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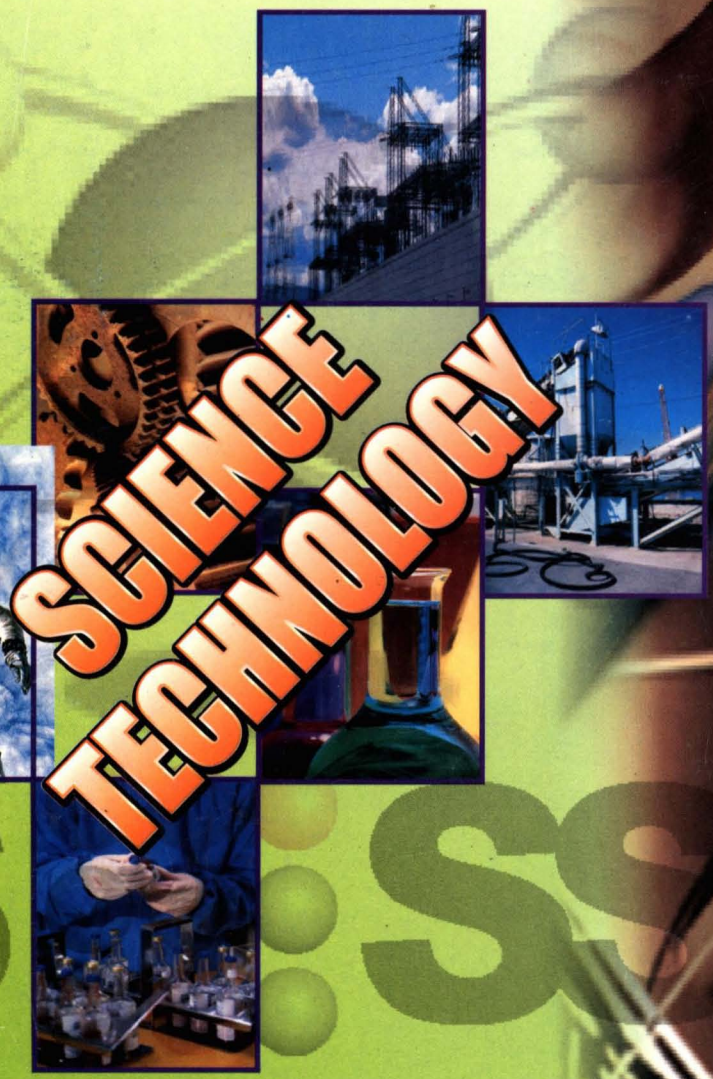

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A Study on Flux Declination in Enzymatic Membrane Reactor (EMR) for Cyclodextrins Production

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ABSTRACT

This paper investigated on the flux declination in ultrafiltration membrane during separation of cyclodextrins from tapioca starch and enzyme CGTase. The Resistance-In-Series Model was used to identify the responsible hydraulic resistances. The result showed that, the declination of flux was obtained as the amount of total resistances increased. The flux was decreased continuously with time until it reached a steady-state stage. In this stage, the cake layer on the membrane surface has been achieved an equilibrium thickness. These resistances can be eliminated by using hydraulic and chemical cleaning. The results show that 20% of the foulant was removed from the membrane surface after hydraulic cleaning while 27% of the foulant was desorbed from the membrane surface after chemical cleaning.

Keywords: *Cyclodextrins; Ultrafiltration; Enzymatic Membrane Reactor; Fouling Mechanism; Hollow Fiber Membrane*

Introduction

The combination of membrane separation and enzymatic reactor are called enzymatic membrane reactor (EMR). The EMR can separate enzymes from products and/or substrates by semipermeable membrane. The convective force across the membrane can selectively enhance the separation of substrate and products from the reaction mixture. The enzymes is retained within the system by the membrane, while the product passes through the membrane as a permeate. The EMR present advantages such as high enzyme loads, prolonged enzyme activity, high flow rates, reductions in costs, energy and waste products by recycling, easy reactor operation and control, straightforward scale-up to large systems and high yields of pure material (Katchalski-Katzir 1993; Lopez et al. 2002).

