Hybrid membrane bioreactor for water recycling and phosphorous recovery

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Abstract This paper deals with the performance of hybrid membrane bioreactor (MBR) combining the pre-coagulation/sedimentation and membrane bioreactor. The hybrid MBR not only produces the treated water with excellent permeate quality but also shows much lower membrane fouling than the conventional MBR. It may come from its extremely low F/M ratio to maintain the low viscosity even in the high MLSS concentration range of about 20,000 mg/l. Some results of microbial community analysis in MBRs was conducted to demonstrate the other reason for its lower membrane fouling. Hybrid MBR has a high potential to be used for the recycling use of the municipal wastewater.
Coagulated sludge produced in the hybrid MBR is a promising phosphorous resource. This paper also contains a recent progress of phosphorous recovery technology, which uses a new phosphoric acids absorbent, i.e., the hexagonal mesostructured zirconium sulfate (ZS). The ZS has the extremely high adsorption capacity of phosphoric acids through the anion exchange. The adsorbed phosphoric acids are released from the ZS in a high pH range of about 13. .

Keywords Water recycling, Phosphorous recovery, Hybrid MBR,
Pre-coagulation/ sedimentation

Introduction

Necessity of recycling use of water has been recognized to resolve the shortage of water resources. Municipal wastewaters seem to be an important water resource for recycling use. Membrane bioreactor (MBR) is a key technology for creating the reclaimed water resource. MBR has been applied to the municipal wastewater treatment since 1980s. The first generation MBR combines a cross-flow type membrane filtration with outside bioreactor and mixed liquor is re-circulated into the bioreactor. The operation pressure is high and re-circulation pump is needed. In addition, it is reported that microorganism activity decreases due to the re-circulation of the mixed liquor. The second generation MBR submerges membrane module directly in the bioreactor (Yamamoto et al.,1989). As a result, circulation pump is not needed and the operating pressure is low. However, it is reported that accumulated dissolved organic matter in the bioreactor decreases the membrane permeability in the submerged MBR more seriously compared with the first generation MBR. Therefore, chemical cleaning of membranes must be frequently carried out. In order to reduce the chemical cleaning frequency, the authors have combined the pre-coagulation/ sedimentation process with the submerged MBR, which is called hybrid MBR. The authors (Itonaga, Kimura and Watanabe, 2004; Watanbe and Itonaga, 2004) demonstrated several advantages of hybrid MBR. We have reported an interesting relationship among the membrane fouling, mixed liquor viscosity and microbial communities in the MBR. In this paper the previous research results of the hybrid MBR are summarized and some new findings about the efficient removal of organic micro-pollutants are reported.
The amount of rock phosphorous remained in the world is limited. Therefore, it is important to develop the technology and social system for the recycling use of the

phosphorous. Municipal wastewater contains 5 to 10 mg /l of phosphorous as suspended and soluble forms. Japan imported about 3.5 x 10^5 tons of rock phosphorous as P_2O_5 and 1.0 x 10^5 tons of phosphorous as P_2O_5 were contained in the burned ash of sewage sludge in 1999. Therefore the municipal wastewaters are significant phosphorous resource. This paper also deals with a new recovery technology of phosphorous from municipal wastewaters using a new adsorbent i.e., hexagonal mesostructured zirconium sulfate.

Material and methods

Hybrid MBR

The hybrid MBR combining pre-coagulation/sedimentation with submerged membrane bioreactor is described in Fig.1. Pilot plants of the hybrid MBR have been located in a municipal wastewater treatment plant, Sapporo city. The details of the pilot plant study are included in the previous papers (Itonaga and Watanabe, 2004;. Watanbe and Itonaga, 2004). Coagulated sludge separated in JMS was used as a source of phosphorous recovery.

