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Formation and characteristics of zirconium ultrafiltration dynamic membranes of various pore sizes

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Abstract

A dynamic membrane was formed by deposition of colloid particles on a ceramic support. The $ZrOCl_2$ and H_2SO_4 mixing method was found to be the best method for obtaining regular size particles. The size of the colloid particles increased linearly with the increases of the $[H_2SO_4]/[ZrOCl_2]$ ratio, and ranged from 20 to 200 nm. The dynamic membrane was prepared under a pressure of 0.8 MPa and the particles remained intact and were homogeneously deposited on the ceramic support surface. It is possible to prepare dynamic membranes of molecular weight cut-off greater than 100,000 dalton, and the cut-off increases linearly with the colloid particle size. The dynamic membrane separated BSA from glucose solution effectively. © 1998 Elsevier Science B.V.

Keywords: Dynamic membranes; Ultrafiltration; Particle size; Pore size; Zirconium

1. Introduction

Crossflow ultrafiltration has been in common use for processing of fluid foods for many years. The filtration is carried out by a membrane made of various structural materials, including polymers, sintered metals, and ceramics. These membrane systems offer good filtration but suffer from a number of disadvantages, such as difficulty in cleaning, high costs of installation, and high initial and replacement capital costs.

Membranes suitable for ultrafiltration can be formed by depositing upon a porous support a colloidal substance from a dilute suspension. The suspension is pumped over the support under pressure so that the colloid is deposited from the solution passing through the support. These membranes are called dynamic membranes [1]. Past studies of dynamic membranes have focused on the performance of membranes for salt rejection. The best results were obtained with hydrous metal oxides, especially Zr(IV) oxide [2,3], and the dual layer membranes consisting of a layer of Zr(IV) oxide followed by a layer of polyacrylic acid [4–8]. Only a few studies on the formation of a dynamic membrane on a crossflow porous tube for the purpose of ultrafiltration [9–11], and the method to form different molecular weight cut-off dynamic ultrafiltration membranes could not be found in the literature. However, it was noticed that the molecular weight cut-off of dynamic membranes might be controlled by the colloid particle size. Therefore, the objectives of this study were to investigate the

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relationship between the colloid particle size and the pore size of dynamic membranes, to establish the procedures which could be used for preparing different molecular weight cut-off ultrafiltration dynamic membranes, and to study the characteristics of the prepared dynamic membranes, so that its potential applications in food processing can be further explored.

2. Experimental

2.1. Apparatus

The experimental apparatus used is schematically shown in Fig. 1. The dynamic membranes were deposited on a ceramic tube (0.2 μm pore size, module 1T1-70, SCT, France). The ceramic tube having an o.d. of 1.0 cm, an i.d. of 0.7 cm, a length of 25.0 cm and a wall thickness of 0.15 cm was inserted into a stainless steel housing. The effective membrane area of the ceramic tube was 50 cm^2.

2.2. Materials

Inorganic colloids of zirconium compounds were used as the materials for forming the dynamic membranes. Chemical reagent zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) manufactured by Nacalai Tesque, Inc. (Kyoto, Japan) was used. The colloid suspension was formed by adding 10^{-3} M $ZrOCl_2$ to various sulfate solutions (H_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$ and

