

Adsorption Behavior of Aromatic Carboxylic Acids on A Cyclodextrin-Based Metal-Organic Framework

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Abstract

A cyclodextrin-based metal-organic framework (CD-MOF) was crystallized by methanol vapor diffusion. The performance of CD-MOF was compared with commercial available adsorbents (faujasite zeolite, activated carbon and activated clay) for the adsorption of ferulic acid at 298 K in methanol. The adsorption behavior of aromatic carboxylic acids on the CD-MOF was also investigated. The initial adsorption rate of ferulic acid in methanol on the CD-MOF was lower than that for activating carbon and faujasite zeolite, due to the alternating passage of ferulic acid through hydrophilic pore and hydrophobic pore in CD-MOF. The saturated adsorption amount on the CD-MOF was highest among those on the other adsorbents. The high adsorption amount was obtained for aromatic carboxylic acids with high values of pKa(W). A single saturation state of benzoic acid on the CD-MOF was obtained at a concentration of more than 1.0 mmol/L. The molar ratio of benzoic acid to the (γ -CD)₆ unit was evaluated to be 4.4 from the saturated adsorption amount.

Keywords: Adsorption, Aromatic Carboxylic Acid, Cyclodextrin, Porous Crystal, Adsorbent

1 Introduction

Metal-organic frameworks (MOFs) are highly ordered materials with a large adsorption amount that is built by combining multifunctional organic molecules (linkers) and metal ions into a three-dimensional network. Recently, cyclodextrin-based MOF (CD-MOF) has been synthesized from γ -cyclodextrin (γ -CD) and alkali metal salts [1-3]. The (γ -CD)₆ cubic units are connected to form the porous framework. The crystal structure of the CD-MOF was body-centered cubic packing of the (γ -CD)₆ units. As shown in Figure 1, a large spherical pore of 1.7 nm in diameter exists at the center of each (γ -CD)₆ unit [1-3]. The spherical cavities show a hydrophilic nature by the free primary 6-OH groups in the (γ -CD)₆ unit. These large pores are connected through a circular window of 0.78 nm in diameter in each γ -CD tori. A pair of γ -CD forms nanopore with the hydrophobic nature. In addition, infinite pores with a triangular shape propagate along the (111) direction with an aperture of 0.4 nm. Thus, CD-MOF is considered to be the porous crystal having amphiphilic nanopores.

The porous CD-MOF crystal is able to adsorb a large amount of CO₂ at ambient atmosphere [1,2,4]. Chemisorption of CO₂ occurred to the OH groups in CD-MOF, rather than reacting with adventitious free OH⁻ in the pores [5]. The adsorptive separation of alkylaromatic compounds by CD-MOF under HPLC conditions at ambient temperature was reported [6]. CD-MOF was found to separate benzene, toluene, ethylbenzene and the regioisomers

with high selectivity. Adsorption of 4-phenylazophenol on CD-MOF in CH₂Cl₂, was investigated [3], but no quantitative description of the experimental conditions was reported.

The crystallization of CD-MOF with the inclusion of ferulic acid (FA) was investigated [7]. Ferulic acid like many phenolic compounds exhibits antioxidant effect in response to free radicals and also inhibits growth of colon cancer in vitro. Thus CD-MOF is thought to be one of the candidate of drug carrier. Phenolic acids constitute an important class of phenolic compounds with bioactive functions, and they are usually found in plant and food products [8]. Usually, these bioactive compounds are recovered from natural sources by solid-liquid extraction employing organic solvents in heat-reflux systems [9,10]. However, the fundamental research on adsorption behaviors of phenolic compounds on CD-MOF is insufficient to assess the adequacy of CD-MOF as the drug carrier and drug release [11,12].

In this research, CD-MOF was formed from γ -CD and potassium hydroxide by the methanol vapor diffusion method. The adsorption amount of ferulic acid on the CD-MOF was compared with similar quantities of commercial inorganic adsorbents such as activated carbon, faujasite zeolite (X-type) and activated clay. The adsorptions of various aromatic carboxyl acids on the CD-MOF were investigated. The adsorption isotherm curve of benzoic acid on the CD-MOF was also measured.