Hexagonal mesostructured zirconium sulfate (ZS)

A few research groups found that phosphoric acid can be adsorbed in the pore structureof zirconium sulfate. Iwamoto et al.(2002) have synthesized the hexagonal mesostructured zirconium sulfate (ZS). The ZS was synthesized from $Zr(SO4)_2 \cdot 4H_2O$ and hexadecytrimethylammonium bromide($C_{16}TMABr$, template) by the procedure

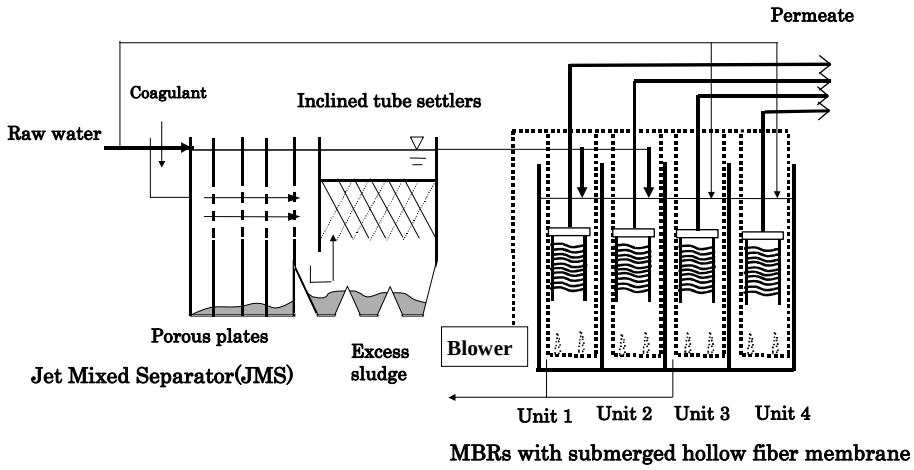


Fig. 1 Schematic diagram of hybrid MBR pilot plant

reported previously. The ZS powders show characteristics (100), (110), and (200) XRD diffractions of the hexagonal structure with d spacing of 4.28-4.06, 2.47-2.36, and 2.17-2.03 nm. The chemical formula of the ZS is $Zr\ (HSO_4^-)\ (OH)_{3.5}\ (C_{19}H_{42}N)_{0.5} \cdot 2H_2O$. Fig.2 shows the structure and ion exchange model for ortho-phosphate of the ZS.

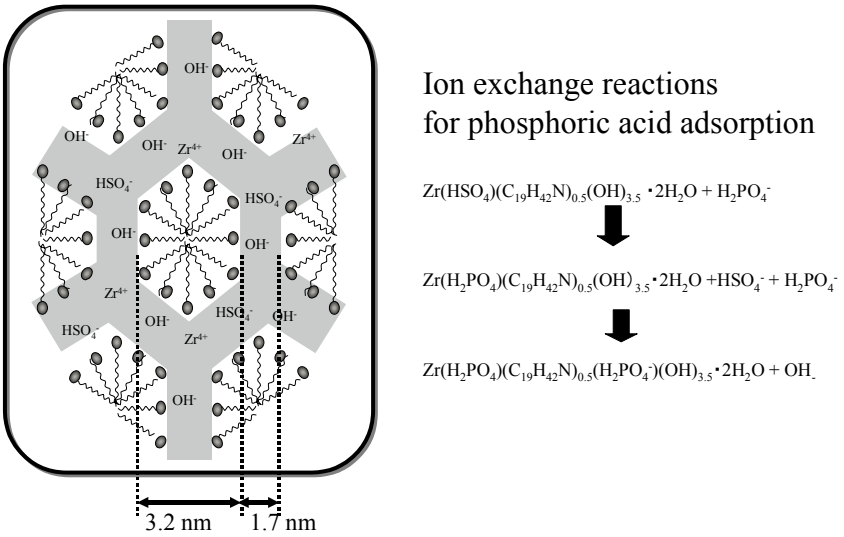


Fig. 2 Structure and ion exchange mechanism of hexagonal mesostructured zirconium sulfate

Results and discussion

MBR performance

Fig.3 shows variation of trans membrane pressure (TMP), and the average DOC concentration of mixed liquor and permeate during the operation period of 0-70 days and 71-120 days in hybrid MBR (HMBR, Unit 2) and conventional MBR (CMBR, Unit 4), into which the effluent from the JMS and primary clarifier was fed, respectively.