In this study, the EMR was applied to produce and separate cyclodextrins (CDs) from tapioca starch. The cyclodextrins glucosyltransferase (CGTase) and starch degradation products were retained within the system by membrane, allowing the establishment of a continuous operation with starch and enzyme feed and CDs withdrawal (Lopez *et al.* 2002; Giono and Drioli 2000; Prazeres and Cabral 2001). CGTase is an enzyme which is capable of converting starch and related substrate into CDs. CDs are cyclic oligosaccharide composed of α-1,4-glycosidic-linked glucosyl residues produced from starch or starch derivatives using CGTase. CDs can solublize hydrophobic materials and entrap volatile components by forming inclusion complexes with organic compounds and thus enhance their chemical and physical properties. These properties have led to the commercial application of CDs (Ibrahim 2005; Biwer, Antranikian and Heinzle 2002) in food, pharmaceutical, cosmetic, agricultural and plastic industries as emulsifiers, antioxidants and stabilizing agent (Szejtli 1997). However, the extensive use of CDs is still restricted by high production cost of CDs (Kim, Lee and Kim 1993).

Although there are many advantages of membrane, the application of membrane technology in EMR is still limited. This is due to the fouling problem, which reduces the membrane performance. Fouling in membrane separation occurred when the flux decline as the function of time due to the increment of hydraulic resistance. Parallel with this scenario, this study focuses in determining the flux declination and quantitave study of hydraulic resistances occurred during the CDs separation by using EMR.

Materials and Methods

Experimental system

The EMR system was developed to evaluate the performance of our locally produced hollow fiber ultrafiltration membrane. As shown in Figure 1, the EMR system is comprised of an enzymatic stirred reactor with installed temperature controller, a membrane module unit, a pump, feed and retentate pressure gauges. The ultrafiltration membrane module has a length of 30 cm and a diameter of 22 cm. The locally produced PES membrane with a MWCO of 32,000 Dalton was used in this experiment. Membrane diameter and effective area are 600 μm and 0.027 m^2, respectively. The enzymatic reactor consists of a stainless steel vessel with a mechanical stirrer attached. This vessel was

filled with 2 % of raw tapioca starch solution mixed with CGTase enzyme (200 µl/100 ml reaction volume which has an enzyme activity of 0.8 unit/ml-optimal conditions suggested by Novo Nordisk, Denmark). The reaction mixture was continuously pumped to the membrane module and recycled back to the enzymatic reactor. The temperature and pH of the enzymatic reactor was maintained at 60°C and 6.0 respectively. The operational transmembrane pressure (TMP) for membrane filtration was kept constant at 2 bars.

