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Mechanism of nitrogen removal by a hybrid membrane bioreactor in municipal wastewater treatment

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ABSTRACT

A pilot scale experiment was conducted to evaluate the characteristics of nitrogen removal in a hybrid membrane bioreactor (HMBR) which was developed by introducing biofilm carriers into a conventional membrane bioreactor (CMBR) in municipal wastewater treatment for more than three months. During the experimental period, the HMBR performed well on organic matter and nitrogen removal. The COD, NH_4^+-N, and TN removal rate in the HMBR was enhanced by 3.8, 5.4, and 12.7%, respectively, compared to the CMBR. The effluent TN in the CMBR ranged from 21 to 33 mg L^{-1}, while it dropped to 15–24 mg L^{-1} in the HMBR. Further investigation was conducted on the property of activated sludge such as biomass quantity, sludge volume index, particle size distribution, and sludge particle structure. Results showed that the activated sludge particle size in HMBR was increased by nearly 100% comparing with that in CMBR, and the sludge in HMBR was more compact, which means that the effect of simultaneous nitrification and denitrification (SND) can occur in the HMBR sludge more easily. Like in the sludge, SND can also occur in the thick biofilm. According to the experiment, the contribution of activated sludge and biofilm in HMBR to the enhancement of TN removal rate was 7.7 and 5%, respectively.

Keywords: Hybrid membrane bioreactor; Nitrogen; Simultaneous nitrification and denitrification; Activated sludge; Biofilm

1. Introduction

The adverse environmental impacts of nitrogenous compounds in waters are well known. These impacts include promotion of eutrophication, toxicity to aquatic organisms, and depletion of dissolved oxygen (DO) due to bacterial oxidation of ammonia to nitrate [1]. Thus, the removal of nitrogenous compounds from wastewater is very important.

Biological nitrogen removal is achieved by aerobic nitrification and anoxic denitrification using autotrophic nitrifying bacteria and heterotrophic denitrifying bacteria [2]. In order to remove nitrogen, it is necessary to provide different conditions in two

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separate reactors due to the existence of nitrifying bacteria and denitrifying bacteria. In general, a conventional biological nitrification–denitrification system must contain two separated tanks, one is an aerobic tank and the other is an anoxic tank [3]. In the aerobic tank, the ammonia is oxidized to nitrite and the unstable nitrite is readily oxidized to nitrate. This process is called nitrification. In the anoxic tank, denitrification occurs and bacteria utilize nitrate as a terminal electron acceptor in place of oxygen. Nitrate is ultimately reduced to nitrogen gas (N_2) and released into the atmosphere.

In recent years, studies have revealed that nitrification and denitrification can occur in a single reactor. This process has been termed as simultaneous nitrification and denitrification (SND) [4]. SND has gained significant attention due to its potential to eliminate separate tanks required in conventional treatment plants and consequently to simplify the plant design, saving space and time. Some researchers have documented that SND could occur as a consequence of DO concentration gradients within microbial flocs or biofilms, due to diffusion limitation [5,6]. Oxygen may be depleted at significant rates within the granules so that the DO cannot penetrate the entire granule depth. In other words, nitrifiers will be more active on the surface of the granules, whereas the anoxic microzones in the center of granules allow heterotrophic denitrifiers to produce nitrogen gas. In biological nitrogen removal activated sludge process systems that operate with a mixed liquor suspended solids (MLSS) concentration of approximately 3,000–5,000 mg L^{-1}, the SND process was promoted under DO concentrations around 0.5 mg L^{-1} [5,7].

