Performance of diatomite/iron oxide modified nonwoven membrane used in membrane bioreactor process for wastewater reclamation

Yueling He, Wenqi Zhang, Pinhua Rao and Peng Jin

ABSTRACT

This study describes an approach for surface modification of a nonwoven membrane by diatomite/iron oxide to examine its filterability. Analysis results showed that nonwoven hydrophilicity is enhanced. Static contact angle decreases dramatically from 122.66° to 39.33°. Scanning electron micrograph images show that diatomite/iron oxide is attached on nonwoven fiber. X-ray diffraction analysis further proves that the compound is mostly magnetite. Fourier transformed infrared spectra results reveal that two new absorption peaks might be attributed to Si—O and Fe—O, respectively. Modified and original membranes were used in double nonwoven membrane bioreactors (MBRs) for synthetic wastewater treatment. High critical flux, long filtration time, slow trans-membrane pressure rise and stable sludge volume index confirmed the advantages of modified nonwoven. Comparing with original nonwoven, similar effluent qualities are achieved, meeting the requirements for wastewater reclamation.

Key words | diatomite/iron oxide, double nonwoven MBR, nonwoven, wastewater reclamation

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INTRODUCTION

Membrane bioreactors (MBRs) have distinct advantages over conventional wastewater treatment for high pollutant removal efficiency, complete solid–liquid separation and little sludge waste (Seo *et al.* 2007; Judd 2008; Meng *et al.* 2009). However, membrane cost and energy consumption are still comparatively high. Low-cost filter materials like mesh, fabric cloths and nonwovens have been rapidly developed in the MBR process. Fan & Huang (2002) and Fuchs *et al.* (2005) found that the dynamic membrane formed on the mesh surface had a high solid–liquid separation efficiency. Loderer *et al.* (2012, 2013) reported that mesh filter system had excellent performance in effluent quality, and high filtration flux of 150 L/(m^2·h) was obtained with frequent cleaning for dynamic filtration.

Nonwoven has outstanding properties like variable pore size distribution, inexpensive filter material and uncomplicated design (Chang *et al.* 2006). Both Meng *et al.* (2005) and Chuang *et al.* (2011) reported that nonwoven could be used in submerged MBR system for wastewater treatment. Seo *et al.* (2003) showed that it could be used in gravity filtration for solid–liquid separation. Recently, Ren *et al.* (2010) used a nonwoven fabric filter bag (NFFB) as MBR under gravity flow for activated sludge separation. However, nonwoven is relatively hydrophobic and there is an interest in the exploration of antifouling methods to improve its hydrophilicity.

For nonwoven MBR system, methods of grafting polymer onto the membrane surface, activating the surface by plasma and adsorbing suitable hydrophilic polymers on its surface have been developed (Zhang *et al.* 2008). However, those methods are quite complex and not suitable for large-scale application. Diatomite has been developed as filter aids, adsorbent and in other techniques in many industrial areas for its good hydrophilicity, high porosity and favorable adsorptive properties. Methods of hydrous ferric oxide incorporated into diatomite are eco-friendly, cost-effective and simple (Jang *et al.* 2006). Diatomite precoated on stainless steel mesh forming a bio-diatomite dynamic membrane reactor has been proved to be effective for water treatment (Chu *et al.* 2010). However, nonwoven filter materials modified with diatomite/iron oxide and their application in MBR systems have not been reported.

A method of coating diatomite/iron oxide on nonwoven surface for membrane modification was investigated. Contact

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angle, scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transformed infrared (FTIR) analysis were used to detect physical and chemical property changes with nonwoven membranes. The modified membrane used in MBR was tested with effluent qualities, and its filtration performance was compared with an original nonwoven.

MATERIALS AND METHODS

Materials and chemicals

Diatomite and other chemical agents were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd. The polyethylene nonwovens with nominal pore size of 5 and 10 μm were obtained from Shanghai Zhihe Filtration Material Co., Ltd.

