Adsorption of chloramphenicol onto cobalt-based zeolitic-imidazolate framework (Co-ZIF-67)

Adsorción de cloranfenicol sobre un marco imidazolato zeolítico basado en cobalto (Co-ZIF-67)

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ABSTRACT

Releasing pharmaceuticals like chloramphenicol (CHL) into water sources will likely pose potential risks to human health and aquatic life. Adsorption is preferably adopted to remove chloramphenicol from water. This study reported the microwave-assisted production of a cobalt-based zeolitic–imidazolate framework (ZIF67) for adsorptive removal of CHL in water. ZIF-67 was characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray (EDX), and scanning electron microscopy (SEM). ZIF67 showed a uniform morphology with a mean particle size of about 350 nm. For CHL uptake, the effect of time (0-120 min), concentration (2.5-20 mg/L), pH (3-9), and dosage (0.1-1.0 g/L) was investigated. It was found that pseudo-second-order (PSO, Radj.2: 0.998) and Langmuir (Radj.2: 0.991) models best described the kinetic and isotherm of CHL, respectively. Based on the Langmuir fitting of the isotherm model, the maximum adsorption capacity (Qmax) was found at 25.73 mg/g. This study suggests that ZIF67 can be a potential adsorbent for CHL removal and a modification should be considered in future research to improve its performance in the environmental field.

Keywords: Chloramphenicol, water treatment, ZIF67, adsorption, modeling.

RESUMEN

Los residuos de productos farmacéuticos como el cloranfenicol (CHL) en las fuentes de agua representan un riesgo potencial tanto para la salud humana como para la vida acuática. La adsorción se adopta preferentemente para eliminar el cloranfenicol del agua. El presente estudio describe la producción asistida por microondas de un marco imidazolato zeolítico (ZIF67) basado en cobalto para la eliminación por adsorción de CHL en agua. ZIF-67 se caracterizó mediante difracción de rayos X (DRX), espectroscopia infrarroja por transformada de Fourier (FTIR), dispersión de energía de rayos X (EDX) y microscopía electrónica de barrido (SEM). En el caso del ZIF67 se observó una morfología uniforme con un tamaño medio de partícula de unos 350 nm. Se investigaron los efectos sobre la absorción de CHL del tiempo

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(0-120 min), la concentración (2,5-20 mg/L), el pH (3-9) y la dosis (0,1-1,0 g/L). Los modelos de pseudo-segundo orden (PSO, Radj.2: 0.998) y Langmuir (Radj.2: 0.991) describieron mejor la cinética y la isoterma de CHL, respectivamente. A partir del ajuste de Langmuir del modelo de isoterma, la capacidad máxima de adsorción (Qmax) se encontró en 25,73 mg/g. Estos resultados sugieren que ZIF67 puede ser un adsorbente potencial para la eliminación de CHL y que en futuras investigaciones debería considerarse una modificación para mejorar su rendimiento en el campo medioambiental.

Palabras clave: Cloranfenicol, tratamiento de aguas, ZIF67, adsorción, modelling.

INTRODUCTION

Antibiotic drugs are necessary for human therapy and animal disease treatment. However, the excessive use of antibiotics has been increasingly alarming, leading to the release of these pharmaceuticals into the environment [1]. Chloramphenicol (CHL) is one of the most consumed antibiotic drugs and has become an emerging antibiotic contaminant in the environment [2]. This compound significantly functions by binding to bacterial ribosomal subunits, thereby inhibiting protein synthesis [3]. The applications of CHL for livestock and aquaculture activities have recently surged [4]. Many studies have detected this antibiotic in surface water at elevated contents, related to the discharge of untreated wastewater, such as hospital effluents and aquaculture wastewater, into aquatic environments [5]. This situation is likely to pose potential risks to human health and aquatic life [6]. As a result, employing sustainable techniques, like adsorption should be considered to remove chloramphenicol from water.

