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Research of groundwater denitrification using a plate-and-frame composite membrane bioreactor

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ABSTRACT

A plate-and-frame composite membrane bioreactor (PFCMBR) integrating the immobilized cell technique and the membrane separation technology was developed for groundwater denitrification. In PFCMBR the groundwater and external carbon source (ethanol solution) are separated by the plate-like immobilized cell, molecules of nitrate and ethanol diffused from the respective frames into the plate-like immobilized cell where nitrate was reduced to gaseous nitrogen by the denitrifying bacteria present there with ethanol as carbon source. The microporous membrane attached to one side of plate-like immobilized cell is used to separate product water from a plate-like immobilized cell or to provide effective retention of the biomass. Using the PFCMBR for groundwater denitrification, the over dosed external carbon source can be reused, and its treatment performance was perfect during continuous operation up to 98 days, and almost all effluent NO_3^--N, NO_2^--N, and COD_{Mn} concentrations are below their maximum contaminant levels.

KEYWORDS

Groundwater;
Nitrate;
Denitrification;
Plate-and-frame composite membrane bioreactor;
Plate-like immobilized cell.

INTRODUCTION

Groundwater is the most important source of drinking water in northern China; in some rural areas, it is the only readily available source of drinking water. As a result of excessive use of urea and/or other nitrogen fertilizers, nitrate contamination of the groundwater has become a common issue in northern China[1, 2]; as an example, 58 mg·l^{-1} of nitrate-nitrogen (NO_3^--N) was found in the sample of a drinking well in Zhangqiu County of Shandong Province[3]. Consumption of drinking water contaminated with nitrate may cause infant methemoglobinemia and contributes to cancer formation[4]. Because of nitrate's potential adverse health effects, World Health Organization (WHO) and European Community have regulated the amount of nitrate in public drinking water supplies to below a maximum contaminant level (MCL) of 50 mg NO_3^{-1}.l^{-1}[5], United States Environmental Protection Agency (US-EPA) and Chinese Ministry of Health have established a MCL of 10 mg·l^{-1} for NO_3^--N[6, 7].

The conventional methods for nitrate removal are ion exchange (IX) and reverse osmosis (RO). Both of these processes, however, yield concentrated waste brines requiring further treatment or disposal at a high cost[8]. Biological denitrifcation is an attractive treatment alternative for nitrate removal due to the high specificity of denitrifying bacteria for nitrate, low cost and high denitrification rates[9]. Although direct biological denitrification of surface water is used in some European countries, like France and Germany[9, 10], it is still not widely accepted as a drinking water treatment strategy. The main reason is the potential risk of microbial contamination of the treated water and presence of residual carbon source. To overcome these limitations, several types of membrane bioreactors, mainly using hollow fiber microfiltration or ultrafiltration modules, have been proposed and studied[5, 11-13]. While in most cases the microbial contamination of the treated stream was avoided, it was found that bioreactors utilizing porous membranes could not prevent pollution of the treated water with incompletely degraded substrate[14, 15].

To overcome such stated disadvantages of the groundwater denitrification processes, research was conducted in our lab to develop an innovative nitrate removal process employing the plate-and-frame composite membrane bioreactor (PFCMBR) which integrates immobilization cell technique with membrane separation technology for groundwater denitrification. The PFCMBR consists of plate-like immobilized cells, microporous membranes, frames and flat covers, and the frames include W frames and C frames. The W and C frames represent the water and carbon sources go through corresponding chambers of frame, respectively. The flat covers, plate-like immobilized cells, microporous membrane and frames are arranged in the following order (see Figure 1): flat cover, W frame, microporous membrane, plate-like immobilized cell, C frame, plate-like immobilized cell, microporous membrane, W frame, microporous membrane, plate-like immobilized cell, C frame, plate-like immobilized cell, microporous membrane, W frame, and flat cover. The groundwater is delivered into the inlet of the first W frame and fills up its chamber, then the groundwater flow into the inlet of the next W frame through a pipe from the outlet of this W frame. And so on, the groundwater flows through the third and fourth W frames orderly, and flows out from the outlet of the fourth W frame. At the same time, a dilute ethanol solution is delivered into the inlet of the first C frame and fills up its chamber, then the ethanol solution flow into the inlet of the second C frame through a pipe from the outlet of this C frame, finally the ethanol solution return to its storage tank for recycling use. Molecules of nitrate and ethanol diffused from the respective chambers into the plate-like immobilized cell where nitrate was reduced to gaseous nitrogen (N_2) by the denitrifying bacteria present there with ethanol as carbon source. The microporous membrane attached to one side of plate-like immobilized cell is used to separate product water from a plate-like immobilized cell or to provide effective retention of the biomass. The main objectives of this research are therefore to investigate the possibility of the novel plate-and-frame composite membrane bioreactor (PFCMBR) for groundwater denitrification and the ability to control contamination of the product water by adding organic carbon source. In addition, the long term treatment performance of the PFCMBR was evaluated.

