Membrane Technology in Fishery Industry – A State of the Art

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ABSTRACT

A large amount of raw materials is processed with the demand of fishery products. Membrane technology and bioprocessing have been increasingly involved in fishery industry, particularly for the treatment of fishery wastes. A critical review on application of membrane technology in fishery industry has been reported. Fishery wastes including both solid and liquid contain high content of organic compound which may cause the pollution to the environment. Membrane technology could recover valuable compound from fishery wastes, therefore not only reduce the risk of pollution but also improve economic benefit of fishery industry. Comparing to other competing methods, membrane technology could serve as a simple, large scale and mild method to achieve both high efficiency and maximum preservation of natural property of recovered compounds. A series of valuable compounds such as protein, enzymes, collagen and marine flavor could be recovered from fishery byproducts by membrane technology. Different membrane processes mostly microfiltration, ultrafiltration, reverse osmosis and nanofiltration have been employed. These membrane processes could work individually or be combined with other biochemical reactions to develop a hybrid multistage membrane process for the desirable recovery rate, high purity of recovered compound and development of new product. The performance of these processes could be improved by model design or other additional techniques such as gas sparging. In addition to recovery of valuable compounds, membrane process has also been applied for treatment of both fish pond and fishing process water to achieve water recycle. In the future, more industrial success of membrane technology in fishery industry is expected.

Key words: Fishery, membrane

1 INTRODUCTION

Fishery has been a fast-growing industry because of the increasing demand of fish as food. Fish are processed in fishery industry by defrosting, cooking, canning and cleaning to all lines (sauce filling, washing of cans, sterilization and packing). For illustration, mussel and tuna are processed by washing, trimming, cooking, size classifying, dehydrating and finishing. Sardine processing includes scraping, cutting, conveying, canning and finishing. The processing operations differ with species (octopus, squids, mackerel, etc). Fishery processing wastewater and processing of fishery products may leave a solid waste up to 50 % by weight with a high organic content(bone, skin, dark meat, viscera and pieces from flaking) and liquid wash water, cooking water, oil, blood, mucus, condensate. For example, the production of surimi, a product obtained from minced fish that is washed with water from Pacific whiting (*Merluccius productus*) results in about 80 % of the original raw materials. In the case of canned tuna processing, there are 25-23% solid waste (e.g. head, skin, viscera) and about 35% liquid waste (e.g. blood, tuna condensate, oil). Now fish production by aquaculture is new art since the last decade and growing constantly at a rate of 10% per year. However, waste discharges of aquaculture facilities may have environmental problems not known. There are numerous ways for by-product recovery in the fish processing industry, such as production of pet food, fertilizers, fish silage, protein hydrolysates, chitin and chitosan, gelatin, collagen, food flavors, bone meal, bait and fish scales.

Membrane processing is to separate different materials by semi-permeable membranes using two bulk phases physically separated by a third phase, the membrane. The membrane is an interphase between the two bulk phases. The membrane phase may be any one or a combination of the following: nonporous solid, microporous or macroporous solid with a fluid (liquid or gas) in the pores, a liquid phase with or without a second phase, or a gel. Different membrane processes, include reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), nanofiltration (NF), dialysis (DA), electrodialysis (ED), gas permeation (GP), pervaporation (PV) and liquid membrane to concentrate, purify or fractionate temperature sensitive solutions (food and drug industry, biotechnology) by microfiltration, ultrafiltration, reverse osmosis and nanofiltration have been adopted for both promotion of product and treatment of wastes. Pressure plays a role as driven force.

2. WHAT IS MEMBRANE TECHNOLOGY AND OPTIMAL CONDITIONS

The pressure driven membrane process rely on the preferential retention and passage of at least one solute and one solvent. Both these processes often involve selective separation of multiple solutes.

2.1 FUNDAMENTALS OF PRESSURE DRIVEN MEMBRANE PROCESS

The function of pressure driven membrane process is affected by a series of factors. Major factors include pressure, feed velocity, solute concentration and temperature. Interaction between feed solution and membrane, characteristic of solute and cleaning operation also should be considered in many cases. During pressure driven membrane process, the flux (J) of permeate is normally described as a function of the driving force and the total resistance shown in equation, called Darcy's law.

