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Determination of Fouling Mechanisms in Enzymatic Membrane Reactor (EMR) for Cyclodextrins Production Based on Resistance-In-Series Model

A. M. Mimi Sakinah[1, 2] A.F. Ismail[1] M.I. Rosli [1, 3] H. Osman[4]

[1]*Membrane Research Unit, Faculty of Chemical Engineering and Natural Resources, University Technology of Malaysia, 81310 Skudai Johor, Malaysia*
Tel: +60-075535592, Fax: +60-075581463, E-mail: afauzi@utm.my

[2]*Faculty of Chemical Engineering and Natural Resources, University of College Engineering and Technology of Malaysia (KUKTEM), Kuantan Pahang, Malaysia*
Tel: +60-095492322, Fax: +60-095492322, E-mail: mimi@kuktem.edu.my

[3]*Bioprocess Engineering Department, Faculty of Chemical Engineering and Natural Resources, University Technology of Malaysia, 81310 Skudai Johor, Malaysia*
Tel: +60-075495564, Fax: +60-075581463, E-mail: r-rosli@utm.my

[4]*School of Chemistry and Food Science, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43000 Bangi Selangor, Malaysia*
Tel: +60-0389213805, Fax: +60-0389213232, E-mail: osman@psikukm.my

Abstract

This study investigates the fouling mechanisms in ultrafiltration membrane during separation of cyclodextrins from starch and CGTase. The Resistance-In-Series Model was used to identify the responsible hydraulic resistances. The result showed that the weak adsorption fouling resistance (r_{a1}) was the main factor that contributed the rate and extent of flux decline. Moreover the significant organic fouling that is contributed by starch, CDs, CGTase and intermediate by-products in organic colloids and/or macromolecular revealed that the fouling potential was $r_{a1} > r_g > r_{cp} > r_{a2}$. The overall results indicate that the fouling mechanisms may consist of pore mouth adsorption and subsequently narrowing of the pores as those components (starch and CGTase) are small enough not to be excluded by steric considerations. In the latter stage unreacted starch would be accumulated to form gel/cake layer. The measured flux recovery of enzymatic membrane reactor for CDs production was about 95%.

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

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharide composed of α-1,4-glycosidic-linked glucosyl residues produced from starch or starch derivatives using cyclodextrin glucosyltransferase (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 CDs commercial application in food, pharmaceutical, cosmetic, agricultural and plastic industries as emulsifiers, antioxidants and stabilizing agent as shown in Figure 1 [1-3]. However, the extensive use of CDs is still restricted by high production cost of CDs [4].

CDs can be synthesized using chemical and enzymatic process. CGTase is an enzyme which capable of converting starch and related substrate into CDs. The CDs can be separated using selective chemical precipitation, chemical precipitation coupled with filtration or an integrated reaction-purification system utilizing size exclusion separation mode such as membrane separation [4-6]. In membrane separation, the starch source, CGTase and CDs can be selectively separated from the reaction mixture by the action of a driving force across the membrane

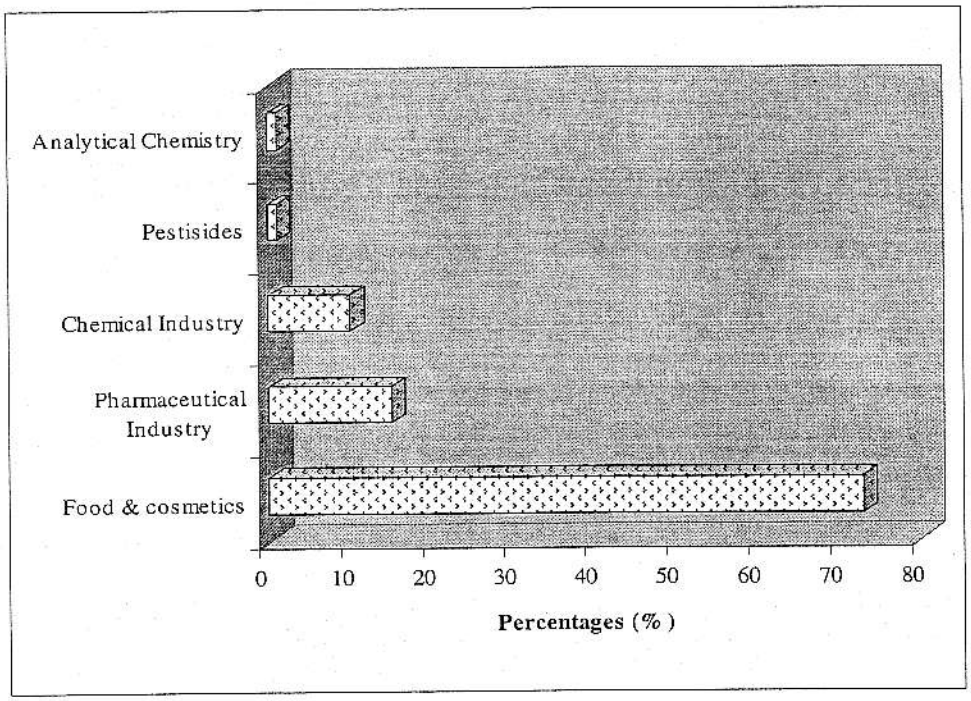

Figure 1 – Estimated Segments of the CDs Markets.

