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Diatomite- and polyvinyl alcohol-modified nonwoven fabric in membrane bioreactor for wastewater reclamation

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ABSTRACT

In the current study, diatomite- and polyvinyl alcohol (PVA)-modified nonwoven fabric was applied in membrane bioreactor (MBR) for wastewater reclamation. The characteristics of the modified nonwoven were elaborated via water contact angle, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy measurements. It showed that the hydrophilicity of nonwoven was enhanced, and water contact angle was decreased from 112.71° to 53.83°. SEM images show that the nonwoven fibers are uniformly covered with PVA, and diatomite deposited on nonwoven fabrics is glued by PVA polymer. The performance of modified nonwoven was evaluated in MBR system at a flux of 6.2–16.5 $L/m^2 h$. Results showed that the anti-fouling property of modified nonwoven membrane was enhanced, and the effluent qualities could meet the requirements for water reclamation.

Keywords: Nonwoven fabric; Wastewater reclamation; Diatomite; Polyvinyl alcohol (PVA); Anti-fouling property

1. Introduction

Due to the high pollutant removal efficiency, superior solid–liquid separation performance, and little excessive sludge generation, the membrane bioreactor (MBR) exhibited obvious advantages over conventional wastewater treatment process, which attracted attentions in recent years. However, high membrane cost, intensive energy consumption, and serious membrane fouling become critical barriers for the further development of MBR systems [1–4].

Some coarse filters like mesh, nonwoven fabric, and filter cloth had been tested in MBR process for wastewater treatment [5–11]. Fan and Huang [5] and Wang et al. [8] used mesh filters in MBRs by applying gravity at a flux of 15–41.7 $L/m^2 h$ for wastewater treatment. Ye et al. [9] applied terylene filter cloth (56 μm) in MBR at a flux of 18.6 $L/m^2 h$, and that the effluent had low permeate chemical oxygen demand (COD) (<20 mg/L on average). What's more, Seo et al. [12] and Ren et al. [13] showed that nonwoven fabric filters could also be operated with gravity when flux was operated at 16.7 and ~5 $L/m^2 h$, respectively. However, studies had found that large pore coarse filters in MBR system had membrane fouling problems, which were related to the hydrophobic surface. What's more, the coarse filters were generally poor in solid retention capacity and resulted in prolonged start-up time.

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To enhance the retention capacity and hydrophilic property, dynamic membrane (DM) and surface modification technology had been developed in recent years [14,15]. Reportedly, DM technology had the advantage of good effluent quality and could also alleviated membrane fouling in MBR process [16–18]. Diatomite particles could be used as the pre-coating materials and micro-organism carriers in aerobic dynamic MBR, and thus bio-diatomite was named [19,20]. The bio-diatomite dynamic membrane reactor (BDDMR) at lab scale had been tested for the treatment of micro-polluted surface water [21]. It was found that the BDDMR allowed high pollutant removal efficiency at a constant flux of 50 L/m^{2}h for a 74 µm-stainless steel mesh filter.

The hydrophobic membrane modification by polyvinyl alcohol (PVA) had been proved to be an effective way of enhancing the hydrophilic property [22–25]. PVA polymer is a kind of good membrane hydrophilic material, whose hydrogels can provide smooth and hydrophilic membrane surface. Coarse filter modification by PVA or TiO_2/PVA had been developed for wastewater treatment [22,23].

Therefore, dynamic membrane and PVA modification had different effects on large pore coarse filters in MBR system. In this paper, the nonwoven material would be modified by combining diatomite and PVA. The diatomite was first pre-coated on nonwoven surface to enhance the retention capacity. Then PVA modification was carried out to improve the hydrophilic property. Water contact angle, scanning electron microscope (SEM), and Fourier transform infra red spectroscopy (FTIR) analysis were measured to detect property changes with nonwoven membranes. Compared with original nonwoven, the modified nonwoven was tested in MBR process to evaluate the filtration performance.

