

Removal of phthalate from papermaking wastewater by MIL-101(Fe) in the presence of persulfate

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ABSTRACT: Phthalates are found in most papermaking wastewater, as are various other pollutants. Phthalates such as diethyl phthalate (DEP) and dibutyl phthalate (DBP) are endocrine-disrupting compounds (EDCs). The objective of this research was to use metal organic frameworks (MOFs) MIL-101(Fe) as a new-style adsorbing material and persulfate (PS) activator for removing DEP and DBP from artificial aqueous model solutions. We used X-ray diffractometer, scanning electron microscope, and Fourier transform infrared spectroscopy technologies to characterize the MIL-101(Fe). More than 80% of the DEP and DBP were removed with a MIL-101(Fe)/PS system over a 5 h period when the initial concentrations of the pollutants (DEP or DBP) were around 3 ppm. MIL-101(Fe) was able to absorb the pollutants and activate persulfate, which together contributed to phthalate removal. As the amount of MIL-101 and PS was increased, the percentage of removed phthalate increased gradually. We concluded that the MIL-101(Fe)/PS system removed phthalate effectively from papermaking wastewater.

Application: Metal organic frameworks MIL-101(Fe) could be applied to activate persulfate for phthalate removal, which would reduce the risk for exposure to EDCs from papermaking wastewater.

Pulp and paper mills discharge various pollutants in wastewater. Of increasing concern are the endocrine-disrupting compounds (EDCs) among the various pollutants from wastewater of paper mills. EDCs include mainly phthalates (phthalic acid esters [PAEs]), such as dimethyl phthalate, diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate, etc. [1]. Additives in the papermaking process, bleaching process, and recyclable paper can be sources of phthalates in wastewater. Different articles have investigated the presence of PAEs in papermaking wastewater [2-4].

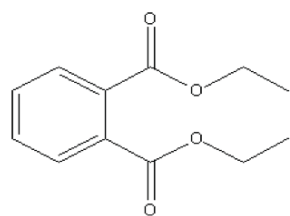
We chose to investigate compounds identified in requirements of the European Union Water Framework Directive (2000/60/EC and 2008/105EC) and the laws of certain countries. Chinese laws limit specific levels of only some typical PAEs. The integrated wastewater discharge standard (GB8978-1996), for example, sets the specific levels of dibutyl phthalate (DBP), one kind of PAE, as 0.2 mg/L, 0.4 mg/L, and 2.0 mg/L for grade I, grade II, and grade III, respectively. Although the amounts of these pollutants are not so large, they could cause great disruption to endocrine and greatly affect the development of wildlife, and even human beings. PAEs have been found in aqueous effluents of paper mills even after aerobic or aerobic-anaerobic treatment [1]. Incomplete degradation of EDCs by biological treatment results in significant levels of EDCs that might still affect human life. Scientists and engineers have developed various technologies to further remove these pollutants. Particularly, filtration technology and advanced oxidation processes (AOPs) are methods for removing

pollutants that are hard to remove by biological methods [5].

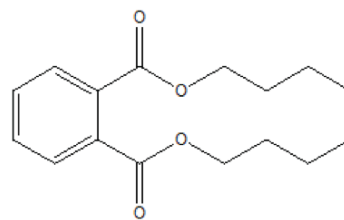
Traditional AOPs are mainly based on hydroxyl radicals ($\text{HO}\cdot$), which can effectively degrade various pollutants. In addition to the traditional AOPs, sulfate radical ($\text{SO}_4^{\cdot-}$)-based AOPs have attracted increasing attention in recent years [6-8]. Sulfate radicals are produced mainly by activation of persulfate. Sulfate radicals have oxidation-reduction potential similar to that of hydroxyl radicals and can be used to degrade various pollutants. Sulfate radicals also have longer effective half-lives than do hydroxyl radicals [9-11]. This advantage makes it possible to break down trace amounts of EDCs pollutants in the papermaking wastewater.