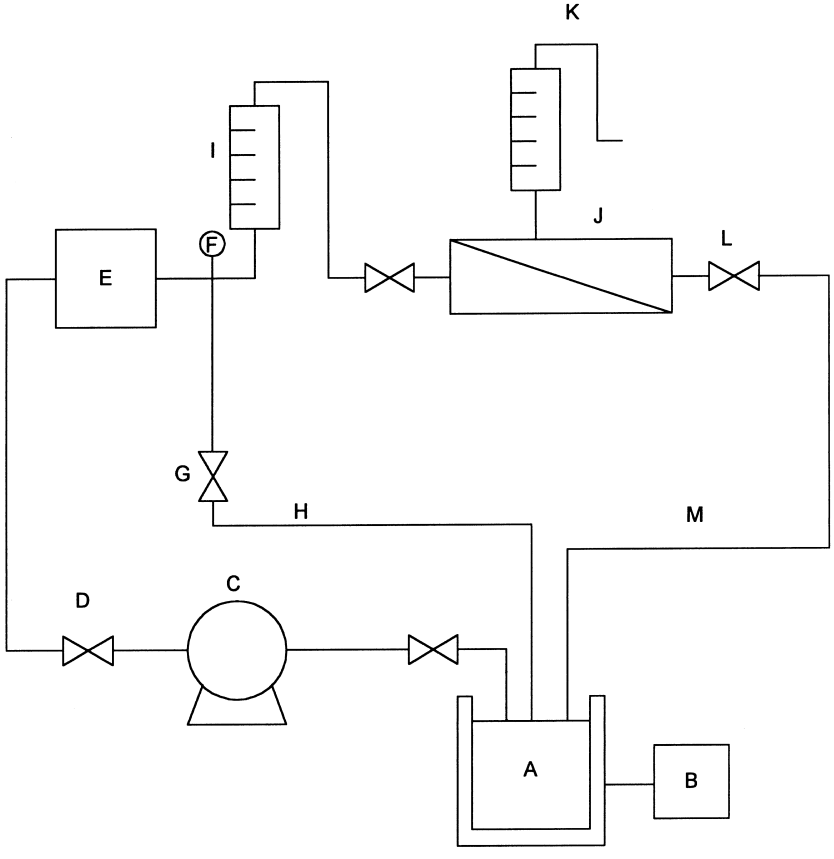

Fig. 1. Schematic diagram of the experimental apparatus used for forming dynamic membrane. (A) Feed tank, (B) temperature controller, (C) pump, (D) manual valve, (E) pressure-stabilized unit, (F) pressure gauge, (G) manual bypass valve, (H) bypass loop, (I) flow meter, (J) membrane module, (K) permeate, (L) manual control valve, (M) retentate.

K_2SO_4) with concentrations ranging from 0.6 to 1.5×10^{-3} M at room temperature, and then aged for overnight [12].

2.3. Procedures

Dynamic membranes were formed on the ceramic support by circulating colloid solution through the experimental apparatus for 1 h at 0.8 MPa pressure, flow rate 10 l/min, and 25 °C. The dynamic membranes obtained were stored in a closed container of 100% relative humidity before analyzing for its characteristics and process performance.

2.4. Analyses

To measure the molecular weight cut-off of the dynamic membranes formed, solutions containing 0.012% of dextran of various molecular weights (Sigma, St. Louis, MO, USA) were ultrafiltered under the standard conditions of pressure 0.2 MPa, flow rate 5 l/min, and 25°C. The dextran concentration was measured by phenol–sulfuric acid method [13]. A piece of dynamic membrane was oven dried at 50°C, and pore size and structure analyzed by a mercury pore size analyzer (Micromeritics, Autopore II 9220, Norcross, GA, USA). The rejection (R) of the membranes were determined by: $R=1-C_p/C_b$, where C_p was the concentration of the dextran in the permeate, and C_b the concentration of dextran in the bulk solution.

The average particle sizes of the colloids were determined by transmission electron microscope (TEM, Hitachi H-7100, Japan). To observe the surface structure, a fraction of the ceramic tube deposited with dynamic membrane was freeze dried and shadowed with gold under vacuum, and then examined by scanning electron microscope (SEM, Hitachi S-2400).

After the colloid suspension was centrifuged, the precipitate was washed with distilled water. This procedure was repeated three times. The structures of the colloid particles were analyzed by X-ray scattering (Philips PW1729, Philips, The Netherlands) at 30 kV voltage and 20 mA current.

2.5. Model food solution filtration test

A solution containing glucose (mw 180) 120 ppm and bovine serum albumin (BSA, mw 80,000) 200 ppm was filtered through the dynamic membrane at pressure 0.2 MPa, flow rate 2.7 l/min and room temperature. While the retentate was circulated back to the feed tank, the permeate was collected and analyzed. The glucose concentration was determined by phenol–sulfuric acid method [13] and the BSA was by Lowry method [14].