Synthetic wastewater used as raw influent was prepared including: sucrose (222.9 mg/L), NH_4Cl (76.9 mg/L), KH_2PO_4 (37 mg/L), $CaCl_2$ (20 mg/L), albumen flakes (15 mg/L), $MgSO_4 \cdot 7H_2O$ (30 mg/L), $MnSO_4 \cdot 7H_2O$ (1.5 mg/L) and $FeSO_4 \cdot 7H_2O$ (0.2 mg/L) as trace elements. The characteristics of synthetic wastewater are listed in Table 1.

Preparation of diatomite-modified membrane

The following procedure was developed to coat diatomite/iron oxide on the nonwoven surface. A nonwoven bag (23 cm × 23 cm × 100 cm) was immersed in a submerged module. According to the pre-test data, diatomite and iron power were mixed at a proportion of 1:3, and added into water with a dose of 200 mg/L. The contents were kept suspended by an air pump and mixture pH was kept at 3.5. The compound intercepted on nonwoven filter was carried out by circulation filtration. The effluent turbidity was measured every 15 minutes. The filtration process was stopped when effluent turbidity become below 5 NTU and the aeration of system was continued for 48 h. The nonwoven filter was taken out and dried at room temperature for 4 days. Later, the filter membrane was placed into the MBR system for use.

Table 1 | Characteristics of synthetic water

Synthetic wastewater parameters	Range
Chemical oxygen demand (mg/L)	200.23–589.94
NH_4^+-N (mg/L)	13.31–34.17
Chromaticity (degree)	121–426
Turbidity (NTU)	9.87–39.8
pH	6.67–8.32
Temperature (°C)	15–28

Experimental setup and operational process

Double submerged nonwoven MBR systems (inner bag and outer bag) used in this study are shown in Figure 1. Physicochemical properties of the bags are listed in Table 2. The modules were defined as MBRa (original nonwoven) and MBRb (modified nonwoven). Stainless steels were used as support module of nonwoven bags.

The total effective volume and filtration area for the inner bag were 84.2 L and 0.58 m^2, respectively. Synthetic wastewater was fed into the inner bag continuously by a

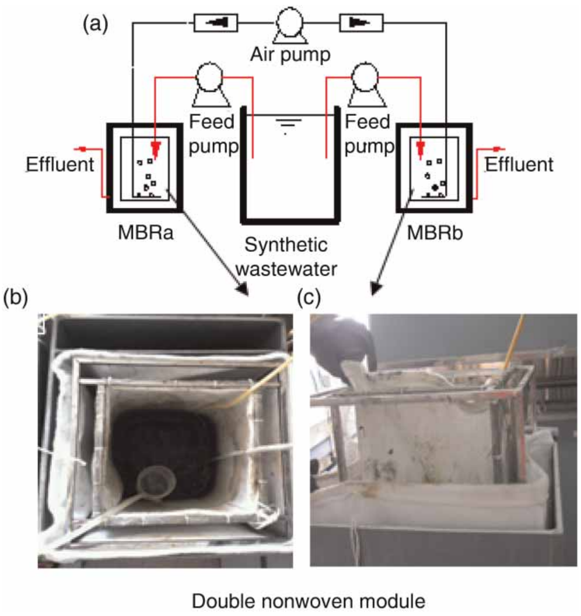

Figure 1 | Schematic of the experimental setup.