2. Materials and methods

2.1. Materials and chemicals

Polyethylene terephthalate (PET) nonwoven (nominal pore size of 5 µm and 10 µm) were obtained from Shanghai Zhihe Filtration Material Co., Ltd. Polyvinyl alcohol powder (PVA, 1,750 ± 50) and glutaraldehyde (GA) 25% (w/w) were from Shanghai Lingfeng Chemical Reagent Co., Ltd. Diatomite and other chemical agents were obtained from Sinopharm Chemical Reagent Shanghai Co., Ltd.

Synthetic wastewater used as raw influent was prepared using Sucrose (250 mg/L), NH_4Cl (80 mg/L), KH_2PO_4 (40 mg/L), $CaCl_2$ (20 mg/L), albumenflakes (15 mg/L), $MgSO_4·7H_2O$ (30 mg/L), $MnSO_4·7H_2O$ (1.5 mg/L), and $FeSO_4·7H_2O$ (0.2 mg/L) as trace elements.

2.2. Surface modification of nonwoven membrane

The modification procedure of nonwoven membrane was summarized in Fig. 1. The nonwoven bag (23 cm × 23 cm × 100 cm) was immersed in absolute acetone for 3 h, followed by washing with water and dried at 70℃ [24]. After the nonwoven bag was placed in the reactor, diatomite was also added into the nonwoven bag. The reactor was operated continuously by feeding water with a peristaltic pump and draining the effluent under gravity flow. Contents were kept suspended by air pump. Permeate effluent turbidity was measured for every 15 min. The pre-coating was continuously operated until permeate turbidity concentration was below 5 NTU. Then nonwoven bag was taken out from the module.

According to pre-test data, the diatomite coated nonwoven bag was immersed in PVA solution, containing 1 wt.% PVA, at 45℃ for 2 h. Then the nonwoven bag was removed from the solution and immersed in the cross-linking solution which contained 5 wt.% GA, 10 vol.% methanol, 10 vol.% acetic acid, and 10 vol.% sulfuric acid, at 45℃ for 15 min. After cross-linking reaction, modified membrane was dried at 70℃ for 2 h in the oven and then placed in water for 48 h to remove the residues by continuous recirculation.

2.3. Experimental set-up and operational process

As shown in Fig. 2, double nonwoven MBR system consisted of inner nonwoven reactor, outer nonwoven bag (38 cm × 38 cm × 100 cm), and an aeration tank with

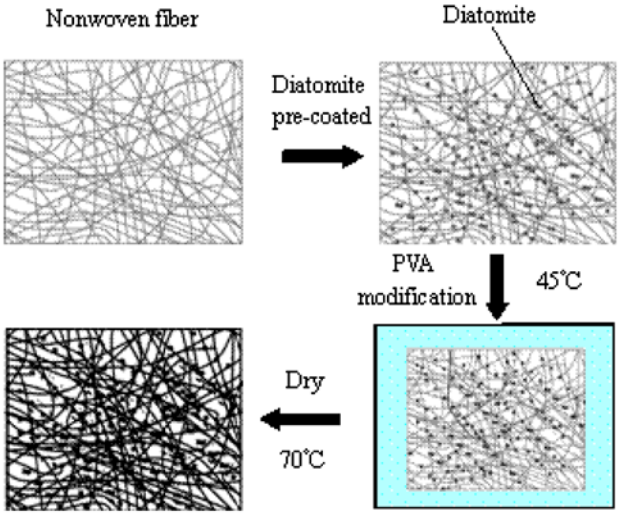

Fig. 1. Schematic illustration of the nonwoven membrane surface modification procedure.

