

GO@ZIF-67/PAN Mixed Matrix Membrane for the Adsorptive and Photocatalytic Removal of Methylene Blue

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ABSTRACT

GO@ZIF-67/PAN mixed-matrix membrane (MMM) was prepared using casting method. The adsorption and photocatalytic activity of GO@ZIF-67/PAN MMM towards the removal of methylene blue dye (MB) in water was evaluated. It was found that the MMM performs better when GO@ZIF-67 composite with higher amount of GO were used as the filler. The GO@ZIF-67/PAN MMM with 25 wt% of GO in the composite was able to remove about 72.9%, 90.5%, and 86.4% of MB in dark, UV-A, and visible light, respectively, within 9 hours of reaction time. The photocatalytic removal of MB by GO@ZIF-67/PAN MMM was well fitted to Langmuir-Hinshelwood pseudo-first order reaction kinetics model, which indicates that the removal process requires the adsorption of MB on the surface of MMM followed by the photocatalytic decomposition of MB on the surface of GO@ZIF-67/PAN MMM. Besides, the results also revealed that GO@ZIF-67/PAN MMM can be photoexcited under UV-A and visible light irradiation. This study opens a new pathway for the exploration of MMM in pollution control under a wider light responsive range, *i.e.* UV-visible regions.

KEYWORDS: Adsorption; Photocatalytic degradation; Graphene oxide; Metal-organic framework; Polyacrylonitrile.

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INTRODUCTION

Various techniques have been employed for the removal of organic pollutants in wastewater. Adsorption is one of the most commonly used treatment techniques as it can occur under low operation temperature in both single and multi-contaminants systems (Abdul Karim *et al.*, 2015; Dalang and Mohd Tuah, 2016; Lin *et al.*, 2014). However, adsorption technique only separates pollutant from the water without breaking the pollutant into biodegradable or less toxic compounds (Wang *et al.*, 2014). Metal-organic frameworks (MOFs) are crystalline porous solids composed from metal ions or clusters that are linked to organic ligands (Rowsell and Yaghi, 2004). The zeolitic imidazolate framework 67 (ZIF-67) is particularly a promising MOF for the removal of organic pollutants due to its good photocatalytic performance under visible light (bandgap energy $E_{BG} = 1.98$ eV). However, its low-density framework structure and fast electron-hole recombination have limited its application in the removal of organic pollutants (Chen *et al.*, 2014, Suzanna, 2016)

Graphene oxide (GO) has been introduced to ZIF-67 (as GO@ZIF-67) in order to enhance the photocatalytic properties of ZIF-67. GO is found to be capable of enhancing photocatalytic activity of ZIF-67 through excellent mobilization of electrons that can reduce the electron-hole recombination and lower the bandgap of ZIF-67. However, heterogeneous photocatalysis involving GO@ZIF-67 requires separation of the composite from solution after treatment (Suzanna, 2016). Here, we report the feasibility of GO@ZIF-67/PAN mixed-matrix membrane (MMM) for the removal of methylene blue dye (MB) in water. Polyacrylonitrile (PAN) has been widely studied for applications such as rechargeable batteries, hydrogen storage, and electrode materials (Idris *et al.*, 2015). Different amount of GO in the composite and light sources towards efficiency of the MMM were evaluated.

METHODOLOGY

Synthesis of GO@ZIF-67 Composites

GO@ZIF-67 composite was synthesized using hydrothermal method (Qian *et al.*, 2012; Zhang *et al.*, 2012). GO solution was first prepared using modified Hummer method (Chen *et al.*, 2013; Marcano *et al.*, 2010). To prepare Mixture A, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.225 g, AR grade, Sigma-Aldrich) was dissolved in 1.5 mL of GO solution. Subsequently, Mixture B was prepared by dissolving 2-methylimidazole (1.375 g, AR grade, Sigma-Aldrich) in 10 mL of GO solution. The Mixture B was then slowly added into the Mixture A with continuous stirring for 3 hours. The final mixture was filtered and washed with deionized water for three times. The product was dried at 100 °C for 4 hours and sieved with a 250- μm laboratory test sieve. This was then followed by another drying at 100 °C for 8 hours to obtain GO@ZIF-67 composite. GO@ZIF-67 composites with different weight percent of GO (*i.e.* 8, 14, and 25 wt%) were synthesized. The composite was denoted as GO@ZIF-67 (x wt%), where x represents magnitude of the weight percent of GO in the composite.

