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# Partial nitrification in a membrane-aerated biofilm reactor with composite PEBA/PVDF hollow fibers

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ABSTRACT

Ammonia removal via nitrite was performed in membrane-aerated biofilm reactors (MABR). Two types of hollow fiber (HF) modules, uncoated microporous polyvinylidene fluoride (PVDF) and composite polyether-block-polyamide copolymer (PEBA) coated PVDF, were used as supports for the growth of ammonia oxidizing microorganism biofilm system. For the composite HF, a suitable coating material was selected between hydrophilic and hydrophobic types of PEBA. Results reveal that hydrophobic PEBA 2533 was more suitable for bacterial adhesion. The formation of coating layer was successfully confirmed through field emission scanning electron microscope. Other surface characterizations were performed through atomic force microscopy and contact angle measurements. Partial nitrification experiments at varied feed concentrations and hydraulic retention times reveal that MABR with uncoated PVDF HF exhibited slightly higher ammonia removal than the MABR with composite HF. In terms of nitrified products, MABR with composite HF produced > 90% of the removed ammonia in nitrite form. On the other hand, around 50% of nitrite was converted to nitrate in the MABR with uncoated PVDF. Thus, between the two membranes tested, PEBA 2533 coated PVDF is the more suitable HF for ammonia removal via nitrite formation in the MABR system.

*Keywords:* Ammonia; MABR; Nitrite; Partial nitrification; Polyether-block-polyamide; PVDF

## 1. Introduction

Nitrogen removal via nitrite is a promising cost-effective and energy-efficient alternative method for the treatment of ammonia-laden wastewaters [1–3]. This technique promotes partial nitrification in which further conversion of nitrite (i.e. from ammonia oxidation) to nitrate is inhibited. With the bypassed nitrate formation route, the process becomes more straightforward and requires less alkalinity, oxygen and electron donor (i.e. carbon source) supplies than the conventional nitrification and denitrification processes [4,5].

Particularly, the so-called single reactor system for high ammonia removal over nitrite process has been

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developed wherein the growth of nitrite oxidizing bacteria (NOB) is selectively inhibited while that of ammonia oxidizing microorganisms (AOB) is promoted [1]. Various operating conditions such as temperature, ammonia feed concentration, pH, inorganic carbon (IC) supply, dissolved oxygen (DO), and sludge retention time have been manipulated for an effective partial nitrification [6].

However, it is known that ammonia oxidation is the rate-limiting step in a nitrogen removal process, mainly due to the slow growth rate and low cell yield of AOB [7]. Thus, to improve AOB microbial density, immobilization techniques using suitable support matrices such as polyurethane have been employed [6,8]. Alternatively, hollow fiber (HF) membranes are excellent support matrices due to their high specific surface area that provides ample space for microbial growth [9]. HFs have been utilized in membrane-aerated biofilm reactors (MABR) for the treatment of various types of wastewater, including nitrification and denitrification [9,10]. In MABR, oxygen ($O_2$) is typically supplied at the lumen side of the gas permeable HF to promote its fast diffusion into the biofilm that is grown on the outer surface of the HF. Microporous HF had been popular in MABRs due to high gas transfer rates but bubbling must be avoided to prevent biofilm damage and loss [10]. Alternatively, dense tubular membranes (i.e. silicone and polypropylene) have been used but they are less attractive than the microporous HFs due to their lower specific surface areas [10,11]. Composite HFs have also been developed by coating the outer wall of a microporous HF with a thin dense polymeric layer. The use of composite HFs in MABR features several advantages which include the prevention of bubble formation; it also provides the opportunity to tailor the membrane surface properties for effective biofilm development. Some reports used polyethylene/polyurethane and polyolefin membrane with skin layer on the outer surface [12,13]. But so far, there are limited reports available regarding the selection of suitable coating materials for composite HFs in MABR application.

Polyether-block-polyamide copolymer (PEBA) is an elastomeric polymer frequently used in gas separation and pervaporation [14]. Hence, PEBA can be used as a dense-coating material through which the $O_2$ required for the development of AOB biofilm could be permeated. PEBA has a tunable hydrophobic/hydrophilic character since its copolymer compositions can be varied [15]. Thus, it is possible to find a suitable type of PEBA as a coating material for effective attachment and growth of AOBs.

