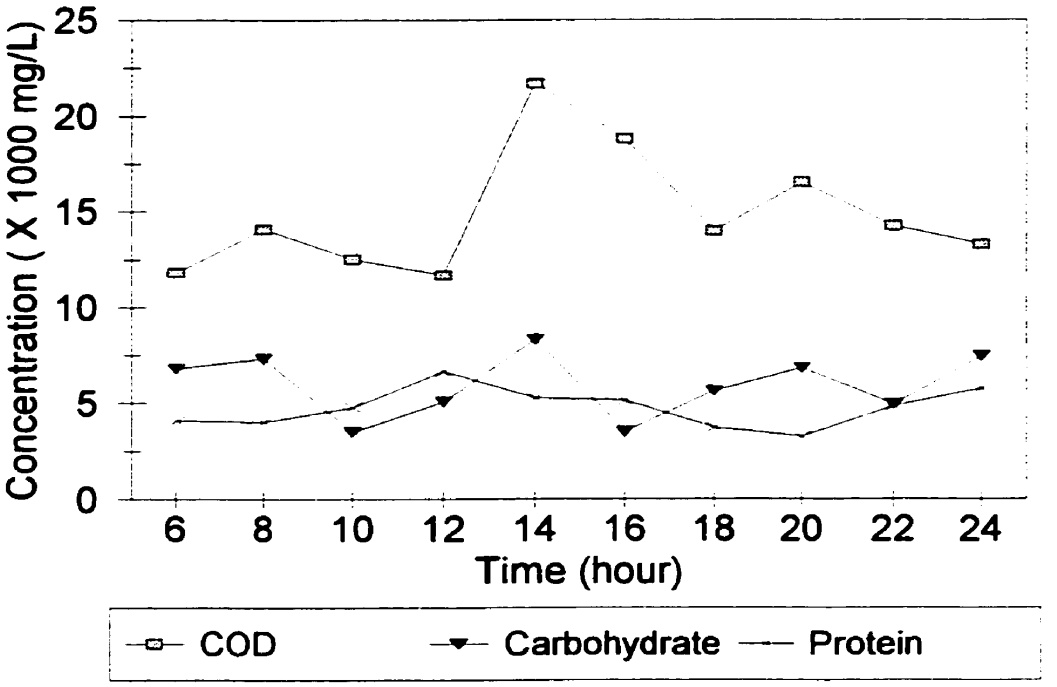

Figure 8. **Hourly protein desludger effluent strength.**
Effluents collected every 2 hours on October 8, 1995.

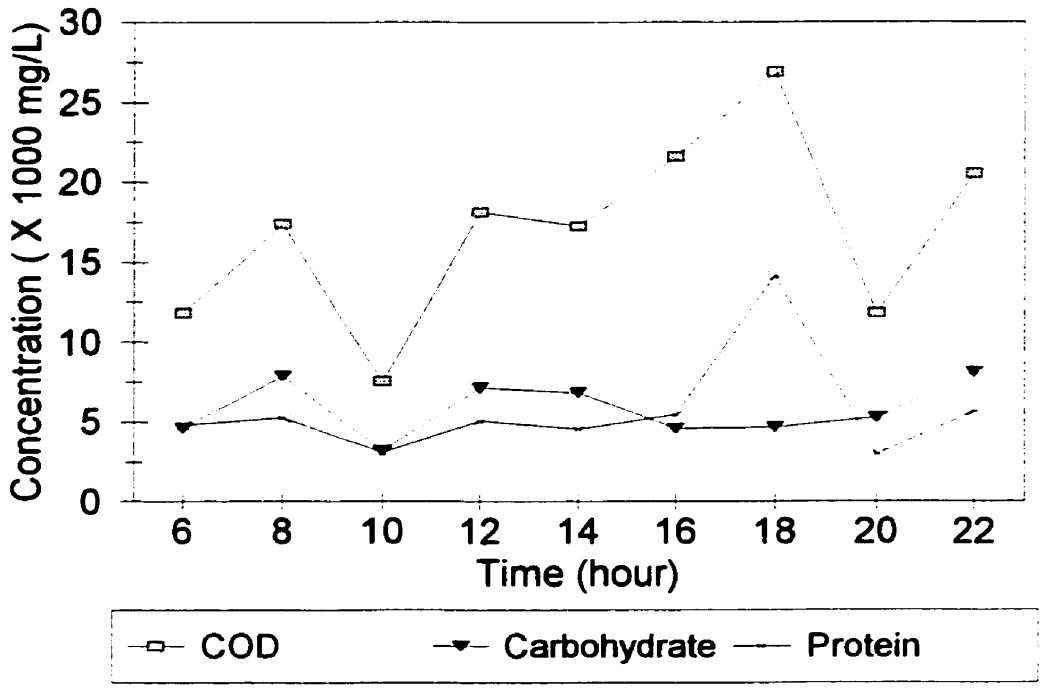

Figure 9. **Hourly protein desludger effluent strength.**
Effluents collected every 2 hours on November 4, 1995.

In terms of operational parameters, both pH and temperature showed variation from the optimum values of pH 4.5 and temperature 50°C respectively. The pH ranged from 4.15 to 4.80 and temperature showed a range from 41°C to 51°C. These deviations could partially account for the variability in organic loading of desludger effluent. Fluctuating process conditions in downstream operations would also contribute to variability in results.

As evident in Figs. 7 - 9, some large deviations were evident, especially in terms of COD measurement. Protein and carbohydrate components showed less variability. Grabowecky (1989) also noted that desludger effluents were highly variable in strength, resulting from fluctuating process conditions. Because of the high organic strength of the protein desludger effluent, and potential economic value of recovering the protein, the company wished to focus on this point source for membrane processing.

The value of the project to the company is evident from an economic analysis of the value of protein to the company. An estimate of 1434 kg/day of protein is lost into the effluent (Table 7) at the desludger operation. A 130 day process run per year and a commercial value of $4.40/kg protein (1996 value) translate to a potential revenue loss of $820,000/year and an estimated sewage surcharge exceeding $70,000/year from the protein desludger effluent alone.

B. Protein desludger effluent - Pretreatment

Based on a recommendation for work in the area of enzyme use for cleaning or to minimize fouling of membranes (Grabowecky, 1988), the Woodstone company began evaluating amylases for pre-treatment of protein desludger effluent prior to membrane treatment. From preliminary studies (Berger, 1995) it was recommended that a heat stable amylase and other carbohydrases be further evaluated. Upon company request, therefore, Termamyl (Novo Nordisk Biochem) was to be used singularly or in combination with other heat stable enzymes.

The enzymes used in this study included Termamyl, Novozym, Viscozyme, Celuclast, and Pectinex. Enzyme properties are outlined in Table 11. The enzymes were selected based on having their optimum activity at 45 - 50°C and at a pH close to 4.5, both characteristics of the protein desludger effluent. To allow for continuous processing, the company did not wish to alter these parameters. The temperature is near the maximum tolerance for most membranes, while the pH is within an acceptable range of most membrane types.

Preliminary studies (Berger, 1995) concluded that the formation of floc upon the addition of Termamyl, and that the absence of starch in the effluent as determined by the iodine test would be indicators of satisfactory enzyme pretreatment prior to ultrafiltration. Breakdown of the starch-like material, and removal of the floc material by physical treatment resulted in the desludger effluent showing more promise for membrane treatment. Once the floc was removed by physical treatment, the starch-free effluent feed did not cause fouling problems when subjected to membrane treatment.

Table 11. Enzyme properties.

Enzyme[a]	Description	Optimum pH	Optimum Temp.(°C)	Function
Termamyl 120L	Endoamylase	4.0 - 9.0	40 - 100	Hydrolyze 1,4 -alpha-glucosidic linkages in amylose and amylopectin to soluble dextrins and oligosaccharides.
Celluclast 1.5L	Cellulase	4.5 - 6.0	50 - 60	Breakdown of cellulose into glucose, cellobiose and glucose polymers.
Novozym 188	Cellobiase	4.0 - 6.5	50 - 60	Breaks down cellobiose to glucose.
Viscozyme L	Multienzyme complex carbohydrases	3.3 - 5.5	40 - 50	Breakdown of cell wall constituents.
Pextinex Ultra SP-L	Multienzyme complex pectinases	3.3 - 5.5	30 - 60	Degrade natural fiber random hydrolysis of alpha (1-4) bonds between galacturonic acid residues in pectic acid.

[a] Enzyme source: Novo Nordisk Biochem, Franklinton, NC.

This study was designed to determine enzyme type, concentration, the effect of enzyme on floc formation, presence of starch, viscosity of the effluent and membrane flux. The use of Termamyl as a single enzyme application, and in combination with other carbohydrase enzymes was investigated.

1. Effect of enzyme (Termamyl) concentration on floc formation

Table 12 shows the effect of enzyme (Termamyl) concentration on the formation of a white floc. The formation of floc occurred at the lowest level of enzyme used, 0.002%(w/v), however the effluent still showed a positive starch test. The protein desludger effluent (control) initially was free from visible suspended solids and also tested positive for starch. Higher levels of Termamyl (0.006% to 0.20%) produced floc formation, and the resulting effluent also tested negative for starch.

Termamyl rapidly breaks starch down to soluble dextrins and oligosaccharides (Novo, 1986). The iodine test gives a positive result (blue-black colored complex) with starch or glucose polymers containing at least six dextrose molecules with α1- 4 glycosidic linkages. The floc formed is believed to be a carbohydrate breakdown product as a result of the enzyme action. The precipitated floc did not produce a positive test based on iodine reaction. However, cellulose-like material does not give a colored complex when reacted with iodine (Novo, 1986), and thus may form part of the floc.

The formation of an instantaneous floc would be advantageous for continuous in-plant treatment of desludger effluent. As indicated in Table 13, low levels of enzyme took up to 40 seconds for floc formation, however doses of 0.01 % or greater provided virtually

Table 12. Qualitative tests for the effect of Termamyl concentration on starch and cellulose degradation in field pea protein desludger effluent.

Termamyl concentration (% w/v)	Iodine test[a]	Floc formation[b]
Control (no enzyme)	+ ve	- ve
0.002	+ ve	+ ve
0.006	- ve	+ ve
0.010	- ve	+ ve
0.020	- ve	+ ve
0.100	- ve	+ ve
0.200	- ve	+ ve

[a] The reaction of iodine with starch to give a dark blue-black colored complex and serve as an endpoint indicator for degradation of starch into dextrins..

[b] Parameter established by Woodstone Foods as a method for monitoring carbohydrate reactions.

Table 13. Effect of Termamyl concentration on floc formation in field pea protein desludger effluent[a].

Enzyme concentration (% w/v)	Time required for floc formation
0.002	40- 60 sec
0.006	10 - 20 sec
0.010	0 - 5 sec
0.020	0 - 5 sec
0.100	0 - 5 sec
0.200	0 - 5 sec

[a] Temperature = 50°C

instantaneous floc formation. The results indicated that use of enzyme Termamyl would be feasible in terms of time of formation of floc, however, subsequent removal of the floc prior to membrane treatment would require another treatment stage.

2. Effect of enzyme (Termamyl) concentration on viscosity

According to models proposed for predicting flow rate through a membrane (Cheryan, 1998), flux is inversely proportional to the viscosity of the feed solution. A lower feed viscosity should have a positive effect on membrane flux. Viscosity reduction is therefore an advantage of using enzymes in filtration operations (Novo, 1986). Enzymatic reactions can break long chain carbohydrates which exhibit a resistance to flow into smaller fragments or can remove branches of polymers with a resulting drop in viscosity.

As shown in Table 14, increased enzyme concentration from 0.002% to 0.2%(w/v) decreased the viscosity of the desludger effluent. The desludger effluent initially showed a measured kinematic viscosity of 1.1073 m^2s^{-1}, and this decreased to 1.0455 m^2s^{-1} at 0.002% enzyme and 0.9837 m^2s^{-1} at 0.20% enzyme.