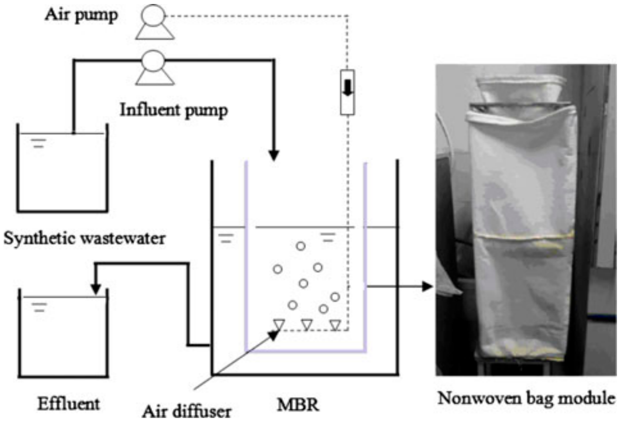

Fig. 2. Schematic diagram of MBR system and nonwoven bag module.

effective volume and filtration area of 84.2 L and 0.58 m^2, respectively. A stainless steel mesh was equipped into the reactor used as the support of nonwoven bags. Synthetic wastewater was continuously fed into the inner bag by metering pumps, and the effluent was discharged into a drain by naturally filtered through the nonwoven fabric. Air diffuser was equipped at the bottom of nonwoven bag to scour the membrane and mix the contents. The dissolved oxygen (DO) concentration was maintained at 3–4 mg/L. The activated sludge was seeded and maintained in the inner nonwoven bag. The systems were operated at three different hydraulic retention times (HRTs) of 23.4, 11.7, and 7.8 h during the operation with different fluxes. Trans-membrane pressure (TMP) was obtained by water head difference between both sizes of inner nonwoven bag. The filtration was not stopped until water head reached 30 cm. The water between inner bag and outer bag was called inner bag permeate.

2.4. Analytical methods

The samples were collected from the reactors, the influent, and the effluent once a day. DO and pH were measured by DO (Jenco-9010, USA) and pH (pHS-3C, Shanghai) meters, respectively. Chromaticity and turbidity were measured by color (SD9011, Shanghai) and turbidity meter (2100 N, USA), respectively. COD, ammonia (NH_4^+-N), and mixed liquor suspended solid (MLSS) were analyzed according to the standard methods [26]. Dynamic water contact angles of modified and original nonwoven were measured by DCA300 (Thermo Cahn, USA) to quantify the change of membrane surface. Surface morphologies of the modified and original nonwoven before and after used in MBRs were observed by SEM (Hitachi S-3400 N, Japan). FTIR of modified and original nonwoven was analyzed by a Nicolet Avatar 380 Instrument (Thermo Fisher Nicolet iS10, USA).

3. Results and discussion

3.1. Characterization and surface properties of the diatomite/PVA modified nonwoven fabrics

In this study, SEM images are employed to examine the surface structure of modified and original nonwoven in Fig. 3. After cross-linking reaction, in comparison with the micrograph of original nonwoven (Fig. 3(a)), the nonwoven fiber was coated with PVA. Diatomite deposited on nonwoven fabrics is glued by PVA polymer (Fig. 3(b)). The amount of diatomite might be larger and the membrane pore size might be reduced greater when the fibers were closely packed.

The modified and original membrane surfaces were monitored by dynamic contact angle measurement with ultra-pure water. The values obtained from the samples are listed in Table 1. Comparing with the