In this study, two types of PEBA (i.e. hydrophobic and hydrophilic) polymers were coated on microporous polyvinylidene fluoride (PVDF) HF for MABR. Bacterial adhesion tests were performed to select the most suitable PEBA coating material. Partial nitrification experiments in MABR were performed to determine whether the use of composite PEBA/PDVF HF would be more beneficial than the uncoated PVDF membrane. Ammonia feed concentrations and hydraulic retention times (HRT) were varied during the MABR operation, while other parameters such as pH, IC, and temperature were controlled and monitored.

## 2. Materials and methods

### 2.1. Membrane preparation

PVDF HF membranes (pore size = 0.07 μm, $d_{\text{in}}$ = 0.8 mm, $d_{\text{out}}$ = 1.2 mm) were generously provided by Toray, Co., South Korea. PEBA resins were purchased from Arkema Technical Polymers (Colombes, France). Hydrophobic Pebax 2533 is composed of 80% polytetramethylene oxide and 20% polyamide, whereas hydrophilic Pebax MH 1657 contained 60% of polyether block segment [16,17]. The resins were dried in an oven at 60–70°C before use and were stored in a desiccator.

To prepare 5 wt.% PEBA solution, anhydrous ethanol (PEBA 2533) or n-butanol (PEBA 1657) were used as solvents. The mixture was stirred at 150 rpm while being heated under closed reflux at 80°C for 2 h (PEBA 2533) or 24 h (PEBA 1657). The cooled PEBA solutions were poured into cylinders in which the pre-wetted (overnight soaking in water) PVDF HFs were individually immersed. The PEBA solution was slowly drained at a controlled rate through a valve at the bottom of the cylinder to assure uniform coating. The coated membranes were dried at room temperature for 12 h; coating was repeated several times before it was finally air-dried for at least 12 h and cured for 2 h at 70°C in a drying oven.

### 2.2. Membrane characterization

The surface morphologies of uncoated and coated HFs were observed under a field emission scanning electron microscope (FE-SEM, Jeol JSM-6700F) at 15.0 kV acceleration voltage. The surface roughness and asperities were inspected using atomic force microscopy (AFM; Autoprobe CP Research, Veeco, USA) under tapping mode; samples were observed within 25 $\mu m^2$ at 1 Hz scan rate. Contact angles were measured using flat sheet membranes to determine the intrinsic hydrophobicity of different polymeric materials.

### 2.3. Bacterial adhesion test

The rates of bacterial adhesion on different types of HFs were performed according to the method of Terada and co-workers [18]. Uncoated PVDF and PEBA coated HFs were cut into 4-cm long. Each fiber was sealed on both sides to avoid the penetration of the cell suspension inside the HFs. Two representative strains were used as cell suspensions: gram-positive bacteria *Bacillus* sp. and gram-negative *E. coli*. The cultures were harvested via centrifugation (6,500 rpm) and re-suspended in 0.1 N phosphate buffer. For each test sample, 50 mL cell suspension and membrane sample with 2.08 $cm^2$ effective surface area were made in contact in a 100 mL flask. The decline in optical density at 600 nm ($OD_{600}$) was measured every 30 min using HP 8453 UV–vis spectrophotometer. The inoculum concentrations (CFU/mL) were also quantified through colony counting of incubated samples on nutrient agar plates [19].

### 2.4. Nitrifying sludge enrichment

Nitrifying sludge from Yongin Wastewater Treatment Plant (Yongin, South Korea) was collected and acclimatized by adding P-media at 1:1 volume ratio with the sludge. The composition of P-media was detailed elsewhere [20]. The mixed liquor was aerated and incubated at 38℃. When the decrease in ammonia concentration was > 100 mg/L, the sludge was collected via centrifugation at 7,000 rpm for 10 min. The sludge pellets were re-suspended in fresh P-media; replenishment of media solution was repeated several times until > 200 mg/L $NO_2^-$–N and minimal $NO_3^-$–N concentration were achieved (<10 mg/L). The enriched sludge was finally collected and re-suspended in fresh P-media before it was pumped into the MABRs for immobilization.