Cobalt-based zeolite imidazole framework-67, abbreviated as ZIF67, is a novel type of metal-organic framework. This adsorbent has several advantages, such as a high surface area, and thermal stability. For applications, ZIF67 has been used as a catalyst for benzimidazole synthesis [7], an adsorbent for desulfurization of dibenzothiophene [8], a supercapacitor [9], and a photocatalyst for hydrogen evolution [10]. For example, ZIF67 was used to remove oxytetracycline with an efficiency of 88.3% at ten mg/L [11]. However, the yield for removing this contaminant was relatively low. Moreover, insights into mechanisms and role of electrostatic-attraction and pi-pi interaction were not fully assessed. In another study, Nguyen *et al.* used the same adsorbent to remove dyes, including congo red, rhodamine B and methylene blue, obtaining capacities of 50.5-714.3 mg/g [12]. It should be remarked that this ZIF67 was synthesized using a microwave-assisted method, which may have led to high performances. However, there are very rare studies investigate the uptake of ZIF67 for removing contaminants, particularly CHL. At present, adsorption of CHL by ZIF67 is not still reported.

Therefore, this study aimed to synthesize ZIF67 and investigate its kinetic and isotherm adsorption of CHL. The current work is significant in better understanding the performance of ZIF67 for water treatment applications.

MATERIALS AND METHODS

Materials

Chloramphenicol, 2-methylimidazol, and cobalt nitrate hexahydrate were obtained from Sigma Aldrich, Singapore. Others, including methanol and N, N-dimethylformamide, were purchased from Chemsol, Vietnam. All of the chemicals have been of analytical grade and were used untreated.

Synthesis of ZIF67

ZIF67 was synthesized through a microwave-assisted procedure [11]. 1.873 g $Co(NO_3)_2{\cdot}6H_2O$ and 1.681 g of 2-methylimidazole were separately dissolved in each 100 mL of mixed N,N-dimethylformamide and methanol (1:1 by vol.). Afterward, two solutions were slowly mixed and transferred into a teflon-lined autoclave. The microwave processing was initiated at 450 W for 15 min. The resulting ZIF67 was collected, washed with methanol, and dried.

Adsorption test

The effect of time was examined by adding ZIF67 (0.1 g/L) to 100 mL of 10 mg/L CHL solution at pH seven and stirring for 0, 10, 20, 20, 30, 60, 90,

and 120 min. After each interval, 2mL of the sample was extracted, centrifuged to remove ZIF67, and used to determine CHL concentration using UV-Vis calibration. For the concentration test, CHL solution was prepared at 2.5, 5.0, 7.5, 10.0, 15.0, 20 mg/L, and pH 7. ZIF67 (0.1 g/L) was added to 100 mL of each solution, and after 120 min of shaking, the sample was extracted to determine CHL concentration. For the pH test, CHL solution was adjusted at 3, 4, 5, 6, 7, 8, and 9, while for the dosage test, ZIF67 (0.1, 0.3, 0.6, and 1.0 mg/L) was added into 100 mL of 10 mg/L CHL. The same procedure for concentration determination was employed at 120 min.

RESULT AND DISCUSSION

Characterization

Firstly, the crystallinity of ZIF67 was measured using an XRD pattern profile. Figure 1a shows that ZIF67 has a certain degree of crystallinity with characteristic peaks at 7.25º, 10.31º, 12.66º, 17.92º, 22.04º, and 26.66º. The appearance of peaks at these positions was indexed as (011), (002), (112), (222), (114), and (233). The finding was also in harmony with the past literature [13], [14], revealing that ZIF67 was produced. The surface chemistry of ZIF67 was determined using an FTIR spectrum. Figure 1b shows a wide range of peaks between 400.0 and 4000.0 cm^{-1}. Evidently, two peaks at 429.8 and 694.5 cm^{-1} could be attributable to a metal-nitrogen coordination bond of Co-N [15]. Multiple peaks between 800 and 1600 cm^{-1} could be due to the characteristic stretching of imidazolate [16]. To be more specific, C = C and C = N bonds may be ascribed to two peaks at 762 and 1425.7 cm^{-1}, respectively. The methylene group with C-H bond of imidazole was confirmed at 2931.5 cm^{-1}. The N-H bond of unreacted 2-methylimidazole or O-H of adsorbed H2O could be observed at 3441.3 cm^{-1}.