$$J = \frac{\Delta P}{\mu R_{\mathrm{tol}}} \tag{1}$$

where, ΔP is the differential pressure(or transmembrane pressure); μ is the dynamic viscosity of the permeate; R_{tol} is total resistance. During pressure-driven membrane process, solution is separated by a membrane. Due to the membrane osmosis, the liquid level at concentrated side increases. A hydrostatic pressure difference, called osmotic pressure will be built up between the two sides of membrane. In ultrafiltration and microfiltration process, osmotic pressure is normally negligible. However, due to the high salt concentration during the process, the effect of osmotic pressure in reverse osmosis and nanofiltration process should be considered. In order to obtain a flux from bulk side (higher concentration) to permeate side (low concentration), the applied pressure should be larger than osmotic pressure shown as:

$$J = \frac{\Delta P - \Delta \pi}{\mu R_{\mathrm{tol}}} \tag{2}$$

where $\Delta\pi$ is osmotic pressure. The flux is dependent on the driven force, i.e. transmembrane pressure and total resistance. In practice, if feed solution contains particular materials or macromolecules, the permeate will decrease with filtration time to a level which is much lower than initial flux. The decrease of flux is due to the build-up of a concentration gradient onto membrane surface caused by convective transport of solutes towards membrane (concentration polarization), formation of macromolecule gel layer on membrane surface and other membrane fouling (i.e. narrowing or blocking membrane pore by solutes). The total resistance increases with filtration time due to the different types of membrane fouling and leads to a decline of flux when a constant pressure is applied. Thus the total resistance is the sum of all sub resistances as:

$$R_{\mathrm{tol}} = R_{\mathrm{m}} + R_{\mathrm{cp}} + R_{\mathrm{f}} \tag{3}$$

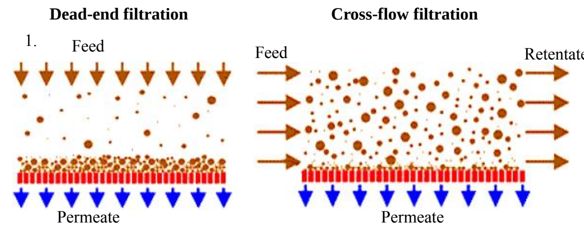

Figure 2. Dead-end and cross-flow filtration..

where, R_{m} is membrane resistance, a membrane constant; R_{cp} is the resistance caused by concentration polarization; R_{f} is the resistance caused by membrane fouling.

There are two fundamentally different (1) ways of running pressure driven membrane process, i.e. dead-end filtration and cross-flow filtration (Figure 2).

In dead-end filtration, feed solution is pressurized through the membrane. The pressure is constant over the whole membrane surface. In cross-flow filtration, the feed solution is pumped tangentially along the membrane surface. By the pressured applied, the permeate is induced. However, there is a pressure drop along the membrane because of the tangential flow over the membrane. Cross-flow filtration has several advantages comparing to dead-end filtration. The cross-flow filtration is more widely employed, especially in industrial applications.

The transmission of a partially rejected solute through a membrane is expressed by the apparent sieving coefficient S_{a}.

$$S_{\mathrm{a}} = \frac{C_{\mathrm{P}}}{C_{\mathrm{b}}} \qquad \Psi = \frac{S_{\mathrm{a1}}}{S_{\mathrm{a2}}} \tag{4}$$

where C_{b} is the solute concentration in the bulk feed; C_{p} is the solute concentration in permeate, Ψ is the selectivity, and S_{a1} and S_{a2} are the observed sieving coefficients for the lesser- and greater- retained solute, respectively. From equation (5), a larger value of Ψ is correlated with a better separation between two solutes. With great potential for concentration, fractionation, and purification of soluble and insoluble materials, pressure driven membrane processes are just beginning to emerge for applications in fishery industry. This method provides two essential characteristics: (a) it is a purely physical separation principle; and (b) it is a modular design. Membrane process is therefore an ideal choice for waste treatment in fishery industry.

