報　文

Adsorption properties of Bisphenol A(BPA) in honey on Ultrafiltration membranes during cross-flow ultrafiltration

Shinji Itoh[*1] · Mika Terakawa[*1] · Naoki Kogure[*1]
Kazuho Nakamura[*2,†] · Kanji Matsumoto[*2]

[*1] Kato Brothers Honey Co., Ltd. 2-1-8, Fukuura, Kanazawa-ku, Yokohama, 236-0004, Japan
[*2] Yokohama National University, Graduate School of Engineering, 79-5, Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan
[†] Corresponding author. Tel : +81-45-339-3980, Fax : +81-45-339-4012, E-mail : naka1@ynu.ac.jp

Abstract :

Removal of Bisphenol A(BPA), which is considered as one of endocrine disrupting chemicals, in honey by ultrafiltration(UF) membranes were studied. It was shown that the BPA was removed from feed honey solution by adsorption to UF membrane during cross-flow UF. The adsorption isotherm could be explained by Frendlich isotherm. The adsorbed BPA decreased with the increase in operating temperature. The BPA adsorbed onto PS membrane was not eluted by 1% citric acid solution but by 0.05N sodium hydroxide. The adsorption properties were also affected by the types of membrane material. The amount of adsorbed BPA increased in the order of PAN, PS, and PES and increased with the decrease in MWCO.

Keywords : Bisphenol A, honey, ultrafiltration, adsorption, ultrafiltration membrane

1. Introduction

Honey is produced and consumed all over the world. In Japan the production of honey is about 3,000 t per year and the consumption is about 40,000 t per year[1]. The most of the consumption is covered by imports and the percentage of the imports from China is over 90%[2]. The steel drum coated with epoxy resin is usually used as a container for honey transporting. Bisphenol A(BPA) is a raw material used in the epoxy resin and is considered as one of endocrine disrupting chemicals(EDCs)[3]. The molecular weight of BPA is 228 and its chemical formula is shown in **Figure 1**. The undesired contamination of honey with BPA and its effect are concerned. Although there have been some studies of BPA for activity as estrogens[4], analysis method[5～6] and transition to foods[7], the studies of its removal from foods are hardly reported.

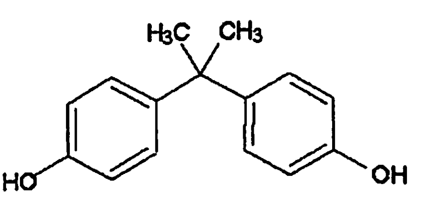


Fig.1 Bisphenol A

Honey consists of carbohydrate, pigment, protein, and other substances. The carbohydrate is the main substance of honey and consists of monosaccharides such as fructose and glucose. The pigment composition in honey is a flavonoid[8]. The molecular weight of the protein in honey is larger than 10 kDa[9]. The protein is one of impurities in honey and causes puff-failure in baked sweet stuffs such as sponge cake and precipitation in soft drinks when honey is added to processed foods. Ultrafiltration(UF) has been used for removing the proteins in honey[10].

The removal of EDCs by membranes is mainly interested in the drinking water production and wastewater treatment processes. As almost of EDCs have molecular weights from 100 to 400 Da, it is expected that reverse osmosis (RO) membrane or nanofiltration(NF) membrane would be effective to retain EDCs. RO membrane was effective in removing EDCs and pharmaceutical active compounds(PhACs) and the rejection depended on membrane material and the physic-chemical properties of target molecules[11~12]. NF membrane showed more complex rejection behavior because NF membrane could retain EDCs due to both adsorption and size exclusion[11, 13~15]. The rejection is depend on experimental condition, such as the molecular size[13], hydrophobicity of the molecule[11, 14] and electric repulsion between the molecule and membrane[16, 17]. UF membrane was also studied for removal of EDCs. In UF process the BPA removal is mainly attributed to the adsorption on the membrane material[18~20]. Hybrid processes of membranes and bioreactor or catalytic oxidation were also studied for EDCs removing[21~23].