3. Results and discussion

3.1. Preparation of colloid particles of different sizes

Among the sulfates tested for forming Zr(IV) colloid, the H_2SO_4 was the most effective one for controlling the particle size. It appeared that the cation might interfere with the polymerization. The presence of the cation in the solution would encourage the development of new polymerizing cores rather than growing on the old polymers. The particle size increased with increasing the $[SO_4^{-2}]/[Zr^{+4}]$ ratio (Fig. 2). Their relationship could be expressed by the following equation with a regression coefficient (r^2) of 0.99:

$$Y = 5.69X + 53.84X^2 - 6.26X^3 \quad (1)$$

where Y is the particle diameter in nm, and X is the $[SO_4^{-2}]/[Zr^{+4}]$ ratio. The TEM photos of the particle also showed that the higher the $[H_2SO_4]/[ZrOCl_2]$ concentration ratios, the larger are the particles formed, and the particles were spherical and uniform (Fig. 3). The particles of size ranging from 10 to 200 nm could be prepared by changing the $[H_2SO_4]/[ZrOCl_2]$ ratio.

The pH of the colloid suspension prepared at various $[H_2SO_4]/[ZrOCl_2]$ ratios ranged from 2.48 (ratio=1.5:1) to 2.68 (ratio=0.7:1). It appeared that the pH might not be a major factor affecting the particle size in this study. The X-ray diffraction pattern of the particles shows two to three broad diffraction peaks, indicating that the colloid particle is a microcrystalline materials.

3.2. Preparation of dynamic membranes

When the colloid suspension was circulated through the ceramic membrane system, the colloid particles deposited on the inner surface of the ceramic tube, and

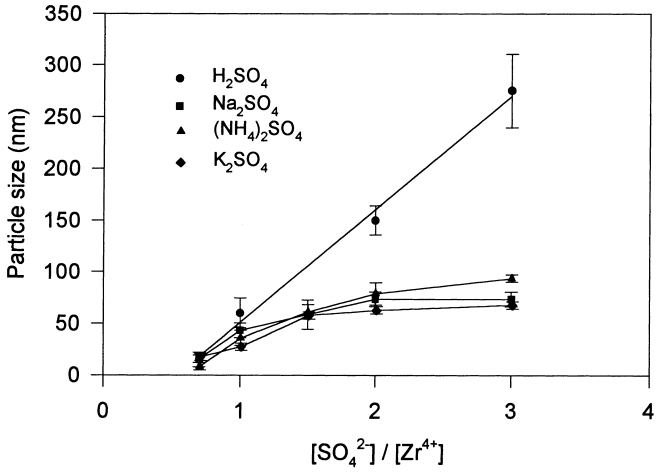

Fig. 2. The relationship between colloid particle size (nm) and $[SO_4^{2-}]/[Zr^{4+}]$ ratio.

the permeate flux decreased with time as shown in Fig. 4. The colloid particles accumulated on the ceramic surface, compacted by pressure, thus, the dynamic membrane was formed. The longer the circulation time the lower the permeate flux obtained. However, the flux reached a steady state after ≈1 h of circulation, indicating that a stable layer of dynamic membrane was formed. Furthermore, the smaller the colloid particle size, the lower the flux was observed during the circulation of the colloid suspension, suggesting that a more compact dynamic membrane with higher hydraulic resistance was formed by smaller particles.