MATERIALS & METHODS

Materials

The denitrifying bacteria employed for the study were obtained from acclimation of the SBR activated sludge of the wastewater treatment plant located in East China University of Science and Technology, Shanghai, China. The culture medium consists of tap water, KNO_3(2000mg·l^{-1}), CH_3CH_2OH (1500 mg·l^{-1}), trace elements and the dilute phosphate buffer (pH = 7.2).

Polyvinyl alcohol (PVA) with an average degree of polymerization of 1750 was obtained from Shanghai Chemicals Factory. All other reagents were analytical grade commercial chemicals.

The microporous membrane (average pore opening 0.45μm) was obtained from Shanghai Diqing Filtration Technology Company.

The simulate groundwater contained 16-100 mg·l^{-1} NO_3^--N were used in batch and continuous experimental process, respectively, and the dilute ethanol solution with a few trace elements and phosphate buffer (pH=7.2) was used as external carbon source.

Cell immobilization

The culture medium containing known concentration of denitrifying bacteria was centrifuged at 3000 r·min^{-1} for 15 min; the cell fraction was washed with normal saline and centrifuged twice. The concentrated cells were then added to the solution of 15% (w/v) PVA and 4% (w/v) glycerol (cryprotectant) and stirred to ensure uniformity; the concentration of cells was about 2% (w/v) in the PVA solution. This mixture was poured into a plate-and-frame mold (350mm×100mm×4mm); the mold containing the mixture was frozen overnight at –20°C, then thawed at room temperature. After five repeated processes of freezing and thawing, the formed gel sheet was washed thoroughly with distilled water to produce the plate-like immobilized cell. The thickness of plate-like immobilized cell was about 4 mm.

The plate-and-frame composite membrane bioreactor

The PFCMBR consists of plate-like immobilized cells, microporous membranes, frames and flat covers, and the frames include W frames and C frames. The W and C frames represent the water and carbon sources go through corresponding chamber of the frame, respectively. The flat covers, plate-like immobilized cells, microporous membrane and frames are arranged in the following order (see Figure 1): flat cover, W frame, microporous membrane, plate-like immobilized cell, C frame, plate-like immobilized cell, microporous membrane, W frame, microporous membrane, plate-like immobilized cell, C frame, plate-like immobilized cell, microporous membrane, W frame, and flat cover. Bolts and nuts are used to press them together.

After assembling of the PFCMBR, the effective volume of each chamber was 60 ml (30cm×2cm×1cm), and the total effective area of the immobilized cell membrane was 0.024 m^2 (0.3m×0.02m×4).