### 2.5. MABR setup and operation

The HF modules were constructed in the laboratory; each contained 69 40-cm filaments which were fixed on both ends by an epoxy mold attached to an acryl ring. Two types of HF modules were prepared: bare or uncoated PVDF and PEBA coated PVDF. Each module has a total membrane surface area of 0.10 $m^2$ and was installed into a 2 L acryl MABR. Total bed height of the MABR was 40 cm with inner diameter of 5 cm. The reactors were covered with thermostatic jacket for temperature control between 35 and 37℃. The feed solution was delivered by a peristaltic pump (Masterflex, GT-150D, South Korea) at the shell side of the HFs. Air was supplied in the HFs from the bottom of the MABRs using air pumps and exited at the top of the reactor.

Synthetic P-media with nitrifying sludge enriched with AOBs were re-circulated to the MABRs for 30 days to allow biofilm development on the HFs. Synthetic wastewater was prepared with the following composition (per liter of solution): 0.7 g $KH_2PO_4$, 13.5 g $Na_2HPO_4$, 0.1 g $MgSO_4{\cdot}7H_2O$, 5 mg $CaCl_2{\cdot}2H_2O$, 1 mg Fe-EDTA, $(NH_4)_2SO_4$ as ammonium source, and 0.6 g $NaHCO_3$ as IC source. The two MABRs were then operated at varying ammonium feed concentrations (as N) and HRT. The columns were then evaluated for nitrogen removal by ammonium removal as well as nitrite and nitrate formations.

### 2.6. Analytical methods

Ammonium, nitrate, and nitrite concentrations were analyzed using Automatic Analyzer 3 (Bran and Luebbe, Germany) and reported as N. The pH was measured using Orion 4 Star pH/ISE meter and 91-57 Orion pH electrode (Thermo, USA). Temperature and DO concentrations were using Testo digital thermometer (South Korea) and YSI DO meter (South Korea), respectively.

## 3. Results and discussion

### 3.1. Membrane characterization

Fig. 1 illustrates the optical image of the PVDF HF module prepared in the laboratory. Morphologies of the uncoated and PEBA-coated HF are also shown in the same figure. FE-SEM images reveal the asymmetric (cross-section) structure of the HF.

The pores of the uncoated PVDF are evident on the surface with size < 0.1 μm. Meanwhile, the presence of PEBA 1657 and PEBA 2533 on PVDF HF resulted to dense surfaces, indicating that the pores were concealed after PEBA coating. Unlike the cross-section image of the bare PVDF, a dense layer with thickness around 18 μm was measured on the PEBA 2533 coated HF. The thickness of PEBA 1657 layer (data not shown) was around 22 μm. It is also evident that the structure underneath the dense PEBA layer remained unclogged or free from infiltration. This indicates that proper coating procedure was followed as it prevented the penetration of PEBA solution within the pores of the HF. It is known that infiltration of coating solution increases the overall membrane resistance [21], which could significantly reduce the oxygen transfer rate that is essential for the growth of the biofilm.

Fig. 2 illustrates the surface topographies of the bare PVDF and PEBA coated HFs. In Fig. 2(A), uncoated HF exhibited closely spaced asperities with