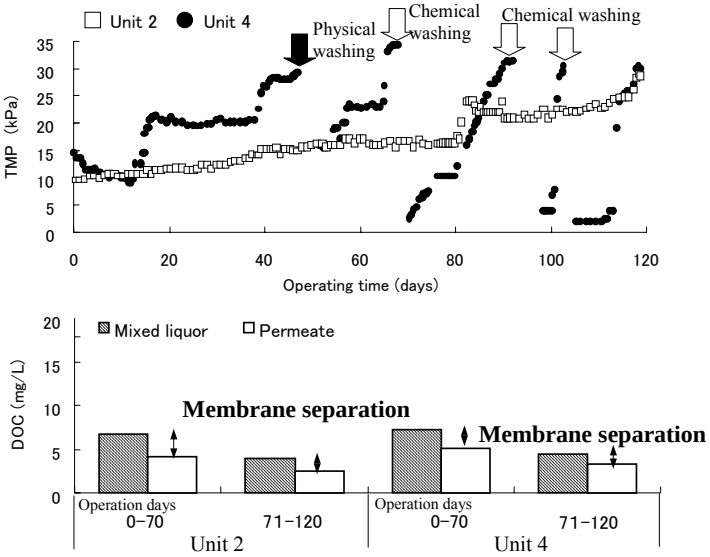


Fig. 3 Trans membrane pressure and DOC concentration during the operating period

The mixed liquor in each MBR was centrifuged with 3000 rpm for 5 min, and the supernatant was filtered through a membrane with the average pore size of 0.45 μm,

then DOC concentration was measured. DOC concentration in the mixed liquor and permeate in Unit 2 was lower than those in Unit 4. Fig.4 shows the comparison of non-biodegradable and biodegradable DOC among the treated water by the activated sludge process, CMBR (Unit 4) and HMBR (Unit 2).

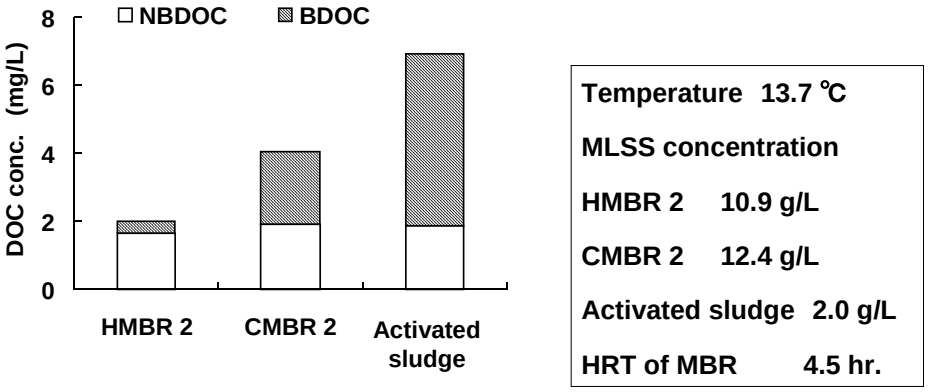
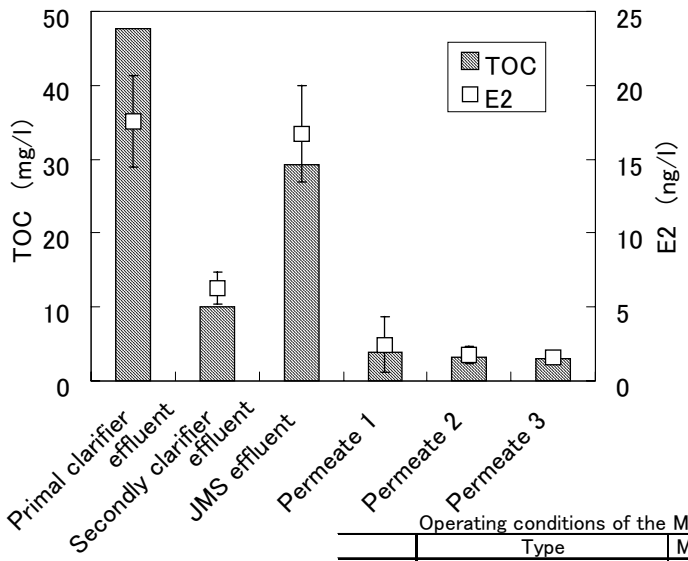


Fig.4 Comparison of biodegradable DOC among HMBR, CMBR and AS

HMBR produces the treated water with much lower biodegradable DOC (BDOC) compared with the other processes. Lower BDOC is required in the transport process of the reclaimed waters. If MBR effluent is discharged into a clean water environment for indirect recycling use, the effects of micro-pollutants such as the estrogenic substances and pharmaceuticals on the ecological system should be considered. Figs.5 and 6 show the removal efficiency of estrogenic substance (17 β -estradiol, E2) and pharmaceuticals (Kubo et al., 2003; Kimura et al., 2004), respectively. Pharmaceuticals with 2 aromatic rings such as ketoprofen, mefenamics and naproxen were effectively removed by the MBRs.