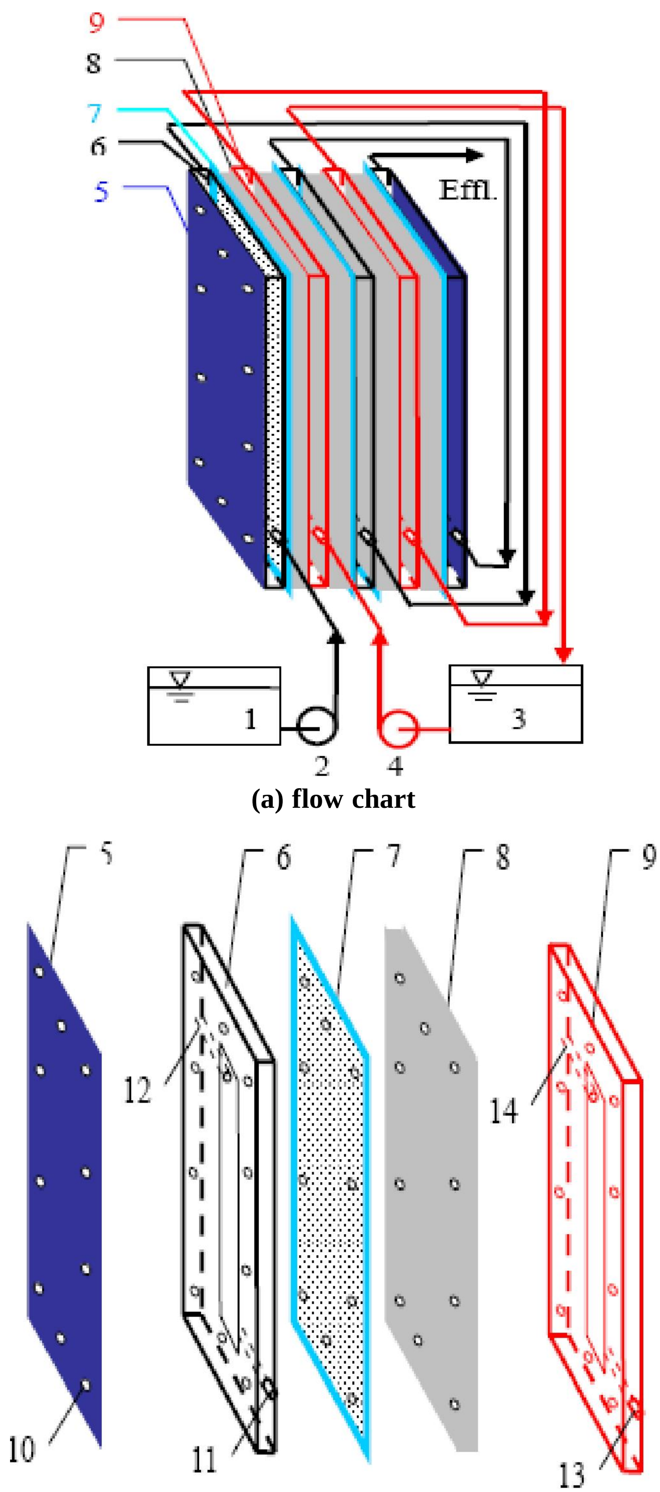
Batch denitrification of the PFCMBR

Put the PFCMBR into a 20±1°C thermostatic room, nitrate containing simulate groundwater is delivered into the inlet of the first W frame and fills up its chamber. Then the groundwater flows into the inlet of the second W frame through a pipe from the outlet of the first W frame. And so on, the groundwater flows through the third and fourth W frames orderly, and then returns to groundwater tank for recycling. At the same time, a dilute ethanol solution is delivered into the inlet of the first C frame and fills up its chamber, then the ethanol solution flows into the inlet of the second C frame through a pipe from the outlet of the first C frame, and then returns to ethanol solution tank for recycling. The total volumes of both simulate groundwater and ethanol solution are 4000 ml and ethanol content in ethanol solution is 138 mg.l^{-1}, and samples were taken from each tank at various time intervals. The samples of simulate groundwater tank were analyzed for nitrate, nitrite and COD_{Mn} (potassium permanganate was used for measuring chemical oxygen demand) concentrations, and the samples of ethanol solution tank were analyzed for nitrate and nitrite concentrations. Fresh samples of the groundwater and ethanol solution were employed for each treatment run.