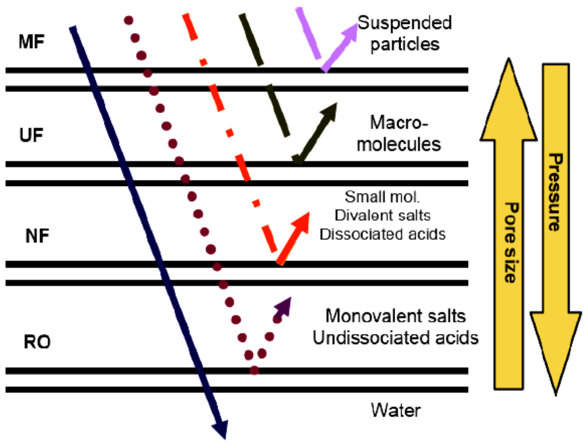

Figure 1: Pressure driven membrane technology

3 APPLICATION OF PRESSURE DRIVEN MEMBRANE PROCESS IN FISHERY INDUSTRY

3.1 Microfiltration of fish water: Microfiltration is filtering a suspension colloidal or fine particles in the approximate range of 0.02 to 10 µm based on size. Membranes are made up of ceramics, teflon, polypropylene, or other polymers. Two microfiltration system, Zenon ZW500 ((PVDF, nominal pore size 0.04 µm, membrane area 10 m^2) and Eido-HF-PP-M6 for (PP, nominal pore size 0.1 by 0.7 µm, membrane area 12.75 m^2) in pilot scale (in 6 culture tanks, each with a volume of 1 m^3 and a fish stocking density of about 20 to 60 kg/m^3) was standard at the aquaculture company Fischwirtschaftsbetrieb Andreas von Bresinsky, Oelzschau, Germany. 'Surimi' is Japanese technology to recover the suspended myofibrillar proteins from mince fish wash water at refrigerated temperatures (12-15^{o}C) using polysulfone microfiltration membranes with a nominal pore size of 0.2 µm for the proteins recovered. Other microfiltration process uses Whatman filter No. 1, pore size of 5-10 µm as pretreatment before ultrafiltration of effluent from fish meal production in a fish meal factory. For example, recovery of protease from the spleen of yellowfin tuna, a solid waste from tuna canning process, microfiltration has been applied as a pretreatment process by hollow fiber membrane with pore size 0.1 µm.

3.2 Ultrafiltration: Ultrafiltration is applied to recover brines, process water treatments, separate marketable compounds in wastes or works as pretreatment for nanofiltration and reverse osmosis. Ultrafiltration is effective in the organic matter recovery in fish canning industry. At average transmembrane pressures of 2.2 and 3.8 bar and tangential flow rates of 6.0 and 0.47 m/s for Ceraver and PCI membranes, protein concentration in the feed solution was increased from 5 to 35 g/dm^3. Fish skin waste could be used to isolate collagen and gelatin by three-step membrane bioreactor having three hollow fiber ultrafiltration membranes with molecular weight cut-off of 10 (first step), 5 (second step) and 1 (third step) kDa respectively at operation conditions including temperature, pH, type of enzyme, substrate-to enzyme ratio, flow rate and reaction volume, to achieve degree of hydrolysis in the first, second and third membrane bioreactor were 87%, 77% and 70% respectively. These hydrolysates are rich in bio-proteins. The ZrO_2 membranes (6 mm inner diameter, 1.2 m long, 0.16 m^2 filtering area) need 10 kDa nominal molecular weight cut-off for 2.4 mg/dm^3 of enzyme, 32 g/dm^3 of APC with a conversion rate of 75.9%, flow rate of 2.22 cm^3/min, reactor volume of 400 cm^3, residence time of 180 minutes. For example, catheptic L proteases from fish mince wash water needs pretreatment of fish mince wash water at 60 ^{o}C, acidification to pH 6, and centrifugation doubled ultrafiltration membrane flux and significantly improved protease purity by reducing a majority of the 35–205 kDa proteins, purity100-fold, yield 80%. Stability (frozen and freeze-dried protease). Tryptic enzyme was obtained by ultrafiltration of fish sauce made from cod viscera using polysulphone membranes at very high salt concentrations (20-25%). Protease from yellowfin tuna spleen by extraction process and microfiltration membrane was purified up to 12-fold with possible trypsin-like serine protease with low cost by membrane technology involving microfiltration (pretreatment step) and ultrafiltration (separation and purification steps) as shown in Figure 1.

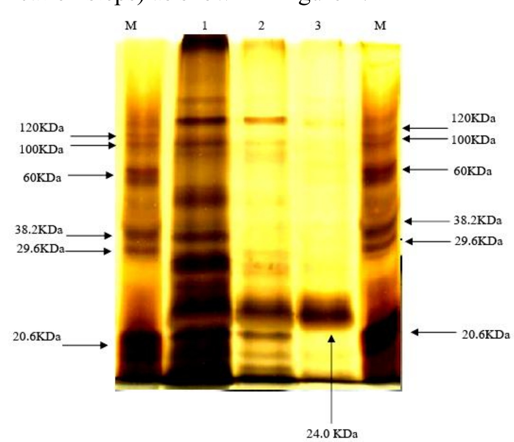

Figure 2. Protease isolated and purified from yellowfin tuna spleen by membrane filtration (SDS-PAGE with 12% gel, stained by silver staining; Lane M, standard marker; Lane 1, raw spleen extract before membrane filtration; Lane 2, spleen extract treated by microfiltration; Lane 3, spleen extract treated by ultrafiltration).