Table 2 | Physicochemical characteristics of the experimental nonwoven

Parameters	PE 5 μm (outerbag)	PE 10 μm (inner bag)
Materials	polyethylene	polyethylene
Thickness (mm)	2.3	2.3
Weight per unit area (g/m^2)	400	350
Production mode	Needle	Needle
Surface treatment	Singeing calender	Singeing calender
Gas permeability ($m^3/(m^2 \cdot min)$)	30–45	75–105

metering pump. The system was operated continuously under gravity without a suction pump. The trans-membrane pressure (TMP) across the bag was obtained by water head reached. The filtration was stopped once the TMP in the water head reached 30 cm. An air diffuser was placed at the inner nonwoven bag bottom to scour the nonwoven membrane and keep dissolved oxygen (DO) concentration above 3 mg/L for aerobic microorganism growth. Nonwoven systems were operated at three different influent flow rates during operation period using metering pumps. No dedicated excess sludge was discharged and the sludge retention time was prolonged. TMP was calculated by the following formulae:

$$\mathrm{TMP} = \rho g \Delta h$$

where Δh is the water head drop (cm), ρ is the density of mixed solution (1.0×10^3 kg/m^3), g is the acceleration of gravity (9.8 m/s^2) (Chen & Cong 2006).

Analytical methods

The chemical oxygen demand (COD), ammonia (NH_4^+-N), chromaticity, turbidity, sludge volume index (SVI), DO and pH were measured according to standard methods (Wei & Qi 2002). All the parameters were determined once a day during the first month. After that, COD and NH_4^+-N were measured once every 2 days. DO and pH were measured by DO (Jenco-9010, USA) and pH (pHS-3C, Shanghai) meters, respectively. Turbidity and chromaticity were measured by a turbidity (2100N, USA) and color meter (SD9011, Shanghai), respectively. Static contact angle of the modified membrane and original nonwoven was measured by static contact angle SL200C (Solon Tech, Shanghai). Surface morphologies of modified membrane and original nonwoven were observed by SEM (Hitachi S-3400N, Japan). The compound was analyzed by XRD (Bruker D2 Phaser, GER). The modified and original nonwoven membranes were analyzed using attenuated total reflection (Thermo Fisher, Nicolet AVATAR 380).

RESULTS AND DISCUSSION

Characterization and surface properties of the diatomite/iron oxide modified nonwoven fibers

The water contact angles of original and modified membrane are shown by the images in Figure 2 and the measured data are listed in Table 3. Results showed that the hydrophilicity of nonwoven was enhanced greatly and contact angle decreased dramatically from 120.66° (original nonwoven) to 39.33° (modified nonwoven) because of Si—O and Fe—O groups from diatomite/iron oxide compound.

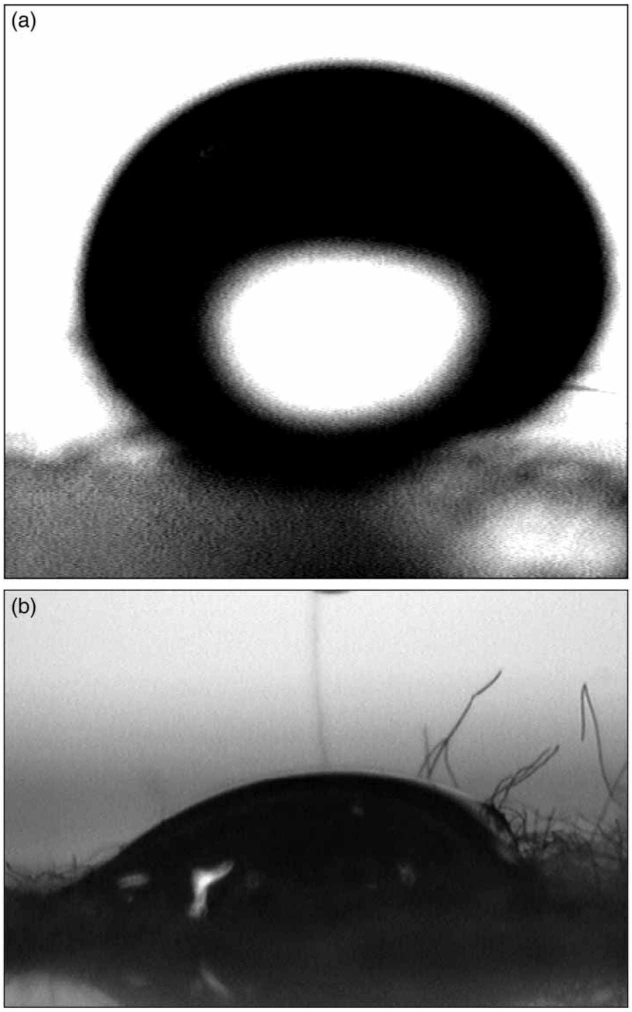

Figure 2 | Water contact angles: (a) original nonwoven, (b) modified nonwoven.