Operating conditions of the MBRs

	Type	MLSS	HRT
MBR 1	Hollow fiber (MF : HMBR)	5 g/l	4.5 h
MBR 2	Flat type (UF : HMBR)	8 g/l	2 h
MBR 3	Flat type (MF : HMBR)	15 g/l	4.8 h

Fig.5 Removal efficiency of estrogenic substance in MBRs

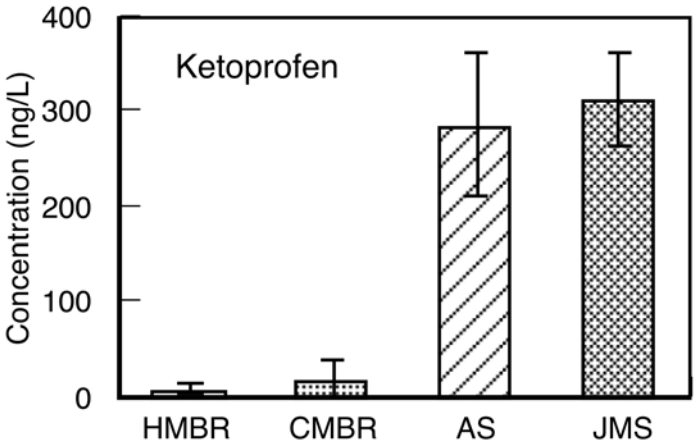


Fig.6 Removal efficiency of pharmaceuticals among HMBR, CMBR and AS

The TMP increased more rapidly in Unit 4 from the beginning of the operation, compared with Unit 2. The physical washing of the membranes by water jet in Unit 4 was carried out after 47 days' operation. After the physical membrane washing of Unit 4, the TMP was decreased from 29 to 16 kPa. This washing effect means that the TMP increased mainly due to the cake formation on the membrane surface. In the previous paper (Watanabe and Itonaga, 2004), we compared the activated sludge floc size distribution among the hybrid MBR, conventional MBR and conventional activated sludge process. We have found that higher the organic loading larger the activated sludge floc size. We also investigated the relationship between the MLSS concentration and mixed liquor viscosity. The hybrid MBR (Unit 2) kept low mixed liquor viscosity even in the high MLSS concentration range. On the other hand, the mixed liquor viscosity in the conventional MBR (Unit 4) increased with increasing MLSS concentration. The sticky cake layer will be formed on the membrane surface in the high mixed liquor viscosity. We may conclude that membrane fouling occurs due to the sticky cake layer formation, which can not be detached by the physical washing in the conventional submerged MBR, but such a sticky cake layer does not formed in the hybrid MBR because of lower mixed liquor viscosity due to extremely low organic loading. Lower organic loading results in less production of EPS, where the size of activated sludge is smaller due to poor agglomeration ability. The authors (Itonaga et al., 2004) also demonstrated that pre-coagulation/sedimentation reduced the irreversible membrane fouling caused by the adsorption of soluble organic matter such as the EPS inside the pores.

Microbial community analysis in MBR

The microbial community structure of HMBR, CMBR and activated sludge process (AS) was analyzed by polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) and fluorescence in situ hybridization (FISH) techniques (Hiraiwa et al.). Dice coefficient of similarity (Cs) was introduced to study the microbial community similarity among the HMBR, CMBR and AS. DGGE fingerprints were manually scored by the presence or absence of comigrating bands (each band representing a single bacterial species), independent of intensity (species abundance). Pair wise community similarity was quantified using Dice coefficient of similarity, Cs=