Metal organic frameworks (MOFs) have drawn more and more attention. Their porous character resembles activated carbon or molecular sieves. One way that MOFs could help to remove pollutants is by adsorption. In addition, the active transition metal center could behave as the effective heterogeneous activator for AOPs. MOFs have been investigated for many applications, including absorption or catalysis in aqueous solution [12-14]. However, most of the reported works on MOFs so far are mainly for dye removal [15-17]. Some researchers found that MOFs could effectively absorb certain dyes, such as methyl orange, methylene blue, and so on. Moreover, some researchers showed that ferrous (Fe)-based MOFs, including MIL-53(Fe), MIL-101(Fe), and MIL-88(Fe), effectively activate water or persulfate for dye removal [18,19]. However, these works mainly focus on discoloration of dye-containing pollutants with iron-based MOFs and activated PS.

MIL-101(Fe) was one kind of MOF with comparable stabil-



(A)



(B)

1. Structure of (A) diethyl phthalate and (B) dibutyl phthalate.

ity in water and good performance in absorbing pollutant or activating oxidants for pollutant removal [20,21]. This work focused on MIL-101(Fe) developed for absorbing and degrading PAEs. DEP and DBP were used as the model for PAEs found in papermaking wastewater treated by traditional methods.

To our knowledge, ours is the first work about MOF/PS systems for PAEs removal. As mentioned, DEP and DBP could be found in papermaking wastewater. Even after traditional treatment, the level of PAEs in effluents still could be harmful to human beings. Therefore, we applied MIL-101(Fe) to activate PS for DEP and DBP removal. **Figure 1** shows the structures of DEP and DBP. In the traditional paper mills, the concentration of PAEs was less than 1 mg L⁻¹ before and after water treatment. However, the model concentration of PAEs in our works was about 3 mg L⁻¹, which could help to tell the ability of MOF/PS systems for PAEs removal [3]. The concentration of PAEs might vary in different kinds of paper mill streams because of specific papermaking techniques, thus it is hard to provide one typical concentration of PAEs in paper mill streams. However, the concentration of 3 mg/L in our model system was based on our measurement in some paper mill streams collected in Zhongshan and Dongguan in China, so that the PAE concentrations of 3 mg/L in our model system is relevant.

EXPERIMENTAL

Chemical

Iron (III) chloride hexahydrate (FeCl₃·6H₂O) and dimethylformamide (DMF) were bought from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). DEP, peroxydisulfate, and terephthalic acid (H₂BDC) were obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). The chemicals were used without purification.

Sample preparation

Fe-MIL-101 was prepared to match other studies [22,23], with some modifications. In a typical procedure, 2.7 g of FeCl₃·6H₂O, 0.824 g of H₂BDC, and 60 mL of DMF were mixed together and heated at 110°C for 20 h in a Teflon-lined stain-

less steel reactor. The raw product was filtered off and washed twice with hot ethanol at 60°C for 3 h each time. Finally, the purified product was dried in a vacuum drying oven (70°C) overnight.

Synthetic aqueous solution of DEP or DBP were prepared to be 3 ppm after being stirred for 2 days.

Characterization

Technologies including X-ray diffractometer (XRD) (Bruker; Ettlingen, Germany), Fourier transform infrared spectroscopy (FTIR) (Bruker), thermal field-emission scanning electron microscope (FESEM) (Quanta 200, FEI Co.; Eindhoven, The Netherlands) were used to characterize the morphology and crystallographic structures and so on.

Evaluation of catalytic activity

To investigate the ability of pollutants removal, batch tests were carried out in glass conical flasks. The flasks were shaken in a Zhicheng (Shanghai, China) ZHWY-20102C rotary shaker at 180 rpm at room temperature (25±0.5°C). A certain amount of solution sample was withdrawn at specified intervals, then immediately the same amount of ethanol was added for detection by high performance liquid chromatography (HPLC) using a Shimadzu (Kyoto, Japan) LC-20A with an InertSustain C18 column. For detection of DEP, the mobile liquid was water and methanol mixed at a rate of 65:35 (V/V) at a wavelength of 236 nm and temperature of 40°C. But for detection of DBP, the mobile liquid was water and methanol mixed at a rate of 90:10 (V/V) at a wavelength of 225 nm and temperature of 30°C. The HPLC technique was applied to detect the residual PAEs in water, which could tell the amount removed by MIL-101(Fe)/PS system.