In addition to the treatment of wastes, membrane technology also shows its potential for product promotion in fishery industry. Ultrafiltration was applied for fractionation of cod frame protein hydrolysate to improve its functional property. Membrane-assisted hybrid bioreactor for wastewater treatment is new art in a fish canning factory by a hybrid circulating bed reactor coupled in series to an ultrafiltration membrane module. In this technology, aerobic reactor couples to an external submerged hollow-fiber ultrafiltration membrane module (average pore size of 0.045 μm, nominal surface area of 0.093 m^2 and typical operating transmembrane pressure of 10-50 kPa.) contained in a vessel of 1.2 liter. The system can operate simultaneously with high COD and ammonia conversion rates at high nitrogen loading rate and organic loading rate.

3.3 Reverse Osmosis: Reverse osmosis across semi-permeable membrane contains tiny pores restrictive to salt and other natural minerals, bacteria and disease-causing pathogens. The Calembo Company, Sfax, Tunisia uses 50 m^3/d of drilling water per ton of fish to condition cuttlefish (before freezing) with hard water, high sulphate concentration and salinity (67 g/l), high organic load (COD of 10-20 g/l), high pressure (70 bars), salinity of the drilling water (permeate salinity around 2.5 g/l). However the application of reverse osmosis membrane for aquaculture wastewater treatment has been largely limited. One of the major problems is the energy cost during the reverse osmosis process. Low cost wind-driven reverse osmosis system for aquaculture wastewater treatment reduces the wastewater from fish tank sent to membrane unit by a piston pump driven by windmill to make it suitable for fish production recirculated to the fish tank. Authors reported temperature and pH play significant role in fish acquarium in different months in year [1]. The brine is sent back to the storage tank, where it mixes with the wastewater from the fish tank. The system can process aquaculture wastewater at flow rates ranging from 230 to 370 l/h. The wind-driven reverse osmosis system for nitrogen removal from aquaculture wastewater is feasible and environmentally friendly. Depending on the wind speed, it can generate and recycle freshwater at a flow rate of 228-366 L/h. About 70-84% of aquaculture wastewater can be recycled using this system, which was capable of removing 90-97% of nitrogenous waste present in tilapia culture effluent. The average recovery rate of the membrane used in this system is about 39.2–57.5%.

3.4 Nanofiltration

Nanofiltration is present state of art in membrane processing in fishery industries and can perform separation applications that are not otherwise economically feasible, such as demineralization, color removal, and desalination. In general, application of nanofiltration could be defined as three areas: (a) removal of monovalent ions from waste water or reaction mixtures; (b) separation between ions with different valences; (c) separation of low- and high-molecular weight components. Nanofiltration membranes (molecular weight cut-off of 550, 342 and 500 Da) show retention rates of COD and protein nitrogen increase with pore size diminution. Retention of COD ranged from 87% to 93% while retention of protein nitrogen ranged from 52 to 82.5% for nanofiltration membranes used. Blue whiting is mainly used for the production of fish meal and fish oil to avoid excessive concentration of salt, Membrane enzymatic bioreactor uses both ultrafiltration and nanofiltration membranes. Nanofiltration membranes have also been evaluated and employed in pre-treatment facilities for both reverse and thermal process for seafood washing and processing. The reports showed that the nanofiltration membrane with molecular weight cut-off of 200 Da was effective for the removal of natural organic matter and reducing the sulphate concentration in drilling water. Organic materials rejection with this membrane is about 89%. The nanofiltration as a pre-treatment process allows to standardize the water quality.

4 SUMMARY

Fishery industry is one of the most important industry sectors throughout the world. The avoidance of waste formation and pollution is always a key task, but on the other hand, waste prevention, minimization and valorization, and the use of energy efficient process technologies are more and more desirable options in waste management as these streams from fishery industry are usually rich in valuable compounds (e.g. oils, protein, enzyme, etc.). The controlling of raw material, water and energy use, as well as the utilization of by-products and reducing the effluent discharge leads towards exploring new applications of membrane process and new modules. Pressured driven membrane process has made significant advantages in fishery industry. According to the selection of membrane configuration from an economic point of view, either hollow fiber or spiral wound membranes are preferred. However, with a strongly fouling or a highly viscous solution tubular or plate and frame systems have to be applied. It is also necessary to focus on the fouling process and the way it affects the separation. Generally, specific components in the feed can be related to the fouling process and therefore techniques to overcome the fouling (e.g. by a pre-treatment) can be developed. With the further development of membrane material, module design and great knowledge of membrane fouling, membrane processes will show their great potential to achieve desirable process and reduce operation cost and investment in fishery industry.

5 REFERENCE

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