The chemical composition of ZIF67 was analyzed using an EDX spectrum. Figure 1c reveals that there are four main elements in ZIF67, including

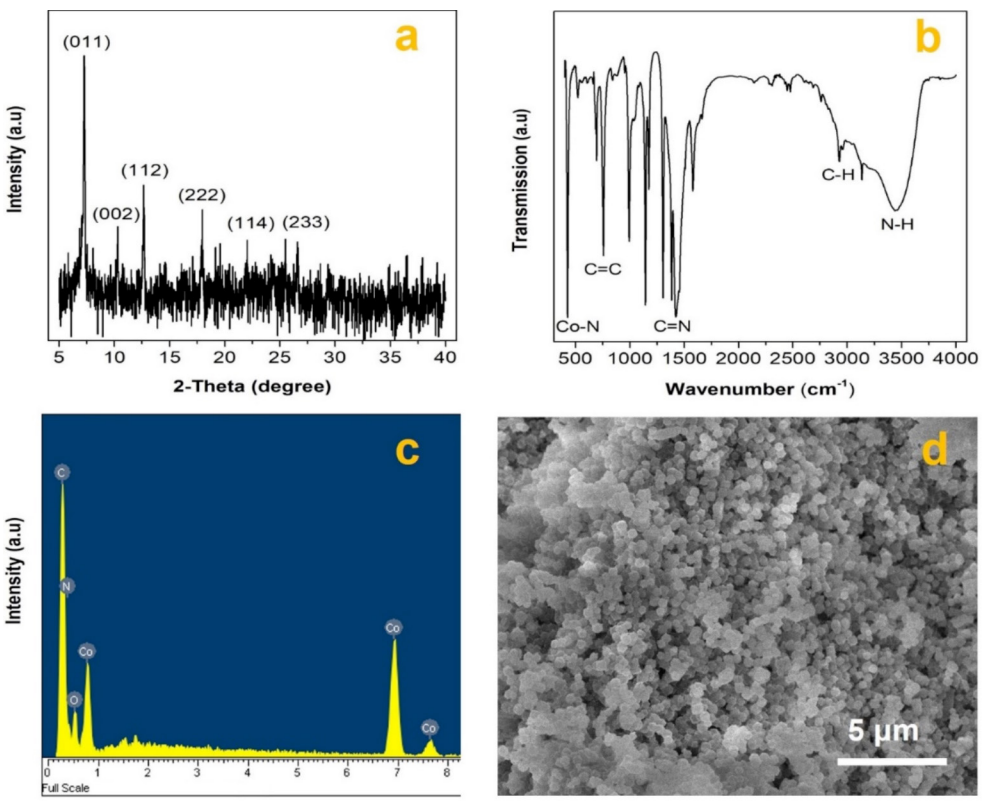

Figure 1. a) XRD diffraction pattern, b) FTIR spectrum, c) EDX spectrum, and d) SEM image of ZIF67 adsorbent.

Co (20.07% by wt. %), C (48.43% by wt. %), and N (18.46% by wt. %). With such a composition, ZIF67 may correspond to the formula as $Co(CH_3C_3H_3N_2)_2$ [17]. Moreover, another element, O (13.03% by wt. %), was found, suggesting that this material could incorporate H2O in its structure through the synthesis. Several published studies also confirmed the presence of O in the EDX spectrum [18]–[20]. Otherwise, no strange elements were found in the EDX spectrum. The morphological image of ZIF67 was recorded using the SEM technique. Figure 1d reveals the presence of uniformly and highly dispersed particles. ZIF67 particles have a microspherical shape with an average particle size of 350 nm. This finding was agreeable with the other studies [21]-[23]. Moreover, there was no specific aggregation among ZIF67 crystals, indicating good morphology of an adsorbent.

Adsorption study

The first investigation was to have insight into the impact of time on CHL adsorption capacity (Q_t) by ZIF67. Figure 2a shows that the Q_t sharply increased within 20 min due to available sites or pores of ZIF67. Then, no significant increase in Q_t value was observed between 60 and 120 min, indicating the established equilibrium point [12]. The highest Q_t value was found at 18.05 mg/g in 120 min.