Preparation of GO@ZIF-67/PAN Membranes

The GO@ZIF-67/PAN MMM (with 1:10 of GO@ZIF-67 to PAN ratio) was prepared through casting method (Xie *et al.*, 2011). Typically, 0.026 g of GO@ZIF-67 was added into a 100-mL beaker containing DMF as the solvent (10.5 mL, AR grade, Sigma-Aldrich) followed by sonication for 5 min. Subsequently, 0.523 g of PAN powder ($M_w = 150,000$, AR grade, Sigma-Aldrich) was added to the mixture followed by stirring for 12 hours to obtain a homogenous mixture. After that, the solution was poured into a glass petri dish and dried at 80 °C for 4 hours. The obtained GO@ZIF-67/PAN MMM was then cooled to room temperature and immersed in deionized water to detach GO@ZIF-67/PAN MMM from the glass petri dish. Finally, the GO@ZIF-67/PAN MMM was rinsed with deionized water and dried in air.

Photocatalytic Activity

The photocatalytic activity of GO@ZIF-67/PAN MMM was evaluated through the degradation of MB in aqueous condition and under irradiation of white light (Apluses 5-W 28-LED desk lamp) at nominal wavelength of 450 nm and UV-A radiation (Vilber T-6L 6-W Mercury UV-A lamp) at nominal wavelength of 365 nm, respectively. The wavelength components of the lights sources have been further confirmed using ASEQ LR-1 portable spectrometer (see Figure 1).

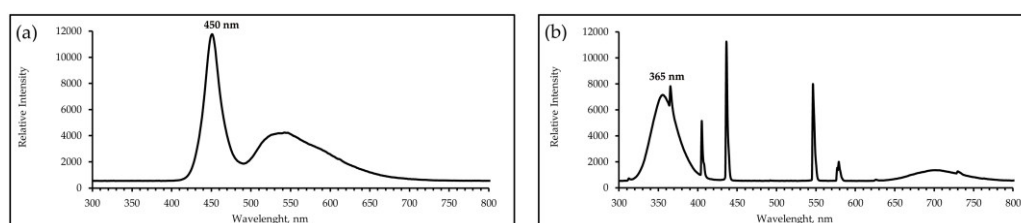


Figure 1. Relative amplitude of the wavelength components of lights from two different sources. (a) Lights with 450 nm of nominal wavelength produced by Apluses 5-W 28-LED desk lamp, and (b) Lights with 365 nm of nominal wavelength produced by Vilber T-6L 6-W Mercury UV-A lamp.

In this study, 50 mL of 20-ppm of MB solution was first added into a cylindrical dish with continuous stirring. Then, GO@ZIF-67/PAN MMM was placed on the MB solution. The samples that collected at different time intervals were then analyzed using UV-Vis spectrophotometer (Agilent, Cary 60) at its maximum absorption wavelength of 665 nm for the Absorbance value. The percentage of dye removal for each time interval, % Removal was calculated using Equation 1:

$$\% \text{ Removal} = (A_0 - A_t)/A_0 \times 100 \quad (1)$$

Langmuir-Hinshelwood kinetics model was used to evaluate the reaction kinetics of the photocatalytic process (Lin *et al.*, 2015, Zainal *et al.*, 2006, Konstantinou & Albanis, 2004):

$$\text{Pseudo-first order:} \quad \ln [A_0 - A_t] = k_1 t \quad (2)$$

where A_0 is the initial absorbance of dye at $t = 0$ min, and A_t is the absorbance of dye at t min, k_1 is pseudo-first order rate constant in min^{-1} and k_2 pseudo-second order in $\text{mg}^{-1}\text{L}\cdot\text{min}^{-1}$.