(chemical potential, pressure, electric field) that causes the movement (diffusion, convection, electrophorectic migration) of solutes [7]. The 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 continuously [7-9].

The combination of membrane separation and enzymatic reactors are called enzymatic membrane reactor (EMR). In this study, the ultrafiltration hollow fiber (UF HF) membrane was locally produced from polyethersulfone (PES). The ultrafiltration hollow fiber membrane has a molecular weight cut-off (MWCO) of 32000 Dalton and was horizontally assembled besides the enzymatic reactor.

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 [7,10].

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 fouling characteristics associated with the type of fouling mechanisms occurred, quantitative determination of hydraulic resistances and determination of flux recovery during separation of CDs.

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 2, the Enzymatic Membrane Reactor comprises of an enzymatic stirred reactor equipped with 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 that equipped with a mechanical stirrer. 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.

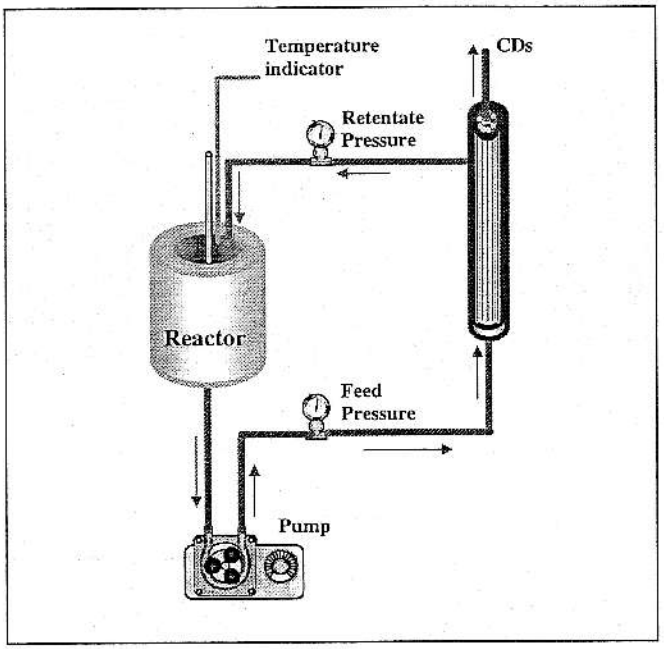

Figure 2 – Schematic diagram of Enzymatic Membrane Reactor.

Resistances-In-Series Model

Resistances-In-Series model is most widely use 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 [11]:

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

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, several types of resistances contributed to both reversible and irreversible foulant. 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 foulant. 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 on the membrane surface and pores. The fourth J_{pwp} was measured and the r_{a2} were calculated using Equation 1.

Results and discussion

Determination of hydraulic resistances

The resistance-in-series model was used in this study is to obtain the hydraulic resistances (m^{-1}) exhibited during CDs separation. The values of the hydraulic resistance in this study are shown in Figure 3.

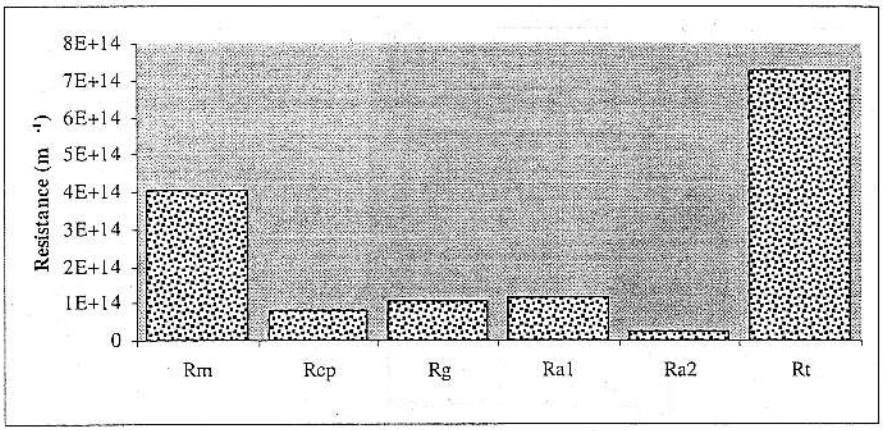

Figure 3 – Amount of hydraulic resistances of the UFHF membrane.

As shown in Figure 3, 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}).

The amount of the hydraulic resistance can also be converted into the ratio of the hydraulic resistance to the amount of the total hydraulic resistance as shown in Table 1. Based on Table 1, the result showed that 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.

Table 1 – Percentages of hydraulic resistance of the PES UF membrane in separation of cyclodextrin.

Type of resistances	Percentage (%)
r_m	56
r_{cp}	11
r_g	14
r_{a1}	16
r_{a2}	3

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 is 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.

Flux decline in the UF crossflow filtration

The flux decline in this EMR system was due to the membrane fouling. Initially, the particles from the reaction mixture arrived to 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 [15].