Membrane bioreactor (MBR) system is characterized by high-quality effluent, short hydraulic retention time (HRT), small sludge production and perfect nitrification, which are induced from high MLSS condition [8–10]. However, the denitrification in the conventional membrane bioreactor (CMBR) with high DO level is unsatisfied. Some researches have introduced the alternating aerobic and anaerobic conditions in a CMBR by intermittent aeration for simultaneous removal of nitrogen [11,12], but the filtration operation was limited only during aeration period because of membrane fouling control. Subsequently, a continuous aerated MBR with a separated anoxic tank for denitrification, pre-denitrification/nitrification MBR, was developed for continuous filtration operation [13]. Although this MBR system can remove nitrogen effectively, the cost is higher. In consequence, studies on SND in the MBR were conducted. Sarioglu et al. indicated that a total nitrogen (TN) removal efficiency of greater than 95% could be obtained by the means of SND when operating a MBR system without an anoxic reactor with biomass concentrations greater than 16,000 mg L^{-1} and maintaining the bulk DO level below 1.0 mg L^{-1} [14]. Murat Hocaoglu et al. evaluated the effect of low DO concentrations on SND in a CMBR system treating black water and found that when the CMBR was operated at a sludge age of 60 d, nitrogen removal remained optimal within the DO range of 0.15–0.35 mg L^{-1} [15]. Paetkau and Cicek investigated the nitrogen removal in a SND-MBR with low DO concentrations and a CMBR with high DO levels, and the comparison results showed that the SND-MBR was able to remove 80% of the TN with 48% of influent TN being removed by SND [16]. Dramatically, Ding et al. exploited a novel integrated vertical membrane bioreactor (IVMBR) composed of both anoxic and aerobic zones based on the installation of a three-phase separator to remove nitrogen, and the optimal TN removal efficiency of about 76.4% in the IVMBR was obtained when the internal recycle rate is 400% [17].

In the author's previous study [18], a hybrid membrane bioreactor (HMBR) was developed by introducing biofilm carriers into a CMBR, which operated for about one year for municipal wastewater treatment. Results showed that the HMBR can not only remove chemical oxygen demand (COD) and ammonia nitrogen (NH_4^+-N) effectively, but also decrease TN significantly. The TN removal rate in the CMBR was only about 37%, while it exceeded 50% in the HMBR. However, the mechanism of TN removal enhancement by the HMBR was unclear.

In this paper, a pilot scale HMBR and a CMBR operated for municipal wastewater treatment at the same conditions for more than three months and the attention was mainly focused on the mechanism of nitrogen removal by the HMBR.

2. Materials and methods

2.1. Raw wastewater characteristics

The experiment was conducted at a municipal wastewater treatment plant in Xi'an, China. The raw wastewater fed to the experimental set-up was from the inlet of the plant and its characteristics are shown in Table 1.

2.2. Experimental set-up and operational conditions

As shown in Fig. 1, the pilot set-up used in this study consisted of a rectangular aerated tank equipped with a hollow fiber microfiltration (MF) membrane module and associated with biofilm

Table 1
Characteristics of the raw water

COD (mg L^{-1})	243–857
NH_4^+-N (mg L^{-1})	20.3–47.1
TN (mg L^{-1})	24.7–55.8
TP (mg L^{-1})	4.7–13.5
TSS (mg L^{-1})	210–1,260
pH	7.1–7.7
Temperature (°C)	14.1–26.3

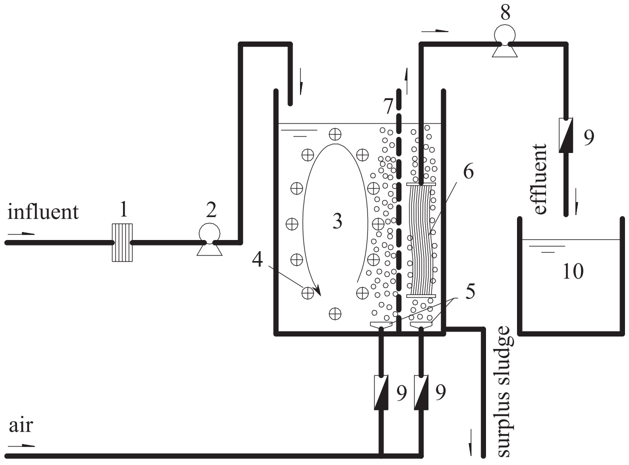

Fig. 1. Schematic diagram of the pilot set-up. (1) Screen; (2) feed pump; (3) aeration tank; (4) biofilm carrier; (5) air diffuser; (6) MF membrane module; (7) perforated wall; (8) suction pump; (9) flowmeter; (10) effluent tank.

carriers, pump, air diffusers, flowmeters and so on. To avoid the biofilm carriers entering the membrane module and hindering the fibers trembling, the aerated tank was partitioned by a perforated wall into two rooms, one as the aeration tank with biofilm carriers and the other as the membrane tank holding the MF membrane module. With or without the biofilm carriers in the aeration tank, the set-up could perform the function of HMBR or CMBR.