RESULT AND DISCUSSION

Characterization of GO@ZIF-67/PAN

Figure 2a shows the XRD patterns of GO, ZIF-67 compound, PAN membrane, ZIF-67/PAN membrane, and GO@ZIF-67/PAN MMM. The synthesized GO has shown a characteristic peak at $2\theta^\circ = 10.4^\circ$ (Zhang *et al.*, 2015). The diffraction peaks of GO@ZIF-67/PAN MMM also matched well with that of ZIF-67 compound and PAN membrane (Qian *et al.*, 2012; Xie *et al.*, 2011). However, the GO peak was absent in the MMM. This may be due to overlapping of the GO diffraction peak with that of ZIF-67 at 10.4° of 2θ degree. To confirm the presence of GO in MMM, FTIR was employed. Figure 2b shows the ATR-FTIR spectra of GO powder, ZIF-67 powder, PAN membrane, ZIF-67/PAN membrane, and GO@ZIF-67/PAN MMM. A small peak at 1789 cm^{-1} in MMM was characteristic of C=O stretching of carboxylic groups of GO (Krishnamoorthy *et al.*, 2011). The absorption bands at 1198 cm^{-1} and 1069 cm^{-1} were attributed to epoxy group (C-O) and alkoxy group (C-O-O) of GO, respectively. This confirms the presence of GO in the GO@ZIF-67/PAN MMM. The SEM images revealed that the PAN membrane has a rough surface topography (Figure 3a), while the GO@ZIF-67/PAN MMM has a rugged surface, which indicates the successful introduction of GO@ZIF-67 to the PAN (Figure 3b). However, the morphology of GO@ZIF-67 composites could not be observed clearly in the PAN membrane due to the thicker surface of PAN membrane in this study. This is different from our previous study in which the MIL-53(Fe) crystals are clearly seen as embedded in the PAN membrane (Mohd Tahir *et al.*, 2017).

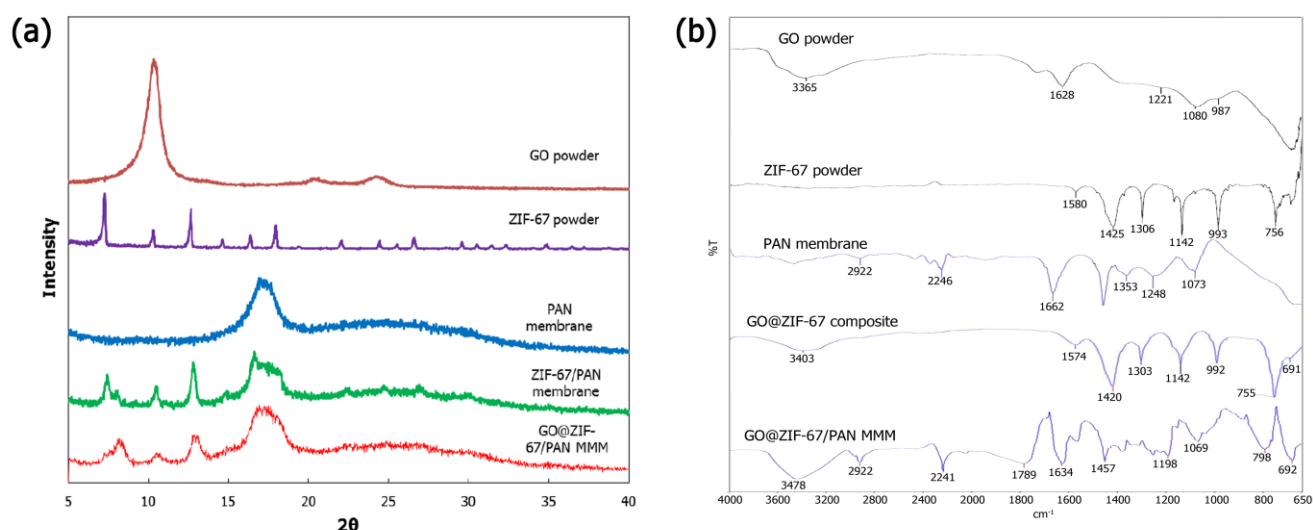


Figure 2. (a) XRD patterns, and (b) ATR-FTIR spectra of GO, ZIF-67 compound, PAN membrane, ZIF-67/PAN membrane and GO@ZIF-67/PAN MMM.