2j / (a + b) where j is the number of common bands between samples A and B, respectively. This coefficient ranges from 0 (no common band) to 100 % (identical bands patterns). The similarity of microbial community structure in HMBR 1 (unit 1), HMBR2 (unit 2), CMBR1 (unit 3), CMBR2 (Unit 4) and AS taken after 78 days of operation were quantified using Dice coefficient of similarity. The HMBR supported a significantly different microbial community structure comparing with those in the CMBR as it was only 46.9 to 59 % similar to the CMBR and 37.5 to 44.8 % similar to the AS microbial community. A more quantitative analysis of the microbial community structure was carried out by FISH analysis. It revealed that the population of Chloroflexi bacteria (formerly known as green nonsulfar bacteria) was four times greater than the HMBR and two times greater than the AS. It is consistent with the microbial community analysis by PCR-DGGE. The filamentous Chloroflexi is ubiquitous and conspicuous members of AS wastewater treatment plant microbial communities. However, their roles in the wastewater treatment have not been well studied in relation to the ecophysiology of Chroroflexi. Therefore, we have been further conducting the identification and characterization of this group of bacteria. Miura et al. (2005) have found that Chloroflexi is an important bacterium in the formation of the microbial flocs, as seen in Fig.7

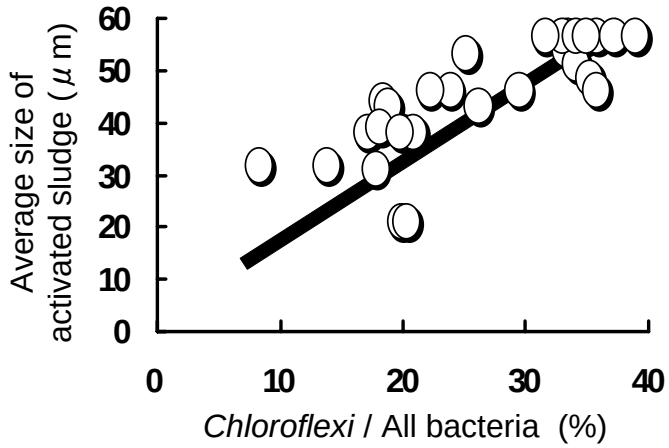


Fig.7 Relationship between Chloroflexi/all bacteria ratio and floc size

As already described, floc volume or size has a significant effect on the mixed liquor viscosity. We have concluded that flocculation effect of Chlororoflexi increases the viscosity of mixed liquor to cause more rapid membrane fouling. However, we should consider the positive role of Chlroroflexi as a scavenger of cells with low rRNA content, which are high in CMBR. Fig. 8 shows the change of TMP, water temperature, Chloroflexi/ all bacteria ratio and soluble saccharide concentration in CMBR with increasing operation time when MLSS was kept around 10 g/l.

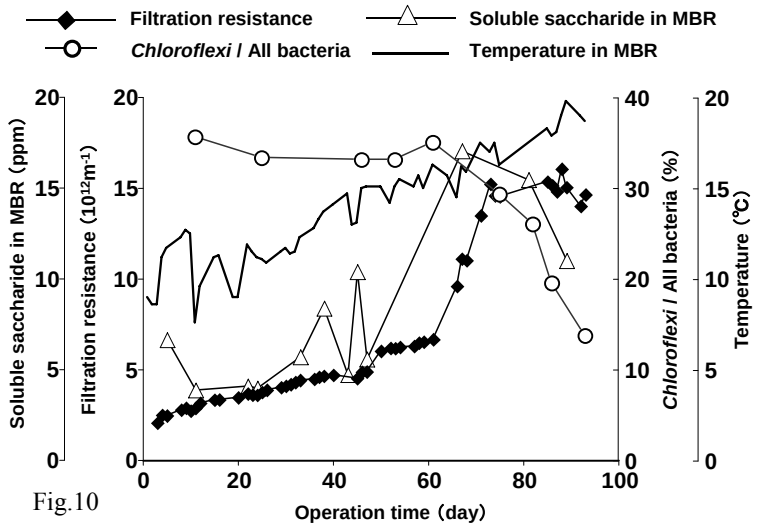


Fig. 8 Trans membrane pressure change and Chloroflexi/all bacteria ratio

Until 60 days of operation, TMP and saccharide concentration seemed to be stable even in water temperature range of 10 to 15 ℃. Chloroflexi /all bacteria was about 35 % during the operation time. After 60 days of operation, TMP decreased and saccharide concentration increased along with the decrease in Chloroflexi/all bacteria with increasing water temperature. These phenomena may be because higher water temperature stimulates the growth of other bacteria, which have less decomposing ability of soluble saccharide than Chloroflexi. However, we do not have sufficient information to support this hypothesis, and further studies should be conducted.