Continuous denitrification of the PFCMBR

Put the PFCMBR into a 20±1°C thermostatic room, and nitrate containing simulate groundwater is delivered into the inlet of the first W frame and fills up its chamber, and then the groundwater flows into the inlet of the second W frame through a pipe from the outlet of the first W frame. And so on, the groundwater flows through the third and fourth W frames orderly, and finally the treated groundwater is discharged from the outlet of the fourth W frame. At the same time, a dilute ethanol solution is delivered into the inlet of the first C frame and fills up its chamber, and then the ethanol solution flows into the inlet of the second C frame through a pipe from the outlet of this C frame, and returns to ethanol solution tank for recycling use. The flowrate of simulate groundwater is 50 ml.min^{-1} and the recycling flowrate of ethanol solution is 500 ml.min^{-1}. The total volume of ethanol solution is 8000 ml, and fresh ethanol is added to ethanol solution tank each day based on the stoichiometry of denitrification reactions, and the used ethanol solution is replaced completely by fresh one after continuous operation of 5 days. The samples from groundwater tank, final effluent, and ethanol solution tank were taken each day. The samples of groundwater tank were analyzed for nitrate nitrogen concentration, and the samples of final effluent were analyzed for nitrate, nitrite and COD_{Mn} concentrations. The samples of ethanol solution tank were analyzed for nitrate and nitrite concentrations.

Analysis and calculation



(a) flow chart

(b) assembly drawing

Figure 1 : Schematic diagrams of PFCMBR; 1 - tank of simulate groundwater, 2 - metering pump of simulate groundwater, 3 - tank of ethanol solution, 4 - metering pump of ethanol solution, 5 - flat cover, 6 - W frame, 7 - microporous membrane, 8 - plate-like immobilized cell, 9 - C frame, 10 - bolt hole, 11 - inlet of W frame, 12 - outlet of W frame, 13 - inlet of C frame, 14 - outlet of C frame

The concentrations of nitrate and nitrite were determined according to Standard Methods[16]. COD_{Mn} was analyzed according to Water and Wastewater Monitoring and Analysis Methods[17].

The average denitrification rate of the PFCMBR was calculated using the following equation:

$$r = \frac{V(N_0 - N_t)}{A \cdot t}$$

Where: r - the average denitrification rate ($g \cdot m^{-2} \cdot h^{-1}$) of the PFCMBR, V - the volume (m^3) of groundwater, N_0 and N_t - the nitrate nitrogen concentrations ($g \cdot m^{-3}$) at the beginning and at the end of each run, A - the effective area (m^2) of the plate-like immobilized cell, and t - the time (h) of the batch experiment.

RESULTS AND DISCUSSIONS

Feasibility of using the PFCMBR for groundwater denitrification

Figure 2a and 2b show the time profiles of nitrate nitrogen and nitrite nitrogen concentrations in simulate groundwater tank and ethanol solution tank, respectively, during initial batch treatment run. The nitrate nitrogen concentration in simulate groundwater tank decreased with the treatment time; it was less than 10 $mg \cdot l^{-1}$ after 4 days treatment. Throughout the entire treatment run, the nitrite nitrogen concentrations in both tanks were very low and that the nitrate nitrogen concentration in ethanol solution tank was fairly low. These results suggest that the nitrate in groundwater in chamber of W frame diffused into the plate-like immobilized cell where the denitrifying bacteria mediated denitrification process reduced most of them to nitrite and then N_2 by the electrons coming from the oxidation of ethanol molecules which moved in from the ethanol solution in chamber of C frame; only a small amount of nitrate nitrogen ended up ethanol solution. Therefore, it is feasible to employ the PFCMBR for groundwater denitrification. In addition, the COD_{Mn} value of simulate groundwater sample picked at the fourth day was about 3.8 $mg.l^{-1}$. This means only a little of carbon source (ethanol) from diffusing into the groundwater.