3. Effect of enzyme (Termamyl) concentration on flux

As indicated in Table 14, increased enzyme concentration decreased viscosity of the desludger effluent. Two concentrations of enzyme (0.01% and 0.10%) were used to determine the effect of Termamyl activity on flux. The viscosity of the treated effluents averaged 0.9929 and 0.9888 m^2s^{-1}, respectively. The corresponding membrane flux is

Table 14. Effect of Termamyl concentration on viscosity[ab] of field pea protein desludger effluent.

Enzyme concentration (% w/v)	Time (sec)	Viscosity (m^2s^{-1})
Control (no enzyme)	21.50	1.1073
0.002	20.30	1.0455
0.006	19.47	1.0027
0.010	19.28	0.9929
0.020	19.20	0.9888
0.100	19.20	0.9888
0.200	19.10	0.9837

[a] Ubbelohde viscometer

[b] Conditions: Temperature = 50°C
Instrument constant = 0.05150
Kinematic viscosity = Instrument constant x Time

illustrated in Fig. 10. The lower viscosity effluent permeated the membrane at a slightly higher flux over the range of concentration up to 10:1 VCR. Both flux profiles showed similar trends in this range of VCR, but the lower viscosity effluent consistently showed a higher flux. The concentration of enzyme ultimately used by the company will depend on economics. A small gain in flux was achieved by increasing the enzyme concentration by a factor of 10.

4. Effect of enzyme combinations on viscosity

Other carbohydrases were evaluated in combination with Termamyl to determine the combined enzyme effect on reduction of viscosity of the protein desludger effluent. The results using Termamyl in combination with Viscozyme, Novozyme, Celluclast and Pectinase are shown in Table 15. As would be expected, all enzyme combinations produced an effluent with a lower viscosity than the control (no enzyme addition). All the mentioned enzymes have the ability to reduce viscosity (Novo, 1986). The results did not clearly suggest a combination of enzymes would be a necessity , as Termamyl alone reduced viscosity in the range of the other enzyme treatments. For example, Termamyl reduced the viscosity of the effluent from 1 .0877 m^2s^{-1} to 0.9734 m^2s^{-1} while a combination of Termamyl and Viscozyme reduced the value to 0.9631 m^2s^{-1}. Combinations of Termamyl and Novozyme or Celluclast slighly increased the viscosity compared to Termamyl alone. Preliminary studies also showed that Termamyl was necessary for floc formation, which was considered by the company as an indicator for effective pretreatment prior to membrane filtration. The other enzymes used singularly did not produce the floc.

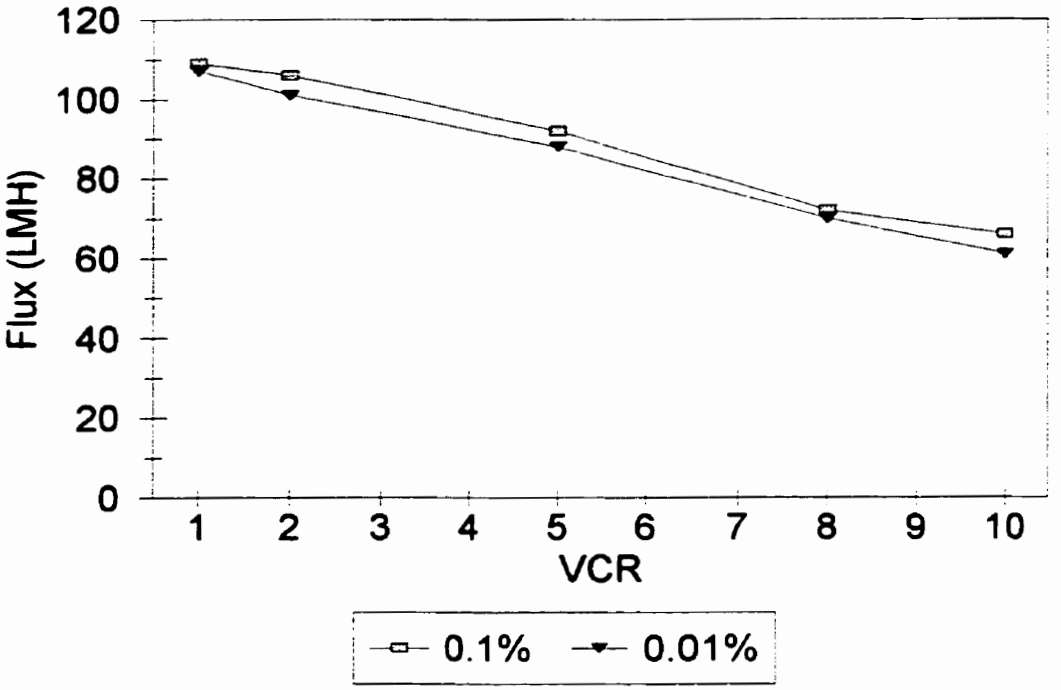

Figure 10. **Effect of enzyme concentration on membrane flux.** Pea protein desludger effluents were pretreated with Termamyl at 0.01% (w/v) and 0.1% (w/v), and ultrafiltered with Amicon H5P30-43 hollow fiber, 30,000 MWCO UF membrane.

Table 15. Effect of Termamyl and combined enzyme effect on viscosity of field pea protein desludger effluent.

Enzyme	Total concentration[a] (% w/v)	Temperature (°C)	Time (seconds)	Kinematic viscosity[bc] (m^2s^{-1})
Termamyl	0.01	50	18.9	0.9734
Termamyl + Viscozyme	0.01	50	18.7	0.9631
Termamyl + Novozyme	0.01	50	19.2	0.9888
Termamyl + Celluclast	0.01	50	19.4	0.9991
Termamyl + Pectinase	0.01	50	18.9	0.9734
Termamyl + all enzymes	0.01	50	19.0	0.9785
Control (no enzyme)	0.00	50	21.1	1.0877

[a] Concentration is the total of equal amounts of each enzyme added.
[b] Ubbelohde viscometer
[c] Conditions: Temperature = 50°C
Instrument constant = 0.05150
Kinematic viscosity = Instrument constant x Time

Based on these results and considering the added cost of using an enzyme combination, Termamyl as a single enzyme treatment was the recommended treatment option. In this study Termamyl at a concentration of 0.01 % was used for pretreatment prior to membrane filtration.

5. Floc removal

Floc formation as a result of Termamyl enzyme treatment required an additional processing step to remove the suspended solids prior to membrane treatment. Specifications for membranes recommend prefiltering the feed solution through a 100 μm screen to prevent plugging of the cartridge flow channels (Amicon, 1995).

The removal of the formed floc from the effluent was investigated by settling, settling with added celite, filtration using a pre-coated (celite) filter, and by centrifugation. For subsequent membrane studies, the protein desludger effluent was clarified by settling with the use of a settling-aid (celite), and decanted through a 100 mesh screen (Fig. 11). Centrifugation produced a clear effluent, however, this may not be cost effective for pre-treatment. The pre-coated filter system worked effectively, however, it was not available for the majority of the research work.

Settling of the floc would be the least expensive option in terms of equipment, however, time of settling is an important factor when considering continuous processing. As shown in Table 16, settling of the floc required approximately 15 - 20 min. The floc was readily separated by centrifugation, and a pre-coated filtration system designed by Berger (1995) using celite also was effective in removing the suspended floc quickly. The

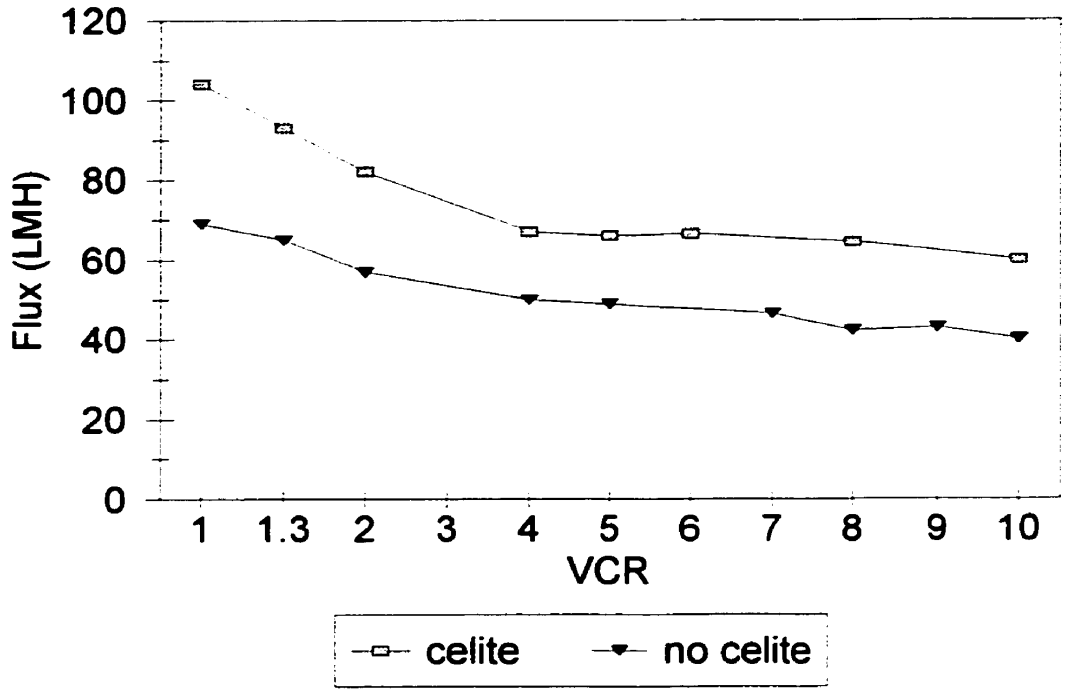

Figure 11. **Effect of celite addition on membrane flux.** Effluents were enzyme pretreated with Termamyl at 0.01%, and ultrafiltered with Amicon H5P30-43 hollow fiber, 30,000 MWCO membrane.

Table 16. Effect of celite on settling time for floc formed by enzyme pretreatment of field pea desludger effluent.

Pre-treatment	Concentration (% w/v)	Time to settle[a]
Termamyl	0.01	15 - 20 min
Termamyl + Celite	0.01 0.02	2 - 4 min

[a] Based on Imhoff cone measurement for settleable solids.

filter-aid celite used in the pre-coat system was also used as a settling-aid by adding to the enzyme treated effluent as the floc formed, and dispersed throughout the liquid. The settling aid (celite) was effective in settling the fine floc prior to decanting of the effluent. The time to settle the floc was reduced to approximately 2 - 4 min hold time, a considerably lower time factor (Table 16). The level of celite used for rapid settling was 0.02% which was determined in preliminary studies by the company (Berger, 1995) and was considered economically feasible by the company.

6. Effect of pretreatment on desludger composition

The change in composition of the protein desludger effluent as a result of pretreatment (including enzyme treatment) and use of celite to settle the floc is shown in Table 17. The composition of the desludger effluent was altered only slightly after treatment. Total solids and COD showed a reduction from levels of 20,500 mg/L for both to 17,960 mg/L and 17,900 mg/L respectively. Protein meanwhile decreased from 5900 mg/L to 5300 mg/L. This could have been due to further protein precipitation at its isoelectric point or enhanced settling out of protein by Celite or occlusion of the protein in the carbohydrate floc. Other suspended organics could be expected to settle, contributing to a lower value of COD and solids. Measured carbohydrate increased in value from 6800 mg/L to 8400 mg/L after enzyme treatment. Measured carbohydrate increased perhaps due to the formation of smaller chain carbohydrates from enzyme activity, which could be more readily measured in standard analyses.

Table 17. Effect of pretreatment on field pea desludger effluent composition.