Phosphoric acids adsorption by ZS

The authors (Tatsumi et al., 2004) have carried the research on phosphorous recovery using the ZS based on the concept as shown in Fig.9.

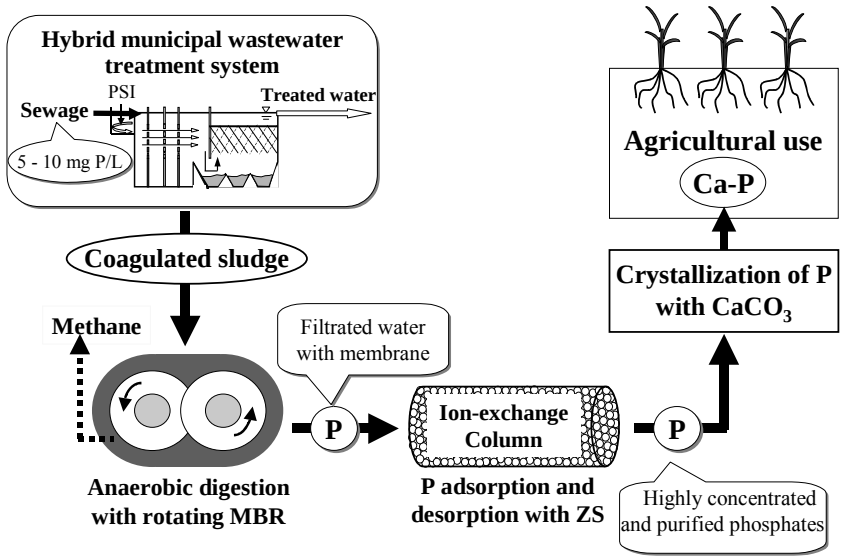


Fig. 9 Phosphorous recovery system from municipal wastewater

Phosphorous contained in the municipal wastewater can be concentrated through the recovery processes. The ZS may be used after anaerobic membrane bioreactor to purify and condense phosphoric acids. The optimum adsorption pH is in the range of 3 to 6.5 where $H_2PO_4^-$ is predominant. Table 1 describes the comparison of the saturation capacity of phosphoric acids in various adsorbents.

Table 1 Adsorption ability of various adsorbents

Adsorbent	Amount of P adsorption (μ mol/g)
ZS	3330
Zirconium hydrous oxide	2066
Zirconium ferrite	969
Complex of zirconium hydrous oxideand and activated carbon	387
Impregnated activated alumina with aluminum sulfate	1195
Activated alumina	613

The ZS has extremely high saturation capacity. Fig.10 shows the desorption results of phosphoric acids from the ZS by NaOH (pH=13) or 50 mmol/l of Citric acid (pH=5.0).

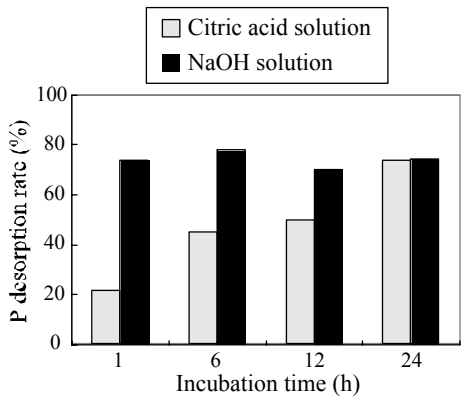


Fig. 10 Desorption efficiency of phosphoric acids from ZS

Through the adsorption and desorption process of the ZS, phosphoric acids was purified and condensed.

Conclusions

This paper reported the experimental results regarding the performance of the hybrid MBR (HMBR) combining of pre-coagulation/sedimentation with submerged MF membrane bioreactor. HMBR had better permeate quality and less membrane fouling compared with conventional MBR. Phosphorous contained in the coagulated sludge can be recovered by the hexagonally mesostructured zirconium sulfate-surfactant micelle (ZS). The experimental results of adsorption and desorption of phosphoric acids by the ZS were reported. The ZS has the highest saturation capacity of phosphoric acids among

the existing absorbents.

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