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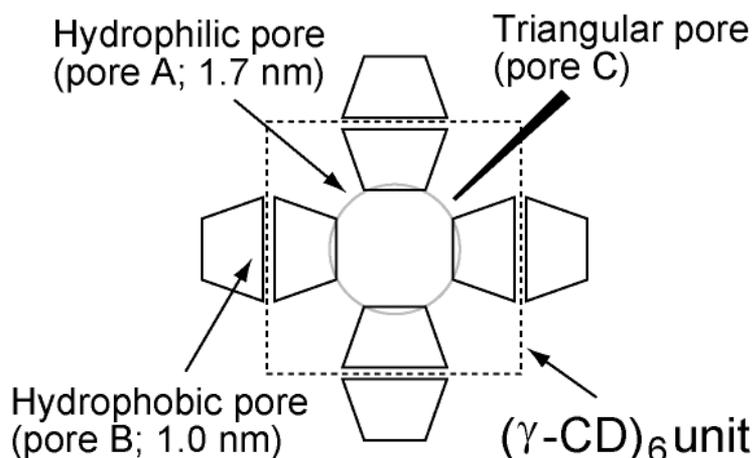


Figure 1 Pore structure of CD-MOF

2 Experimental

Benzoic acid, terephthalic acid, isophthalic acid, phthalic acid, L-phenylalanine, methanol, dichloromethane (CH_2Cl_2) and potassium hydroxide (KOH) were obtained from Wako Pure Chemical Industries, Ltd. (Japan). Gallic acid, 4-hydroxybenzoic acid, ferulic acid, trans-coumaric acid, trans-cinnamic acid and γ -CD were obtained from Tokyo Chemical Industry, Ltd. (Japan). All reagents were analytical graded and used without further purification. Activated carbon, activated clay and faujasite zeolites (F-9 Powder, X-type) purchased from Wako Pure Chemical Industries, Ltd. (Japan) were also used as adsorbent for comparison.

The vapor diffusion method was applied to the crystallization of CD-MOF [1-3,7]. In a typical procedure of CD-MOF preparation, γ -CD (163 mg, 0.126 mmol) was dissolved in a KOH solution (200 mmol/L, 5.0 mL). After filtering the mixed solution through a syringe filter (0.45 μm), the clear solution was divided into three polyvinyl chloride test tubes. They were put into a methanol pool (50 mL) in a glass jar with a cap. Vapor diffusion of methanol into the solution was performed at room temperature for 14 days. Colorless, cubic CD-MOF crystals with sizes less than 1 mm were washed with methanol and dipped in CH_2Cl_2 for three days prior to use.

The crystallization of CD-MOF with incorporating L-phenylalanine was performed by the addition of L-phenylalanine (294 mg) into the mixed solution of γ -CD (291 mg) and KOH (100 mg) in deionized water (10 mL). The procedures for the subsequent vapor diffusion of methanol were identical to those for pure CD-MOF.

Batch adsorption experiments were conducted using glass bottles. In each bottle, 100 mg of the adsorbent and 100 mL of a methanol solution of ferulic acid with a low initial concentration

($C_0 = 0.1$ mmol/L) were added at 298 K for comparison of the adsorption rate. The final concentration of ferulic acid (C) was measured at a prescribed period of time. The adsorption amount of ferulic acid (q , mmol/g) was calculated as follows:

$$q = (C_0 - C) V / m \quad (1)$$

where V is the initial solution volume, and m is the weight of the adsorbent. To evaluate the adsorption properties of various aromatic carboxylic acids as the adsorbate, identical experiments were performed using 100 mg of the CD-MOF and a methanol solution of aromatic carboxylic acid (1.0 mmol/L, 100 mL) for 5 h. The isothermal adsorption curves of benzoic acid on the CD-MOF and activated carbon were determined with the same procedures for seven days by changing the initial concentration from 0.2 mmol/L to 2.5 mmol/L.

Powder X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (Rigaku, Cu-K α radiation) to examine the crystal structure of the CD-MOF. The Brunauer-Emmett-Teller (BET) specific surface area and the mean porous equivalent diameter were determined using a TriStar3000 automatic surface area analyzer and a porosimetry system (Micrometrics, Shimadzu). The concentration of aromatic carboxylic acid in the solution was determined using UV-Vis spectroscopy (JASCO H550 spectrophotometer). Scanning electron microscope (SEM VE-9800, Keyence, Japan) was used in the visualization of crystal shape of CD-MOF.