Desludger effluent pretreatment	Component (mg/L)			
	Protein	Carbohydrate	Total solids	COD
Untreated	5900	6900	20500	20500
Enzyme[a]	5200	8400	20370	19500
Enzyme[a] + Celite[b]	5300	7400	17960	17900

[a] Enzyme - Termamyl added at concentration of 0.01% (w/v).
[b] Celite added at concentration of 0.02% (w/v).

C. Membrane Studies

A major objective of this study was the recovery of protein from the desludger effluents by membrane separation. To determine the feasibility of ultrafiltration, several process variables were studied. The process variables studied included the size of membrane in terms of nominal molecular weight cutoff, membrane type, temperature of operation, pH of operation, feed composition, and feed concentration. Other factors studied included membrane cleaning, diafiltration of concentrate and treatment of permeate for recycle opportunities within the plant.

The feed source was protein primary desludger effluents #1 and #2 obtained from the processing plant. The effluent was heated to 50°C, enzyme treated, celite was added to assist in floc removal by settling, and the decanted effluent was filtered through a 100 μm mesh screen prior to UF. The process scheme for effluent treatment is illustrated in Fig. 12.

1. Effect of MWCO and membrane type - operating effects

a. Effect of MWCO and membrane type on flux

Molecular weight cut-off (MWCO) is a term used to describe the potential separating capabilities of a UF membrane. The size of proteins are commonly characterized by reference to their molecular weight. Membranes rated with a MWCO rating of 30,000, 20,000 or 10,000 are often used in fractionation or concentration of protein from a liquid stream (Cheryan, 1998).

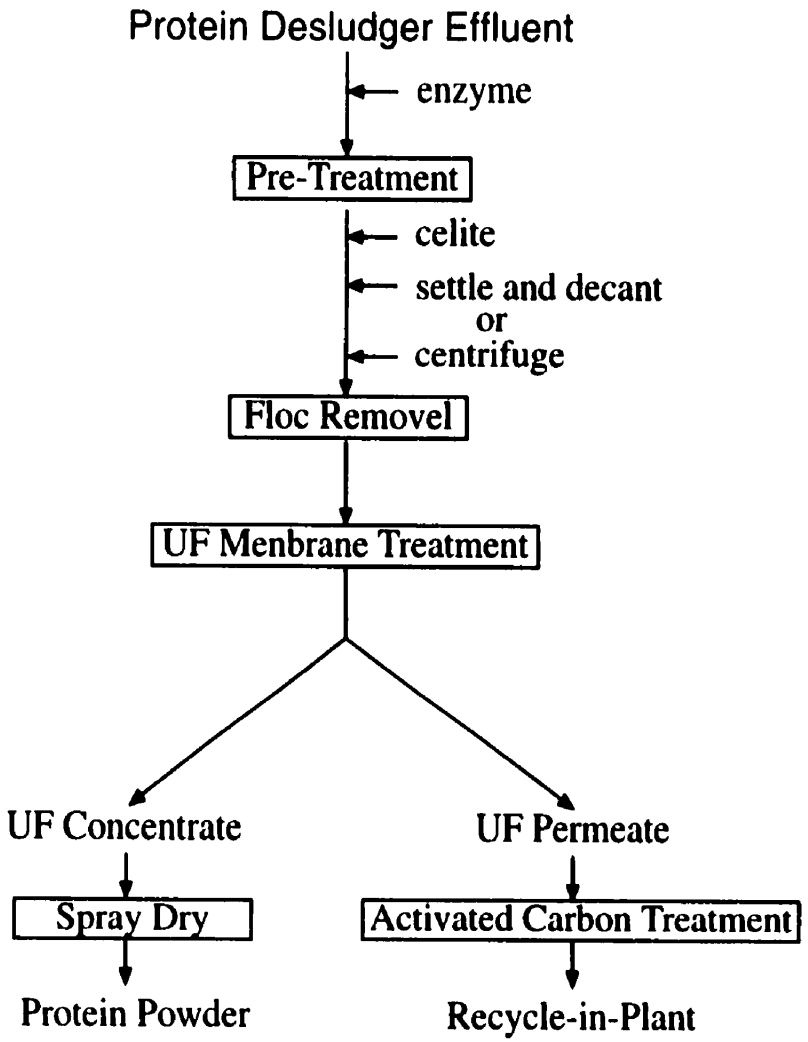

Figure 12. Effluent Treatment Process Scheme

During the course of this study, a spiral wound membrane with a 10,000 MWCO rating, and both a spiral wound and a hollow fiber membrane of 30,000 MWCO rating were used. The spiral wound membranes were cellulose acetate based, while the hollow fiber was constructed from polysulfone. Membrane characteristics are presented in Table 18.

During initial studies, the three membranes were evaluated by concentrating the protein desludger effluent by a factor of 10 (VCR = 10:1). This VCR was chosen as Woodstone Foods determined this concentration factor would be sufficient for further processing by spray drying or for use as protein concentrates for other food or feed use. The resulting membrane flux is shown in Fig. 13. The 30,000 MWCO hollow fiber membrane exhibited the highest flux throughout the concentration process. As would be expected, the tighter membrane of 10,000 MWCO exhibited the lowest flux. The flux was approximately 50% of that exhibited by the hollow fiber membrane. The 30,000 MWCO spiral membrane produced a flux about 10 - 15% lower than the hollow fiber membrane.

At 10:1 VCR, the flux of the 30,000 MWCO hollow fiber membrane was 54 LMH. This represented a loss of approximately 50% of the original flux. During the concentration period, the flux declined slowly to this value. The company was satisfied with the high flux values obtained with the 30,000 MWCO membranes for this range of concentration. Both the hollow fiber and spiral wound membranes were acceptable in performance. However, the small difference in membrane flux indicates that membrane type has an effect on flux as has been reported previously (Cheryan, 1998). This study also demonstrated that it is possible to scale up the membrane process from a membrane

Table 18. Membrane characteristics.

Cartridge type	Nominal cutoff molecular weight	Surface area (m^2)	Deionized water flow rate (ml/min)	pH range	Temperature Max. (°C)	Construction material
Amicon H5P30-43 Hollow fiber	30,000	0.45	2100 - 2350	1.5 - 13.0	50	Polysulfone
Amicon SIY30 Spiral wound	30,000	0.09	150 - 270	3 - 11	55	Cellulose acetate
Amicon SIY10 Spiral wound	10,000	0.09	50 - 90	3 - 11	55	Cellulose acetate

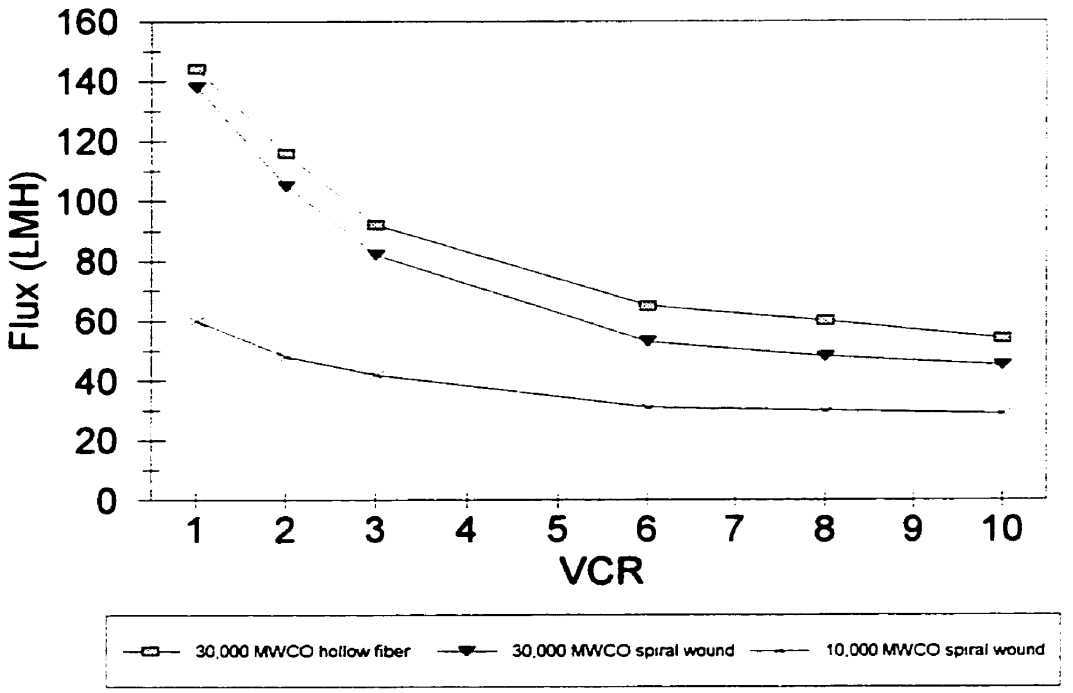

Figure 13. **Effect of MWCO size and type of membrane on flux.**
Pea protein desludger effluents were pretreatment with Termamyl at 0.01% (w/v) dosage level and ultrafiltered using:
1) Amicon H5P30-43 hollow fiber, 30,000 MWCO membrane,
2) Amicon SIY30 spiral wound, 30,000 MWCO membrane,
3) Amicon SIY10 spiral wound, 10,000 MWCO membrane.

surface area of 0.09 m^2 to 0.45 m^2 with a similar flux being obtained, even with membrane type changing from a spiral wound configuration to a hollow fiber configuration.

Use of the 10,000 MWCO membrane with a lower flux rating could only be warranted if the separation of protein was considerably improved over that of the 30,000 MWCO membranes.

b. Effect of MWCO and membrane type on composition of membrane streams

The effect of MWCO on the composition of the resulting retentate and permeate fractions is presented in Tables 19 - 21. Total solids and COD were equally concentrated to the same extent during the volume concentration using the 30,000 MWCO hollow fiber membrane. At 10:1 VCR, the rejection values were 75.1% and 73.5%, respectively. Rejection measures how well a membrane retains or allows the passage of a solute component. The permeate fraction, however, contained 9390 mg/L COD, which is still considerably over the maximum allowable limit of 300 mg/L. The plant would still face considerable surcharge due to the high organic loading if the permeate was to be discharged. Protein was concentrated nearly 7 fold, showing a rejection of 92.1%. There was, however, carbohydrate contamination in the protein enriched fraction, although the carbohydrate fraction showed a rejection value of only 17.1%. Because of the low rejection value of the carbohydrate fraction, protein was concentrated to a much greater degree than carbohydrate resulting in a more concentrated protein fraction. The concentrations of protein and carbohydrate in the retentate were 21,195 mg/L and 6640 mg/L, respectively.

Table 19. Effect of 30,000 MWCO hollow fiber UF membrane on component value of separated streams[a].

Component (mg/L)	Desludger[b] feed	Desludger concentrate	Desludger permeate	% Rejection
Total solids	12220	38640	9610	75.1
COD	10800	35900	9390	73.8
Protein	3120	21000	1650	92.1
Carbohydrate	5400	6730	5580	17.1

[a] VCR = 10:1.
[b] Field pea primary desludger effluent.

Table 20. Effect of 30,000 MWCO spiral wound UF membrane on component value of separated streams[a].

Component (mg/L)	Desludger[b] feed	Desludger concentrate	Desludger permeate	% Rejection
Total solids	12220	37740	9740	74.2
COD	10800	34660	9480	72.7
Protein	3120	19900	1730	91.3
Carbohydrate	5400	6660	5750	13.7

[a] VCR = 10:1.
[b] Field pea primary desludger effluent.

Table 21. Effect of 10,000 MWCO spiral wound UF membrane on component value of separated streams[a].

Component (mg/L)	Desludger[b] feed	Desludger concentrate	Desludger permeate	% Rejection
Total solids	12440	39600	9390	76.3
COD	11200	37690	9325	75.3
Protein	3190	22140	1575	92.9
Carbohydrate	5520	6700	5625	16.0

[a] VCR = 10:1.
[b] Field pea primary desludger effluent.