RESULTS AND DISCUSSION

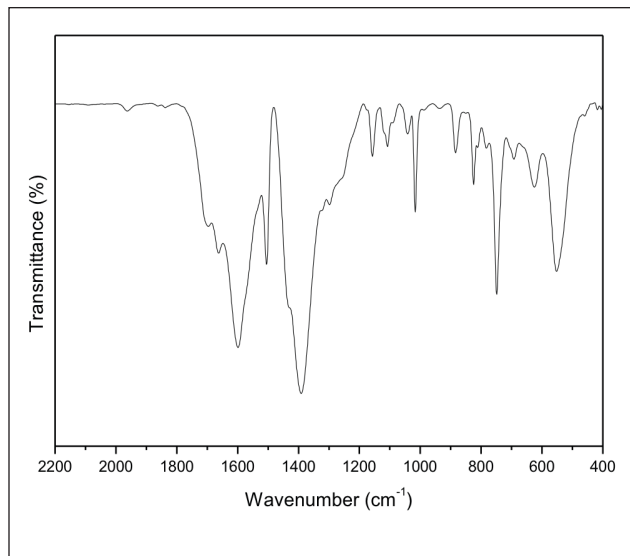
The objective of this research was to study whether MIL-101(Fe)/PS systems could remove PAEs and thereby reduce the environmental impact of papermaking wastewater. The character of MIL-101(Fe) and the ability of MIL-101(Fe)/PS were studied.

Characterization of MIL-101(Fe)

Figure 2 shows the XRD pattern of MIL101 (Fe) before activation. The fresh samples presented the typical peaks near 2θ of 5° and 10° , which agreed well with the previous reports [20,23].

Figure 3 shows the morphology of MIL-101(Fe) that can be observed by SEM. It shows that MIL-101(Fe) has octahedral morphology and is about $0.5\ \mu\text{m}$ to $1.0\ \mu\text{m}$ in diameter. The morphology agreed well with that described in related articles [20,24]. The SEM and XRD patterns together proved the successful preparation of MIL-101(Fe).

FTIR spectroscopy is a sensitive method to detect the vibrations of bonds between different elements, such as metal-oxygen and carbon-oxygen. FTIR was applied to further investigate bonding changes of MIL-101 (Fe). As shown in **Fig. 4**, all peaks of fresh samples were similar to those reported in previous articles [19,20,23]. According to the images, MIL-101(Fe) are built from trivalent metal centers and carboxylate ligands. Typical peaks might result from the carboxylate or Fe-O vibrations. Peaks between $1300\ \text{cm}^{-1}$ and