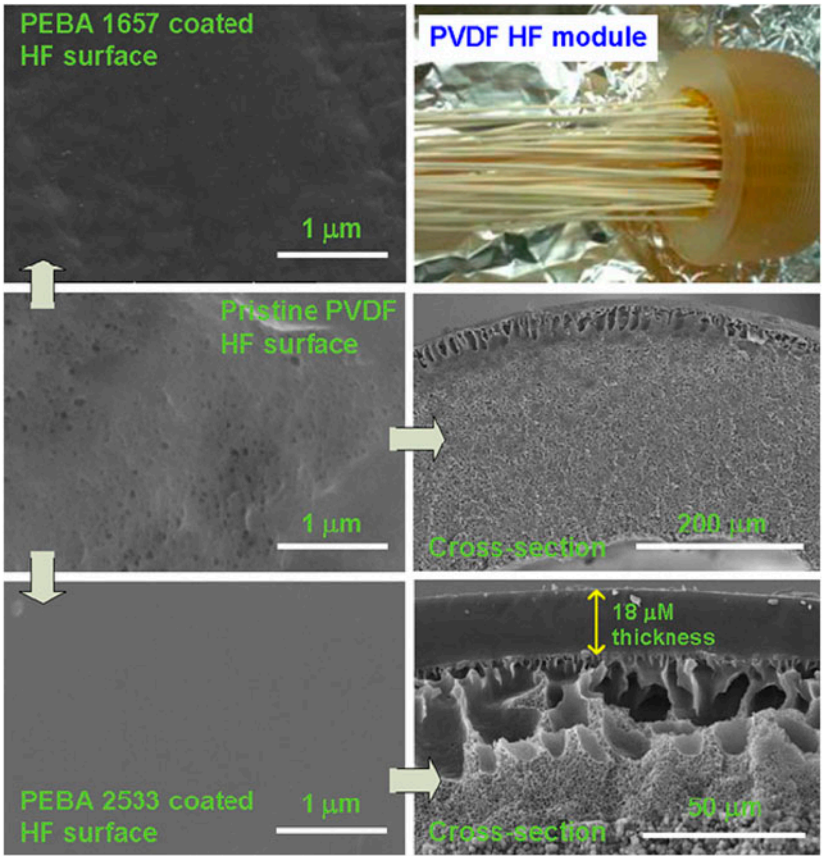

Fig. 1. Optical image of the prepared PVDF HF module and corresponding FE-SEM images of the pristine and PEBA-coated membranes.

maximum ridge elevation of 400 nm while that of PEBA 1657 coated HF in Fig. 2(B) was 650 nm which suggests its rougher surface. This result is in contrast with a previous report, in which polysulfone (PSf) coated with PEBA 1657 showed a smoother surface [19]. This may be possible since different support materials and membrane configurations (flat sheet PSf) had been used. Fig. 2(C) showed the smoother surface of PEBA 2533 coated PVDF with only 125 nm of maximum ridge elevation.

To compare the surface roughness of the HF membranes, root mean square roughness ($R_q$) values were estimated from AFM line profiles according to Eq. (1). In the expression, $N$ is the number of measurements, $Z_i$ is the height of the $i$th point, whereas $Z_m$ is the mean height [22].

$$R_q = \left[ \sum_{i=1}^{N} (Z_i - Z_m)^2 / (N-1) \right]^{0.5} \quad (1)$$

The measured $R_q$ of the membranes are summarized in Table 1 which confirms that PEBA 1657 coated HF has the roughest surface, while PEBA 2533 coated HF has the smoothest.

### 3.2. Bacterial adhesion test

As a surface phenomenon, biofilm formation is affected by the interaction of the microorganisms on the membrane surface. Factors such as roughness, surface energy, and charge have been strongly associated with the initial bacterial adhesion, which is a critical step to biofilm formation [18]. Fig. 2 shows that regardless of the microorganism tested, bacterial concentration decreased in all membrane samples, suggesting that portions of the suspended cells adhered on the membrane surfaces. However, the extent of decline in $C_t/C_o$ is most remarkable in PEBA 2533 coated HF, while both uncoated and PEBA 1657 coated HFs displayed similar profiles. This indicates that PEBA 2533 coated HF has the most favorable surface property among the tested membranes for bacterial attachment and biofilm formation.

To compare the adhesion rates on the membranes, results in Fig. 3 were transformed in Fig. 4 for the