The rejection values for the 30,000 MWCO spiral wound membrane were similar to the values obtained for the 30,000 MWCO hollow fiber membrane. As expected, the rejection values for the components using the 10,000 MWCO membrane were higher, but only slightly. Protein was rejected 92.9% versus 92.1% and 91.3% for the 30,00 MWCO membranes. This small increase in rejection would not warrant the tighter 10,000 MWCO membrane as flux was approximately 50% lower (Fig. 13).

2. Effect of temperature on flux

Ideal plant operating parameters called for a temperature of 48°C - 50°C at the protein desludger unit operation. Deviation from this temperature could affect protein recovery, and also result in variability in desludger effluent composition. Temperature of the feed also affects membrane performance. A temperature range of 41°C to 51°C was noted for the desludger effluents during sampling periods at the pea processing plant.

The effect of temperature of protein desludger effluent on membrane flux is illustrated in Fig. 14. Temperatures of 50°C, 40°C, and 25°C were used for comparison. Membrane flux was higher at elevated temperatures. Flux at 50°C was double that at 25°C. This was a greater difference than predicted by Cheryan (1998) who suggested a temperature increase of 30-45°C would be required to double the flux in model systems.

An increase in flux with temperature is due to temperature effects on both fluid density and viscosity. Diffusivity of protein also increases with an increase in temperature, again affecting flux positively (Cheryan, 1998).

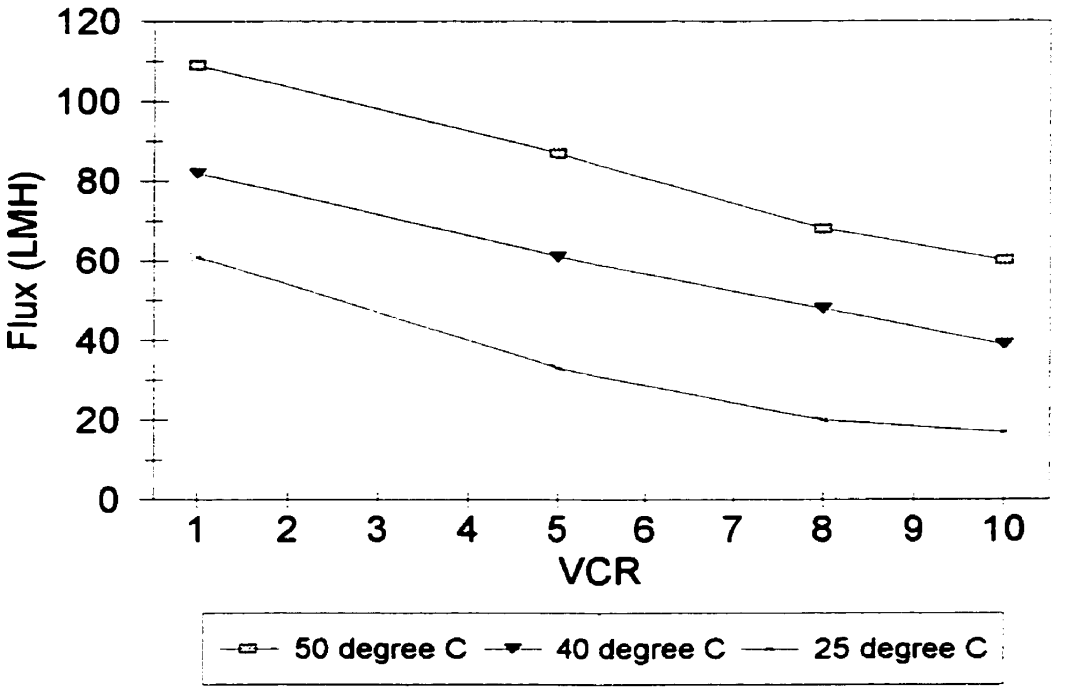

Figure 14. **Effect of operating temperature on membrane flux.** Pea protein desludger effluents were pretreated with Termamyl at 0.01% (w/v), and ultrafiltered with Amicon H5P30-43 hollow fiber, 30,000 MWCO membrane.

It would be most beneficial for the plant to operate at the highest practical temperature. As the desludger is to be maintained at 48 - 50°C, this would be the ideal temperature for membrane treatment. Higher temperatures can also have beneficial effects on lowering energy and horsepower requirements, and temperatures of 50°C or greater can also minimize microbial growth (Cheryan, 1998). However, there are limits of temperature both with the effluent feed (i.e., protein denaturation) and with a specific membrane tolerance to temperature. Maximum operating temperature for the hollow fiber polysulfone membrane is 50°C, while for the spiral wound cellulose acetate membrane is 55°C (Table 18).

3. Effect of pH on flux

The permeability of a solute can be affected by its micro-environmental conditions such as pH (Cheryan, 1998). Shape and confirmation of the macromolecules are affected by pH which can affect solute rejection by the membrane. The pH of the desludger effluent was adjusted by addition of acid or base to determine the effect on flux.

The effect of pH on membrane flux for field pea desludger effluent is shown in Fig. 15. The normal pH for the desludger effluent is pH 4.5, the isoelectric point for the pea protein. By lowering the pH to 3.2, a slight increase in flux was observed, however, when the pH was adjusted upwards to pH 8.5, a decrease in flux was observed.

For proteins, flux is generally lowest at the isoelectric point of the protein and increases as the pH is adjusted away from the isoelectric point (Cheryan, 1998). As the pea protein is more soluble at pH 3.2, an increased flux was observed. At the higher pH,

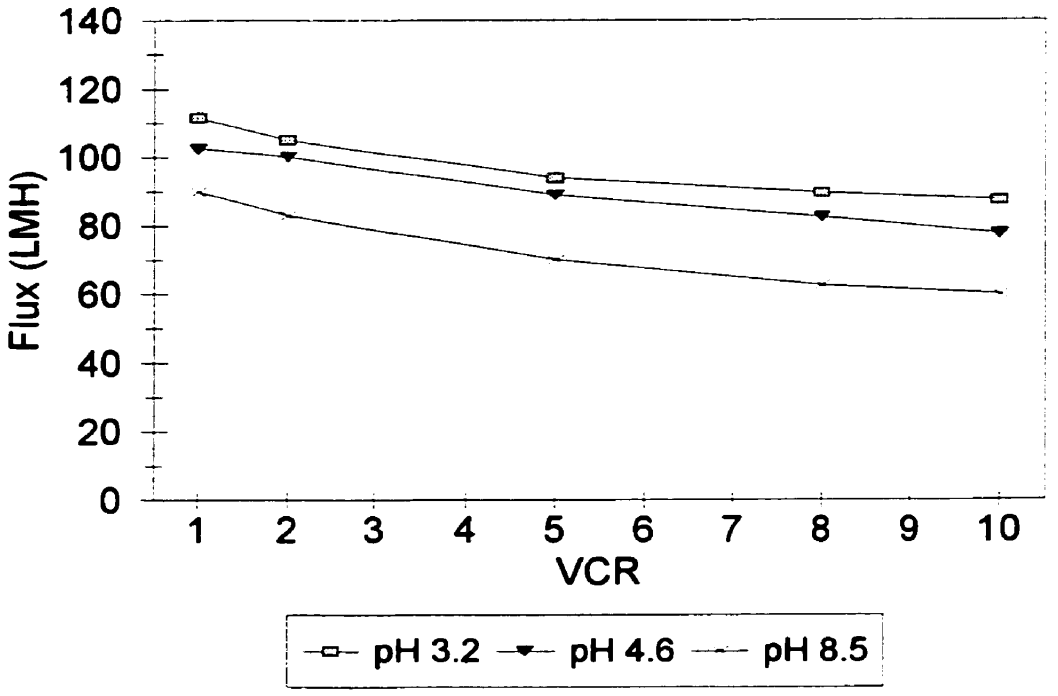

Figure 15. **Effect of effluent pH on membrane flux.**
Pea protein desludger effluent was pH adjusted and pretreated with Termamyl at 0.01% dosage level and ultrafiltrated with Amicon H5P30-43 hollow fiber, 30,000 MWCO membrane.

the decrease in flux may have been due to the decrease in solubility of salts and their deposition on the membrane (Kuo and Cheryan, 1983), or because the protein has a charge similar to the membrane (Cheryan, 1998).

From this study, it is suggested that the effluent be membrane concentrated at its normal pH at discharge. The relatively small increase in flux obtained by lowering the pH may not warrant further addition of acid to the protein slurry which could affect purity and functional properties of the recovered protein. Berry and Nguyen (1988) reported that reducing the pH of soy extracts to 2.0 improved flux but resulted in off-flavours of the recovered product due to hydrolysis of the oligosaccharides.

4. Effect of feed concentration on flux

Feed concentration is a major operating parameter that affects flux. Based on the film theory model (Cheryan, 1998), flux will decrease exponentially with increasing feed concentration. As feed concentration changes, parameters such as viscosity, density and diffusivity will change affecting equations used in predicting flux. Flux will also decline as volume concentration ratio increases. With varying concentration of solute in the feed solution (desludger effluent), flux would be variable and prediction of flux becomes difficult when trying to design a membrane system.

As reported earlier (Table 10 and Fig. 7 - 9), protein desludger compositional strength can be highly variable. In this study, 3 strengths of effluent concentrations were used to evaluate their effect on flux. The COD of the effluent ranged from 10,800 mg/L to 19,760 mg/L, and protein from 3120 mg/L to 6975 mg/L.

For operation of a membrane system, the variable composition could affect operational parameters such as throughput, and membrane surface area required. Fig. 16 illustrates the resulting flux based on a range of feed composition discharged at the desludger operation. As predicted by theory, the flux dropped off sharply from an initial level of 105 LMH as the effluent composition increased and volume concentration proceeded. At 10:1 VCR, the lowest strength effluent showed a flux of 60 LMH, while the highest strength effluent had decreased to 20 LMH. The decrease in flux for the three effluents showed a similar % decrease throughout the concentration process (Fig. 16). The middle strength effluent showed flux values intermediate to the lowest and highest strength effluents.

The variability of desludger effluent composition is related to process efficiency. The above data illustrate the importance of optimizing conditions of pH, temperature, and residence time in desludgers during isoelectric precipitation to minimize organic discharge. High surges of effluent strength will cause flux decline resulting in membrane cleaning sooner than scheduled, or the need for a membrane system with extra capacity. In both cases, this would result in increased costs to the plant. Protein recovery could be affected in terms of purity and the cost of protein recovery would increase.