3 Results and Discussion

Figure 2 shows the XRD pattern of the synthesized CD-MOF. The data were consistent with that reported by Forgan et al. [1]. As shown in an inset of Fig.2, the cubic CD-MOF crystal with the size in the range of 30-150 nm was formed after the vapor diffusion of

methanol for 14 days. The surface of the crystal is flat and smooth. The N_2 adsorption-desorption curves of CD-MOF shown in Figure 3 displayed the type I isotherm, indicating microporous solid and chemisorption. Table 1 summarizes the pore volume, V_{pore} , BET specific surface area, S_{BET} and average pore diameter, D_{BJH} , for CD-MOF, activated carbon, activated clay and faujasite zeolite. The BET specific surface area of the CD-MOF was $915 \text{ m}^2/\text{g}$. Thus, CD-MOF with a large surface area is suitable as an adsorbent.

From the perspective of the crystal structure of the CD-MOF, four K^+ ions link to C6 OH groups in the primary face of the γ -CD tori to form the $(\gamma\text{-CD})_6$ unit [1-3]. In addition, another four K^+ ions link to the C2 and C3 OH group located on the adjacent 1,4-linked D-glucopyranosyl group in the secondary face of the γ -CD tori to connect the $(\gamma\text{-CD})_6$ units to each other. As a result, the CD-MOF still has free C2, C3 and C6 OH groups that are able to adsorb by hydrogen bonding to the functional groups of the carboxylic acid.

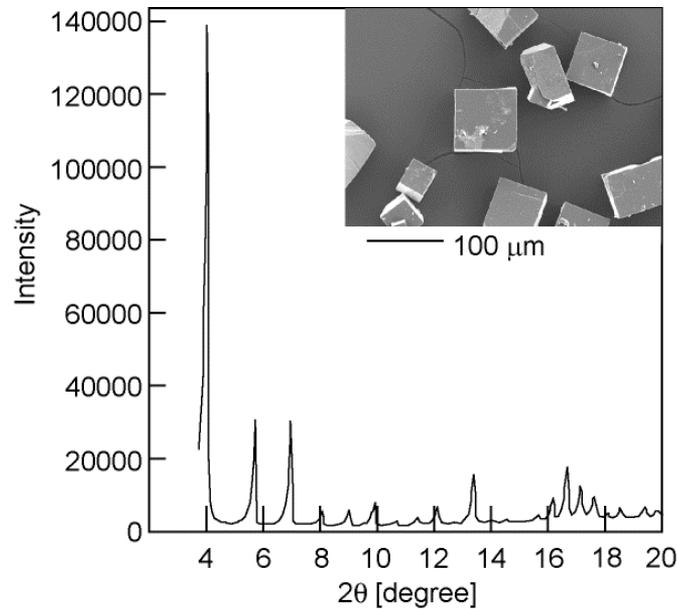


Figure 2 XRD pattern and SEM image of CD-MOF

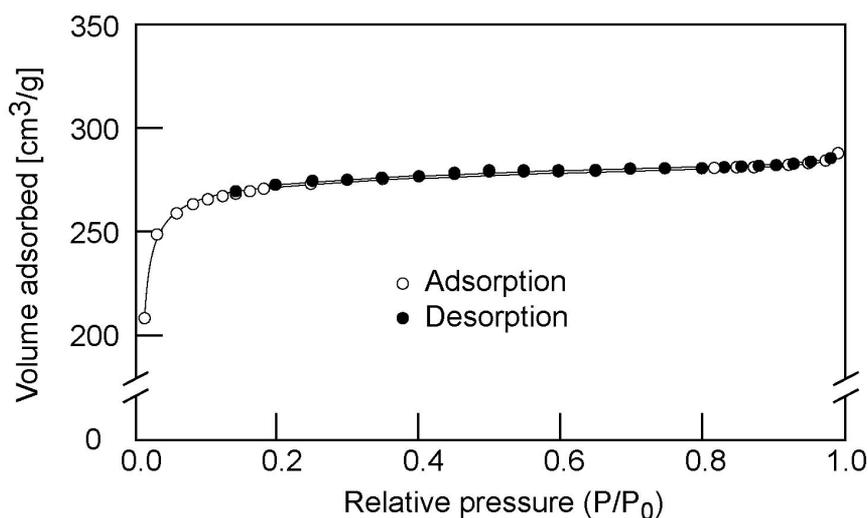


Figure 3 N_2 adsorption-desorption isotherms of CD-MOF; ○ adsorption, ●, desorption