3.3. Characteristics of the dynamic membrane

The retention property of the dynamic membrane was dependent on the size of the colloid particles forming the membrane, which, in turn, was controlled by the $[H_2SO_4]/[ZrOCl_2]$ ratio during colloid particle formation. Table 1 shows the rejections of the dynamic membranes prepared with the colloid particles which were formed at various $[H_2SO_4]/[ZrOCl_2]$ ratios. The membrane formed at the $[H_2SO_4]/[ZrOCl_2]$ ratio of 1.0 retained more than 90% of the dextran molecules of molecular weight 2.2×10^7 dalton. However, the membrane formed at $[H_2SO_4]/[ZrOCl_2]$ ratio of 0.6 could retain more than 90% of the 1.5×10^5 dalton dextran. If one uses 90% rejection as a criterion for determining the nominal molecular weight cut-off of the dynamic membrane, it can be concluded that the dynamic membranes with molecular weight cut-offs ranging from 10^5 and above could be prepared by adjusting the $[H_2SO_4]/[ZrOCl_2]$ ratio using the following equation:

Table 1
The rejection (%) of different molecular weight dextrans by the dynamic membranes which were prepared with colloid particles of different sizes controlled by $[H_2SO_4]/[ZrOCl_2]$ ratios

$[H_2SO_4]/[ZrOCl_4]$ ratio	Dextran molecular weight (dalton)				
	1.1×10^4	1.5×10^5	5.0×10^5	2.0×10^6	2.2×10^7
0.6	66.1	94.2	ND	ND	ND
0.7	19.0	87.6	94.4	ND	ND
0.8	16.0	ND	90.5	99.9	ND
0.9	2.4	ND	61.6	92.0	ND
1.0	ND	ND	42.9	81.8	95.6

ND: not determined.

