Advanced treatment of dyeing wastewater towards reuse by the combined Fenton oxidation and membrane bioreactor process

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Abstract

The performance of combined Fenton oxidation and membrane bioreactor (MBR) process for the advanced treatment of an effluent from an integrated dyeing wastewater treatment plant was evaluated. The experimental results revealed that under the optimum Fenton oxidation conditions (initial pH 5, H_2O_2 dosage 17 mmol/L, and Fe^{2+} 1.7 mmol/L) the average total organic carbon (TOC) and color removal ratios were 39.3% and 69.5% after 35 min of reaction, respectively. Results from Zahn-Wallens Test also represented that Fenton process was effective to enhance the biodegradability of the test wastewater. As for the further purification of MBR process, TOC removal capacity was examined at different hydraulic retention times (HRT) of 10, 18 and 25 hr. Under the optimum HRT of 18 hr, the average TOC concentration and color of the final MBR effluent were 16.8 mg/L and 2 dilution time, respectively. The sludge yield coefficient was 0.13 g MLSS/g TOC and TOC degradation rate was 0.078 kg TOC/(m³·day). The final effluent of MBR can meet the reuse criteria of urban recycling water – water quality standard for miscellaneous water consumption GBT18920-2002.

Key words: dyeing wastewater; Fenton oxidation; membrane bioreactor; Zahn-Wallens Test

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Introduction

Textile dyeing industry demands large quantities of water, which results in large amounts of wastewater streams of complex contaminant matrix from different steps (dyeing, bleaching, printing, soaking and finishing) of textile industry process. The discharged wastewater which has strong color, high value of chemical oxidation demand (COD) and extremely low biochemical oxygen demand (BOD) to COD ratio may exert a great impact on the environment and therefore the related ecology (Kritikos et al., 2007). Nowadays, many dyeing wastewater treatment plants have been built to eliminate the adverse effect of pollution in China. However, the effluents of these wastewater plants are hardly to meet the standards of water reuse. Suspend solid (SS), turbidity, color and the residual non-biodegradable substance are the key factors affecting the reclamation (Brik et al., 2006). Therefore, advanced treatment is necessary to upgrade the treated wastewater quality to reuse criteria. Fenton oxidation (FO) process, based on the generation of highly reactive hydroxyl radicals, is recognized as a valuable method to de-color and increase the biodegradability of dyeing wastewater due to its high oxidative efficiency, non-selective and easy of

implementation (Bae et al., 2004; Ruppert et al., 1993). But it is evident that sole Fenton oxidation is not economical due to its high cost of reagents. Therefore, bio-treatment is more attractive for the final purification of the wastewater. Among the bio-treatment methods, membrane bioreactor (MBR) is a promising bio-technology which involves a suspended growth activated sludge system and a microfiltration/ultrafiltration (MF/UF) membrane for solid/liquid separation. MBR system has a potential to degrade the residual organic matters and to obtain a high effluent quality. It has many advantages such as high quality of effluents, high biomass concentration, high organic loading, less production of sludge and the total retention and enrichment of effective bacteria (Fan et al., 2006). In addition, MBR effluents can be of good quality for water recycle or for further purification steps (Heran et al., 2008).

The main objective of the present study was to investigate the technical feasibility of combined Fenton oxidation and MBR process for reclamation of an effluent from integrated dyeing wastewater treatment plant (IDWTP) in Jiangyin City of China. The optimum operating conditions of the pre-treatment with Fenton oxidation were determined for efficiently chemical reagents use and to achieve the best TOC/color reduction ratios. The supernatant of Fenton oxidation was subsequently fed to the MBR system for the final purification.

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1 Materials and methods

1.1 Wastewater source and characterization

The wastewater sample was obtained from the effluent of IDWTP. The flow chart of IDWTP is presented in Fig. 1, and the characteristics of the raw wastewater and effluent of IDWTP (hereafter refers as EI water) are summarized in Table 1.

Table 1 shows that the residual anthraquinone dye Reactive Blue 4 (RB4) ($C_{23}H_{12}CL_2N_6O_8S_2 \cdot 2Na$) is one of the most recalcitrant pollutes in this treatment system, which can not be degraded completely by sole bio-treatment. Although RB4 resembles only a small fraction of the organic load, the color of effluent should be considered.

1.2 Main reagents

Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), H_2O_2 (30%, *W/W*) and deithylene glycol (DEG) were obtained from Sinopharm Chemical Reagent Company (Shanghai, China). Sulfuric acid, NaOH and CaO were obtained from Shanghai Lingfeng Chemical Reagent Company (China). All the chemical regents are analytical grade and used without further treatment.