Subsequently, the plot of Q_{2h} versus C_i is shown in Figure 2b. Here, CHL's initial concentration (C_i) was investigated between 2.5 and 20 mg/L. Clearly, Q2h was increased with increasing CHL concentration. The highest Q_{2h} value was found at 22.04 mg/g for C_i = 20 mg/L. It can be explained that a higher density of CHL in water triggers a gradient force to push out CHL molecules into ZIF67 pores easily [24], [25]. Chen *et al.* also reported the same trend for CHL uptake on N-doped porous carbons at a range concentration of between 50 and 135 mg/L [26].

pH is a major factor that influences the ionization and disassociation of CHL. Here, the pH of the CHL solution was surveyed at 3-9. Figure 2c illustrates

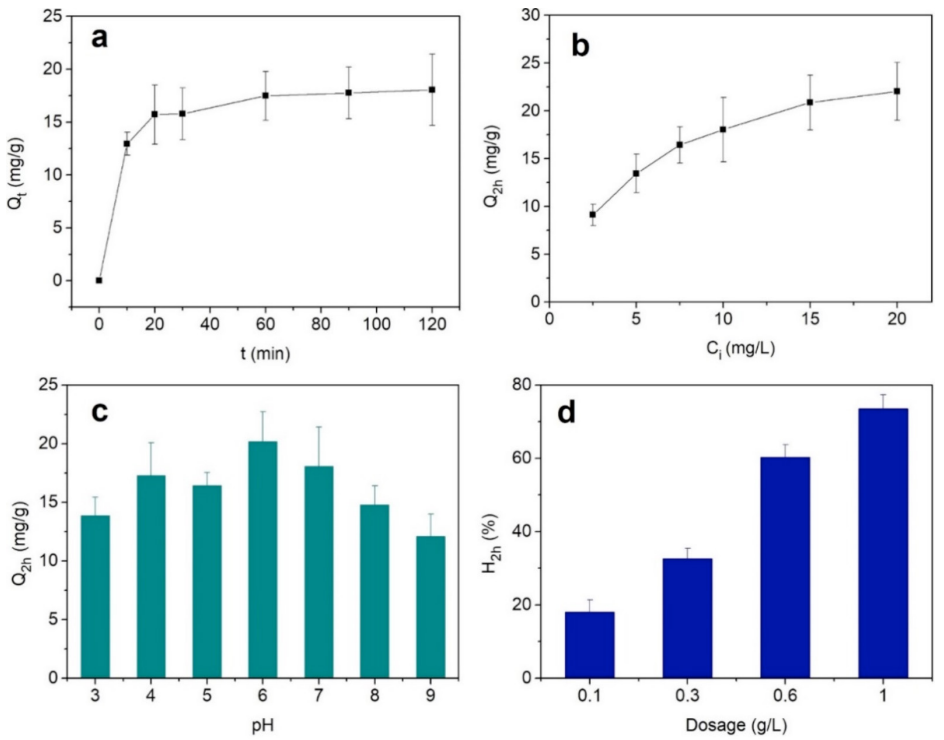

Figure 2. The plots of a) Q_t versus t (0–120 min), b) capacity after 2 h (Q_{2h}) versus C_i (2.5–20 mg/L), c) Q_{2h} versus pH (3–9) of the CHL solution, and d) removal percentage after 2 h (H_{2h}) versus ZIF67 dosage (0.1–1).

that pH at 6 was optimal for removing CHL from water with a high Q_{2h} value of 20.15 mg/g at C_i = 10 mg/L. At acidic or basic pH conditions, CHL adsorption was not favorable. It can be understood that electrostatic repulsion hampers the CHL uptake on ZIF67. This force was generated due to the positive-charged ZIF67 and $CHLH^+$ cations or the negative-charged ZIF67 and CHL– anions [4]. By contrast, at pH 6, electrostatic attraction between positive-charged ZIF67 (zero-charge point measured at 7.5) and CHL– anions (pka of CHL 5.5) [27]. A previous work also found pH 6 as the most favorable condition to remove CHL [26].

The effect of ZFI67 dosage on CHL uptake was recorded at 0.1–1 g/L. Figure 2d exhibits an increased trend in CHL removal percentage at higher dosages. It was found that at a dosage of 0.1 g/L and Ci = 10 mg/L, 73.51% CHL was eliminated by ZIF67. A higher dosage of ZFI67 was likely to supply more sites to adsorb CHL better. Several past works reported the same increase in CHL uptake by N-doped porous carbons [26], green Ag_2O [24], and acid-washed halloysites [27].