In the application of the adsorption phenomenon on membrane for BPA removing from foods the adsorption equilibrium is important because the adsorption process is usually carried out in a batch process including both adsorption and desorption. The Freundlich adsorption[22] or a linear isotherm[20] was reported as the adsorption isotherm of EDCs. The adsorption of BPA was significantly decreased as pH of feed solution approached to pKa(9.6～11.3) of BPA[18, 19]. 2-propanol or ethanol was effective to remove EDCs from porous polysulfone beads[24]. The adsorption kinetics is also important for the design of adsorption processes. In the protein adsorption on microfiltration membrane the adsorption kinetics during filtration, i.e. adsorption breakthrough curve, was studied in detail by a mathematical model[25, 26].

In this study we focused on the removing both protein and BPA from honey by bench scale cross-flow UF. It is expected that protein and BPA are removed by size exclusion and adsorption, respectively. The effects of membrane materials(PAN, PS, and PES), molecular weight cut off(MWCO), operating conditions(BPA concentration, temperature) on the separation properties were studied. The elution condition of the adsorbed BPA was also studied.

2. Materials and methods

Chinese Acacia honey was used. BPA was used as an endocrine disrupting chemical in feed honey. BPA was not detected in the honey in preliminary experiment. The feed honey solution was prepared by adding a given amount of BPA dissolved in a small amount of methanol into 16 L of the honey solution with 20% sugar content. The concentration of the honey solution was adjusted by diluting with pure water treated with RO membrane. The BPA concentration in the honey solution was determined by HPLC. **Table 1** showed the analytical condition. The sample was filtered with a membrane filter(pore size 0.22μm) before injection. In a preliminary experiment BPA was not detected from the experimental equipments. The protein concentration was determined by Bradford method[27]. The water soluble protein in the feed honey solution was about 300 mg/kg. The sugar concentration was determined as sugar content with a refractometer (RX-5000, Atago) at 293 K. The pigment concentration was determined by absorbance at 420 nm, ABS_{420}, with a spectrophotometer(Model 228, Hitachi). The effect of BPA on ABS_{420} could be negligible because the concentration range of BPA in this study is too low.

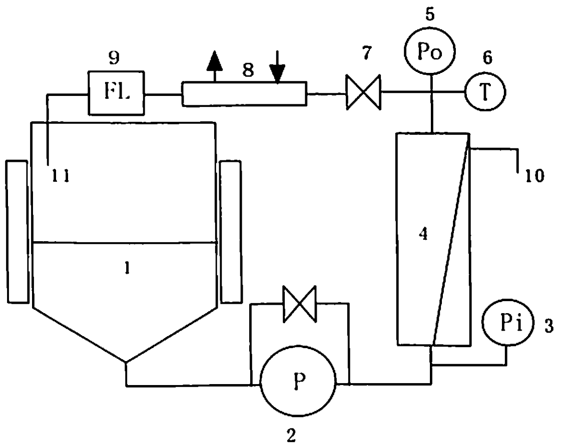
Five kinds of hollow fiber membrane modules were used. **Table 2** shows the membrane modules used. **Figure 2** shows the experimental apparatus. The apparatus comprised of an feed tank(SUS 304, 50L), heat exchanger(SUS 304), pump(cascade type, 0.75

Table 1 HPLC analysis of BPA

Column	Inertsil ODS3 (GL science)
Mobile phase	Methanol/water (70:30)
Flow rate	0.2 mL/min
Detection	UV 276nm

Table 2 Ultrafiltration membranes and modules

Material	MWCO [kDa]	Size [mm] (I.D. × Length)	Effective membrane area [m^2]	Pure water flux [$L\ m^{-2}\ hr^{-1}$] (at 98 kPa)	Model	
Polysulfone(PS)	20	1.1×1000	0.4	250	NTU-3250	Nitto-denko Co.
Polysulfone(PS)	6	0.8×300	0.2		AIP-1013	Asahi kasei chemicals Co.
Polyacrylonitrile(PAN)	30	1.2×300	0.1	150	ACP-1050	Asahi kasei chemicals Co.
Polyethersulfone(PES)	30	1.2×300	0.26		Molsep	Daicen membrane-systems
Polyethersulfone(PES)	150	1.2×300	0.26		Molsep	Daicen membrane-systems