Table 3 | Static contact angles for the diatomite/iron oxide modified nonwoven membrane

Membrane	Contact angle
Nonwoven	122.66°
Modified membrane	39.33°

The SEM images of modified and original nonwoven are shown in Figure 3. The diatomite surface was almost covered by iron oxide and no aperture was seen. The compound deposited well on nonwoven fabric, which made the fiber much coarser than the original nonwoven.

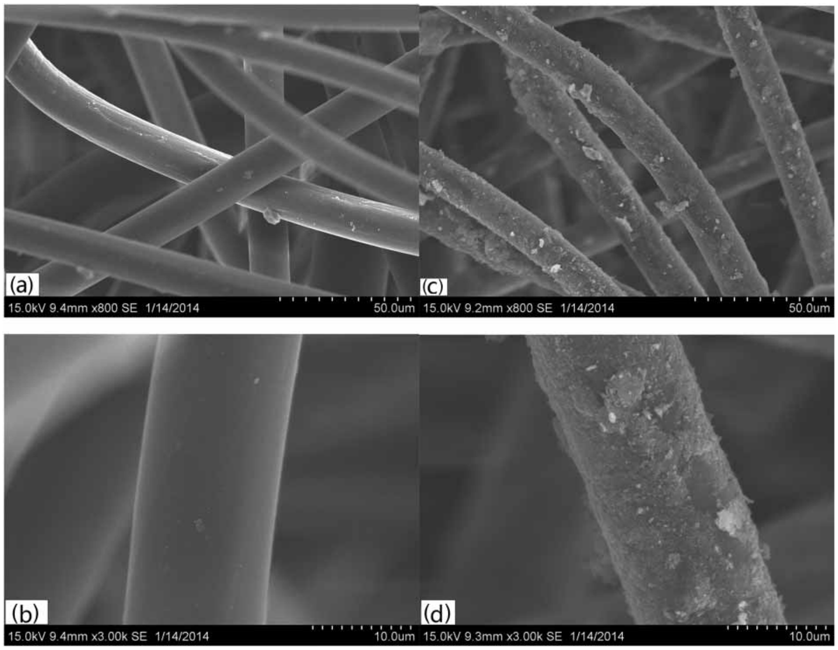

Figure 3 | SEM images of (a) and (b) original nonwoven, (c) and (d) modified membrane.

The changes in SEM images agreed with the result of the following XRD analysis.

XRD shows the peaks of diatomite/iron oxide compound. An amorphous structure is observed in the diatomite/iron oxide compound (Sun *et al.* 2013). XRD results show that the peaks at different degrees (2θ of 30°, 35.5°, 43°, 53.5°, 56.5° and 62.8°) are mostly magnetite (Dong *et al.* 2014). It also suggests that iron is gradually oxidized and formed iron minerals on nonwoven surface.

FTIR spectra of diatomite, diatomite/iron oxide, modified membrane and nonwoven membranes are shown in Figure 4. In spectrum (a), the absorption peaks at 1074 and 794 $\mathrm{cm^{-1}}$ reflect the Si—O group of asymmetric stretching modes and symmetric stretching vibration, respectively (Sun *et al.* 2013). The diatomite/iron oxide typically enhances absorption at 584 $\mathrm{cm^{-1}}$ for its Fe—O group (Tamaura & Buduan 1981). Comparing the two spectra, new absorption peaks are shown in spectra (c). The absorption peak at about 794 $\mathrm{cm^{-1}}$ can be attributed to diatomite in the membrane surface. The absorption peak at about 584 $\mathrm{cm^{-1}}$ for iron oxide can be attributed to Fe—O group.