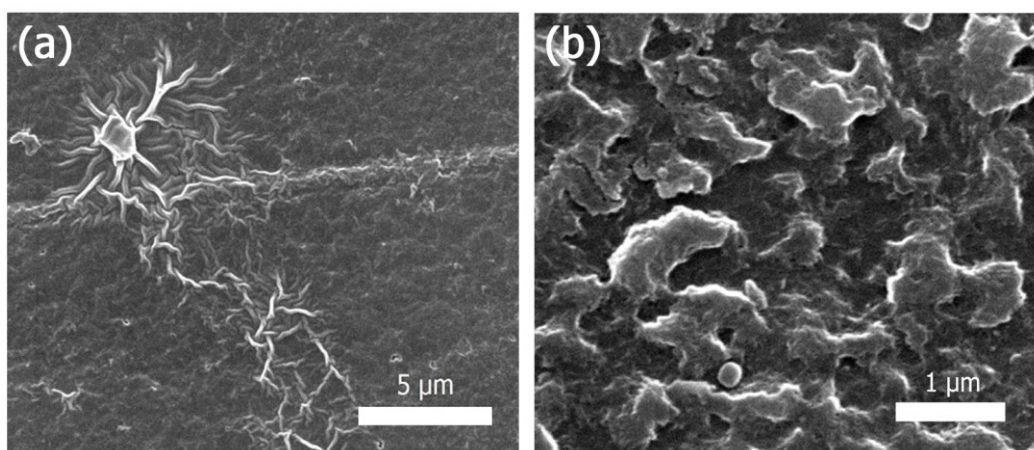


Figure 3. SEM images of (a) PAN membrane, and (b) GO@ZIF-67/PAN MMM.

Adsorption Ability

Figure 4 shows the adsorption ability of MMMs, filled with GO@ZIF-67 at different GO wt%, for the removal of MB in dark. The results showed that MMM with GO@ZIF-67 (25 wt%) gave the highest removal efficiency of 72.9% after 9 hours in dark. Adsorption of MB by MMM with GO@ZIF-67 (8 wt%) and GO@ZIF-67 (14 wt%) were 47.5% and 60.8%, respectively. Each MMM showed a consistent increment of 12.5% of MB removal as the amount of GO increased. ZIF-67/PAN membrane, for instance, gave 14.2% of MB removal whilst PAN membrane showed the lowest efficiency with only 1.5% of MB removal. The results confirmed the positive effect of GO in the adsorption of MB in water. The greater the amount of GO in the composite, the higher is the removal of MB from water. This suggests that higher amount of GO may provide more active sites on the surface of membrane that are favorable to the adsorption of MB in water.

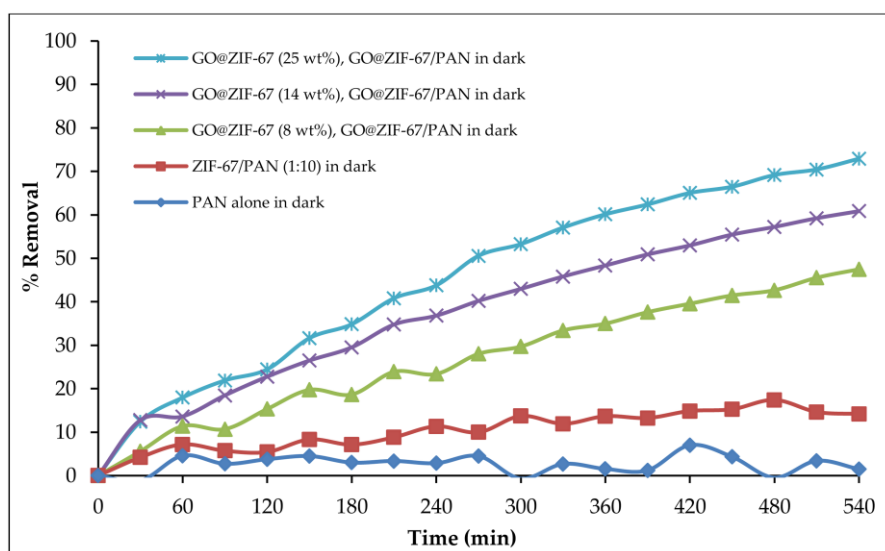


Figure 4. Efficiencies of MMMs prepared with different types GO@ZIF-67 composite (*i.e.* with different amount of GO) towards the removal of MB in dark condition.