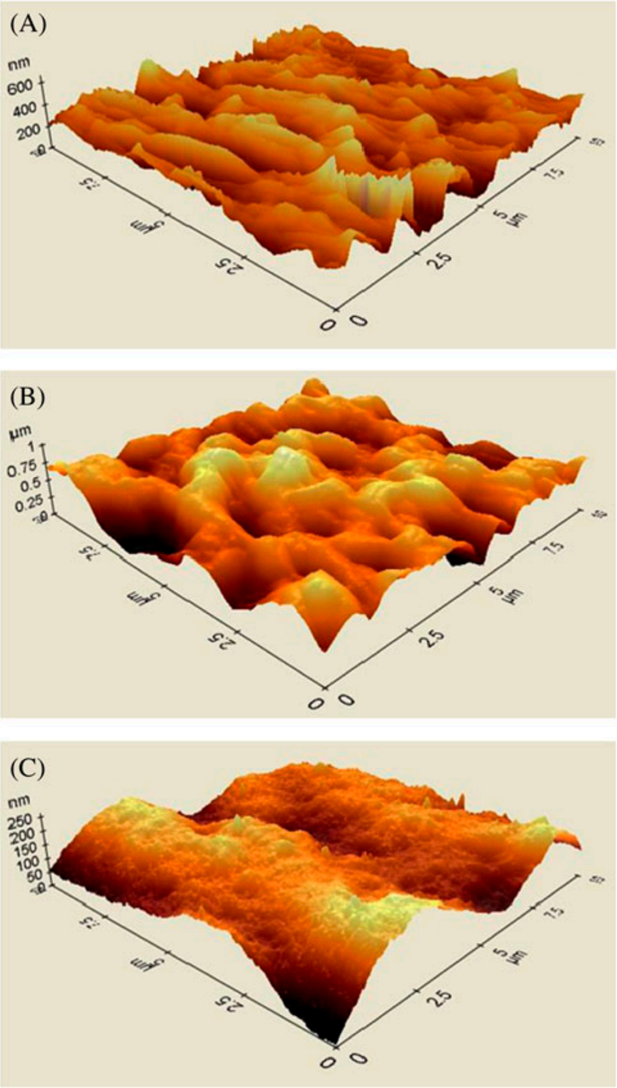

Fig. 2. AFM surface topographies of the investigated membranes: (A) pristine (uncoated) PVDF, (B) PEBA 1657 coated PVDF (hydrophilic) and (C) PEBA 2533 coated PVDF.

estimation of rate constants ($k$) as defined in Eq. (2). In the expression, $V$, $A$, $C_o$, and $C_t$ are the suspension volume, membrane area, initial and bacterial concentration at time ($t$), respectively [18].

$$k = -\left(\frac{V}{A}\right)\left(\frac{1}{t}\right)\ln\left(\frac{C_t}{C_o}\right) \tag{2}$$

The obtained $k$ values are summarized in Table 1 wherein most tested samples exhibited two rate constants except for *E. coli* suspensions placed in contact with uncoated PVDF and PEBA 1657 coated HF (Fig. 4(B)). For samples with two $k$ values, it is apparent that $k_1 \geqslant 3k_2$ values. This result indicates that the deposition of bacteria on the HF surface have occurred at an initially faster rate followed by a slower rate of attachment. This finding is on par with the known mechanism described in a previous work regarding the initial phase of biofilm development [18]. The first step involves the reversible colonization of bacteria on a solid support via physicochemical interactions followed by an irreversible chemical step of bacterial attachment. Results indicate the possibility that these two steps are reflected by the two $k$ values obtained in certain membranes. Consistently, single $k$ values in some samples (i.e. PEBA 1657 coated and uncoated PDVF in *E. coli* suspension) were also the lowest, suggesting that the initial attachment of bacteria on the HF surface was not favored probably due to their weak physicochemical interactions.

Despite having the roughest surface (Table 1), PEBA 1657-coated HF had the lowest $k$ values. Previous results showed that rough surfaces are favorable for bacterial attachment [18,23]. Likewise, hydrophobic surfaces are also susceptible to microbial deposition due to strong hydrophobic–hydrophobic interactions [23]. In Table 1, contact angle is highest in PEBA 2533 which indicates that it has a relatively

Table 1
Adhesion rate constants and membrane surface characteristics

| Membrane type | Gram (+) (*Bacillus* sp. adhesion rate) ($\times 10^{-6}$ m/s) | | Gram (−) (*E. coli* adhesion rate) ($\times 10^{-6}$ m/s) | | Contact angle (degrees) | $R_q$ (nm) |
|---|---|---|---|---|---|---|
| | $k_1$ | $k_2$ | $k_1$ | $k_2$ | | |
| Uncoated HF | 4.49 | 1.44 | 1.18* | | 76 | 87.8 |
| PEBA 1657 coated HF | 4.29 | 1.36 | 0.86* | | 26 | 211.2 |
| PEBA 2533 coated HF | 13.42 | 1.47 | 7.41 | 0.64 | 79 | 29.9 |

*Single $k$ value obtained.