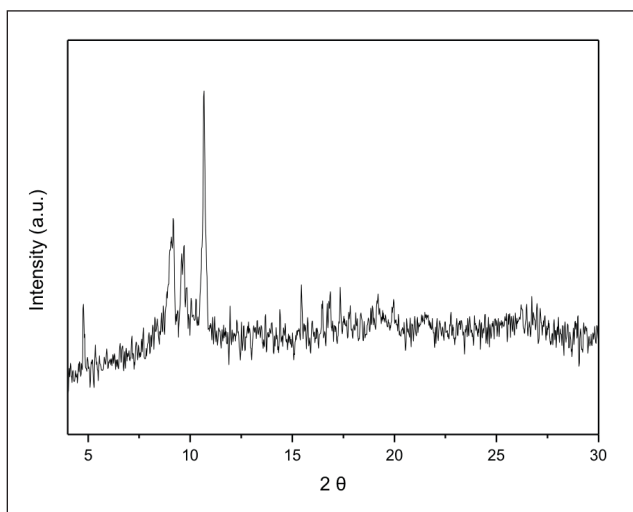


4. Fourier transform infrared (FTIR) spectroscopy spectrum of MIL-101(Fe).

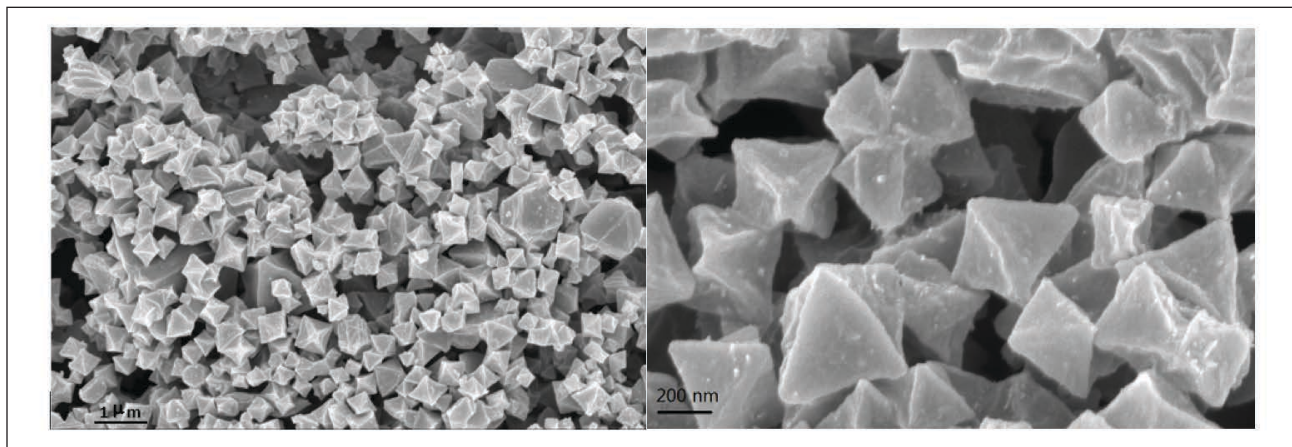
$1750\ \text{cm}^{-1}$ could be indexed to $\nu_{\text{as}}(\text{COO})$, $\nu_{\text{s}}(\text{COO})$, and $\nu(\text{C-C})$ vibrations, which implied that MIL-101 had a dicarboxylate linker. In addition, peaks at about 1110 and $748\ \text{cm}^{-1}$ could be indexed to $\sigma(\text{C-H})$ and $\gamma(\text{C-H})$ vibrations of aromatic rings. The band at $1659\ \text{cm}^{-1}$ could be attributed to the C=O vibration. The peak at about $549\ \text{cm}^{-1}$ could be assigned to the Fe-O vibration. All in all, testing showed that MIL-101(Fe) was prepared successfully.

Removal efficiency of PAEs by MIL-101(Fe)/PS

Degradation tests of DEP and DBP were used to study whether a MIL-101(Fe) system could be applied to PAE removal in papermaking wastewater. As **Fig. 5** shows, more than 80% of DEP and DBP could be removed by a MIL-101(Fe)/PS system in a 5 h period. However, only a little of the PAEs could be removed when PS only was added. This might be because the reduction potential of persulfate was not high enough to degrade PAEs. However, when MIL-101(Fe) was added without PS, around 21% of DEP and 26% of DBP could be removed