Effect of different flux on the operation of the system

Sub-critical flux is considered an important factor in sustainable submerged MBRs. Figure 5 shows SVI and TMP profiles for two double nonwoven MBRs during the test.

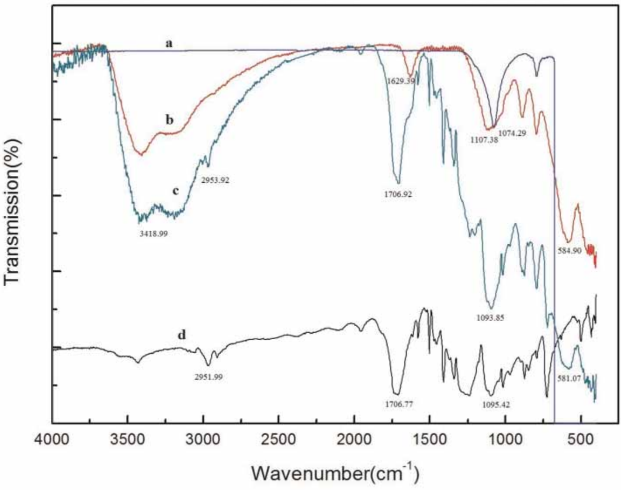

Figure 4 | FTIR spectra of nonwoven membranes: (a) diatomite, (b) diatomite/iron oxide granule generated on the filter surface, (c) diatomite/iron oxide modified nonwoven, (d) original nonwoven.

Both of the operations were divided into three periods, flux of 6 L/($\mathrm{m^2}$·h) for 30 days, 12 L/($\mathrm{m^2}$·h) for 15 days and 18 L/($\mathrm{m^2}$·h) for the rest of the test. The flux was higher than that of the NFFB system, which had a flux between 4.17 and 6.25 L/($\mathrm{m^2}$·h) (Ren *et al.* 2010). The systems were stable for the first 40 days and the SVI showed gradual increase along with biomass growth.

At 33–47 days, TMP of MBRa showed a slow rise. Afterward, the TMP rose to 2978 Pa, and pumping had to be

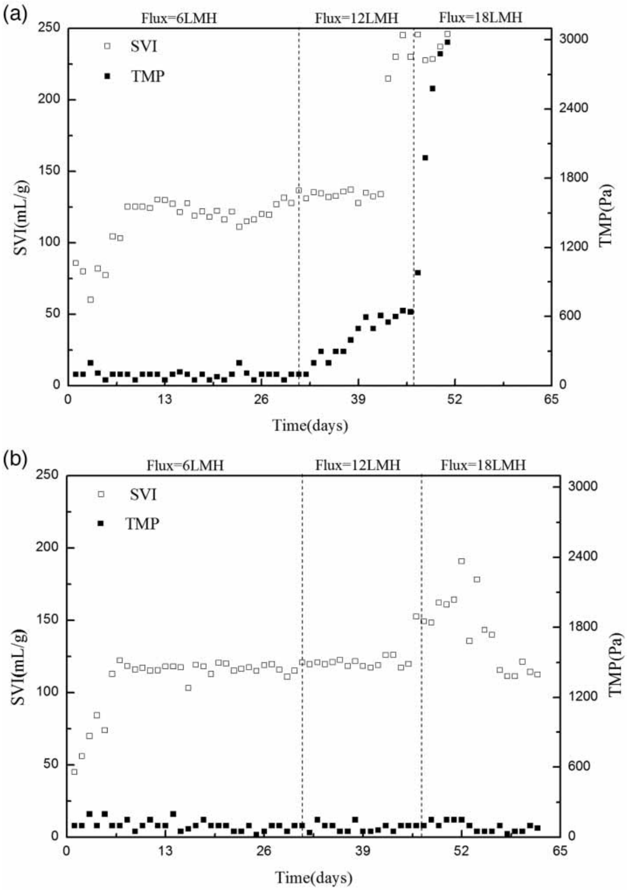

Figure 5 | (a) Flux and TMP in MBRa; (b) flux and TMP in MBRb.