Kinetic models

Kinetic models (PFO-pseudo-first-order and PSO-pseudo-second-order) were adopted to understand the nature and rate of CHL adsorption by ZIF67. Figure 3a and Figure 3b reveal that isotherm data were fitted sufficiently with these nonlinear models. This is because the fitting curves showed a good correlation with kinetic data. According to Table 1, the kinetic adsorption of CHL by ZIF67 could be best described with the PSO model since a high adjusted R2 of 0.998, compared with 0.989 of that of the PFO model. Such an outcome suggests that chemisorption can be a significant contributor to CHL uptake onto ZIF67. The adherence of the PSO model for describing CHL kinetic adsorption in this study was in line with other studies [28]–[30].

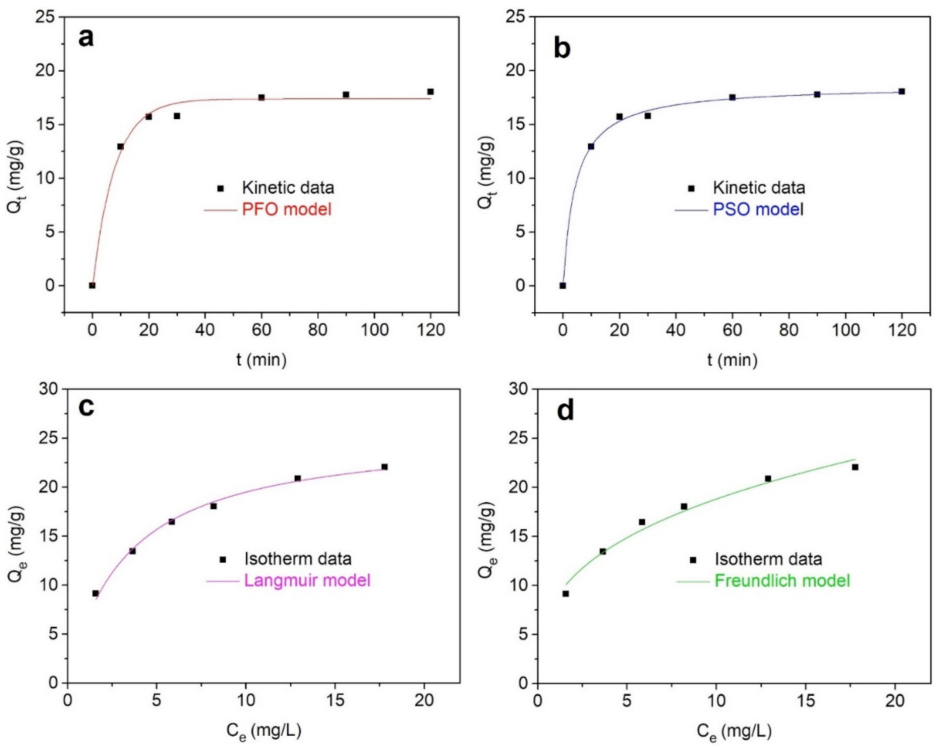

Figure 3. The kinetic (a, b) and isotherm (c, d) models; kinetic data fitted by a) PFO and b) PSO models; isotherm data fitted by c) Langmuir and d) Freundlich models.

Table 1. Kinetic-isotherm constants for the adsorption of CHL by ZIF67.

Kinetic model	Unit	Value	Isotherm model	Unit	Value
PFO model			**Langmuir model**		
K_{PFO}	1/min	0.127	Q_{max}	mg/g	25.73
Q_{PFO}	mg/g	17.39	$K_{Langmuir}$	L/mg	0.313
$(R_{adj.})^2$		0.988	$(R_{adj.})^2$		0.991
PSO model			**Freundlich model**		
K_{PSO}	g/mg min	0.012	$K_{Freundlich}$	$(mg/g)/(mg/L)^{1/n}$	8.63
Q_{PSO}	mg/g	18.63	1/n		0.34
$(R_{adj.})^2$		0.998	$(R_{adj.})^2$		0.973

Isotherm models

Isotherm models (Langmuir, Freundlich) were adopted to understand the CHL adsorption equilibrium onto ZIF67. Similar to kinetic models, Figure 3c and Figure 3d reveal that isotherm data were fitted sufficiently with given nonlinear models due to their good correlation with isothermal data. Table 1 shows that the adsorption isotherm of CHL by ZIF67 could be best described with the Langmuir model since a high adjusted R^2 of 0.991, compared with 0.973 of that of the Freundlich model. As a result, CHL uptake onto ZIF67 was a monolayer behavior. Moreover, with a Langmuir constant ($R_{Langmuir}$) of about 0.14, which lies between 0 and 1, this uptake is a favorable process. The Q_{max} value was found at 25.73 mg/g. This study's adherence to the Langmuir model for describing CHL adsorption isotherm in this study was in line with other studies [27], [28].