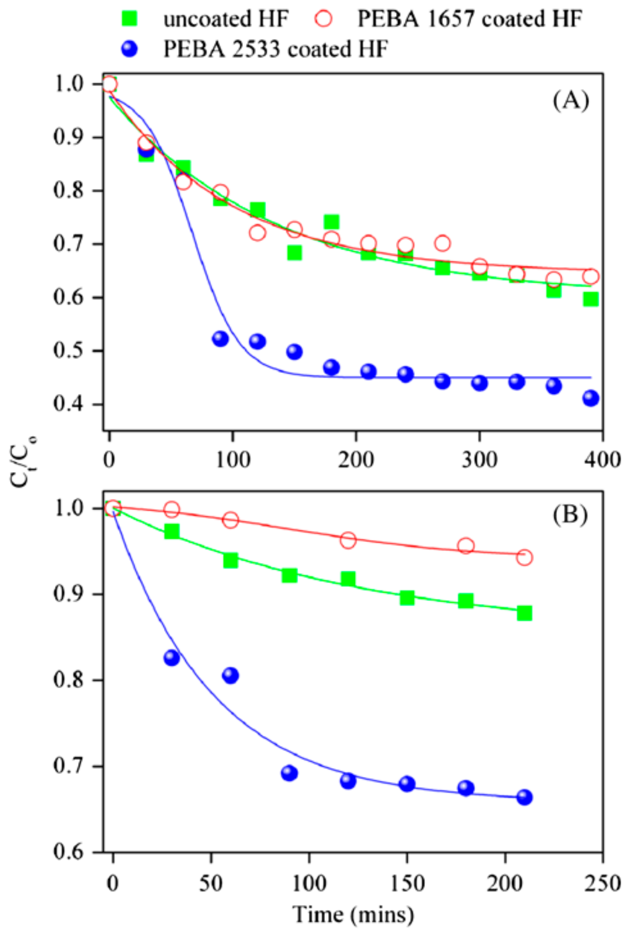

Fig. 3. Bacterial concentration profiles during adhesion test. (A) *Bacillus* sp. ($C_o = 1.2 \times 10^8$ CFU/mL); (B) *E. coli* ($C_o = 9.7 \times 10^8$ CFU/mL).

more hydrophobic surface as compared to PVDF and PEBA 1657. Considering that *k* values from PEBA 2533 coated HF were the highest while those from the other two materials were the lowest, it is apparent in this case that initial bacterial adhesion is more affected by surface hydrophobicity than surface roughness.

Based on the results, hydrophobic PEBA 2533 is more suitable for bacterial adhesion than PEBA 1657 hence was selected as coating material of PVDF HF.

### 3.3. Partial nitrification performance

Partial nitrifications in MABRs were conducted using uncoated and PEBA 2533 coated HF modules and were operated for 115 days. During operation, pH values varied marginally between 7 and 8, while the measured temperatures were within 35–37℃. Both are favorable for the cultivation of AOB because under these conditions, the growth rate AOB is optimal and faster than the NOB [1].

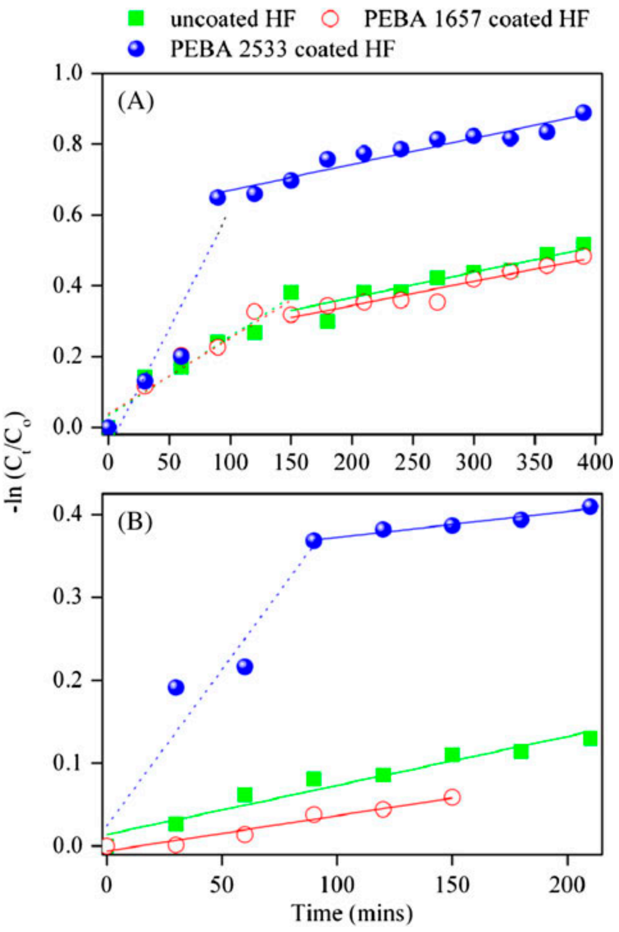

Fig. 4. Profiles for adhesion rate constant calculations in (A) *Bacillus* sp. (B) *E. coli*.