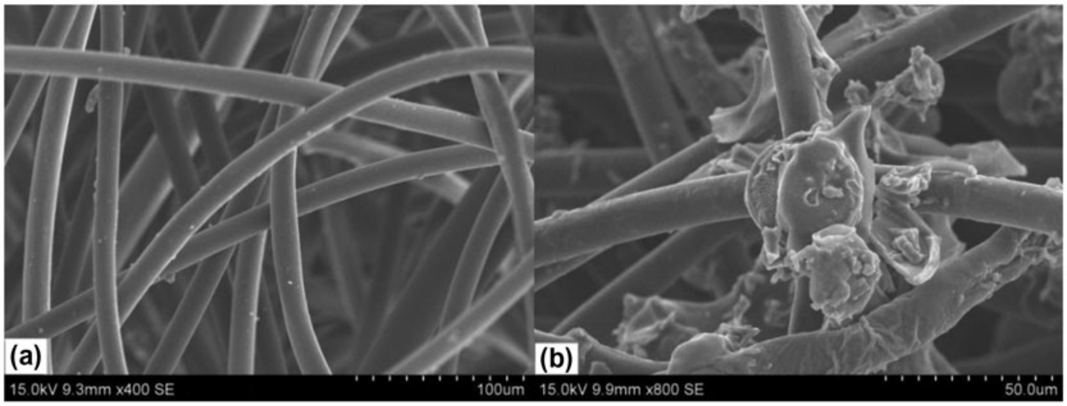

Fig. 3. SEM images: (a) original nonwoven and (b) modified nonwoven.

Table 1.
Dynamic contact angles for the PVA/diatomite modified nonwoven membrane

Membrane	Contact angle (°)
Original	112.71
Modified	53.83

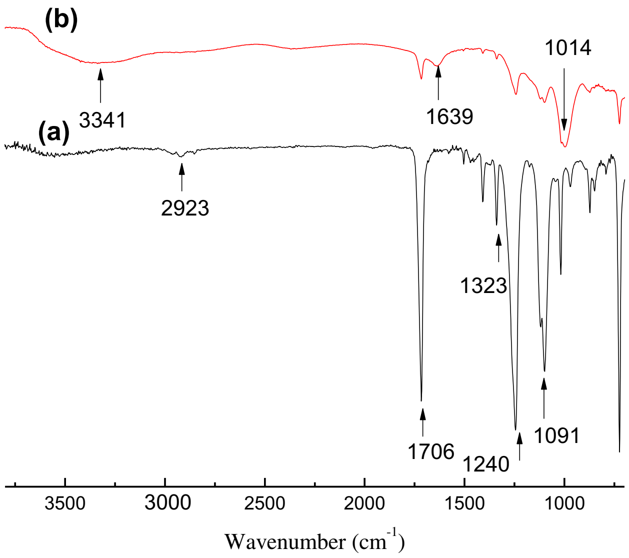

Fig. 4. FTIR spectra of nonwoven fabrics: (a) original nonwoven and (b) modified nonwoven.

original nonwoven, the contact angle of modified nonwoven were decreased from 112.71° to 53.83°, which might be attributed to the introduced Si–O and O–H groups from diatomite and PVA.

FTIR spectra analysis of nonwoven fabric samples are shown in Fig. 4. In Fig. 4(a), the absorption peaks at 1,706 cm^{-1}, 1,523–1,323 cm^{-1}, and 1,240–1,091 cm^{-1} can be attributed to –C=O stretching, benzene stretching, and –C–O–C stretching, respectively [27]. The spectrum of modified nonwoven sample spectra is shown in Fig. 4(b). The characteristic absorption bands at 3,341 cm^{-1} and 1,639 cm^{-1} are attributed to the –O–H stretching of PVA and absorbed water [25]. The PVA is bonded on fabric surface by the reaction of PVA and cross-linkers [24]. The absorption peak at 1,014 cm^{-1} may be from the O–aliphatic carbon interacting with diatomite on nonwoven surface [28]. They all contribute to a more hydrophilic surface of the modified nonwoven.

3.2. Comparisons of original and modified nonwoven MBR performance

The effluent qualities' comparisons of both nonwoven MBRs are listed in Table 2. Turbidity and chromaticity of inner bag permeate could be reduced to below 2 NTU and 40°, respectively. This is consisted with previous studies that cake layer formed on filter surface played a critical role in solid retention capacity [5,8,13]. It was noted that the inner bag permeate turbidity of modified nonwoven was 1.09 NTU, in comparison of the original nonwoven of 1.71 NTU. This indicated that diatomite/PVA pre-coated on nonwoven surface might account for the lower inner bag permeate turbidities. After second nonwoven membrane (5 μm) filtration, effluent turbidity and chromaticity were reduced to below 1 NTU and 20°, respectively. Results turned out that double nonwoven bag had good effect on solid retention capacity.