5. Effect of VCR on flux and fraction composition

The volume concentration ratio (VCR) defined as the ratio of the initial feed volume to volume of retentate, and refers to as the concentration factor. The volume concentration ratio to be targeted for will depend on the purpose of membrane treatment

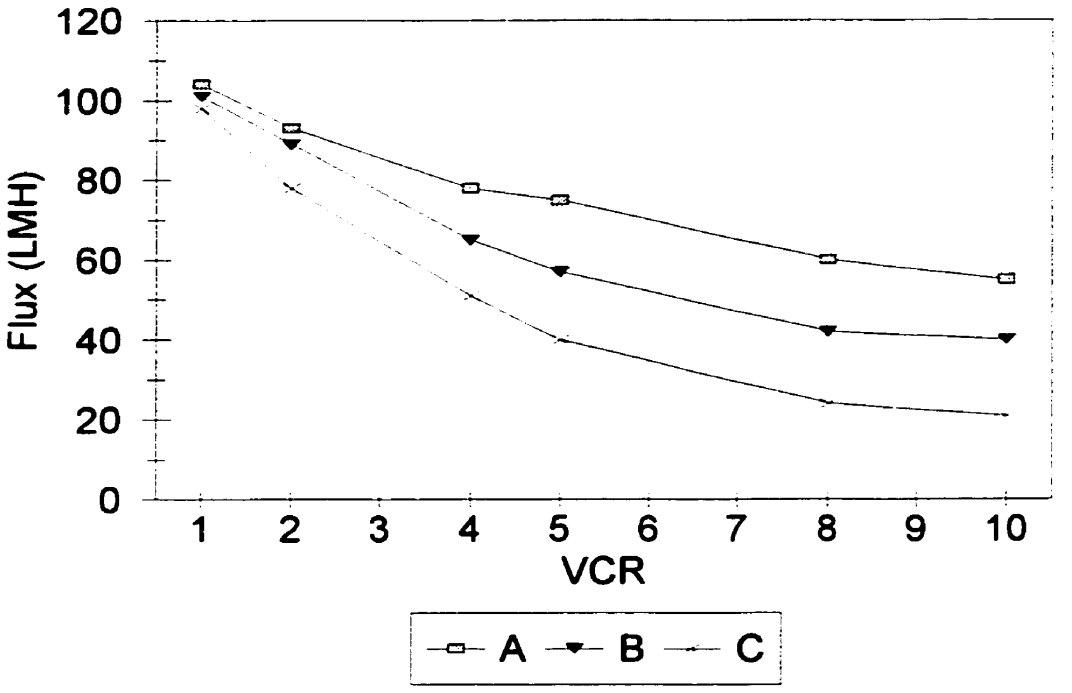

Figure 16. **Effect of effluent strength on membrane flux.**
Pea protein desludger effluents were pretreated with Termamyl at 0.01% (w/v) and ultrafiltered with Amicon H5P30-43 hollow fiber, 30,000 MWCO membrane.
Effluent A: COD 10800 mg/L, protein 3120 mg/L.
Effluent B: COD 16200 mg/L, protein 5400 mg/L.
Effluent C: COD 19760 mg/L, protein 6975 mg/L.

such as protein concentration, but will also be affected by membrane performance. The application of UF in this study was to separate protein from the desludger stream, and to concentrate the protein. The recovered protein concentrate would represent by product recovery and could be added to the protein stream from the desludgers being spray dried or could be dried separately. Fig. 17 illustrates the effect of volume concentration ratio on flux for both the 30,000 MWCO hollow fiber membrane and the 10,000 MWCO spiral wound membrane. As the retained protein concentration increased with increased volume concentration ratio, the flux decreased as would be predicted. At 20:1 VCR, the flux of the 10,000 MWCO membrane was 25 LMH, while the 30,000 MWCO membrane flux was 42 LMH, illustrating the advantage of using the higher MWCO membrane.

A 20:1 VCR was selected for this study as this is approximately the concentration ratio used for dairy whey, an industry where membranes have proven successful. Also, the company is feeding the spray drier from the desludgers at approximately 5% solids. The composition of the retentate stream with increased volume concentration is shown in Table 22. At 20:1 VCR, the protein was concentrated to 38,160 mg/L. The concentration of a solute at any stage of membrane processing is a function of both volume reduction and the rejection value according to the following equation:

$$C_R = C_o(VCR)^R \quad \text{(Cheryan, 1998)}$$

where: C_o = initial feed solute concentration
C_R = solute concentration in the retentate
R = rejection value

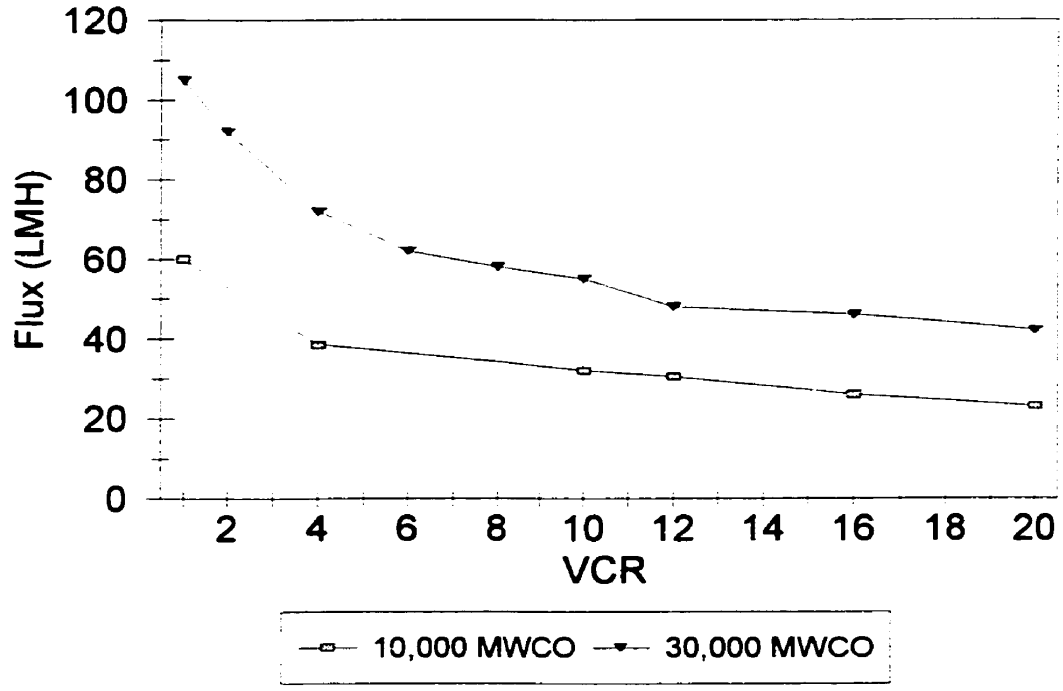

Figure 17. **Effect of volume concentration ratio (VCR) on membrane flux.**

Pea protein desludger effluents was pretreated with Termamyl at 0.01% (w/v) and ultrafiltered with both Amicon H5P30-43 hollow fiber (30,000 MWCO) and SIY 10 (10,000 MWCO) membranes with operating conditions of 45 - 50 degree C and pH 4.5.

Table 22. Effect of VCR[a] on the level of protein, carbohydrate, total solids and COD in retentate[b] from field pea protein desludger effluent.

	Component (mg/L)			
VCR[a]	Protein	Carbohydrate	Total Solids	COD
1:1	3120	5400	12200	10800
4:1	8250	5750	20820	18750
8:1	18655	6260	33380	30400
10:1	21195	6640	38800	36250
12:1	27350	6970	42300	41400
16:1	34775	7110	48760	46350
20:1	38160	7240	52300	49890

[a] VCR = volume concentration ratio.
[b] 30,000 MWCO Amicon H5P30-43 hollow fiber UF membrane.

Deviation from the ideal equation can occur due to several factors including solute adsorption onto the membrane, changes to the rejection value with higher retentate concentrations, or volume exclusion effects with higher solute concentrations (Cheryan, 1998).

At 20:1 VCR, the average solids content of the retentate was 5.23% (Table 23). The protein was concentrated by a factor of 12.2 to 38,160 mg/L. Carbohydrate, having a low rejection value, was concentrated only by a factor of 1.3. The rejection value for protein was 92.9% (Table 24), indicating the possibility of non-protein nitrogen passing through the membrane. Non-protein nitrogen was present in the permeate at 1292 mg/L and had a rejection value of 79.2%.

At 20:1 VCR, the flux had declined to approximately 33% of its original value. However, of prime importance in the economical determination of membrane processing is not flux alone, but productivity expressed as the volume of permeate produced per cycle, or between cleaning (Cheryan, 1998). As the membrane flux becomes lower, pumping costs increase, however, retaining high flux requires additional membranes also at extra cost.

The frequency of cleaning also becomes a critical economic factor as it affects the life of a membrane. The process would have to be optimized to determine the cut-off time for cleaning and restoring membrane flux, rather than operating with a fouled membrane at a low flux. To optimize the process, the membrane type and configuration would have to be determined, working in conjunction with a membrane supplier. Combinations of series and parallel flows can be used in industrial applications.

Table 23. Effect of VCR[a] on composition of field pea protein primary desludger retentate[b].

Volume (L)	VCR[a]	Volume reduction (%)	Protein % (w/v)	Carbohydrate % (w/v)	Ash % (w/v)	Total solids % (w/v)	Protein content of solids % dry basis
40	1:1	0	0.31	0.54	0.36	1.22	25.4
10	4:1	75	0.83	0.58	0.38	2.08	39.9
4	10:1	90	2.12	0.66	0.41	3.88	54.6
2	20:1	95	3.81	0.72	0.44	5.23	72.8

[a] VCR = volume concentration ratio.
[b] 30,000 MWCO Amicon H5P30-43 hollow fiber UF membrane cartridge.

Table 24. Ultrafiltration[ab] of protein desludger effluent.

Component (mg/L)	Desludger Feed	Desludger concentrate	Desludger permeate	% Rejection
Total solids	12200	52300	9390	76.3
COD	10800	49890	9325	75.1
Protein[c]	3120	38160	2709	95.9
Non protein nitrogen	1659	6199	1292	79.2
Carbohydrate	5400	7240	6082	16.0

[a] VCR = 20:1.
[b] 30,000 MWCO Amicon H5P30-43 hollow fiber membrane.
[c] Kjeldahl nitrogen x 6.25.

6. Diafiltration

Because membrane rejection for different solutes differs, it is possible to achieve considerable protein purification by using a membrane with high rejection value for protein and low rejection values for other contaminating solutes. In this study, the R value for protein was established at 95.9%, for carbohydrate 16.0% (Table 24). However with concentration, the flux will drop to low levels causing increased energy cost for pumping due to increased retentate viscosity upon further volume concentration.

Diafiltration, whereby water is added to the retentate, and to be further concentrated to a predetermined concentration volume, can be used to further purify the protein. In this study, a discontinuous diafiltration was employed to remove permeable solutes from the retentate by (1) volume concentration, (2) dilution of retentate with water, (3) further volume concentration. For this study, the feed (40L) was concentrated 20:1 (2L retentate volume), 2L water was added to the retentate for a total volume of 4L, and concentrated again to a final retentate volume of 2L.

The results for discontinuous diafiltration of 20:1 VCR desludger effluent are shown in Table 25. On a dry basis, the protein content of the solids increased from 72.8% to 88.8%. This represented an increase in protein from 3.81 to 3.88% in the effluent. Ash decreased from 0.44% to 0.21%, and carbohydrate reduced from 0.72% to 0.40%. A protein concentrate of higher purity was obtained. Diafiltration may be useful if the resulting protein were to be marketed as a separate product.

Table 25. Discontinuous diafiltration[a] of 20:1 VCR[b] field pea protein primary desludger effluent.

	Volume	Protein		Carbohydrate	Ash	Total solids
Description	(L)	% (w/v)	% d.b.[c]	% (w/v)	%(w/v)	% (w/v)
VCR[b] 20:1	2	3.81	72.8	0.72	0.44	5.23
VCR[b] retentate (diluted)	4	1.90	36.4	0.36	0.22	2.62
VCR[b] 20:1 (discontinuous diafiltration)	2	3.88	88.8	0.40	0.21	4.37

[a] equal volume of water 2 L was added to retentate and reultrafiltered to 2 L using Amicon H5P30-43 hollow fiber 30,000 MWCO membrane.
[b] VCR = volume concentration ratio.
[c] d.b. = dry basis.

D. Membrane cleaning

Membrane fouling is characterized by a decline in flux with time of operation. All feed components will foul membranes to a certain extent. Because of the difficulties in membrane fouling at the company on initial start up in the early 1980s, and subsequent research by Grabowecky (1988), it was thought that membrane cleaning would be a major issue in this study. Desludger effluent pretreatment by carbohydrase enzyme treatment (Berger, 1995) was a breakthrough in membrane application.

Proteins are major foulants in membrane processing (International Dairy Federation, 1995). As protein would be considered a major foulant in this study, an alkali cleaner would be warranted. For the Amicon hollow fiber membrane, the product information bulletin (Amicon, 1987) recommends a 0.1 N sodium hydroxide solution. Three cleaning regimes at 50°C using caustic solution were evaluated:

1. 0.1 N sodium hydroxide.
2. 0.1 N sodium hydroxide + 200 mg/L sodium hypochlorite.
3. Commercial alkaline cleaner + 200 mg/L sodium hypochlorite.