Results from the first 90 days of continuous operation (48 h HRT) at varied feed ammonium (as N) concentrations are shown in Fig. 5. Regardless of the feed concentration, *N* removals in MABR with uncoated PVDF HF were slightly higher than those in MABR with PEBA 2533 coated HF.

Increase in feed concentration resulted in the reductions of N removals in both MABRs. At 50 mg N/L feed, 93 and 88% were attained in uncoated PVDF and PEBA 2533 coated HF, respectively, but both remarkably declined when the feed was increased to 100 mg N/L. After 13 days, the performances of both MABRs were nearly recovered. At higher feed concentrations (i.e. 200, 500 mg N/L), similar trends were observed but removal reductions became more severe hence longer periods were needed to improve the MABR performances. At 500 mg N/L feed, N removal in MABR with uncoated PVDF (37%) was slightly higher than that in MABR with PEBA 2533 coated HF (32%). Due to severe removal reductions, the feed concentration was

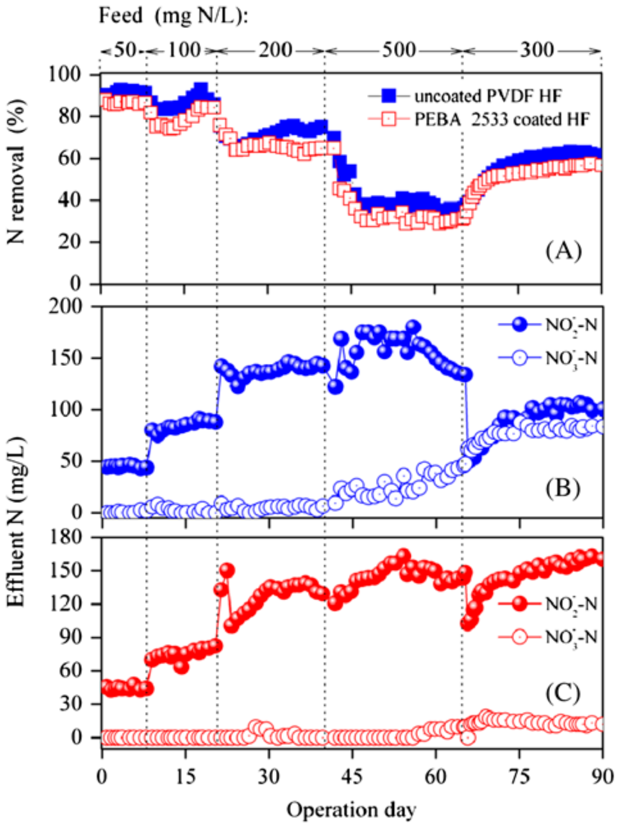

Fig. 5. MABR partial nitrification performance at varied feed concentrations. (A) % N removal; (B) microporous (uncoated) PVDF HF module; (C) PEBA 2533 coated PVDF HF module.