The effluent COD of modified nonwoven MBR was 41.26 mg/L and average 85.71% removal of influent COD (357.8 mg/L), respectively. This system also had low effluent NH_4^+-N of 2.31 mg/L and average 86.38% removal, respectively. The effluent qualities of modified nonwoven bioreactor had similar effluent qualities with other nonwoven equipped MBR systems [13,24].

Table 2.
Effluent qualities of both nonwoven MBR

		Modified		Original	
Items	Unit	Inner bag permeate	Effluent	Inner bag permeate	Effluent
Turbidity	NTU	1.09 ± 0.32	0.76 ± 0.43	1.71 ± 0.55	1.33 ± 0.32
Chromaticity	Degree	15.80 ± 7.56	10.73 ± 4.58	30.94 ± 8.97	15.02 ± 5.79
		Effluent	Removal (%)	Effluent	Removal (%)
COD	mg/L	36.26 ± 17.89	85.71	48.15 ± 18.98	80.93
NH_4^+-N	mg/L	2.31 ± 0.56	86.38	2.78 ± 0.68	79.25
pH	–	6.9 ± 0.25	7.0 ± 0.46	6.8 ± 0.53	7.0 ± 0.34

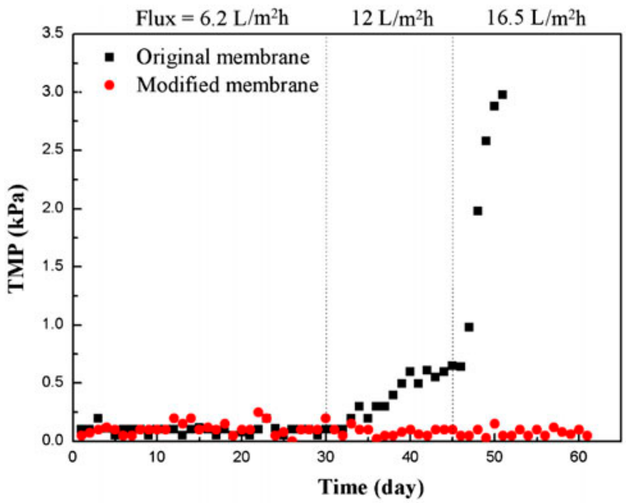

Fig. 5. Flux and TMP profiles: (a) original nonwoven and (b) modified nonwoven.

In this study, the MBR processes were continuously operated under gravity filtration for two months by maintaining proper MLSS level (5,000–6,000 mg/L). TMP variations of the two MBRs at three different imposed fluxes are presented in Fig. 5. It can be seen that at 45th–51st day, the TMP of original membrane increased dramatically from 0.60 to 2.92 kPa when flux increased from 12 to 16.5 L/m^2h. In contrast, the TMP of modified membrane was stable and even had a slight decrease from 0.09 to 0.07 kPa. It was smaller than those in other low-pressure nonwoven or mesh-equipped MBRs [5,13].

TMP of the modified nonwoven was more stable, the filtration time was longer than that of the original membrane (Fig. 5). The diatomite and PVA pre-coated on nonwoven surface might prevent the deposition of pollutants from nonwoven surface, which ensured stable TMP values. In addition, the stable performance of modified membrane indicated that if the flux was set between 16.5 and 20 L/m^2h, and operation parameters were optimized [29], longer operation durability might be acceptable when diatomite/PVA nonwoven MBR system was used.