In addition, an acid wash was used after the alkali wash if warranted. An acid wash is used to remove mineral type foulants. Mineral ions from the pH adjustments of the desludger could be contributing foulants.

A clean membrane refers to a membrane being physically clean of visible impurities or foreign matter; that is, chemically clean with foulants removed, and biologically clean with viable organisms being removed. In practice, restoration of clean water flux is traditionally accepted as a clean membrane. The water flow rate listed by Amicon for the H5P30-43 cartridge is 2100 - 2350 ml/min.

As shown in Table 26, the 0.1N sodium hydroxide solution did not restore the clean water flow rate after concentration of the protein desludger effluent to 20:1 VCR. Doubling of the cleaning cycle time from 30 min to 60 min did not increase permeation to any extent. A sequence of alkaline wash followed by an acid wash again was not successful. This indicated that mineral contaminants were not the major foulants. The chlorinated alkali cleaners were effective in restoring clean water flow rate. Chlorine is recommended at levels of 200 mg/L or less with polysulfone material for sterilizing or cleaning. The chlorine must be used in alkaline solution (pH 10 - 11) to minimize corrosion. After a 5 min wash, the chlorine level had dropped to 80 mg/L, however, it was not necessary to restore it to 200 mg/L as after a 15 min wash, the membrane flux was largely restored. The acid wash following the caustic/chlorine wash again did not improve the permeation rate. The commercial chlorinated alkaline cleaner was effective in restoring membrane permeation, similar to the sodium hydroxide solution with added chlorine. A 30 min recirculation time would be recommended at 50°C (Table 26).

For the cellulose acetate spiral membrane, again a 0.1N sodium hydroxide cleaning solution is recommended by the manufacturer (Amicon, 1987). Sodium hypochlorite (50 - 100 mg/L) can only be used at 23°C or lower. Two cleaning regimes using caustic were evaluated:

1. 0.1 N sodium hydroxide.
2. 0.1 N sodium hydroxide + 75 mg/L sodium hypochlorite.

An acid wash using 0.05 N nitric acid was used following the caustic wash to determine the extent of fouling by mineral contaminants.

Table 26. Effect of cleaning on permeation[a] of Amicon H5P30-43, 30,000 MWCO membrane.

Cleaning regime (agents)	Time (min)	Temperature (°C)	pH	Permeation (ml/min)
1. 0.1N NaOH	30	50	11.2	1740
	60	50	11.2	1820
2. 0.1N NaOH	60	50	11.2	1820
Followed by 0.1N HCl	30	40	2.1	1860
3. 0.1N NaOH & 200 mg/L NaHOCl	15	50	11.2	2190
	30	50	11.2	2240
	60	50	11.2	2280
4. 0.1N NaOH & 200 mg/L NaHOCl	30	50	11.2	2280
Followed by 0.1N HCl	30	40	2.1	2280
5. Commercial alkaline cleaner / 200 mg/L NaHOCl	30	50	11.4	2240

[a] Typical clean water permeation rate 2100 - 2350 ml/min.
Cleaning after 20:1 VCR of field pea protein primary desludger effluent.

The clean water flow rate for the membrane was determined to be 75 ml/min. As shown in Table 27, both sodium hydroxide at 50°C and sodium hydroxide/sodium hypochlorite at 20°C for 1 hr were successful in restoring membrane flux after 20:1 VCR. The sodium hydroxide/sodium hypochlorite wash was used at the lower temperature as membrane tolerance for chlorine. Cleaning of the membrane using caustic washes will require additional time as after a traditional 30 min wash cycle, the membrane clean water flow rate was only restored to approximately 80% of its value. The acid wash following the caustic washes had no effect on membrane permeation.

The membrane pretreatment of enzyme addition and floc removal was effective in reducing the fouling effects of the desludger effluent. Even though considerable salts could be present in the effluent from the protein solubilization and isoelectric precipitation stages, acid cleaning was not required. The study also confirmed that since fouling is a result of specific interaction between the membrane and solutes in the feed, and operating conditions, it is necessary to study each system individually. The polysulfone hollow fiber membrane system and the cellulose acetate spiral wound membrane system responded differently to cleaning. Restoration of flux even after repeated use during a two year period was not a problem with either membrane system. The frequency of cleaning becomes a critical economic factor to the company in terms of chemical costs, down time, and its effect on the life of a membrane. Supplier companies suggest that a membrane can have an operating life of 2-5 years.

Table 27. Effect of cleaning on permeation[a] of Amicon SIY10, 10,000 MWCO membrane.

Cleaning regime (agents)	Time (min)	Temperature (°C)	pH	Permeation (ml/min)
1. 0.1N NaOH	30	50	11.2	61
	60	50	11.2	74
2. 0.1N NaOH	60	50	11.2	74
Followed by 0.05N HNO_3	30	40	2.1	76
3. 0.1N NaOH & 75 mg/L NaHOCl	30	20	11.2	65
	60	20	11.2	77
4. 0.1N NaOH & 75 mg/L NaHOCl	60	20	11.2	77
Followed by 0.05N HNO_3	30	40	2.1	78

[a] Typical clean water permeation rate 75 - 85 ml/min.
Cleaning after 20:1 VCR of field pea protein primary desludger effluent.

E. Permeate Treatment

The permeate resulting from the UF concentration of protein was evaluated for possible reuse/recycle opportunities within the plant. Compositional data (Table 24) indicates that discharge of the permeate would result in a relatively large surcharge to the plant as the COD value (9325 mg/L) greatly exceeds the 300 mg/L allowable limit. The permeate is, however, free of suspended solids.

Reuse opportunities would exist in any downstream operation including the desludger stage, starch separation, or fiber separation. The concentration of organic in the permeate would suppress leaching of further soluble organics as demonstrated by Gallop et al (1976). This would be important especially at the separation stages of starch and fiber as the primary function of water at these unit operations is physical. One limitation of permeate recycling is the amber color of the permeate which could affect final product color of the starch and fiber which are typically white. The company specifications list color as white on product data sheets for these components.

As shown in Table 28, color was readily removed by the activated carbon treatment of the permeate. At a level of 0.25 g carbon/100 ml permeate, a colorless effluent resulted by visual observation. Color measurement by the Hellige Aqua Tester indicated a residual color of 25 units at this carbon level. As indicated from the adsorption isotherm (Fig.18), the extrapolated $(X/M)_{Co}$ value was 2000 color units adsorbed per gram of carbon. This value represents the ultimate capacity of the carbon for color adsorbed per unit carbon weight. The volume of liquid for complete decolorization or decolorized to concentration C_1, can be calculated from the formula (Pittsburgh Activated Carbon Co., 1996):

Table 28. Adsorption Isotherm for decolorization of permeate.

M Weight of carbon[a] (g/100 ml solution)	C[b] Residual solution color	X Color adsorbed	X/M Color adsorbed per unit weight
0.000	120	—	—
0.010	100	20	2000
0.030	70	50	1700
0.050	60	60	1200
0.075	50	70	930
0.100	40	80	800
0.175	25	95	540
0.250	20	100	400
0.375	15	105	280
0.500	10	110	220
0.750	5	115	150
1.000	0	120	120

[a] Atlas chemical industries - powdered Darco activated carbon, Grade S51.
[b] Residual solution color units measured by Hellige Aqua Tester (Hellige Inc. Garden City, NY).

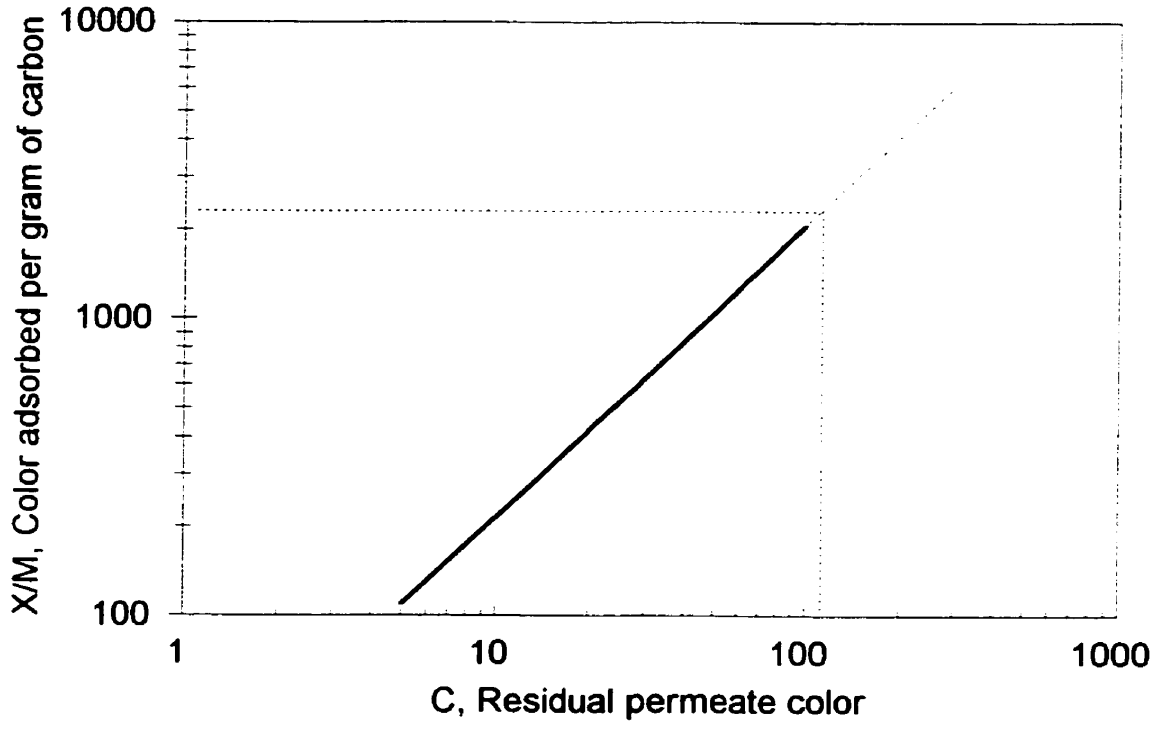

Figure 18: **Adsorption isotherm for permeate decolorization.** Darco activated carbon, grade S51.

$$V_{Co} = (X/M)_{Co} V / (C_o - C_1)$$

where:
- V_{co} = theoretical volume of liquid decolorized per gram (or unit weight) or carbon.
- $(X/M)_{Co}$ = capacity per gram (or unit weight) of carbon at the influent concentration (obtained from Freundlich adsorption isotherm)
- V = volume of liquid used in the isotherm test
- C_o = influent concentration
- C_1 = desired % decolorization

Based on the Hellige color units, for complete decolorization V_{Co} was calculated at 1700 ml/g carbon. Based on visual perception of color, it was estimated that at 25 residual color units (Hellige) that the sample was colorless, resulting in V_{Co} equaling to 2100 ml/g carbon. At the current price of carbon of $1.80 /kg (Van Waters and Rogers), the cost of activated carbon treatment would be 0.0857 cents/L of permeate. In-plant effluent reuse trials would be required to demonstrate if permeate with residual color could be used to justify the cost of treatment. The permeate may have application in reuse at the desludger unit operations where color may not be as critical a factor as at the separation stages for starch and fiber.

The membrane fractions of feed, retentate, permeate, and carbon treated permeate are illustrated in Fig. 19. Evident is the build up of solids in the concentrate, amber color of the permeate, and the clear, colorless permeate after activated carbon treatment.