stopped (Figure 5(a)). It has been accepted that high flux would result in the increase of extracellular polymeric substances concentration and membrane resistance (Chae *et al.* 2006). SVI of MBRa also increased above 200 mL/g when sludge bulking happened. This situation was normally attributed to the growth of filamentous bacteria.

MBRb (Figure 5(b)) had higher flux, slow TMP rise (<200 Pa), more stable SVI (<150 mL/g) and longer filtration time than that of MBRa. The coarser nonwoven surface (SEM analysis) and diatomite/iron oxide coated on nonwoven (FTIR analysis) might be related to stable operation. It was hereby confirmed that modified nonwoven showed good antifouling properties for 61 days continuous operation period.

POLLUTANT REMOVAL EFFICIENCY

Turbidity and chromaticity removal

Chromaticity and turbidity of two MBRs are shown in Figures 6(a)–(d). Although inner bag permeate had relatively high chromaticity and turbidity concentrations of 90 degree and 5 NTU, stable effluent concentrations could become below 20 degree and 0.5 NTU, respectively. This result demonstrated that double nonwoven membrane showed good filtration performance as expected. The turbidity data were lower than those of some other MBR systems (Zhang *et al.* 2008; Wang *et al.* 2012).

Removal of COD and NH_4^+-N

The system was fed with stable synthetic wastewater influent (average 357.8 mg/L COD and 20 mg/L NH_4^+-N). As can be seen in Figure 6(e), COD of both MBR effluents decreased to below 80 mg/L and similar concentrations could be obtained. The results were somewhat similar to the dynamic membrane bioreactor process (Fan & Huang 2002). Unlike organics, as shown in Figure 6(f), effluent NH_4^+-N fluctuated with influent NH_4^+-N concentrations, and then nitrification gradually become stable. During the second stage, effluent NH_4^+-N concentration become below 2.5 mg/L. Comparing with MBRa, effluent NH_4^+-N concentrations of MBRb were more stable and had no significant fluctuation. The double nonwoven MBR provided similar effluent COD and NH_4^+-N concentrations with other nonwoven coupled MBR systems (Chang *et al.* 2006; Zhang *et al.* 2008; Ren *et al.* 2010), and it could meet the requirements for wastewater reclamation in China (GB/T18920–2002).

CONCLUSIONS

Polyethylene nonwoven was modified by coating diatomite/iron oxide on the nonwoven membrane. Measured static contact angle with modified membrane and original nonwoven decreased from 122.66° to 39.33°. SEM images showed that diatomite/iron oxide could be coated on the nonwoven membrane. FTIR spectra of nonwoven surface revealed that two new absorption peaks might be attributed to Si—O and Fe—O groups, respectively. Double submerged nonwoven MBR was used for synthetic wastewater treatment. Results demonstrated that the modified membrane had higher critical flux, longer operation period, lower operation TMP and lower SVI in comparison with original nonwoven MBR. Effluent COD and NH_4^+-N concentrations of both MBRs could be reduced to less than 80 and 2.5 mg/L, respectively. Low effluent chromaticity and turbidity concentrations of 20 degree and 0.5 NTU could be reached after a second nonwoven bag