Table 1 Characterization of the various adsorbents

	V_{pore} (cm ³ /g)	S_{BET} (m ² /g)	D_{BJH} (nm)
CD-MOF	0.434	915	1.9
Activated carbon	1.439	1568	3.7
Activated clay	0.322	258	5.0
Faujasite	0.293	605	1.9

V_{pore} : pore volume, S_{BET} : BET specific surface area, D_{BJH} : BJH average pore diameter.

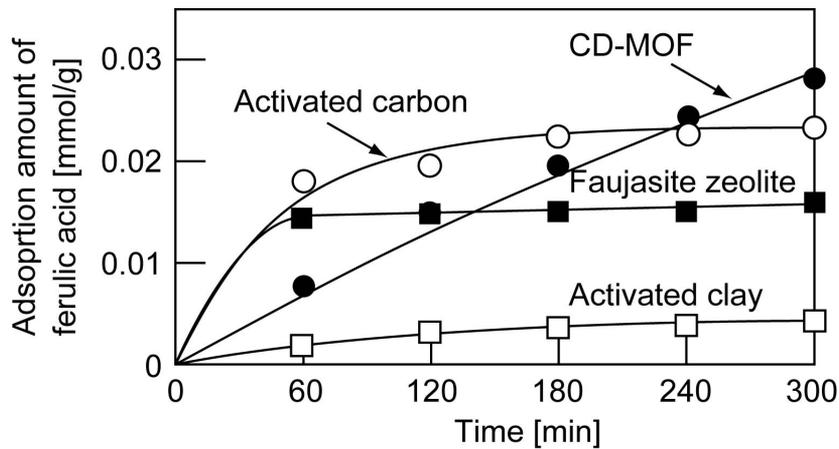


Figure 4 Adsorption amount of ferulic acid on the CD-MOF, activated carbon, faujasite zeolite and activated clay

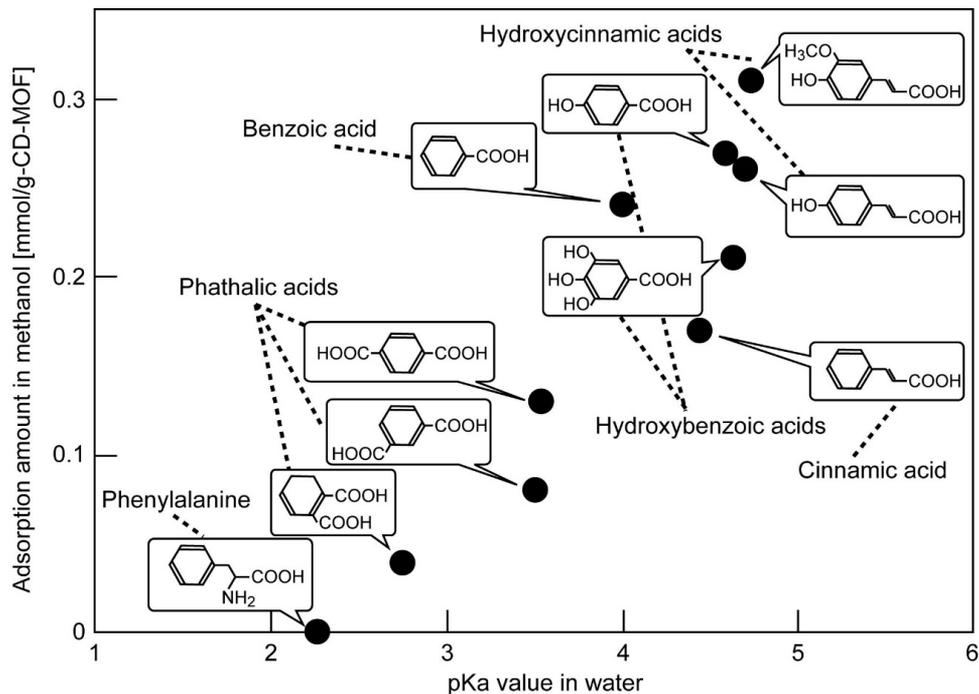


Figure 5. Relationship between the adsorption amount on the CD-MOF and the acid dissociation constant for the aromatic carboxylic acids.