Effects of recycling flowrates of groundwater and

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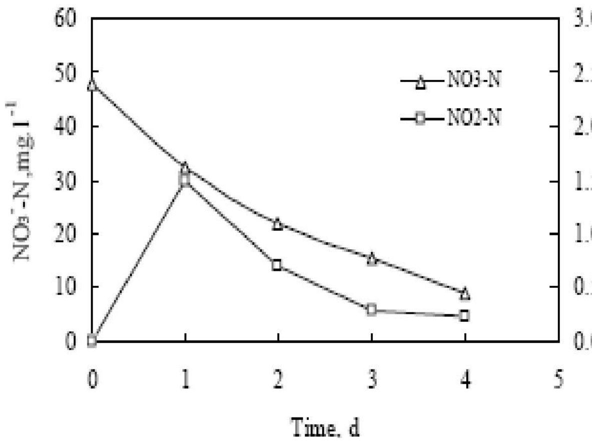

Figure 2a : Profiles of NO_3^--N and NO_2^--N concentrations in simulate groundwater tank during batch denitrification process with PFCMBR

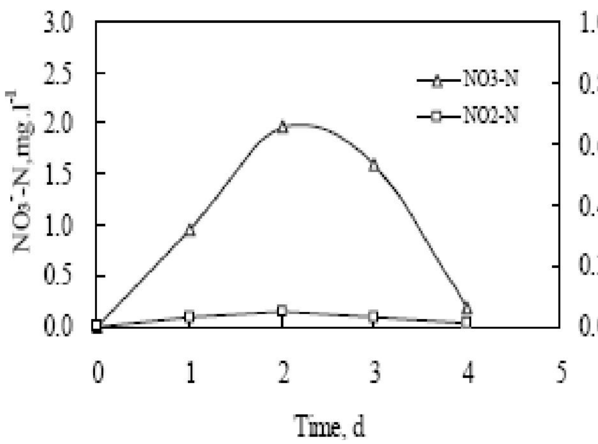

Figure 2b : Profiles of NO_3^--N and NO_2^--N concentrations in ethanol solution tank during batch denitrification process with PFCMBR

ethanol solution

During denitrifying process with PFCMBR, the molecules of nitrate and ethanol diffused from the respective chambers into the plate-like immobilized cell where nitrate was reduced to gaseous nitrogen (N_2) by the denitrifying bacteria present there with ethanol as carbon source. For a given PFCMBR, the internal diffusion of plate-like immobilized cell cannot be changed, but the external diffusion of plate-like immobilized cell could be controlled through adjusting the flowrates of groundwater and/or ethanol solution. Then, the outside diffusion resistance and the denitrifying rate may vary along with the recycling flowrates of groundwater and/or ethanol solution. Therefore, the effects of recycling flowrates of groundwater and ethanol solution on denitrifying rate were evaluated, respectively, and the results were presented at Figure 3a and 3b.

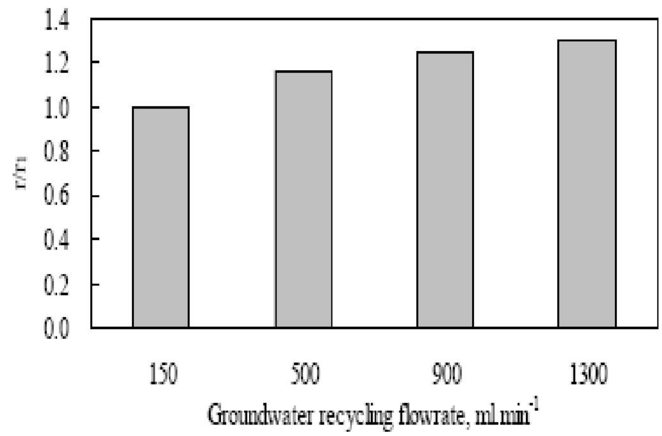

Figure 3a : Effect of groundwater recycling flowrate on denitrifying rate of PFCMBR (The ethanol solution recycling flowrate is 150 ml.min^{-1})