Photocatalytic Performance

Figure 5a shows that the removal of MB in water by PAN membrane under UV-A and visible light were only 3.6% and 7.8%, respectively, which is similar to that of PAN in dark condition. The results confirmed that no photocatalytic activity present under PAN/UV-A and PAN/Vis systems. ZIF-67/PAN membrane, on the other hand, have removed 39.3% and 29.8% of MB under irradiations of UV-A and visible light, respectively. Furthermore, the removal of MB was enhanced through

GO@ZIF-67/PAN MMM under the same operating conditions (Figure 5b-d). The MMM with GO@ZIF-67 (25 wt%), for instance, gave the highest degree of removal where about 90.5% and 86.4% of MB was removed under UV-A and visible light, respectively. The results indicate that GO@ZIF-67/PAN MMM at higher percentage of GO and under UV-A or visible light radiation may promote the removal of MB from water (Figure 6). This can be attributed to narrower bandgap of GO@ZIF-67 that makes the MMM a better light driven photocatalyst with a broader light responsive range. Besides narrower bandgap, it is believed that incorporation of GO can reduce the electron recombination and thus promote the formation of hydroxyl radical, $\bullet\text{OH}$ which is a non-selective species so destructive to most organic pollutants (Suzanna, 2016).

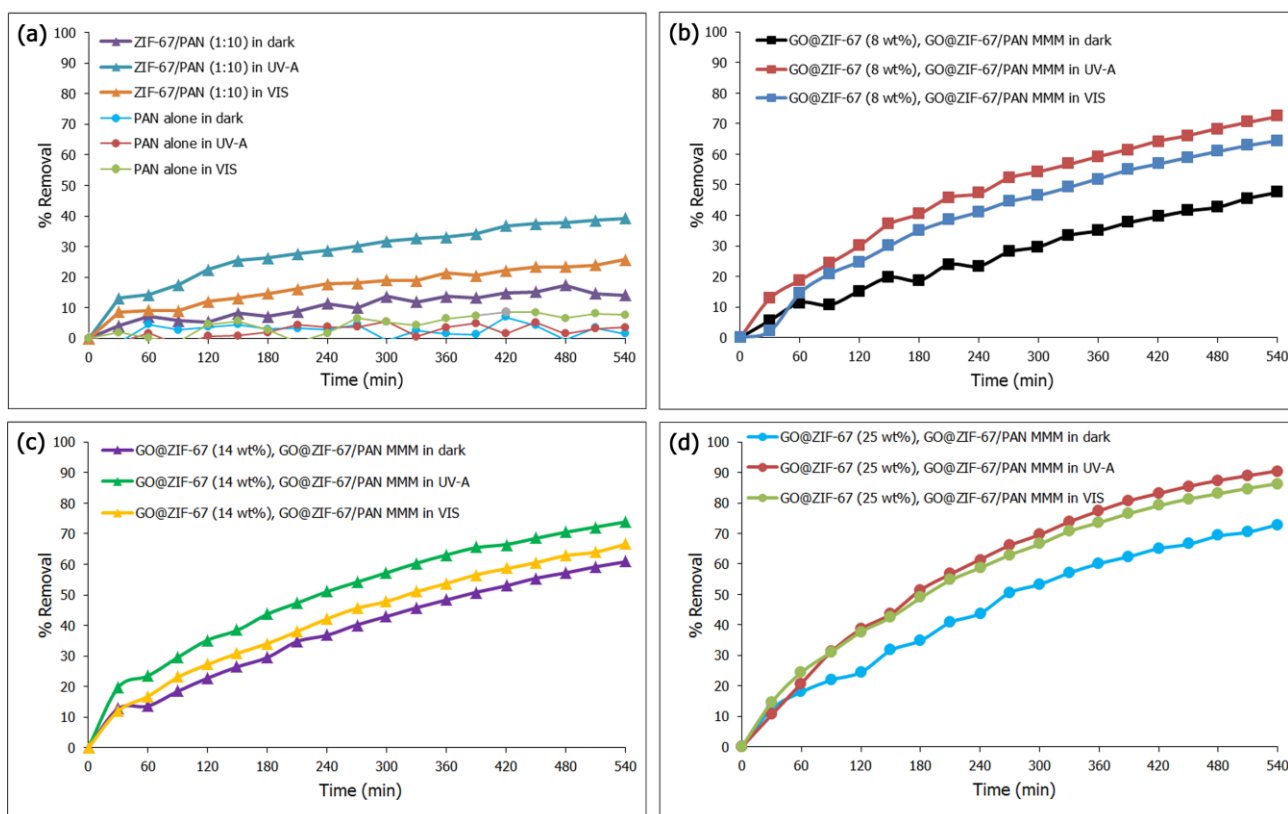


Figure 5. Effect of lights on (a) PAN membrane and ZIF-67/PAN, (b) MMM prepared with GO@ZIF-67 (8 wt%), (c) MMM prepared with GO@ZIF-67 (14 wt%), and (d) MMM prepared with GO@ZIF-67 (25 wt%) towards the removal of MB in water.

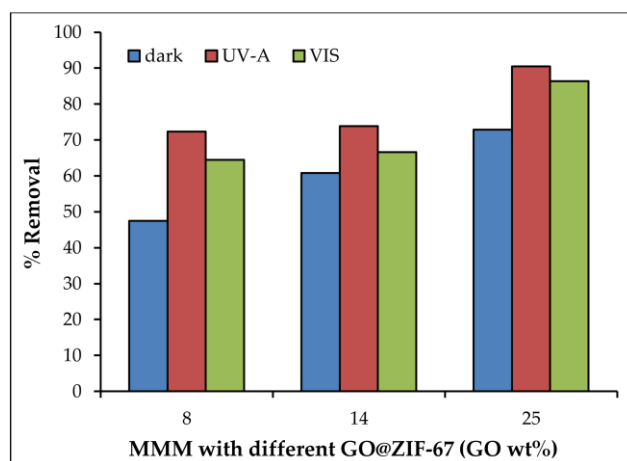


Figure 6. Efficiencies of MMMs prepared with different types GO@ZIF-67 composite (*i.e.* with varying amount of GO) towards the removal of MB in dark, UV-A and visible light conditions.

Reaction Kinetics