3.3. *Membrane surface analysis of the original and modified nonwoven*

The SEM analysis images of original and modified nonwoven membrane surface at the end of the

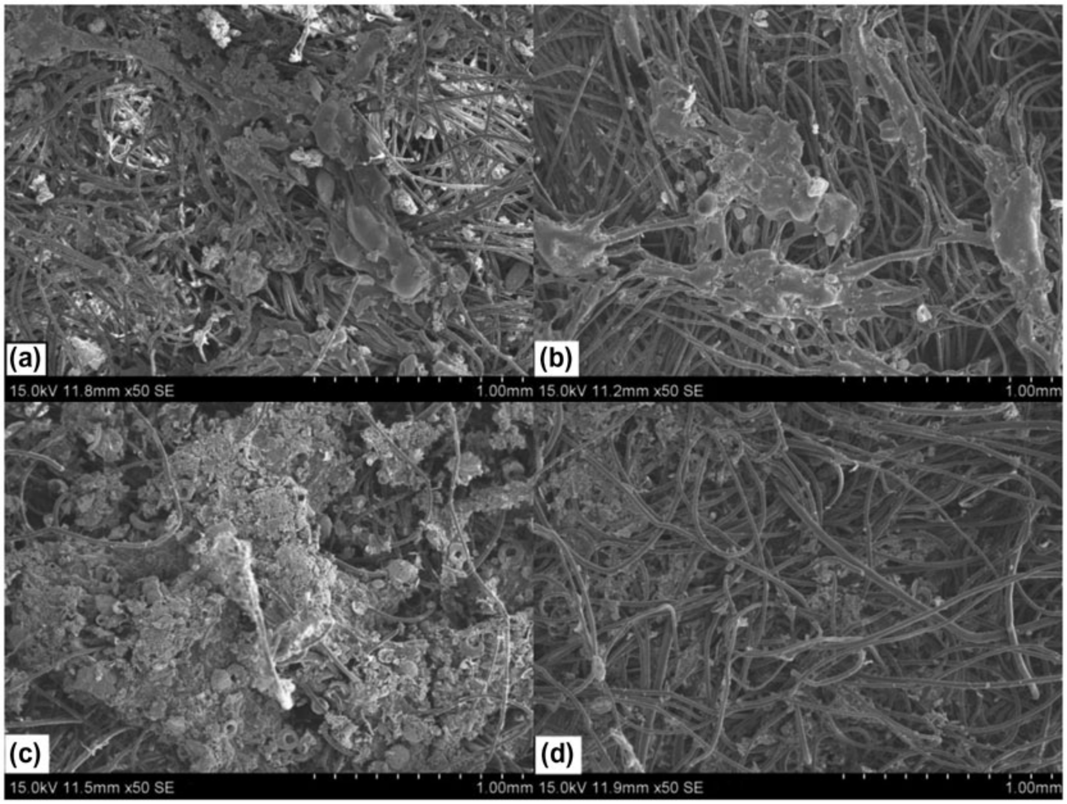

Fig. 6. SEM images of the fouled ((a) and (c)) and cleaned ((b) and (d)) nonwoven surface; (a), (b)—original nonwoven; (c), (d)—modified nonwoven.

operation are shown in Fig. 6(a) and (c). Both of the nonwoven membrane surfaces had fouled layers. It had been reported that the removable fouling could be easily removed from the membrane surface and pores by physical cleaning [30]. Fig. 5(b) and (d) shows the membrane surfaces of original and modified nonwoven after physical cleaning. The pollutants on original nonwoven membrane had a strong adhesion to the surface or pores. The fouled layer on original nonwoven surface might result in the increase of TMP (in Section 3.2). In contrast, the fouled layer on modified nonwoven surface was removed. The fabrics were also exposed to the nonwoven surface (Fig. 6(d)).

4. Conclusions

(1) The nonwoven fabric was modified by diatomite/PVA. SEM pictures demonstrate that PVA uniformly covered the nonwoven fabrics and glued the diatomite. In comparison with the original nonwoven, the contact angle of the modified nonwoven decreased from 112.71° to 53.83°.

(2) MBR experimental results showed that low effluent chromaticity and turbidity levels of 20 and 1 NTU could be obtained after second nonwoven bag filtration. Similar average effluent COD and NH_4^+-N concentrations could be reduced to less than 45 and 2.5 mg/L, respectively.

(3) The modified nonwoven MBR had good antifouling property and no TMP increased when flux was 6.2–16.5 L/m^2 h under gravity flow.

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