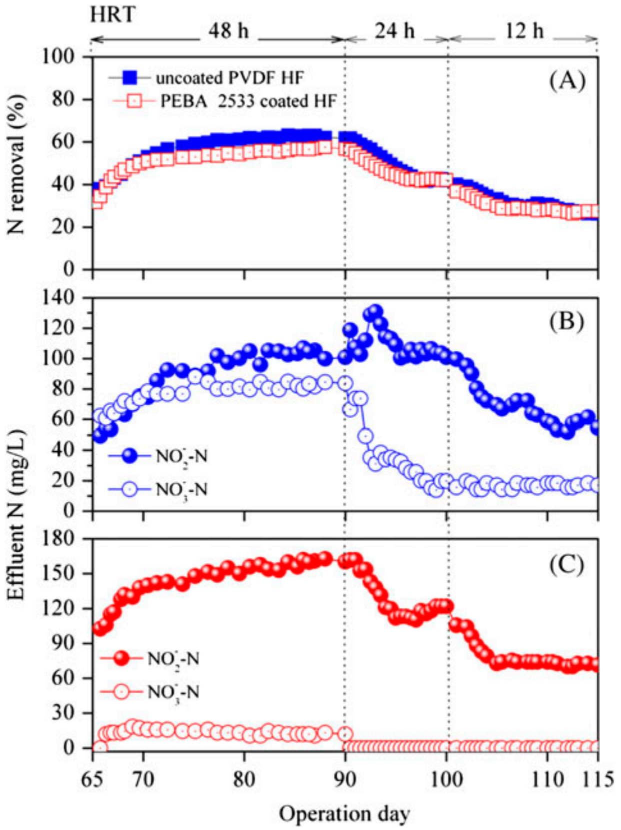

Fig. 6. MABR partial nitrification performance at different HRT. (A)% N removal; (B) microporous (uncoated) PVDF HF module; (C) PEBA 2533 coated PVDF HF module.

decreased to 300 mg N/L. The performance of both reactors gradually increased before reaching steady removals of 61 and 57% for uncoated and PEBA coated HF, respectively, at day 90.

Nitrite and nitrate profiles in Fig. 5(B) and (C) reveal the different nitrification behaviors of the two MABRs. Prolific NO$_3^-$–N formation was observed in MABR with uncoated PVDF HF, which indicates that NOB thrived well in the reactor. At day 40, 20 mg N/mL of NO$_3^-$ was detected which gradually increased up to 85 mg N/L at day 90. On the other hand, minimal NO$_3^-$–N levels were detected in MABR with PEBA 2533 coated HF; highest concentration of 11 mg N/L was measured at day 90.

The different N removals and NO$_2^-$–N/NO$_3^-$–N profiles in the two MABRs can be associated with the difference in gas transfer rates across the HF membranes [10]. The presence of PEBA as coating layer provided an additional membrane resistance for O$_2$ transfer, and hence, O$_2$ permeation in the composite HF would be lower than that in the uncoated PVDF. Consequently, O$_2$ transport might have been limited due to the thick (18 μm) PEBA layer. Thus, despite the favorable surface property of PEBA 2533 for biofilm development, the relatively lower O$_2$ supply across the HF might have curtailed the AOB biofilm to fully develop which led to the slightly lower N removals. On the other hand, it has been known previously that the growth of NOB is inhibited under oxygen-limited environment [19,24]. Hence despite the lower N removals, partial nitrification in MABR with PEBA 2533 coated HF was more successful since > 90% of the nitrified ammonium was in NO$_2^-$–N form. The higher O$_2$ supply in the MABR with uncoated PVDF might have been favorable for both AOB and NOB growths, which could explain the substantial conversion of NO$_2^-$–N to NO$_3^-$–N.

Operation at varied HRTs was observed at 300 mg N/L feed from days 65 to 115. Fig. 6(A) reveals that N removals declined when HRTs were shortened. The declines may be attributed to the lack of contact time between the biofilm system and feed solution. Nonetheless, the performances of both MABRs were similar especially at shorter HRTs (i.e. 24-, 12 h). It is also evident in Fig. 6(B) and (C) that NO$_3^-$–N formation became less prevalent in both MABRs, indicating the wash out of NOB. From day

90 onward, around 20 mg $NO_3^-$N/L was detected in the MABR with uncoated PVDF, while only trace levels (<1 mg N/L) were measured in the MABR with PEBA 2533 coated HF.

During the 115-day operation, highest N removal rates of 92- and 86 mg N/L-day were obtained from MABRs with uncoated PVDF and PEBA 2533 coated HF, respectively. In terms of partial nitrification, highest conversion of nitrite to nitrate was observed at 50% in MABR with uncoated PVDF while that in MABR with PEBA 2533 coated HF was only < 10%. At the highest loading rate of 600 mg N/L (i.e. 300 mg N/L feed at 12 HRT), similar N removal rates of 72 mg N/L-day were measured from both MABRs.

## 4. Conclusions

In this study, the difference in partial nitrification between microporous PVDF and composite PEBA 2533 coated PVDF was investigated. While higher N removal was observed in MABR with microporous HF, it has a higher propensity for the development of NOB as exhibited by its high nitrate production. Hence, coating the HF with dense polymeric layer like PEBA 2533 may assist in the selective development of AOB biofilm system as shown by the low levels of nitrate. To increase the current N removal rate of the MABR with PEBA 2533 coated HF, improvements in the composite membrane preparation such as reduction of PEBA coating layer thickness and optimization of the MABR operation (i.e. air supply feed pressure) are worthy of further investigation.

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