Figure 4 shows the change in the adsorption amount of ferulic acid in methanol ($C_0 = 0.1$ mmol/L) on various adsorbents. The adsorption rate on the CD-MOF was lower than that on the activated carbon and the zeolite during the initial 30 min. The activated carbon, faujasite zeolites and activated clay reached the saturated state at 180 min. Meanwhile, approximately one day was needed to reach the saturation for CD-MOF. Hydrophilic ferulic acid can easily adsorb on hydrophilic pore (pore A) through the hydrogen bonding rather than hydrophobic pore (pore B). The formation and the cleavage of the hydrogen bonding drive the diffusion of ferulic acid. Therefore, the low adsorption rate on the CD-MOF is caused by the slow diffusion due to the alternating passage of ferulic acid through pore A to pore B in CD-MOF. The saturated adsorption amount of ferulic acid (0.1 mmol/g) on CD-MOF was almost four times higher than that on the activated carbon (0.023 mmol/g) regardless of the BET specific surface area.

Figure 5 shows the adsorption amounts of aromatic carboxylic acids on the CD-MOF at 5 h. The adsorption amounts increased with increasing values of the acid dissociation constant in water ($pK_a(W)$). The values of $pK_a(W)$ were obtained from the literature [15]. The initial concentration of the adsorbates in methanol was fixed at a value of 1.0 mmol/L. The relationship between the acid dissociation constant in methanol ($pK_a(M)$) and $pK_a(W)$ is expressed according to experimental data in the following equation [14]:

$$pK_a(M) = 1.02pK_a(W) + 4.98. \quad (2)$$

The pH values in methanol solutions of phthalic acid (0.1 mmol/L, $pK_a(W) = 2.75$) and of benzoic acid (0.1 mmol/L, $pK_a(W) = 4.0$) were 4.04 and 5.76, respectively. This means that the aromatic carboxylic acids are mostly presented as an undissociated molecule contributing to the complexation with γ -CD in CD-

MOF. The $pK_a(W)$ values for phthalic acid, isophthalic acid and terephthalic acid were 2.75, 3.50 and 3.54, respectively. This low $pK_a(W)$ values for phthalic acid can be explained by the effect of intramolecular hydrogen bonding. The adsorption amount of terephthalic acid was higher than that of isophthalic acid due to the steric effects of the molecules. Additional OH groups on benzoic acid ($pK_a = 4.0$) and cinnamic acid ($pK_a = 4.44$) increased $pK_a(W)$ by electron donation from the OH groups, and resulting in high adsorption for the corresponding compounds (4-hydroxybenzoic acid ($pK_a = 4.58$) and coumaric acid ($pK_a = 4.70$), respectively). Ferulic acid exhibited the highest amount of adsorption (0.32 mmol/g) among the aromatic carboxyl acids. The pH value in a methanol solution was 7.48 for phenylalanine, which forms a zwitterion (ionized amino group and carboxylic acid). Accordingly, no obvious adsorption of phenylalanine on the CD-MOF was observed. Therefore, crystallization of the CD-MOF with an aqueous solution of γ -CD, KOH and 4-phenylalanine was performed at room temperature. As a result, the amount of phenylalanine incorporated into the CD-MOF reached 0.12 mmol/g at an initial concentration of 0.17 mol/L.

Figure 6 shows the adsorption isotherms of benzoic acid on the CD-MOF and activated carbon at 298 K. The isotherm data reveals that the adsorption amount rises linearly with the increase of benzoic acid concentration and then reached equilibrium at higher concentration. The isotherm in liquid adsorption can be classified into four classes: S-curves, L-curves, H-curves and C-curves [13]. The isotherm data of the present investigation matches C-2 isotherm behavior. The adsorption indicating C-curve occurs in solid with microporous structure. The saturated adsorption amount on the CD-MOF was much higher than that on the activated carbon. This high adsorption ability might be caused by the developed microporous structure of the CD-MOF.