1 : feed tank, 2 : pump, 3 : presure gauge(inlet), 4 : membrane module, 5 : presure gauge(outlet), 6 : thermometer, 7 : pressure adjusting valve, 8 : heat exchanger, 9 : flow meter, 10 : permeate, 11 : retentate

Fig.2 Experimental apparatus

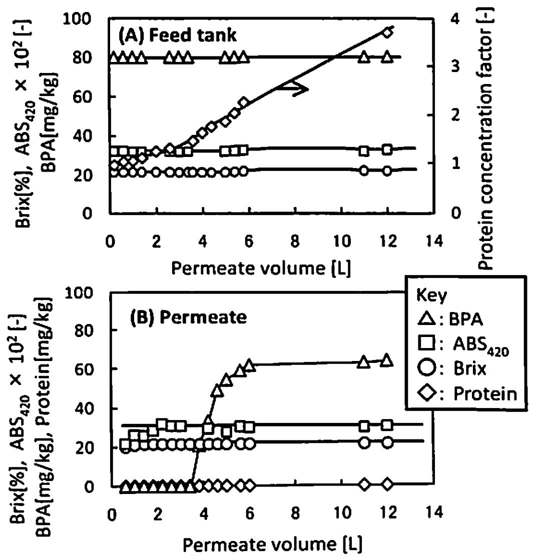


Fig.3 Change in BPA concentration, Brix(an index of carbohydrates concentration), ABS420(an index of pigments concentration), protein concentration in (A) feed tank and (B) permeate solution during cross-flow concentration filtration with PS membrane(MWCO 20kDa)

kW), and flow meter(NF10-PTN, Aichi Tokei Denki). The cross-flow filtration was conducted at 293 K, filtration pressure of 0.12 MPa, cross-flow velocity of 1.5 m/s in the batch concentration mode and the total recycle mode in which all retentate and permeate was returned to the feed tank. After the filtration the apparatus was cleaned by 1% citric acid and 0.05 N sodium hydroxide.

3. Results and discussions

3.1 Separation behaviors of honey components and BPA

In order to confirm the separation behaviors of carbohydrates, proteins, pigments, and BPA, which are components comprising the feed honey solution, the batch concentration of the feed honey solution (16 L) was conducted using polysulfone(PS) membrane with MWCO of 20 kDa. **Figure 3** shows the filtration behaviors. ABS_{420} is an index of pigments concentration and Brix is an index of carbohydrates concentration.

In the feed tank(Figure 3(a)) the protein concentration increased with the increase in the permeate volume and the concentration factor of protein was almost equal to the volumetric concentration factor, while the concentrations of carbohydrates, pigments and BPA showed almost constant values during the concentration filtration. This result shows that proteins will be retained at the membrane surface by size exclusion while other components will not be retained at the membrane surface and could pass through the membrane.

In the permeate(Figure 3(b)) the protein concentration was almost zero and the concentrations of carbohydrates and pigments were almost the same as those in feed tank. These values were almost steady during the concentration filtration, showing that the protein was entirely retained at the membrane surface and carbohydrates, pigments entirely passed through the membrane. BPA concentration in permeate showed a complicated behavior. In the initial stage of the filtration BPA concentration showed almost zero and a rapid increase at permeate volume of about 4 L. After the rapid increasing the BPA concentration became steady at about 80% of that in the feed tank. This change in BPA concentration could be caused by adsorption into the membrane, adsorption to the experimental apparatus, denaturation, or degradation during the filtration. In order to confirm the cause of the change in BPA concentration a comparative experiment was conducted with the experimental apparatus with a straight polysulfone pipe instead of the membrane module. The result showed that denaturation, degradation, or adsorption to the equipment do not occur during the operation and the change in BPA concentration during the filtration will be caused by the adsorption into the membrane.

3.2 Effects of feed solution condition on the BPA adsorption

The amount of adsorbed BPA was determined from the change in the BPA concentration in the feed tank during the total recycle filtration. **Figure 4** shows a typical filtration result with PS membrane(MWCO 20 kDa). The BPA concentration decreased in the initial stage of the filtration and showed a constant steady value after 30 min, reflecting the adsorption equilibrium. The concentration of other components in feed solution showed almost constant value during the total recycle filtration, which means these components did not adsorb into the membrane.