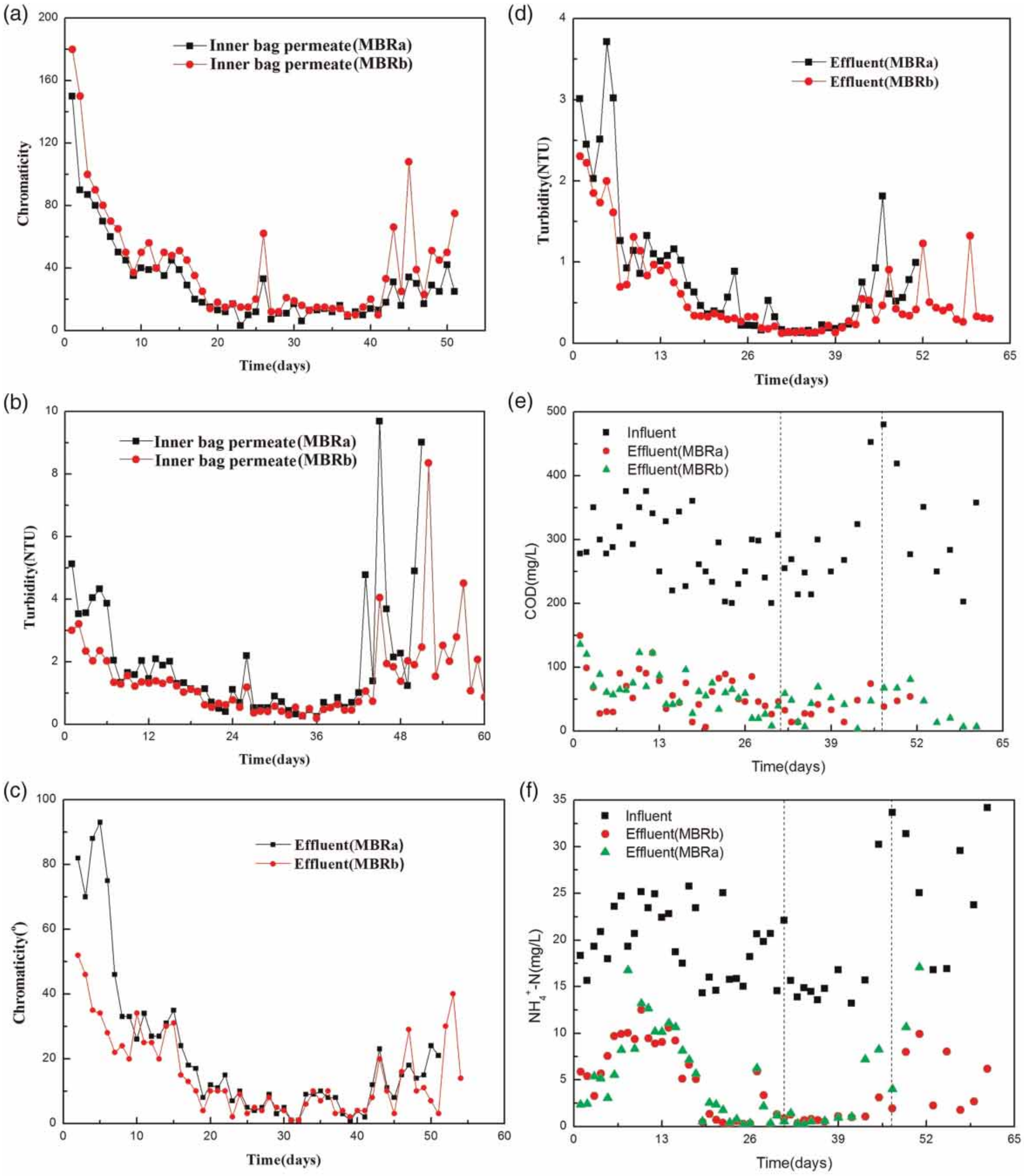

Figure 6 | (a) Inner bag permeate turbidity comparison; (b) inner bag permeate chromaticity comparison; (c) effluent chromaticity comparison; (d) effluent turbidity comparison; (e) variety of COD during operation; (f) variety of NH$_4^+$-N during operation.

filtration. The results could meet the requirements for wastewater reclamation.

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