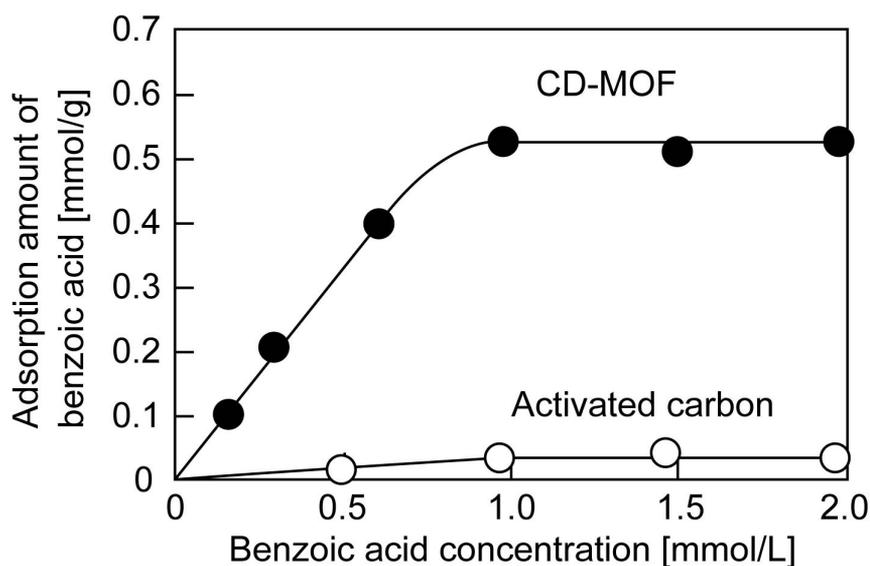


Figure 6 Adsorption isotherm of benzoic acid on the CD-MOF and activated carbon

The saturated adsorption amount of benzoic acid reached 0.52 mmol/g at the concentration of 1.0 mmol/L. The empirical formula of the CD-MOF [3] is $[(C_{48}H_{80}O_{40})(KOH)_2]_n$, and the molecular mass of the $(\gamma\text{-CD})_6$ unit is 8456 g/mol. The molar ratio of benzoic acid to $(\gamma\text{-CD})_6$ was calculated by the product of molecular weight (g/mol) times the adsorption amount (mol/g) and it was as high as 4.4. Smaldone et al. [3] investigated the adsorption of 4-phenylazophenol in CH_2Cl_2 on a CD-MOF(Rb) and reported that approximately four molecules of the dye were absorbed into each $(\gamma\text{-CD})_6$ unit. The adsorption amount of ibuprofen in CD-MOF was investigated by using grand canonical Monte Carlo simulations [11]. As a result, the adsorption isotherm exhibits two well-defined saturation states. Snapshots of the adsorption process reveal that the adsorption of the first molecules occurs in pore B, followed by the saturation of pore A. The molar ratio of ibuprofen to $(\gamma\text{-CD})_6$ was experimentally determined to be 10 [12], very close to the results of simulation [11]. These facts indicate the presence of ibuprofen in both pore A and pore B. A single saturation state of benzoic acid was observed and the molar ratio of benzoic acid to $(\gamma\text{-CD})_6$ was evaluated to be 4.4 from the saturation value. Accordingly benzoic acid might be located in pore A due to its hydrophilicity.

4 Conclusions

CD-MOF crystals with large surface areas were formed by methanol vapor diffusion for 14 days. The initial adsorption rate of ferulic acid in methanol on the CD-MOF was lower than that for activated carbon and faujasite zeolite. This is caused by the slow diffusion due to the alternating passage of ferulic acid through pore A and pore B in CD-MOF. The saturated adsorption amount on the CD-MOF was highest among those on the other adsorbents. The saturated adsorption amount of ferulic acid (0.1 mmol/g) on the CD-MOF reached at 24 hours and was almost four times higher than that on the activated carbon regardless of the BET specific surface area.

The high adsorption amount was obtained for aromatic carboxylic acids with high values of pKa(W). A single saturation state of benzoic acid on the CD-MOF was obtained at a concentration of more than 1.0 mmol/L. The molar ratio of benzoic acid to the $(\gamma\text{-CD})_6$ unit was evaluated to be 4.4 from the saturated adsorption amount.

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