The MF membrane module submerged in the tank was manufactured by Tianjin Motimo Membrane Co. Ltd, China. The membrane was made of polyvinylidene fluoride (PVDF) and its pore size was 0.2 μm. The Kaldnes K_3 biofilm carriers suspended in the tank were provided by AnoxKaldnes Corporation, Norway. Its main parameters are shown in Table 2.

Table 2
Main parameters of the Kaldnes K_3 biofilm carrier

Material	Polyethylene (PEHD)
Density of PEHD (g cm^{-3})	0.95
Nominal diameter (mm)	25
Nominal length (mm)	12
Fill fraction in the tank	50%

This experiment was continuously conducted for more than three months. During the period, the MF membrane module operated under intermittent operation of the suction pump in an 8 min "on" and 2 min "off" cycle. When the transmembrane pressure (TMP) reached 20 kPa, membrane cleaning was conducted according to Huang et al. [19]. The membrane flux was maintained constantly at 10 L m^{-2} h^{-1}, the HRT and sludge retention time (SRT) were controlled at 10 h and 10 d, respectively. When the set-up operated as HMBR mode, the attached biomass was measured at the level of 1,710 mg L^{-1}, the whole biomass in the reactor was nearly 6,000 mg L^{-1}. The operational condition of the pilot set-up is shown in Table 3.

2.3. Chemical analysis

Samples were collected from the raw wastewater and the effluent two or three times per week. Total suspended solids (TSS), volatile suspended solids (VSS), COD, NH_4^+-N, and TN were analyzed by following the Standard Methods [20]. The pH value was determined using a pH meter (Model 525, Thermo Orion). The DO value was monitored using a DO meter (Model 842, ORION). The suspended biomass concentration was determined as MLSS. The TMP value was monitored using a vacuum gauge.

To measure the attached biomass on the carriers, 25 carriers representing about 0.3% of the total number were carefully collected from the reactor and dried for 2 h at 105°C. The total weight of the dried carriers was weighed and the weight of the attached biomass on the carriers was obtained by subtracting the original weight of the clean carriers from the total weight. The attached biomass concentration was finally expressed as mg L^{-1} considering the total number of carriers and the total volume of the reactor.

2.4. Characterization of the activated sludge properties

In this study, the sludge volume index (SVI) was used as a parameter to characterize the settleability of the activated sludge. The morphological characteristics of the sludge particles were observed using an optimal

Table 3
Operational condition of the pilot set-up

DO (mg L^{-1})	0.8–1.1
pH	6.9–7.2
MLSS (mg L^{-1})	4,110–4,350
MLVSS (mg L^{-1})	2,840–3,002

microscope (BX60, Olympus) equipped with a digital camera (Infinity 3, Olympus) and the size distribution of the sludge particles was analyzed using a laser granularity distribution analyzer (LS 230/SVM+, Coulter, USA).

3. Results and discussion

3.1. COD removal

During the experimental period, the vast majority of wastewater temperature in the reactor was stable and varied in the range of 18–23℃. Therefore, temperature likely did not limit the activity of organisms in the reactor. As shown in Fig. 2, the HMBR represented a good performance on COD removal. The average COD in the HMBR effluent was about 20 mg L^{-1} with the average COD removal rate of 95.2%, while it was about 40 mg L^{-1} in the CMBR effluent with the COD removal rate of 90.7%.

The total biomass in the CMBR was approximately 4,200 mg L^{-1}, while it was nearly 6,000 mg L^{-1} in the HMBR. The total biomass enhancement must be the main reason for the high COD removal by the HMBR [18,21,22].

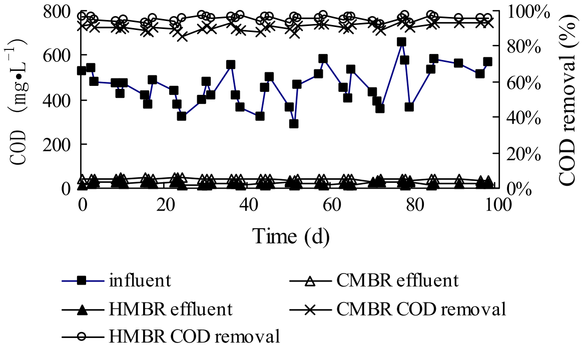

Fig. 2. COD removal in the CMBR and HMBR.