Adsorption mechanism

Shedding light on the CHL uptake significantly improves the treatment efficiency. CHL has a pKa of 5.5 when dissolving in water, as previously reported [27]; this means CHL tends to be deprotonated at pH > 5.5, creating an anionic form and vice versa. In that case, the secondary amine (-NH-) group is deprotonated and negatively charged. Because the optimal pH of this work was found at pH 6, according to Figure 2c, the charge of CHL is negative (-). Meanwhile, the zero charge point (pH_{zcp}) of ZIF67 was experimentally determined at 6.8. This result was very close to the pH_{zcp} data (6.9) reported in a previous study [31]. At the optimal pH 6, the ZIF67 surface tends to be positively charged due to pH (6.0) < pH_{zcp} (6.8). As a result, there is an "electrostatic-attraction" between the ZIF67 and CHL, enhancing this uptake process (Figure 4a). Furthermore, the ZIF67 is structurally constituted of a 2-imidazolate ligand with an aromatic ring and has conjugated π electrons. The CHL also contains another aromatic ring with many π electrons. Therefore, the π-π interaction between these π electrons is expected to aid the adsorption (Figure 4b). Several studies have indicated the importance of electrostatic-attraction and π-π interaction for the adsorption of pollutants [32], [33]. To sum up, two main uptake pathways are suggested, including electrostatic-attraction and π-π interaction.

CONCLUSIONS

In summary, the ZIF67 was synthesized and characterized via a microwave-assisted method. ZIF67 showed a degree of crystallinity, high dispersion, and uniform shape. For CHL uptake, the equilibrium was obtained after 120 min. pH 6 was found to be an optimum condition. It was found that at 73.51%, ZIF67 eliminated CHL at a dosage of 0.1 g/L and C_i = 10 mg/L. Kinetic adsorption of CHL adhered to the PSO model with a high adjusted R^2 of 0.998.

Meanwhile, isotherm adsorption of CHL adhered to the Langmuir model (adjusted R^2 of 0.991). CHL uptake was a favourable process and monolayer behavior. The Q_{max} was found at 25.73 mg/g through the Langmuir equation. The study suggests that two main uptake pathways, including

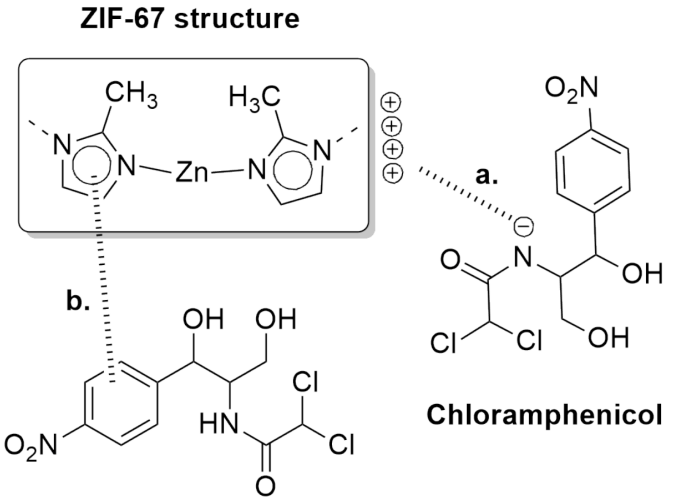

Figure 4. Adsorption routes suggested through a) electrostatic-attraction and b) π-π interactions.

electrostatic-attraction and π-π interaction, may control the adsorption of CHL onto ZIF67. Despite the low Q_{max} obtained by ZIF67, it can be improved with surface modification in future research. This study is expected to expand the application of ZIF67 in the environmental field.

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