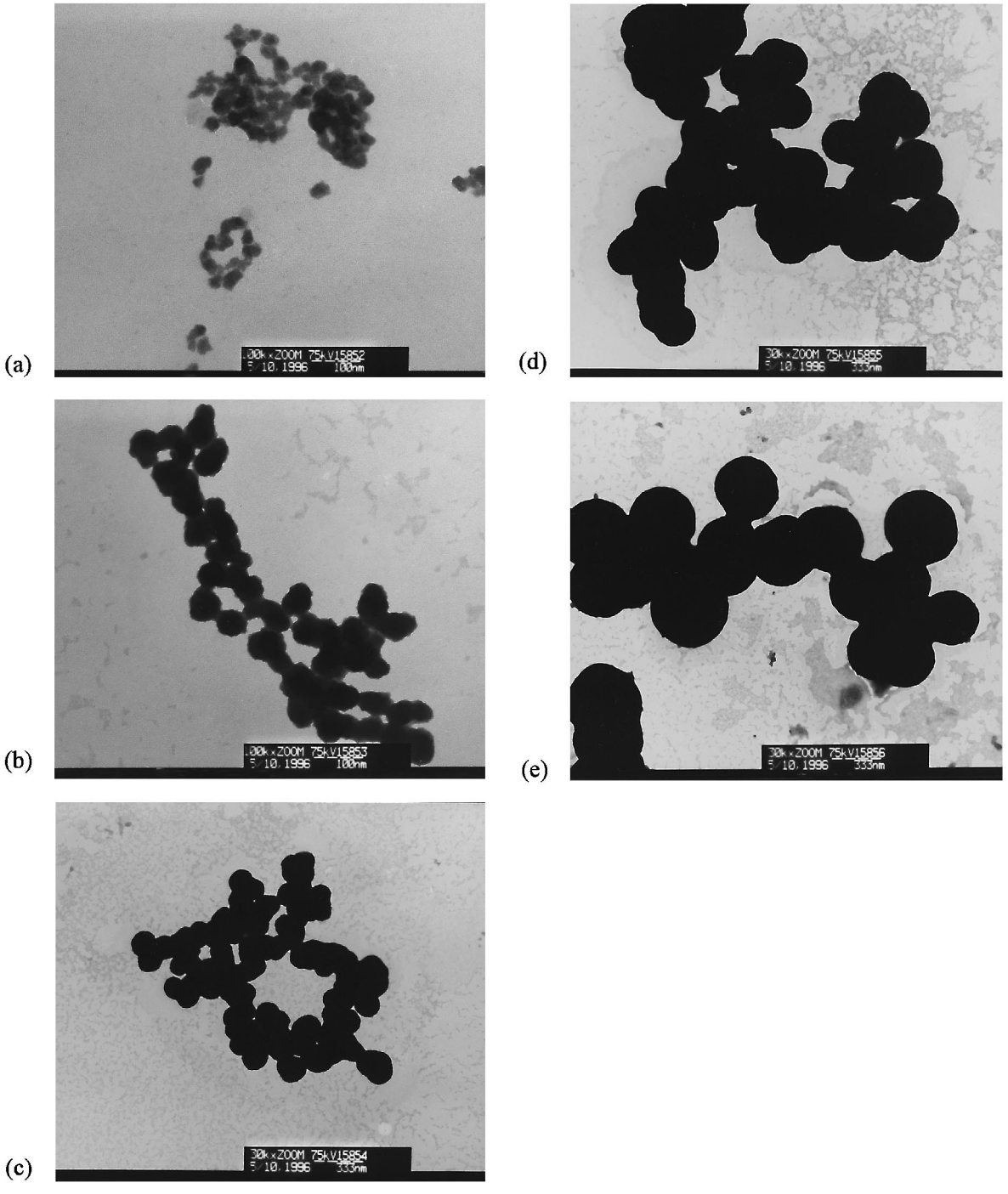

Fig. 3. TEM photographs of the colloid particles formed at different $[H_2SO_4]/[ZrOCl_2]$ ratios. a, b (× 100 k), c, d and e (× 30 k) were 0.7, 1, 2, 3 and 4 $[H_2SO_4]/[ZrOCl_2]$ ratios, respectively.

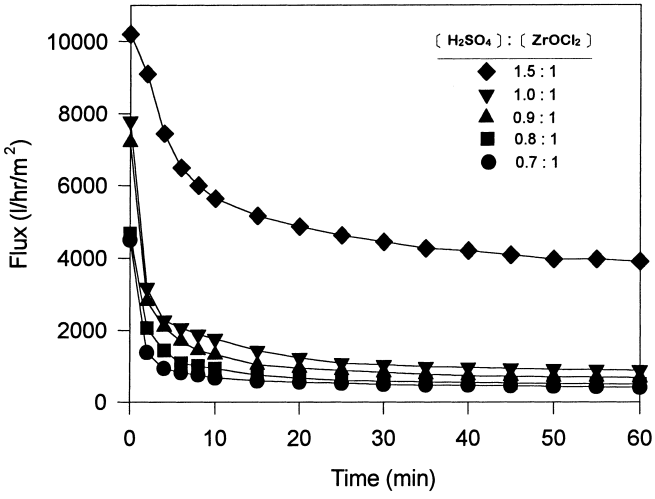

Fig. 4. Flux decline with time during formation of dynamic membranes using various $[H_2SO_4]/[ZrOCl_2]$ ratios.

$$\log Z = 3.71 + 0.054Y \quad (2)$$

where Z is the molecular weight cut-off in dalton, and Y is the particle size of Eq. (1).The regression coefficient (r^2) for Eq. (2) is 0.99.

3.4. The structural properties of dynamic membranes

Fig. 5 shows the SEM photographs of the dynamic membrane deposited on the ceramic support. The colloid particles, in general, remained intact, and were still spherical in shape. However, a close observation of the SEM photograph (Fig. 5(a)) could find some flattened particle contacts on the surface of the membrane, suggesting that the colloid particles were probably partially compressed to form the dynamic membrane.

The average diameters of the colloid particles formed at various $[H_2SO_4]/[ZrOCl_2]$ ratios and the pore diameters of the dynamic membranes formed by these particles are given in Table 2. Again, larger the particle size, bigger is the pore diameter. Considering two possible types of particle packing (Fig. 6), and the cross section areas of the pores of each type of packing were calculated. Based on the pore areas, one could estimate the diameters of the pores by assuming that they were round in shape. The estimated pore diameters of type A and B packings are also given in Table 2. It appeared that the estimated pore diameters of type A packing fitted the actual pore sizes of the membranes formed by smaller particles, while the type B packing matched the larger particle ones. This observation suggested that the smaller colloid particles not only formed smaller pores, but also had more compact stacking than that of the larger particles. However, the deformation of colloid particles as shown by the SEM photograph would complicate the packing phenomena.