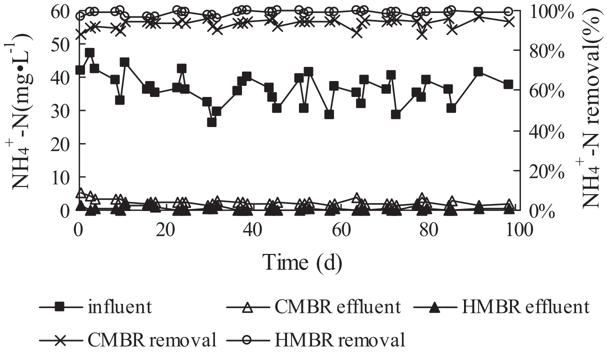

Fig. 3. Ammonia-nitrogen removal in the CMBR and HMBR.

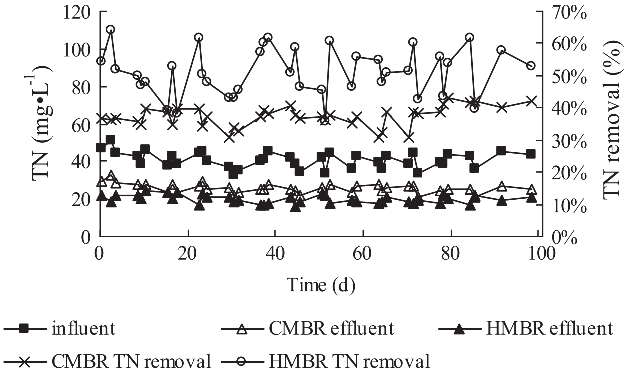

Fig. 4. TN removal in the CMBR and HMBR.

3.2. Nitrogen removal

During the experimental period, the vast majority of wastewater temperature in the reactor was stable and ranged from 18 to 23℃. Therefore, temperature likely did not limit the activity of ammonia-oxidizing bacteria and nitrite-oxidizing bacteria. As shown in Fig. 3, the HMBR performed well on NH_4^+-N removal. The average NH_4^+-N removal rate of the HMBR was

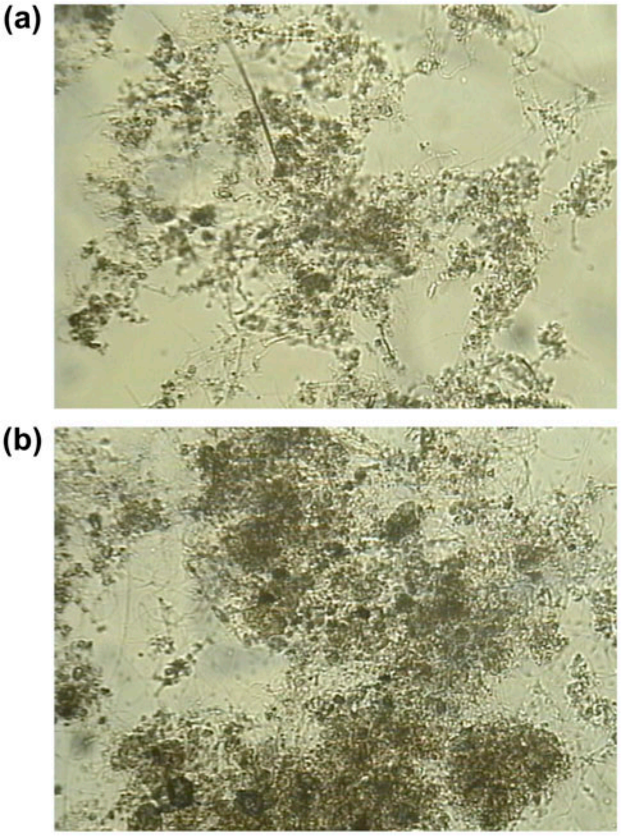

Fig. 5. Microscopic images of the sludge particles in (a) CMBR and (b) HMBR.

98.9%, and 5.4% NH_4^+-N removal enhancement was obtained by the HMBR compared to the CMBR. The SRT for the biofilm was higher than that for the activated sludge, which made it feasible for the growth of nitrifying microorganisms preferentially on the carriers and consequently resulted in a higher NH_4^+-N removal by the HMBR [23].