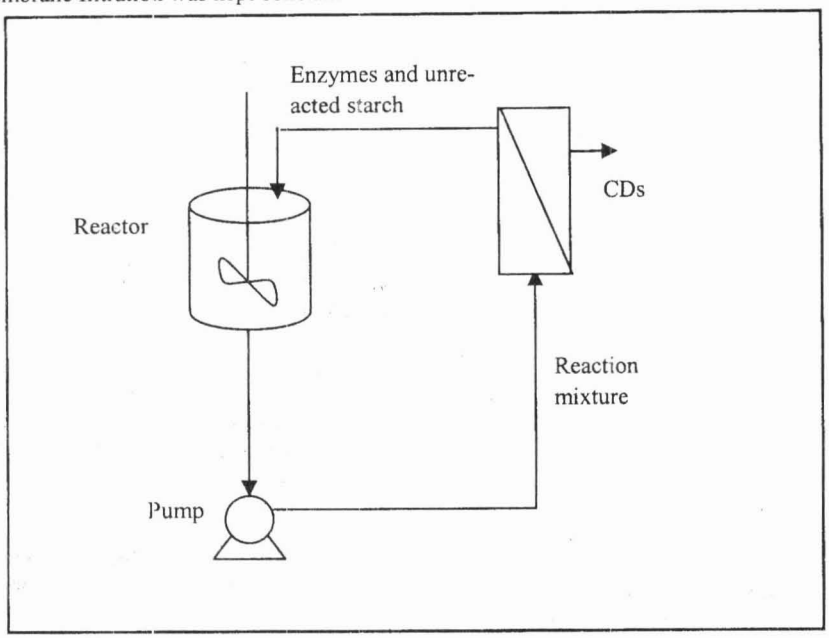

Fig. 1: Schematic diagram of EMR system

Resistances-In-Series Model

Resistances-In-Series model is most widely used in determination of hydraulic resistance in membrane separation. There are five parameters of membrane resistance-in-series model based on Darcy's law which were used to quantify their influences on flux decline (Cho, Amy and Pellegrino 2000):

$$J_v = \frac{\Delta P}{\mu(r_m + r_{cp} + r_g + r_{a1} + r_{a2})} \quad (1)$$

where J_v is flux through the membrane (m/s), ΔP is the transmembrane pressure (Pa), μ is the dynamic viscosity (Pa s), r_m is the membrane hydraulic resistance, r_{cp} is the concentration polarization resistance, r_g is the gel layer resistance, r_{a1} is the weak adsorption resistance, r_{a2} is the strong adsorption resistance (all resistance are in m^{-1}). In this case, the osmotic pressure is considered into the concentration polarization. In this study, there several types of resistances contributed to both reversible and irreversible fouling mechanisms. The concentration polarization (r_{cp}) and gel layer resistance (r_g) were assumed as reversible fouling mechanisms, which could be removed by water. However, the weak and strong adsorptions were categorized as an irreversible fouling mechanism. The weak adsorption was removed by chemical cleaning, while the strong adsorption remained onto the membrane surface.

The distilled water (DI) and reaction mixture were cross-flow filtered using the following procedure to obtain all hydraulic resistances quantitatively. Clean water was first filtered through the membrane to obtain the pure water flux of membrane (J_{pwp}) until a constant flux was achieved. Then, the reaction mixture was fed and the permeate rate was monitored over the time. After the permeate rate reached a constant value (that is, the permeate of fouled membrane), DI replaced the reaction mixture and the applied pressure was released to remove the concentration polarization layer. The next J_{pwp} of the membrane was taken in order to determine the concentration polarization resistance value. The fouled membrane was then rinsed with DI at higher applied pressure. This procedure was conducted to ensure the gel layer was totally removed from the membrane surface. The third J_{pwp} was taken so that r_g value could be determined. The membrane was then rinsed with 0.1M NaOH solution for 20 minutes in order to dissolve the weak adsorption layer off the membrane surface and pores. The fourth J_{pwp} was measured and the r_{a2} were calculated using Equation 1.

Scanning Electron Microscopy

A digital scanning electron microscopy (SEM) was used to study the surface of clean and fouled membrane. The membrane was cut into small tubular about 5 mm in length. The membrane then was coated with a gold-palladium before the photographs were taken.

Results and Discussion

Flux decline in the UF crossflow filtration

The flux decline in this EMR system was due to the fouling mechanism. Initially, the particles from the reaction mixture arrived at the membrane and blocked the smallest pore of the membrane. Then, the inner membrane surfaces of bigger pores are covered. Next, some particles were entered to membrane covered other arrived particles, while others directly blocked some of the pores. Finally, the cake layer begins to be developed (Bowen, Calvo and Hernandez 1995).

Figure 2 shows the flux declined in the ultrafiltration cross flow membrane. The flux of the membrane was first obtained the hydraulic resistance from the membrane due to the intrinsic property of the membrane. Subsequently, by using the Darcy's law, the declination of flux was obtained as the increasing amount of total resistances.

Moreover, once the pressure was released, the flux was increased due to the vanished of the concentration polarization. In addition, after the membrane was cleaned with DI water, the gel layer was moved out from the membrane surface, which effects an increasing of membrane's flux. The flux of the membrane was found to be increase after chemical cleaning as the weak adsorption was purged out off the membrane pores and surface. Nevertheless, the strong adsorption was not removed from the membrane even when the fouled membrane was cleaned several times. It was presumed to be due to dynamic balance between adsorption and desorption of soluble organic matters (CDs) into the matrix of membrane (Mo and Huang 2003).