Table 2
Structural properties of the dynamic membranes

$[H_2SO_4]/[ZrOCl_2]$ ratio	Particle diameter (nm)	Actual pore diameter (nm)	Estimated pore diameter based on type A packing	Estimated pore diameter based on type B packing	Porosity [a] (%)
0.7	28	6	6	15	11
0.9	44	15	10	23	29
1.0	53	23	12	28	38
1.5	108	61	25	57	56

[a] Porosity=total pore volume/total volume of dynamic membrane.

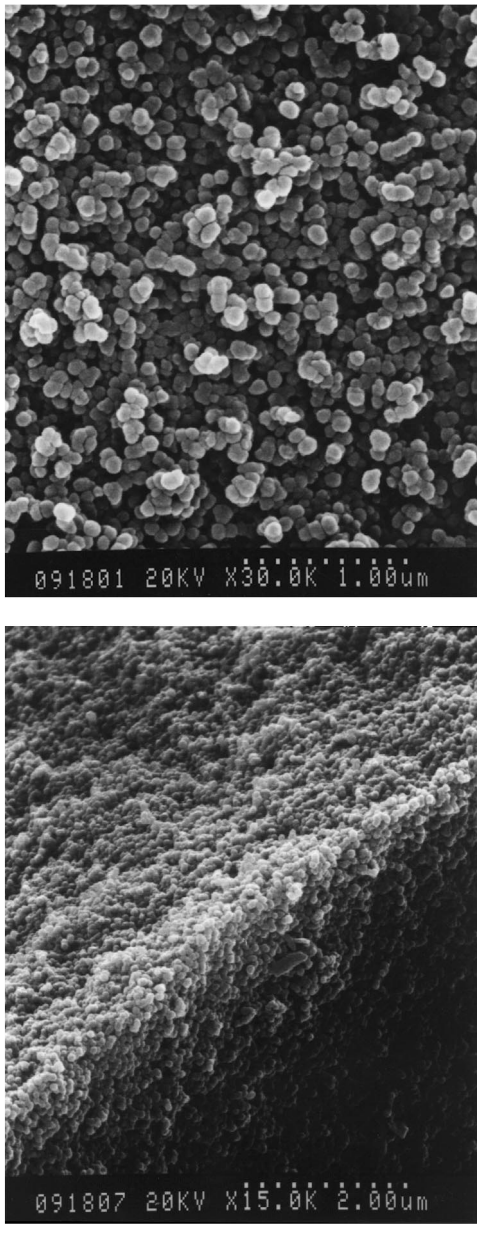

Fig. 5. SEM photographs of the dynamic membranes on the surface of ceramic tube. (a) Top view (× 30 k); (b) side view (× 15 k). The colloid particles were formed using $[H_2SO_4]/[ZrOCl_2]$ ratio of 1:1.

The porosities of the dynamic membranes were estimated by the ratio of total pore volume to the total volume of the dynamic membrane analyzed by the mercury pore analyzer (Table 2). For packing of monosize spheres, the face-centered cubic is the most compact one and has a porosity of 25.9% [15]. The experimental results, however, showed that the dynamic membrane of pore diameter of 6 nm had a 11% porosity. This unexpected low value may be attributed to the particles deformation during membrane formation.