Although organic carbon removal was not the prime objective of treatment, the effect of activated carbon treatment for COD removal was evaluated to determine the potential for lowering the organic loading if the permeate was to be discharged. The adsorption isotherm (Table 29 and Fig. 20) is at a high level and with a steep slope which

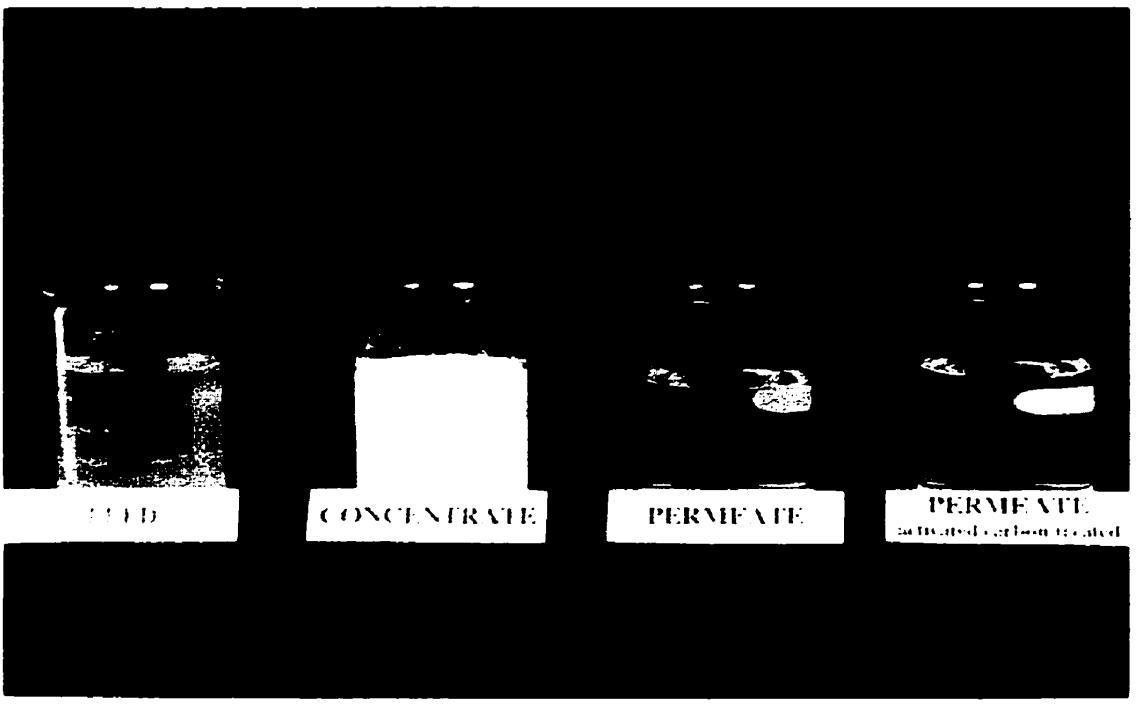

Figure 19. Fractions from protein desludger effluent treated by UF membrane and activated carbon.

Membrane: Amicon H5P30-43 hollow fiber (30,000 MWCO)
VCR = 20:1
Activated carbon concentration = 0.25 g / 100 ml
Carbon source: Darco S51 (Atlas Chemical Industries)

Table 29: Adsorption isotherm for permeate.

Carbon[a] concentration (M) (mg/ L)	COD Final (mg/L)	COD adsorbed (X) (mg/L)	X/M
0	10500	---	---
1000	9800	700	0.70
2500	9200	1300	0.52
5000	8300	2200	0.44
10000	6400	4100	0.41
20000	4000	6500	0.33
40000	2200	8300	0.21

[a] Atlas chemical industries - powdered Darco activated carbon, Grade S51.

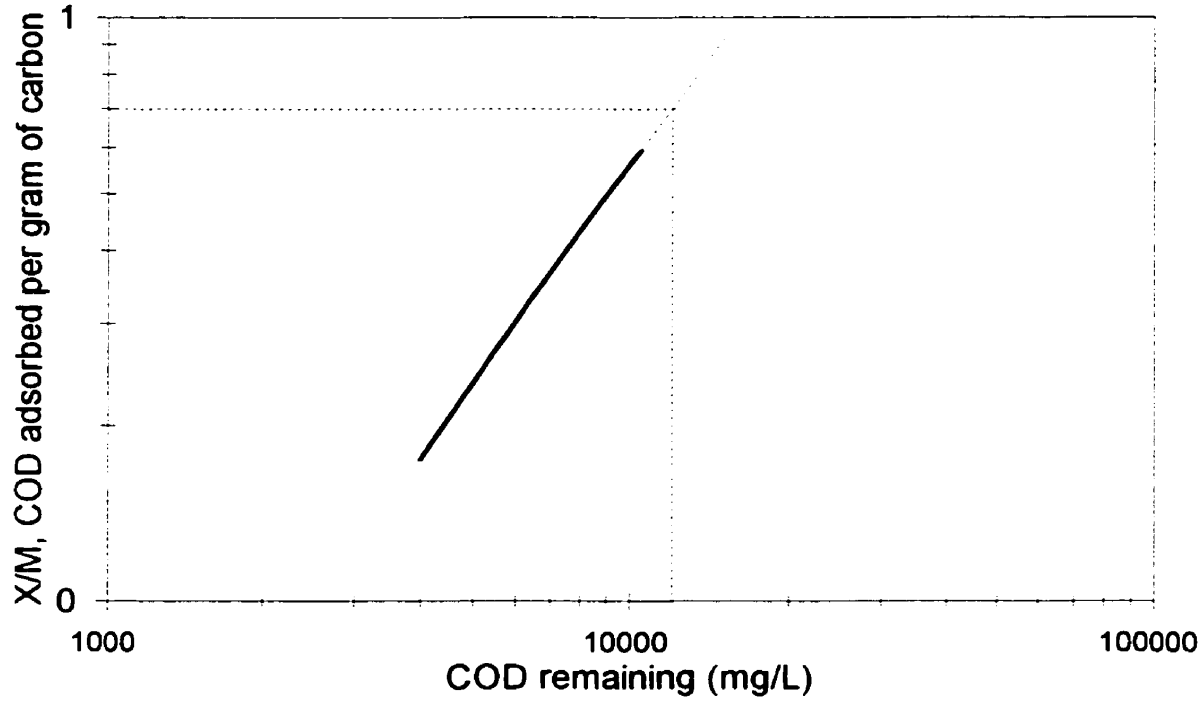

Figure 20: **Adsorption isotherm for permeate COD removal.** Darco activated carbon, grade S51.

indicates that adsorption is large throughout the entire range of organic concentration. The $(X/M)_{Co}$ value, representing the ultimate capacity of the carbon was extrapolated from the adsorption isotherm to read 0.7 (mg COD / mg carbon). An $(X/M)_{Co}$ value >0.1 indicates that an adsorption system is likely to be feasible (Hassler, 1974). The slope of the adsorption isotherm however suggests that the removal of organic matter to low values (<300 mg/L) would require extensive carbon treatment and may not be possible due to refractory organic compounds. The cost of carbon treatment would be prohibitive to the company, based on the initial high COD value of the permeate. The merit of carbon, therefore, would only be appropriate for conditioning the permeate for reuse potential by color removal.

F. Characterization of retentate

The field pea protein fractions have been described by Leterme et al (1990) as consisting of globulins (45 - 50 %), albumins (15 - 20 %), insoluble proteins (15 - 20 %), and non-protein fraction (15 - 20 %), based on % total nitrogen.

The gel filtration elution profile for the UF retentate (Fig.21) indicated protein fractions of molecular weights 20,000 $\pm$ 5,000, 120,000 $\pm$ 5,000, and a fraction estimated $>1,000,000$, coming off at the void volume of the column. This latter fraction could represent aggregated material.

The SDS-PAGE patterns for pea protein flour (Parrheim Foods), UF retentate, and diafiltered UF retentate are shown in Fig.22. Proteins in both a non-reduced and reduced forms were run, as well as protein markers of known molecular weight. The protein flour

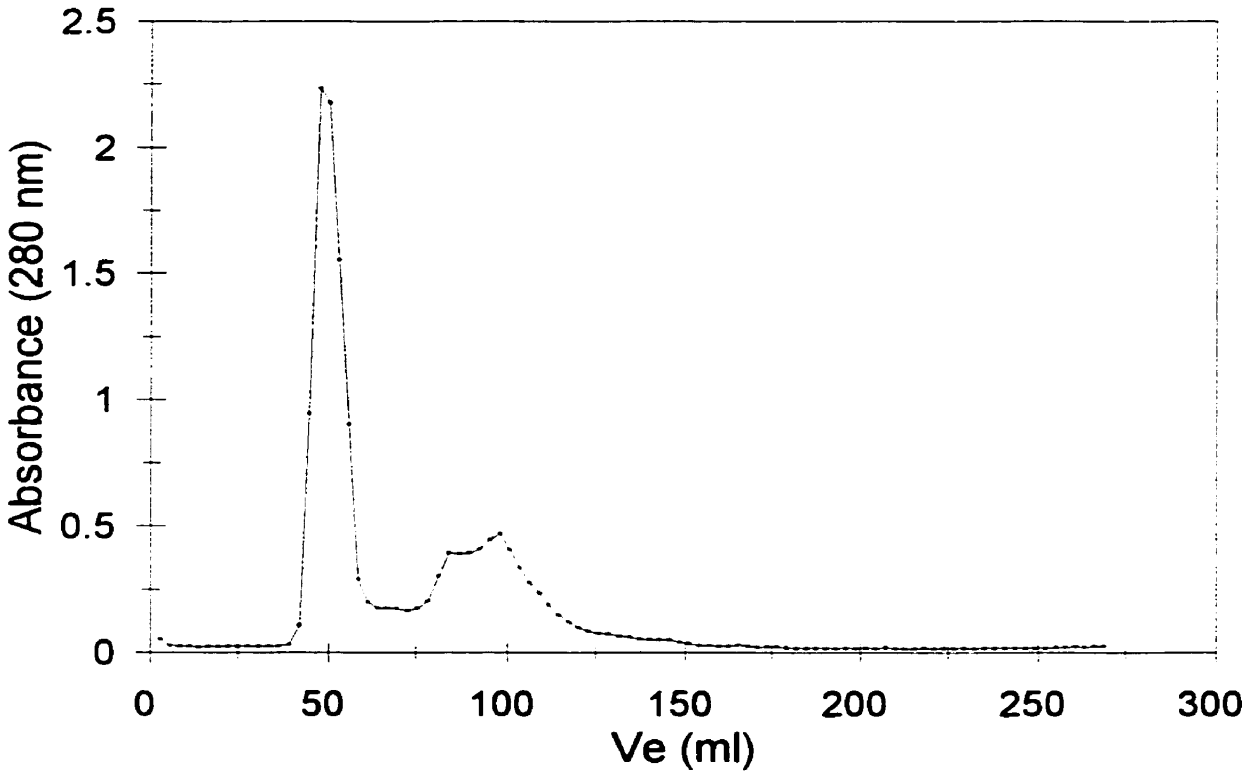

Figure 21: **Elution profile of pea protein desluedger effluent UF retentate.**
Column type: K26/100 packed with Sephacryl-S-300 HR.
Sample size: 5 ml
Eluent: 0.2 M Na acetate buffer (pH 7.5).
Eluted fraction volume: 2.8 ml.