As shown in Fig. 4, the HMBR also performed well on TN removal. The average TN removal by the CMBR was only 37.3%, while the HMBR had a better removal rate of 50%, and 12.7% TN removal enhancement was obtained by the HMBR compared to the CMBR.

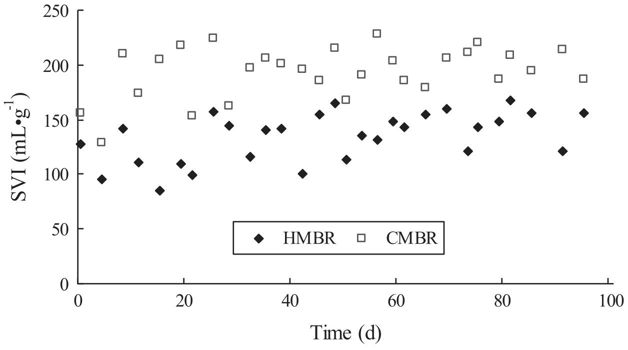

Fig. 6. SVI in the CMBR and HMBR.

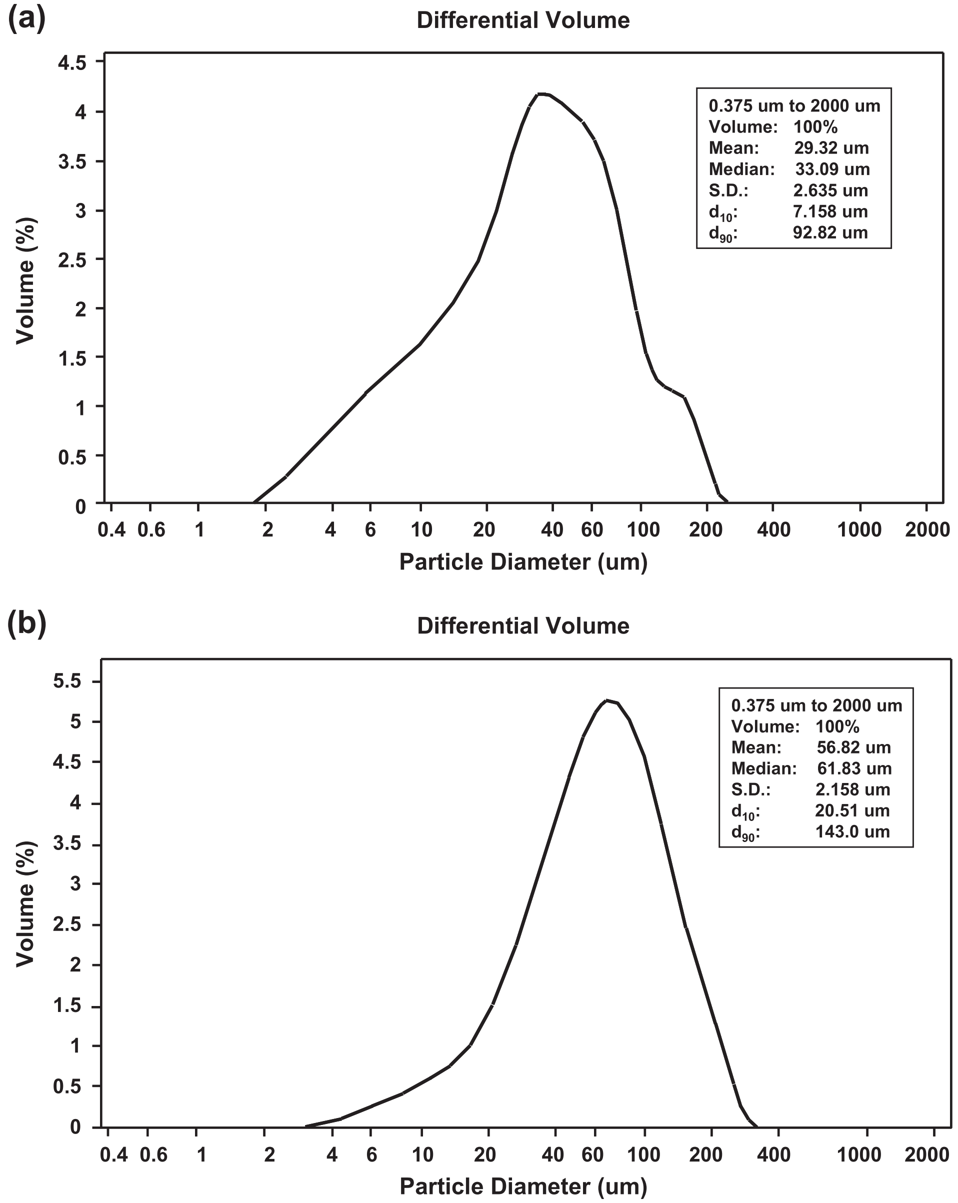

Fig. 7. Sludge particle size distribution in (a) CMBR and (b) HMBR.

3.3. Activated sludge properties

Fig. 5 shows the images of the activated sludge particles in the CMBR and HMBR. It turned out that the sludge particle in the HMBR was much denser than that in the CMBR. Considering SVI, it was approximately 134 mL g^{-1} for the HMBR, while it was about 194 mL g^{-1} for the CMBR (see Fig. 6). This also provided evidence that the density of sludge in the HMBR was higher than that in the CMBR on the other side.

As shown in Fig. 7, the mean value of sludge particle diameter in the CMBR was only 29 μm, while it was 57 μm in the HMBR. It means that the sludge in the HMBR was bigger than that in the CMBR.

In general, as the sludge particle was larger, the resistance of DO's entry into the sludge was higher and the anoxic environment in the sludge would form more easily. Thus, the effect of denitrification would occur. Andreadakis believed that the suitable particle size for SND was 10–70 μm [24], Klangdeun and Jurg believed that the suitable particle size was 50–110 μm [6].

DO was another factor which can affect nitrogen removal. When DO exceeds 2.6 mg L^{-1}, it can pierce through the sludge completely. According to Muuch et al., DO should be controlled at about 0.5 mg L^{-1} [5]. When Helmer and Kunst controlled DO at about 1 mg L^{-1} in a SBR system, the nitrogen removal performance of the system was well and 50% TN removal rate was obtained [25].

In this experiment, DO was controlled at about 1 mg L^{-1}, the density, settleability, and particle size of the sludge in the HMBR were all higher than those in the CMBR. Therefore, the anoxic environment in the HMBR sludge occurred more easily than in the CMBR sludge and the denitrification would happen. It must be one reason why the HMBR can improve TN removal compared to the CMBR.