1.3 Experimental setup

1.3.1 Jar test of Fenton oxidation

Jar test of Fenton oxidation was conducted in a batch mode using a 500 mL jar with an effective wastewater

Table 1 Characteristics of raw wastewater and effluent of integrated dyeing wastewater treatment plant (IDWTP)

| Parameter	Raw	Effluent
COD_{Cr} (mg/L)	1100–1300	220–300
BOD_5 (mg/L)	180–250	20–40
BOD_5/COD_{Cr}	0.15–0.20	0.10–0.12
TOC (mg/L)	720–830	120–150
NH_4-N (mg/L)	65–90	5–10
Reactive Blue 4 (RB4) (mg/L)	12–20	5–8
Total nitrogen (TN) (mg/L)	80–120	30–40
pH	9–10	7.2–7.5
Total phosphates (TP) (mg/L)	10–20	0.5–1.5
Suspend solids (SS) (mg/L)	100–200	50–80
Oil and grease (mg/L)	10–35	ND
Conductivity (μS/cm)	1500–2000	1800–2200
Color (time)	70–90	20–25

ND: not detectable

volume of 350 mL. The reaction was controlled at 20°C for all Fenton experiments. The quantitative ferrous sulfate was added to an appropriate amount of EI solution. After pH adjustment using H_2SO_4 (1 mol/L) and NaOH (5 mol/L), 30% (*W/W*) H_2O_2 was added immediately into the mixture and Fenton oxidation was occurred. The mixed solution was stirred at 30 r/min during the reaction. After the designated oxidation time, CaO was added to the solution to increase the pH to approximately 5. Then, 5 mol/L NaOH solutions were added to neutralize pH to 7–8 and the solids of Fenton sludge were allowed to settle for a few hours. The obtained supernatant were then analyzed and served as the influent of MBR system.

1.3.2 MBR system

The submerged aerobic MBR used in this study was mainly composed of an activated sludge reactor and a hollow fiber membrane module (Fig. 2). The bio-reactor, made of plexiglass, had an effective volume of 6 L. The membrane module (Sadf2590a, Mitsubishi, Japan) was made of Polyvinylidene fluoride (PVDF) with effective surface area 0.04 m^2 and nominal pore size 0.2 μm. The fixed membrane module was aerated vertically through an air diffuser system located at the base of the membrane module, and the aeration rate was in the range of 1.5–2.0 L/min. The membrane module was operated alternately with a cycle of 8-min suction and 2-min off. The operation was stopped when TMP was higher than 35 kPa due to the severe membrane fouling. The membrane module was taken out from the bioreactor and the chemical cleaning was conducted to recover the permeate capacity.