The amount of adsorbed BPA per unit filtration area was determined from the difference in BPA concentration between the initial value and the steady

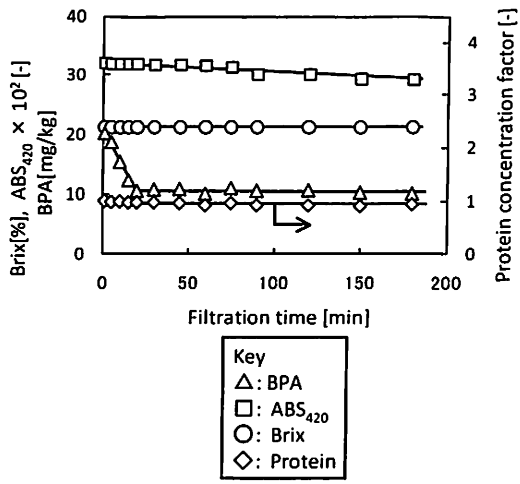


Fig.4 Changes in concentration of components of honey during total recycle cross-flow filtration with PS membrane(MWCO 20kDa)

value.

$$q_{eq} = \frac{C_0 - C_{eq}}{A} V \tag{1}$$

where q_{eq} is the amount of adsorbed BPA per unit membrane area at the equilibrium, C_0 is BPA concentration at the start of the filtration, C_{eq} is BPA concentration at the equilibrium, A is membrane area, and V is feed volume.

Figure 5 shows the relationship between the amount of adsorbed BPA per unit membrane area and BPA concentration in equilibrium state, i.e. adsorption isotherm. In the concentration range studied, the adsorption isotherm followed the Freundlich adsorption, which is also observed in the bisphenol A adsorption onto polyethylene hollow fiber membrane[22],

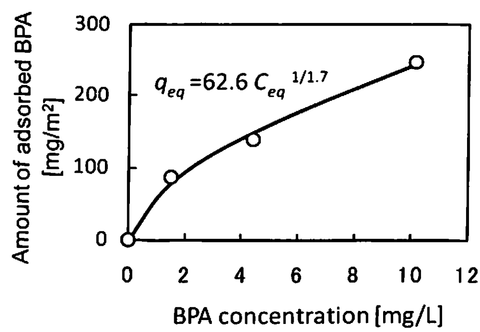


Fig.5 Adsorption isotherm of BPA on PS membrane(MWCO 20kDa)

carbonaceous material[24]. BPA increased with the increase in the BPA concentration. The solid curve in Figure 5 shows a fitting curve of the Frendlich equation,

$$q_{eq} = K_F\, C_{eq}^{\ 1/n} \qquad (2)$$

where K_F is the Freundlich isotherm constant, and n is Freundlich exponent. The experimental plots were well matched ($r^2 = 0.99$) with Eq.(2). The value of n is bigger than 1, reflecting the favorable adsorption.

Figure 6 shows the effect of temperature on the change in BPA concentration in permeates, i.e. breakthrough curve, during batch concentration filtration. The breakthrough curve shifted to left hand as the temperature increases, showing that the amount of adsorbed BPA decreased as the temperature increases. It is expected that the adsorption of BPA on membrane is due to hydrophobic interaction between BPA and membrane[15, 23] as BPA would not be dissociated in the pH range of feed solution(pH=3.4 ~3.7). The dependence of the amount of adsorbed BPA on temperature can be understood from the temperature dependence of the change of energy and entropy by the adsorption due to the dehydration of the membrane and BPA molecule surface[28].

In order to determine the desorption condition of the adsorbed BPA the elution behavior was studied by filtration of water, 1% citric acid and 0.05 N sodium hydroxide with the BPA adsorbed membrane. BPA was not eluted when water or 1% aqueous solution of citric acid were used, whereas BPA was eluted when 0.05 N sodium hydroxide was used. The recovery rate of BPA was about 80% when 0.05 N sodium hydroxide was used. It is expected that BPA dissociate at the pH condition of pKa (9.6~11.3) while BPA does not dissociate under the pH condition of feed honey solution (pH=3.4~3.7). It is likely that the hydrophobic interaction between the adsorbed BPA and membrane is disturbed by the dissociation of BPA, which means the change from neutral molecule to charge molecule.