Figure 4 shows the declination of flux 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

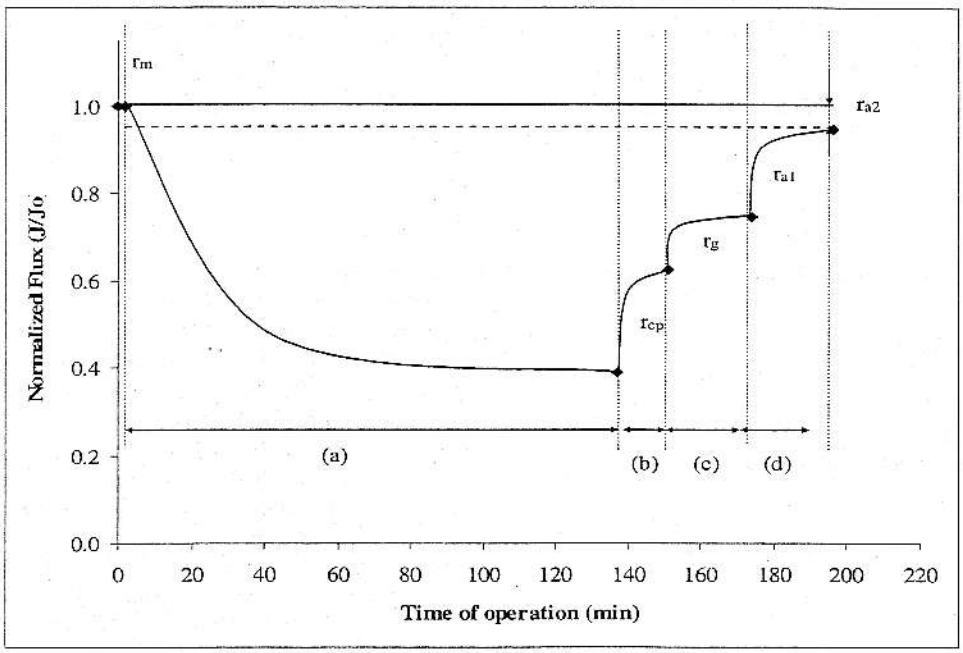

Figure 4 – Flux decline in the UF crossflow filtration; (a) flux decline during filtration, (b) pressure released, (c) water cleaning, and (d) chemical cleaning.

was purged out the membrane pores and surface. Nevertheless, the strong adsorption was not removed from the membrane even 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 [13].

Flux recovery during the separation of CDs

The flux of the cleaned membrane was tested through a filtration with DI water after each membrane cleaning step. The ratio of the specific flux ($m^3m^{-2}h^{-1}m^{-1}$) at room temperature of the cleaned membrane to the new membrane flux was used to evaluate the flux recovery of the membrane [13,14], and the results are shown in Figure 5.

Figure 5 shows the cleaning with DI water could recover the flux of the membrane by about 75%. However, the flux recovery for the cleaned membrane by using 0.1M NaOH solution was about 95%. Nonetheless, about 5% lost in flux come from the irreversible hydraulic resistance (r_{a2}). This is due to the adsorption of solute (CDs) within the matrix of the membrane. The similar observation was found by Mo and Huang [13] in their study using the NOM solutes.

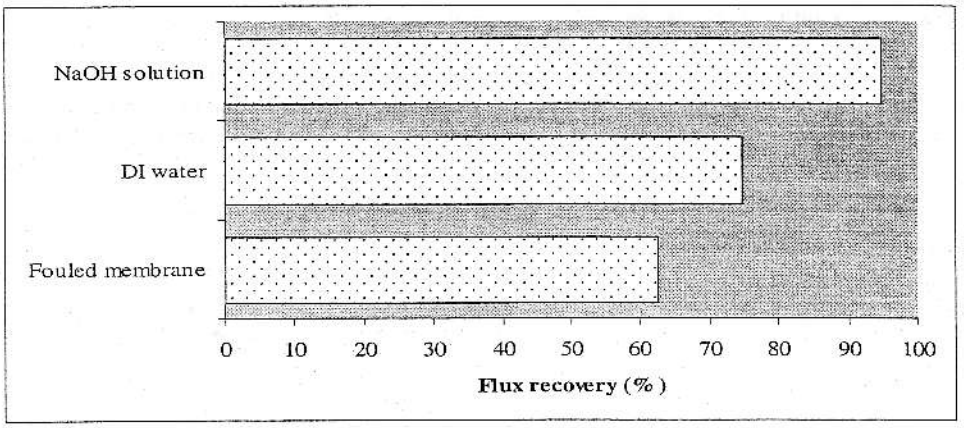

Figure 5 – Percentage of flux recovery during the separation of CDs.

Conclusions

The results of these investigations indicated that:

1) The major fouling mechanism was the irreversible fouling (weak adsorption) which was about 16% of the total hydraulic resistances,
2) The irreversible fouling mechanism could be elevated by chemical cleaning, and
3) The maximum achievable flux recovery of EMR for CDs production was 95% by cleaning with alkaline solution.

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