Table 3
Food model solution containing glucose and bovine serum albumin (BSA) was filtered by the dynamic membrane which was formed by using colloidal solution of $[H_2SO_4]/[ZrOCl_2]$ ratio of 0.6 under 0.2 MPa pressure

Filtration time (min)	Rejection (%)		Flux (l/h/m^2)
	Glucose (mw 180)	BSA (mw 80,000)	
1	5.8	98.3	68.4
30	3.7	98.4	55.2
60	1.8	98.3	42.0
90	1.6	96.4	36.0
120	1.9	97.8	33.0

The pore size distribution of the dynamic membranes is shown in Fig. 7. Smaller the particle size, the narrower is the pore size distribution. Nevertheless, the prepared dynamic membranes, in general, had a rather sharp pore size distribution, which, in turn, could ensure a satisfactory separation during application.

3.5. The food model solution filtration test

A solution containing glucose and BSA was filtered by the dynamic membranes which was formed using the $[H_2SO_4]/[ZrOCl_2]$ ratio of 0.6. The BSA was almost 100% rejected; while, the glucose transmitted through the membrane nearly freely (Table 3). However, the flux declined from the initial value of 68 l/h/m^2 to 30 l/h/m^2 during 2 h of operation. It appeared that the prepared dynamic membrane could provide a satisfactory separation, but the problem of membrane fouling should not be overlooked.

4. Conclusion

The regular size colloid particles ranging from 20 to 200 nm could be prepared by mixing H_2SO_4 and $ZrOCl_2$ at various ratios. Deposition of the colloid particles on a porous ceramic support could form

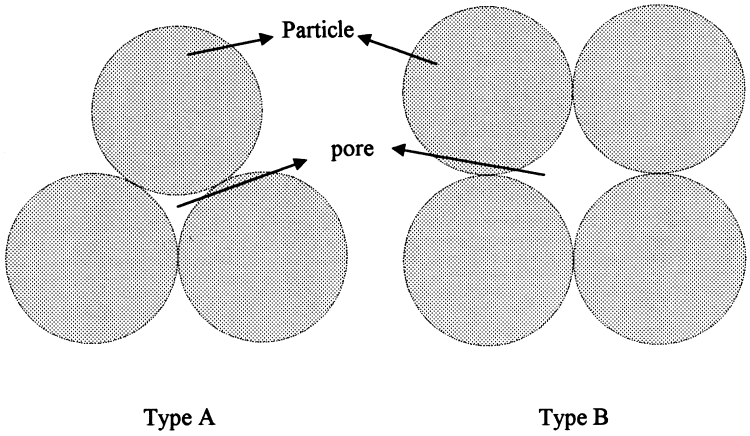

Fig. 6. Various types of colloid particle packing.

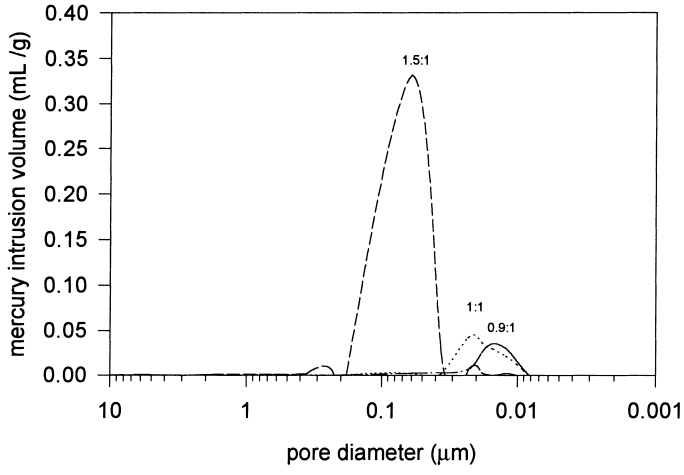

Fig. 7. The pore size distribution of the dynamic membranes prepared by using various $[H_2SO_4]/[ZrOCl_2]$ ratios analyzed by the mercury pore size analyzer.

dynamic membranes of molecular weight cut-off greater than 100,000 dalton. Although the prepared dynamic membrane separated BSA from glucose in a solution effectively, a dramatic flux decline due to fouling was also observed. Further research is needed to reduce the fouling phenomena, possibly by reducing the membrane thickness or preparing an asymmetric dynamic membrane.

Acknowledgements

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