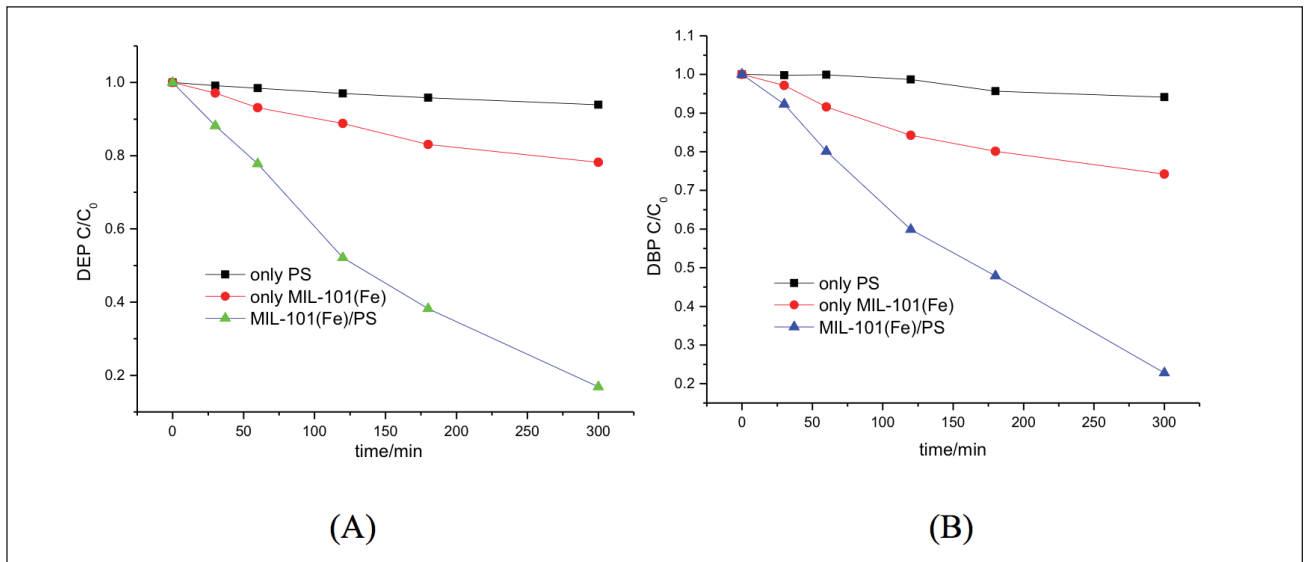


2. X-ray diffractometer (XRD) patterns of MIL-101(Fe).

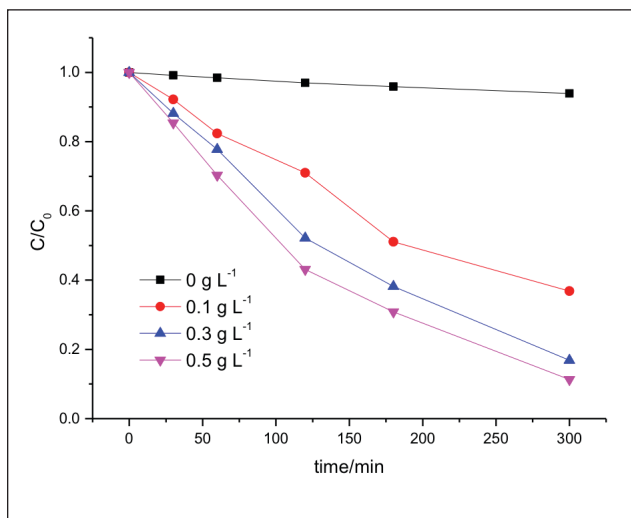


3. Scanning electron microscope (SEM) images of MIL-101(Fe).

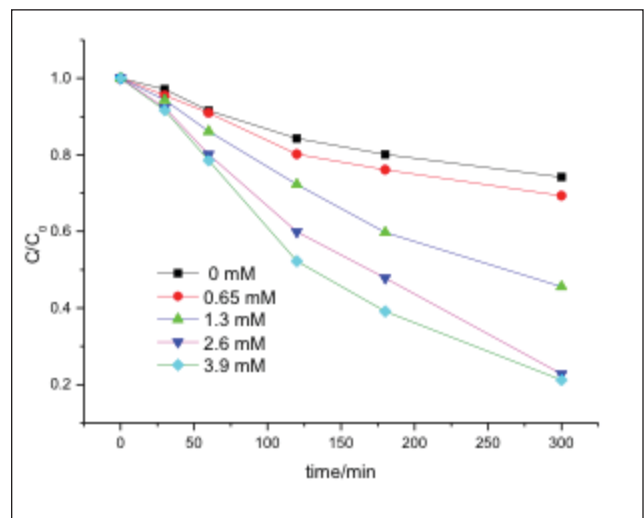
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5. Removal of diethyl phthalate (DEP) and dibutyl phthalate (DBP) in different conditions. Conditions: DEP or DBP = 3 mg L⁻¹, persulfate (PS) = 2.6 mM, MIL-101(Fe) = 0.3 g L⁻¹.



6. Removal of DBP in different amount of MIL-101(Fe). Conditions: DEP = 3 mg L⁻¹, PS = 2.6 mM.



7. Removal of DBT in different amount of PS. Conditions: DEP = 3 mg L⁻¹, MIL-101(Fe) = 0.3 g L⁻¹.

in 5 h. Thus, the MIL-101(Fe) could absorb PAEs. This absorption ability could contribute to PAE removal. According to BET measurement and other studies, the BET surface area could be more than 1000 m² g⁻¹. Such a large area offers effective absorption of PAEs. We know that adding MIL-101(Fe) and PS together greatly increases the efficiency of DBP and DEP removal. This phenomenon indicated that the transition metal center of iron could activate PS, which can produce radicals for removing pollutants. The phenomenon of absorption and PS activation occurred at the same time, and these two pathways together promoted PAEs degradation.