3.4. Contribution to the TN removal by the sludge and the biofilm

The biofilm carriers in the HMBR were all taken out from the aeration tank and the nitrogen removal performance of the system was determined immediately. It was found that without the biofilm carriers in the tank, only 45% TN removal rate was obtained for the set-up. In other words, 5% TN removal rate must owe to the biofilm, because the denitrification can also occur in the thick biofilm like in the activated sludge. This must be another reason for TN removal improvement for the HMBR.

4. Conclusions

A comparison experiment was conducted between a CMBR and a HMBR in municipal wastewater treatment for more than three months and the attention was mainly focused on the mechanism of nitrogen removal by the HMBR. Results showed that the HMBR can remove nitrogen effectively and 12.7% of TN removal enhancement was obtained by the HMBR compared to the CMBR. SND efficiency has a significant correlation with DO and particle size. During the experimental period, DO concentrations in both reactors were controlled at the same low level of about 1.0 mg L^{-1}, thus the TN removal enhancement by the HMBR must owe to the activated sludge particle characteristics improvement and biofilm addition. The activated sludge in the HMBR was found more compact and bigger than that in the CMBR. The average value of SVI was approximately 134 mL g^{-1} for the HMBR, while it was about 194 mL g^{-1} for the CMBR. The mean value of sludge particle diameter in the HMBR was 57 μm, while it was only 29 μm in the CMBR. Therefore, the anoxic environment in the HMBR sludge occurred more easily than that in the CMBR sludge and the denitrification would happen. Like in the activated sludge, the denitrification can also occur in the thick biofilm. According to the experiment, the contribution of activated sludge and biofilm in the HMBR to the TN removal enhancement was 7.7 and 5%, respectively.

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