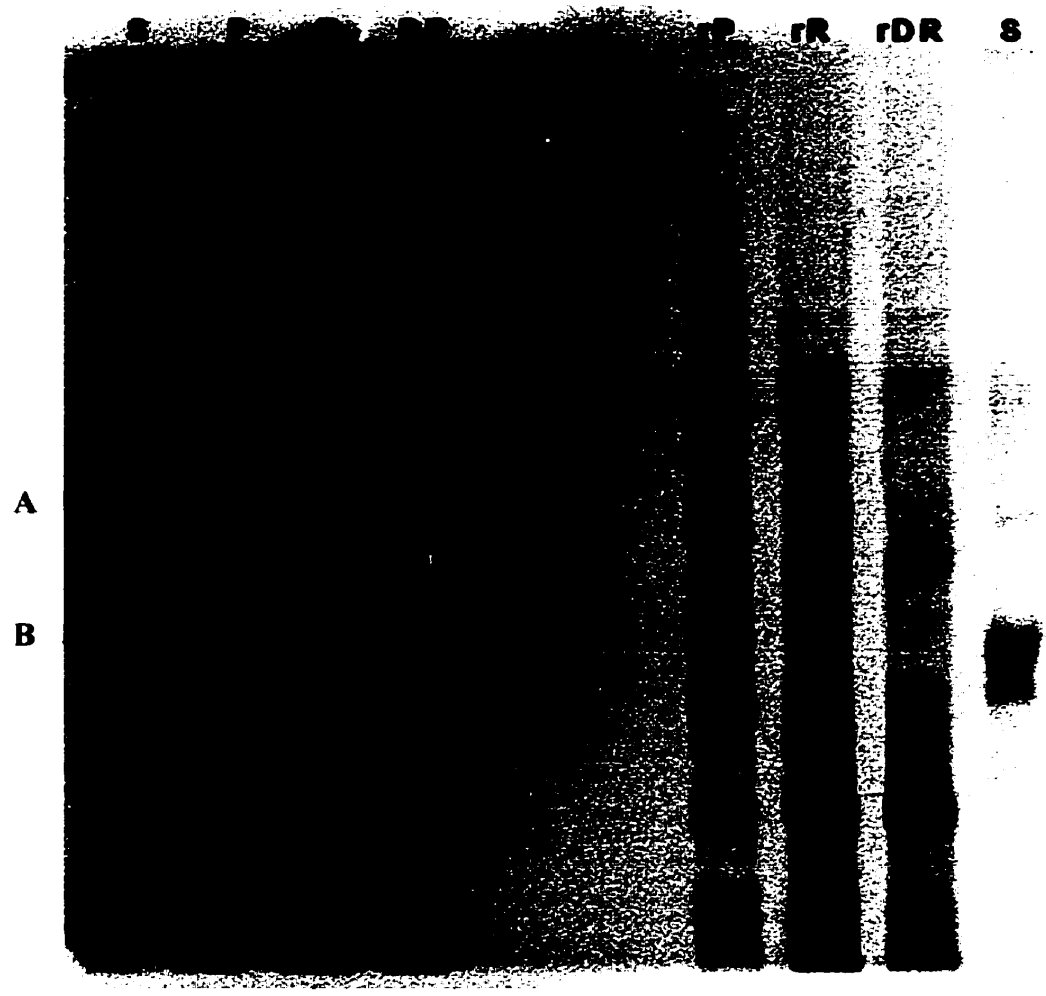

Figure 22. **SDS-PAGE electrophoregrams of pea flour and UF membrane treated pea protein desludger effluent.**
Samples:
P - unreduced pea flour
R - unreduced pea protein desludger effluent UF retentate
DR - unreduced pea protein desludger effluent UF diafiltered retentate
rP - reduced pea flour
rR - reduced pea protein desludger effluent UF retentate
rDR - reduced pea protein desludger effluent UF diafiltered retentate
S - marker protein standards (Sigma SDS-PAGE standards)
A: bovine albumin (66,000), **B**: egg albumin (45,000)
Membrane: Amicon H5P30-43 hollow fiber (30,000 MWCO)
VCR = 20:1

pattern showed at least 20 distinct bands over a wide range of molecular weights. The non-reduced protein patterns for the UF and diafiltered retentate indicated the presence of intense bands at the point of application on the gel, perhaps due to the presence of aggregated protein. In a reduced form, these bands dissipated suggesting the aggregated material was held together by disulfide bonds. The UF retentate and diafiltered retentate samples showed similar profiles. The patterns showed a number of bands that were similar to those of the pea protein flour, although most of the bands were fainter. There were two pronounced bands, and both have molecular weights smaller than the smallest reference standard (egg albumin, 45,000 MW) on the electrophoregrams. These fractions were concentrated during ultrafiltration, and were close to the nominal 30,000 MWCO of the UF membrane. This retentate protein may provide a protein fraction with distinct properties compared to the protein found in the protein flour. The functional properties of this protein requires further investigation.

G. Economics

Process economics based on chemical costs of Termamyl enzyme, celite and activated carbon are calculated in Table 30. On a daily basis, based on 260,000 L of primary protein desludger effluent, a cost of $409 would be incurred by the company. This is in addition to equipment costs and costs related to membrane processing.

By using UF technology, there is a potential of recovering 496 kg of protein in the retentate which could be spray dried for revenue. Based on $4.40 /kg pea protein market value, this could translate into a recovery of $2182.40 per day (Table 31). If the permeate were to be recycled, the saving in surcharge costs was calculated to be $2132, based on the City of Portage la Prairie by-law surcharges. Total savings per day is estimated at $4314.

Table 30. Daily chemical cost of pea protein desludger effluent treatment[a].

Chemical	Price ($ / kg)	Use (w/v)	Volume treated (L)	Cost
Termamyl[b]	$ 5.00	0.01 %	260,000	$ 130.00
Celite[c]	$ 1.33	0.02 %	260,000	$ 69.16
Activated carbon[d]	$ 1.80	1g / 2105ml[e]	247,000	$ 209.95
Total daily chemical cost				$ 409.11

[a] Based on primary desludger effluent = 260,000 L / day.
[b] Price quote from Novo Nordisk Biochem, Franklinton, NC.
[c] Price quote from Van Water and Rogers, Winnipeg, MB.
[d] Price quote from Van Water and Rogers, Winnipeg, MB.
[e] Based on adsorption isotherm value.

Table 31. Potential savings of membrane treatment of field pea effluent.

Savings	Potential amount of savings /day
Savings from protein recovery[a]	$ 2182.40
Surcharge savings[b]	$ 2132.00
Total savings	$ 4314.40

[a] Savings from protein recovery:

260,000 L of primary protein desludger effluent / day
at 20:1 VCR, retentate volume = 13,000 L

Protein in UF retentate (20:1 VCR):
38,160 mg/L X 13,000 L = 496 kg of protein /day
Protein value at $4.40 /kg
Recovery of protein value = $ 2182.40 /day

[b] Surcharge savings:

260,000 L of primary protein desludger effluent /day
BOD = 9312 mg/L (based on BOD/COD ratio = 0.6)
COD = 15520 mg/L (from Table 5)
SS = 1640 mg/L (from Table 5)

Calculation based on City of Portage la Prairie by-law:

$$\frac{0.33 \times (SS - 350)}{350} + \frac{0.46 (BOD - 300)}{300} \times 54.55 \text{ cents /kL} = \$ 8.20 / \text{kL}$$

Surcharge savings for 260,000 L of effluent = $ 2132.00 /day

V. CONCLUSION

This study confirmed the high strength organic loading resulting from the wet milling of field pea into components of protein, starch and fiber. Typical loading values were COD 7655 mg/L, BOD 3952 mg/L, and SS 8190 mg/L and flow 700,000 L/day. Discharge of this effluent to municipal treatment is costly to the plant in terms of sewage surcharge and capacity cost established by the City of Portage la Prairie. The major plant unit operation contributing to the organic loading is the protein desludger.

The technical feasibility of UF treatment of protein desludger effluents to produce a concentrated protein stream was demonstrated. The protein concentrate could be included in the protein stream for spray drying, thus increasing product yield. Pretreatment of the desludger effluents with a carbohydrase enzyme Termamyl (0.01%) prior to membrane treatment was important in reducing fouling aspects. Addition of celite (0.02%) was effective in rapid settling of a fine floc produced by the enzyme treatment allowing for continuous processing.

Both hollow fiber and spiral wound UF membranes were evaluated in this study. A 30,000 MWCO hollow fiber or spiral wound membrane were both effective in concentrating protein. A 10,000 MWCO spiral wound membrane showed only slightly higher protein rejection, however with a significantly lower flux. A 30,000 MWCO membrane would be the recommended membrane size for further research or commercial use by the company.

Operating parameters such as temperature, pH, feed concentration and volume concentration ratio were studied in addition to membrane type and size (MWCO) to determine their effect on flux. This study indicated that the ideal operating conditions of the protein desludger unit operation (temperature 50°C, pH 4.5) were also optimal conditions for UF membrane treatment. Lower temperatures resulted in decreased membrane flux, and pH adjustments to higher or lower values for improved protein solubility did not improve flux appreciably.

As would be predicted, membrane flux decreased with increased feed concentration. Variability in composition of the protein desludger or effluent could result in the plant being required to oversize their membrane requirements to maintain a required throughput.

A VCR of 20:1 was achievable by UF membrane treatment and the protein desludger effluent was concentrated to approximately 5% solids, the solids level at which is used by the plant to feed the spray drier in production of protein powder.

The rejection value for protein was 95.9% using the 30,000 MWCO hollow fiber membrane with some passage of non-protein nitrogen into the permeate. Protein was concentrated approximately 12X by membrane treatment. As carbohydrate was less concentrated by the membrane treatment (1.3X) a more pure protein could be separated from the desludger effluent feed. Further purification of the protein was achieved by diafiltration. On a dry weight basis, the protein content of solids increased from 72.8% to 88.8% by discontinuous diafiltration.

The hypothesis that desludger effluent pretreatment would minimize membrane fouling and allow for efficient membrane cleaning was demonstrated. However, membrane types responded differently to cleaning. A combination of high temperature (45-50°C) and a chlorinated caustic detergent was effective in cleaning of the hollow fiber polysulfone membrane. Caustic wash at high temperature or a chlorinated caustic solution at room temperature (20 - 22°C) was effective in cleaning the spiral wound cellulose acetate membrane. Even though mineral salts would be present due to pH adjustments in isoelectric precipitation of the protein, an acid wash was not required during this study but would be recommended on occasion as preventive maintenance for the membrane. The time required between cleaning would be best determined on a commercial scale membrane process and would depend on membrane surface area.

The resulting permeate stream from membrane concentration was high in organic loading (COD 10,000 mg/L) and had an amber color which could limit reuse opportunities within the plant at specific unit operations. Discharge of this high volume permeate would be costly in terms of surcharge.

The potential for reuse of the UF permeate was demonstrated by activated carbon treatment. The activated carbon treatment could decolorize the permeate at a concentration of 2100 mL/g of carbon. The permeate would be suitable in reuse applications in downstream operations of fiber and starch separation where color is a critical point. However, the cost of treatment, estimated at 0.085 cents/L for activated carbon for complete decolorization, could be prohibitive based on the throughput volume. Further research should be directed at recycle opportunities to determine whether a colorless

permeate would actually be required, whether it could be partially decolorized and still be acceptable, or be used as make-up water with dilution. Another opportunity for recycle would be to use the permeate at the protein desludger operations where color may not be a critical factor.

By use of UF, it was determined that 496 kg of protein could be recovered per day, which could be included in the spray dried protein products produced by the plant. Electrophoretic patterns indicated that a protein with altered subunit distribution compared to the commercial protein fraction was being recovered in the UF retentate. Based on the price of the commercial isolate, the recovered protein value was estimated to be $2182 per day. The protein may have unique properties that could be of value to the company.

The cost to the company in terms of chemical costs for UF pretreatment and treatment of permeate was estimated to be $409. In addition to recovered protein, savings in sewage surcharge costs was calculated at a daily cost of $2132, for both recovery of desludger retentate, and recycle of permeate. Total savings per day is calculated at $4314.

VI. RECOMMENDATIONS

1. Scale up of UF for treatment of primary desludgers to commercial operation using a 30,000 MWCO membrane is recommended. Pretreatment, using Termamyl enzyme and celite should be part of the process scheme.
2. Membrane type, configuration, and cleaning regime should be determined working in conjunction with a membrane supplier.
3. Functional properties of the protein in the retentate should be investigated to determine possible value added potential.
4. Recycle opportunities for the colored permeate should be investigated with option of activated carbon treatment.

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