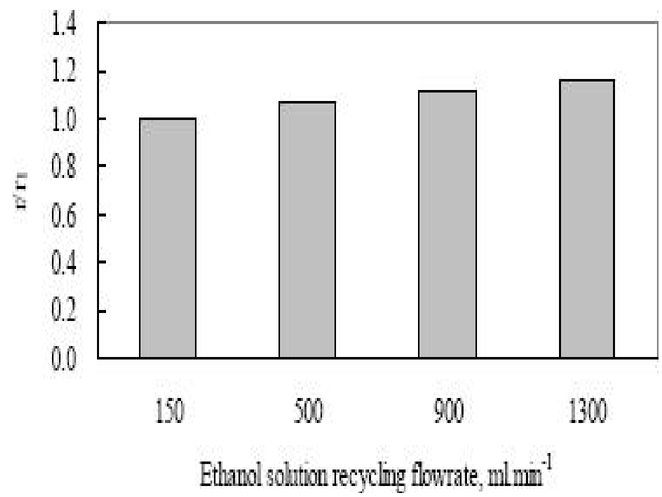

Figure 3b : Effect of ethanol solution recycling flowrate on denitrifying rate of PFCMBR (The groundwater recycling flowrate is 150 ml.min^{-1})

As showing in Figure 3a and 3b, the denitrifying rate increased with increasing the recycling flowrate of groundwater or ethanol solution. When the recycling flowrate is 1300 ml.min^{-1}, the corresponding Reynold's number, Re, is 1435. Re<2000 is the laminar range[18]. Thus, the external mass transfer resistance decreased with increasing the recycling flowrate, resulted in the increase of the denitrifying rate. However, the denitrifying rate only increased 26% even the recycling flowrate increased 9 times. That is the external mass transfer is not the limiting process for groundwater denitrification processes in the PFCMBR.

Effect of the residual carbon source reused on denitrification process of PFCMBR

In biological denitrification process, an important design parameter for denitrification processes is the amount of bsCOD or BOD needed to provide a sufficient amount of electron donor for nitrate removal. Based on the stoichiometry of denitrification process, removal 1 g NO_3^--N need 2.86g COD (ignore cell growth)[19], or the theoretical C/N ratio for denitrification is 2.86. But during the batch denitrification treatment runs, the actual C/N ratio is about 6.0, which is much higher than the theoretical one. Hence, a lot of carbon source was wasted if fresh ethanol solution was employed for each treatment run.

To save external carbon source (ethanol), the possibility for reusing the ethanol solution was investigated. That is, the ethanol solution was not replaced by fresh one at the end of batch testing, or the ethanol solution was reused. Of course, some ethanol was supplemented to the ethanol solution tank before each cycle, and the quantity of supplementation ethanol was calculated based on the stoichiometry of denification reaction.

Figure 4 illustrates the effect of the ethanol solution reused on denitrification process of PFCMBR. The data demonstrate that the residual carbon source (ethanol) could be used for denitrifying reaction of next cycle, but the relative denitrifying rate will was decreased with the ethanol solution reused times. This is because the PFCMBR is an open denitrification system, some other heterotrophic bacteria besides denitrifying bacteria must be presence in this system, and these heterotrophic bacteria also obtain their carbon source for cell growth from ethanol solution. In other words, the available ethanol

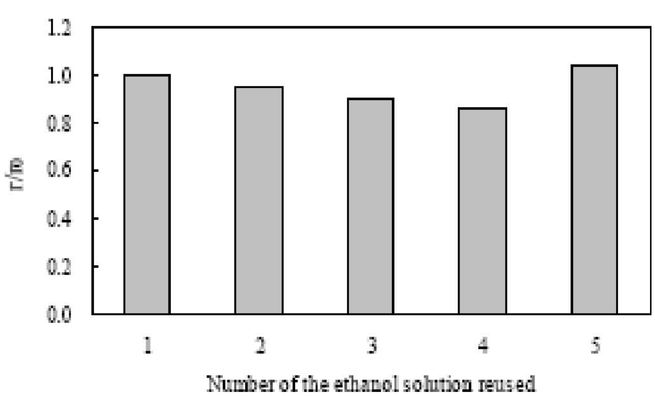

Figure 4 : Effect of ethanol solution reused on denitrifying rate of PFCMBR

quantity for denitrification would be decreased with increasing the ethanol solution reused times if the ethanol is supplemented according to the stoichiometric quantity of denitrification process at beginning of each cycle. Consequently, the denitrifying rates decreased with increasing the ethanol solution reused times. The fact that the denitrifying rate of fifth cycle was higher than the first one can prove that the available ethanol quantity is one of the major reasons affecting denitrification rate in PFCMBR, because the supplementation ethanol was increased about 30% than stoichiometric quantity at beginning of this cycle.