To evaluate the photocatalytic degradation of MB by GO@ZIF-67/PAN MMM, Langmuir-Hinshelwood kinetics model was employed. It was found that the data collected from the photocatalytic experiments of 20-ppm under UV-A and visible light irradiation, respectively, were in good agreement with the pseudo-first reaction kinetics, where the values of correlation coefficient, were close to 1. This is typical for heterogeneous catalysis where it requires adsorption of MB molecules to the surface of the GO@ZIF-67/PAN MMM followed by decomposition of MB molecules by $\bullet\text{OH}$ radicals produced through photoexcitation of GO@ZIF-67 under UV-A or visible light irradiation (Konstantinou & Albanis, 2004). The MMM with GO@ZIF-67 (25 wt%) showed higher value of rate constant, k_1 compared to other MMM with lower amount GO in the composite, which implies that higher amount of GO may favour the photocatalytic degradation of the MB in water.

Table 1. Correlation coefficients, R^2 and rate constants, k_1 obtained by fitting the photocatalytic degradation data to the Langmuir-Hinshelwood pseudo-first order reaction kinetics.

Amount of GO (wt%)	GO@ZIF-67/PAN/UV-A		GO@ZIF-67/PAN/Vis	
	R^2	k_1 (min ⁻¹)	R^2	k_1 (min ⁻¹)
8	0.9936	0.0023	0.9906	0.0019
14	0.9901	0.0023	0.9960	0.0019
25	0.9976	0.0044	0.9993	0.0036

CONCLUSION

Performance of GO@ZIF-67/PAN MMM towards the removal of MB in water increases with the amount of GO in the GO@ZIF-67 composite. The best amount of GO in the composite used to prepare the MMM was found to be 25 wt%. The GO@ZIF-67/PAN MMM gave the best degree of MB removal under UV-A irradiation (90.5%), followed by visible light (86.4%), and in dark condition (72.9%). The results indicate that the GO@ZIF-67/PAN MMM can be a good adsorbent as well as a good photocatalyst that works well under both visible and UV radiation. Larger light responsive range of GO@ZIF-67/PAN MMM relative to other type of photocatalysts such as titania and zinc oxide (which can only be photoactivated by UV radiation) implies that the GO@ZIF-67/PAN MMM can be a good material for environmental remediation under sunlight.

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