3.3 Effects of membrane material and MWCO

It is expected that the adsorption of BPA depend on membrane material and MWCO because these factors will affect both the adsorption interaction and surface area of pore where BPA can adsorb. **Figure 7** shows the effect of membrane types on BPA adsorption during the cross-flow filtration in the total recycle mode. The time course of the amount of adsorbed BPA depended on membrane material and the amount of adsorbed BPA at 150 min increased in the order of PAN, PS, and PES.

Figure 8 shows the effect of MWCO of membrane on BPA adsorption using PES membranes with 30 kDa and 150 kDa. The amount of adsorbed BPA increased with the decrease in MWCO. This trend may reflect the difference in the pore surface area in membranes

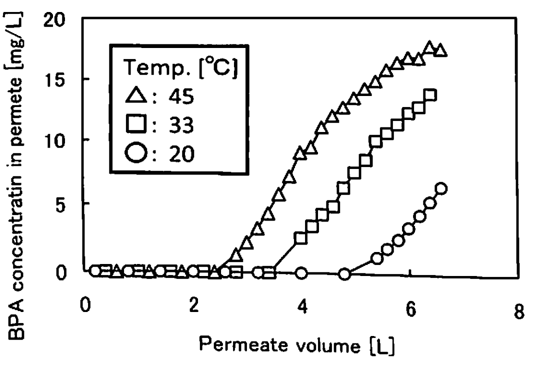


Fig.6 Effect of temperature on adsorption breakthrough curve during cross-flow concentration filtration with PS membrane(MWCO 20kDa)

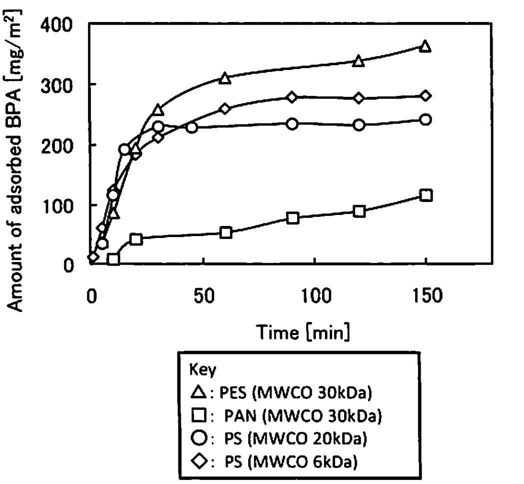


Fig.7 Effects of membrane material on the amount of adsorbed BPA during cross-flow concentration filtration

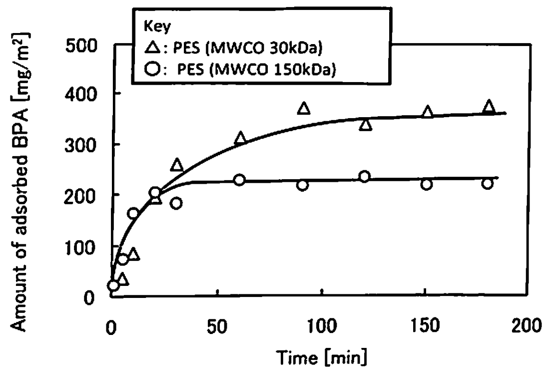


Fig.8 Effects of MWCO on the amount of adsorbed BPA during cross-flow concentration filtration

used because membranes with a smaller MWCO generally have a larger pore surface area.

4. Conclusion

Adsorption properties of BPA from honey solution onto UF membrane during cross-flow UF were studied. It was shown that the BPA was removed from feed honey solution by adsorption onto UF membrane during cross-flow UF. The adsorption isotherm could be explained by Frendlich isotherm. The adsorbed BPA decreased with the increase in operating temperature. The BPA adsorbed onto PS membrane can be eluted by 0.05 N sodium hydroxide. The amount of adsorbed BPA increased in the order of PAN, PS, and PES and increased with the decrease in MWCO.

Although these results show the UF membranes are effective for the removal of BPA from honey solution, further quantitative analysis of process behaviors such as breakthrough curve using a membrane module are necessary for practice and stable operation of BPA removal with UF membranes.

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