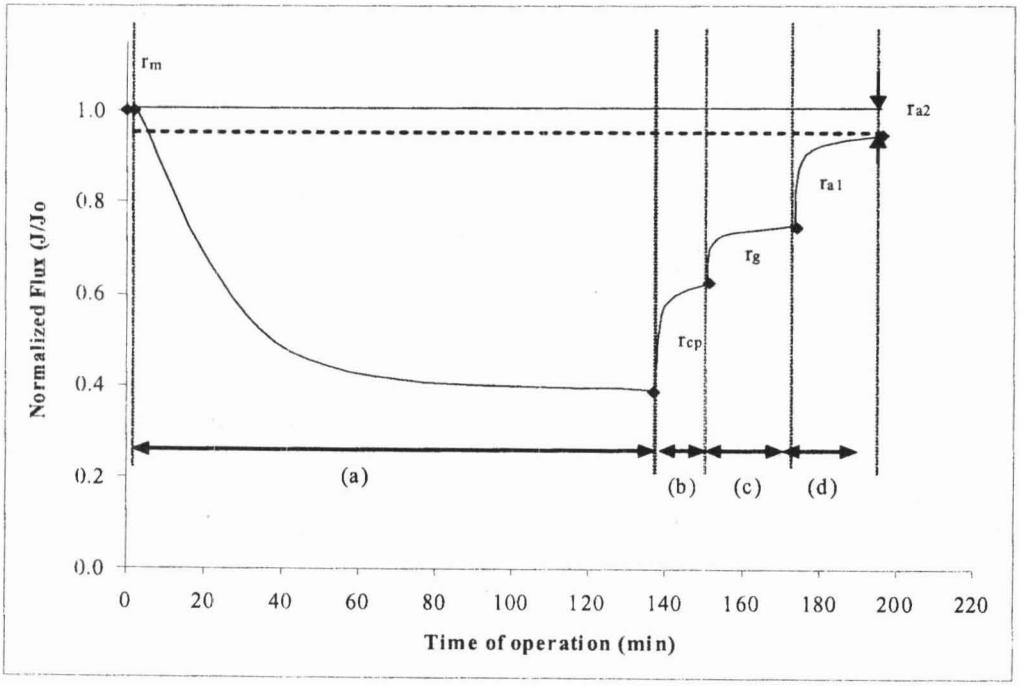

Fig. 2: Flux decline in the UF crossflow filtration; (a) flux decline during filtration, (b) pressure released, (c) water cleaning, and (d) chemical cleaning.

Spectral analysis of UF fouled membrane

The inner and exterior surfaces of the new and fouled membrane were observed under SEM, and the result is shown in Figure 3. The exterior of the membrane surface under 5000 magnification clearly showed the surface was covered with a thick and coarse cake layer.

The membrane used in this study had a pore size of 32 000 Dalton. However the starch, CGTase and CDs were about 10^5 Dalton, 75 000 Dalton and 1135 Dalton (β-CD), respectively. Due to the steric properties of the membrane, neither starch nor CGTase could pass through the membrane pores. As a result, it was presumed that the outer membrane surface was covered by starch and CGTase (reversible fouling), while the inner membrane surface was mainly formed by CDs and starch byproduct (irreversible fouling). As reported by other researchers, the reversible fouling mainly could cause concentration polarization and gel / cake layer onto the membrane surface, while the irreversible fouling mainly could cause adsorption (weak and strong) into the membrane matrix.

Determination of hydraulic resistances

The resistance-in-series model was used in this study to obtain the hydraulic resistances (m^{-1}) exhibited during CDs separation. The values of the hydraulic resistance in this study are shown in Figure 4. As shown in Figure 4, the responsible fouling mechanism that mainly controlled the flux of membrane was the irreversible fouling. This was well supported by the highest value of weak adsorption resistance (r_{a1}) followed by gel layer resistance (r_g), concentration polarization resistance (r_{cp}) and strong adsorption resistance (r_{a2}).