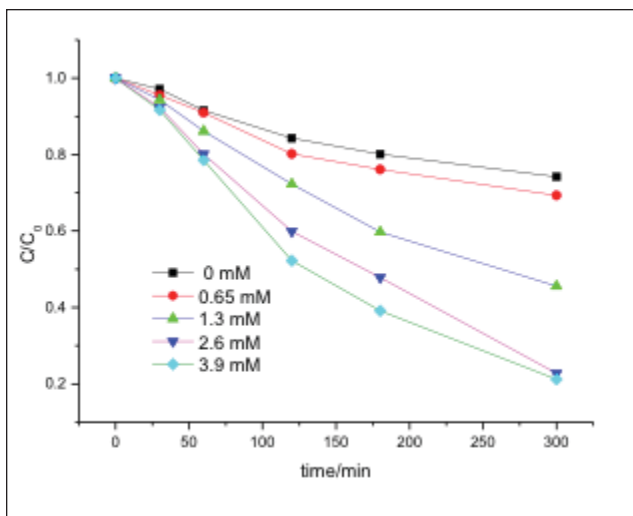
Effect of reaction parameters PAEs removal

Our analysis indicated that MIL-101(Fe) could absorb DEP and DBP, and also help activate PS for further DEP and DBP removal.

To study the effect of the MIL-101(Fe) and PS dosing more easily, DBP was chosen as the target pollutant in the following research.

Figure 6 shows the effect of MIL-101(Fe). The efficiency increased as the amount of MIL-101(Fe) increased. That might be because the increased amount of MIL-101(Fe) offered more sites for PS activation. Removal efficiency did not increase significantly when the amount of MIL-101(Fe) was more than 0.3 g L⁻¹.

Because PS has a great effect on the treatment process and operational costs, it is important to investigate the effects of using differing amounts of PS. As **Fig. 7** shows, the efficiency of degradation gradually increased as the amount of PS increased. More persulfate could offer more opportunities to contact MIL-101(Fe) to produce more radicals for PAEs degradation.



8. Removal of DBT in different initial pHs. Conditions: DEP = 3 mg L⁻¹, MIL-101(Fe) = 0.3 g L⁻¹, PS = 2.6 mM.

dation. However, the removal efficiency did not increase obviously as the PS was more than 2.6 mM. Thus, the material and PS amounts must be controlled when applying a MIL-101(Fe)/PS system for PAEs removal.

The initial pH of traditional Fenton system based on H₂O₂/Fe²⁺ is below 3.5. However, the range of initial pH for persulfate based reaction is larger. As shown in **Fig. 8**, as initial pH changed from 3.0 to 7.5, the reaction ratio changed little.

This is because persulfate is an acid oxidant, which can make the pH of wastewater acid and keep the reaction process.

CONCLUSION

Pulp and papermaking industries make important contributions to the development of society. However, raw wastewater and effluents contain various pollutants, which do harm to human health and affect sustainable development. PAEs, including DEP and DBP, which could be potential endocrine-disrupting compounds (EDCs), were still detected after biological treatment. This research tried to apply metal organic frameworks MIL-101(Fe) to activate persulfate for PAEs removal. We found that a MIL-101(Fe)/PS system could remove DEP and DBP. The method we describe provides a feasible way to remove phthalates from papermaking wastewater. **TJ**

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ABOUT THE AUTHORS

We chose this research topic because it is meaningful to study the removal of phthalates from papermaking wastewater by MIL-101(Fe) in the presence of persulfate. This is the first step in further studies.

The most difficult aspect of this study was that it needed more effort for this technique in the actual application. We learned that advanced oxidation processes based on persulfate activation could degrade phthalates in water. We found it interesting that phthalates in the model system could be effectively degraded.

The results of our study could help mills find more methods for wastewater treatment and pay more attention to phthalates pollution from mills. The next step is to improve the effect of the technique.

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Wan



Ma



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