Long term continuous treatment performance of the PFCMBR

The stability during long-term operation is an essential factor for practical application of the PFCMBR. To evaluate the operational stability of the PFCMBR, a long term continuous treatment study of 98 d was conducted. During the whole experimental course, the influent NO_3^--N concentrations were gradually increased from 16.3 $mg.l^{-1}$ to 99.3 $mg.l^{-1}$, or the NO_3^--N loadings of PFCMBR were gradually increased from 0.813 $g.m^{-2}.d^{-1}$ to 4.968 $g.m^{-2}.d^{-1}$. Accordingly, with the increase of nitrate concentration, the ethanol concentrations in ethanol solution were increased at the same time. The results of the PFCMBR stability study are presented in Figure 5.

As showed in Figure 5, once the influent nitrate concentration was increased, both effluent nitrate and nitrite concentrations were increased slightly during succeeding days, then decreased gradually and tended to stable. Maybe it is a shuck loading affected the performance of PFCMBR. Anyway, almost all effluent samples' NO_3^--N and NO_2^--N concentrations were less than 10 $mg.l^{-1}$ and 1 $mg.l^{-1}$, respectively, except the effluent samples of 63rd, 64th, and 81st-85th days. This is because the influent nitrate concentrations was increased at 63rd and 81st days, respectively, but the ethanol concentration wasn't increased synchronously, the latter was increased at 64th day and 83rd day, respectively. Thus, the reductions of nitrate and nitrite were limited due to insufficient carbon source at these days. In addition, during whole experimental process the effluent COD_{Mn} levels were less than 5 mg/L, which is MCL[6] for COD_{Mn} established by Chinese Ministry of

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Health. Thus, the treated water contaminated by residual carbon source of denitrification can be avoided as the PFCMBR was used for groundwater denitrification.

The maximum NO_3^--N loading of the PECMBR is 4.968 g.m^{-2}.d^{-1}, which is similar to the one of extractive MBR[15], but the organic carbon of product water in the PFCMBR was lower than that in the extractive MBR[15]. Therefore, the performance of PFCMBR is better than that of extractive MBR.

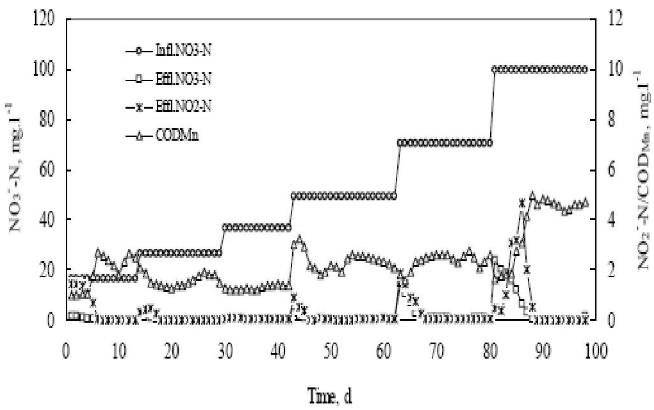

Figure 5 : Long term continuous treatment performance of PFCMBR

CONCLUSIONS

The novel plate-and-frame composite membrane bioreactor (PFCMBR) developed in this research can be used for groundwater denitrification. The residual carbon source and microbial contaminations of the treated groundwater can be avoided during groundwater denitrification process with PFCMBR.

Using the PFCMBR for groundwater denitrification, the over dosed external carbon source can be reused, and its treatment performance was perfect during continuous operation up to 98 days, and almost all effluent NO_3^--N, NO_2^--N, and COD_{Mn} concentrations are below their maximum contaminant levels.

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