Figure 4 also shows the membrane hydraulic resistance was about 56% of the total hydraulic resistance. This is due to the intrinsic property of the membrane. However, the weak adsorption resistance, gel layer resistance, concentration polarization resistance and strong adsorption resistance were exhibited about 16%, 14%, 11% and 3% of the total hydraulic resistances, respectively. The weak adsorption (r_{a1}) was found to be the main determinant of the rate and extent of flux decline. This is due to the precipitation of solute (CGTase and CDs) onto the membrane surface and pores. We presume that the smaller size macromolecular of feed fractions (CDs) is the major components of the adsorbed foulants that lead to significant long term flux decline.

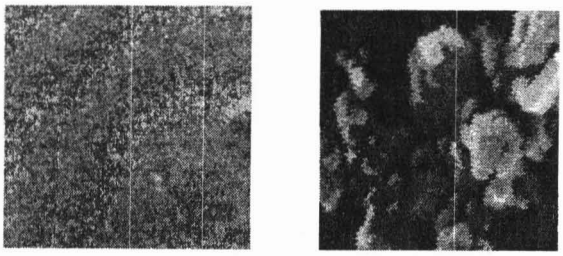

Fig. 3: SEM micrograph of (a) new and (b) fouled PES membrane (magnificent 5000x)

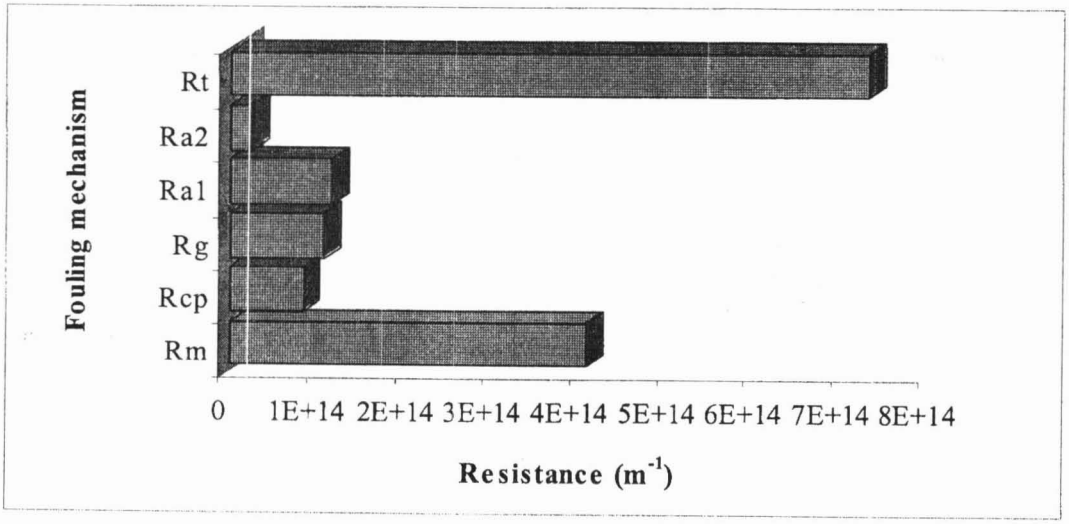

Fig. 4: Amount of hydraulic resistances of the UFHF membrane.

The specific mechanisms may include pore mouth adsorption and subsequently narrowing off the pores, as this component is small enough not to be excluded by steric considerations. Nevertheless, the gel layer resistance (r_g) was due to the formation of a starch deposit located on the upper surface of the membrane. The initial fouling in this system was determined almost entirely by the convective deposition of these large particles/aggregates on the membrane surface. All the fouling mechanisms were observed responsible for fouling that reduces pore size and increases rejection.

Conclusions

The results of these investigations indicated that:

1) The flux declined in ultrafiltration membrane was up to 40% of the initial flux.
2) The highest hydraulic resistance was weak adsorption resistance, which was about 16% of the total hydraulic resistances.
3) The fouled membrane was cleaned by using alkaline solution.

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