1.3.3 Fenton + MBR description

The experiment consisted of two parts: one was Fenton oxidation and the other was MBR. Figure 3 depicts the experimental process. Fenton oxidation was carried out in batch mode under the optimum conditions determined by the jar tests. The product of supernatant was collected into a store tank for the further polishing stage of continuous MBR treatment. The bioreactor was originally seeded with sludge collected from the secondary sedimentation tank of IDWTP. After the acclimation, different parameters and the running characteristics were evaluated during the long-term operation.
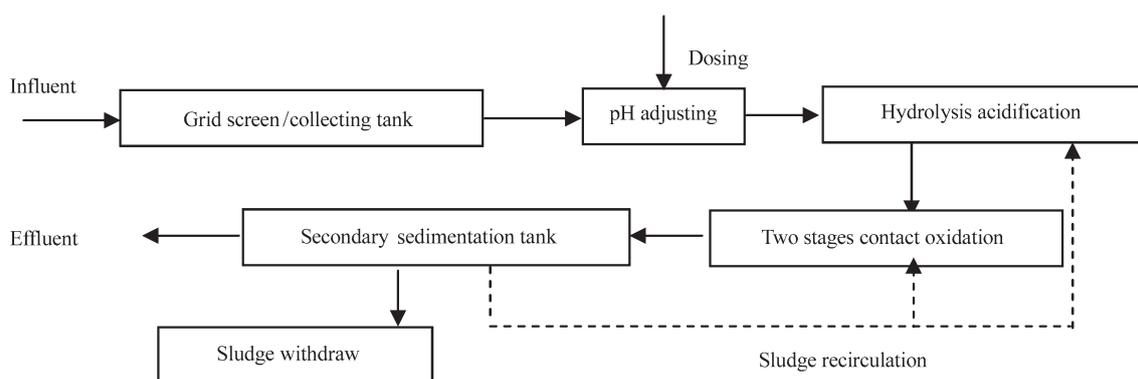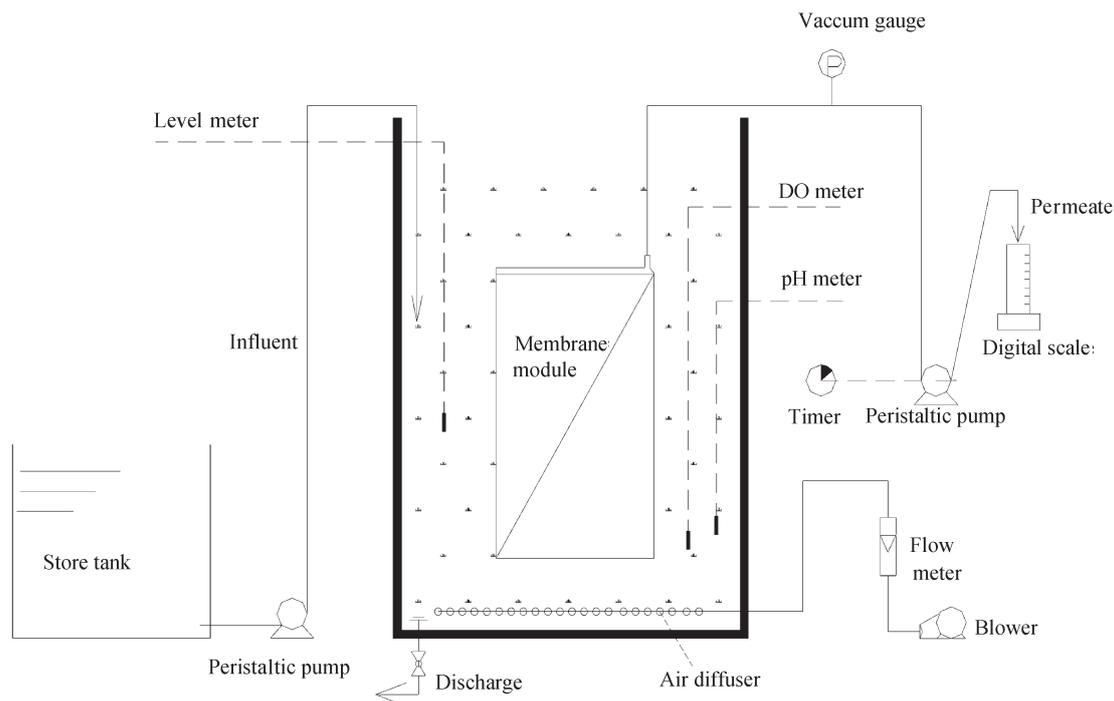

Fig. 1 Flow chart of IDWTP.

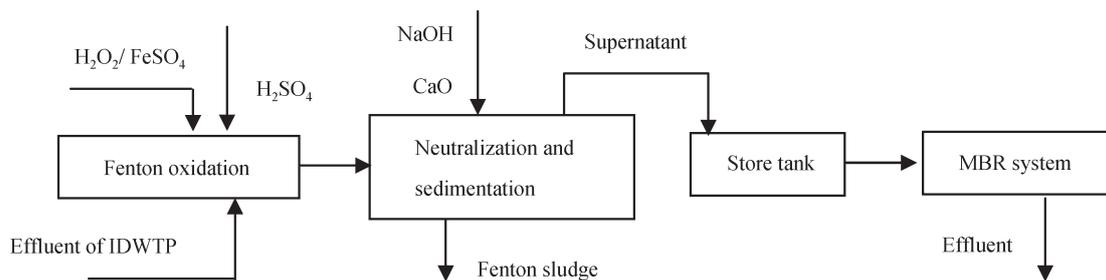**Fig. 2** Schematic diagram of experimental membrane bioreactor (MBR) system.

Fig. 3 Process of Fenton + MBR experiments.

1.4 Analytic methods

The concentration of RB4 was measured by a UV-Vis spectrophotometer (UV-2450, Shimadzu, Japan) with a spectrometric quartz cell (1 cm path length) at the max absorbent wavelength (λ_{max}) 599 nm. Calibration equation was $C = 66.23A - 0.84$, $R^2 = 0.9982$. The RB4 degradation ratio (R_d, %) was calculated as follows:

$$R_d = \frac{A_{initial} - A_{observed}}{A_{initial}} \times 100\% \tag{1}$$

where, $A_{initial}$ is the initial absorbance, and $A_{observed}$ is the measured absorbance after reaction

TOC and TN were measured by the TOC/TN analyzer (TOV-CPN, Shimadzu, Japan). COD_{Cr}, BOD_5, SS, NH_4^+-N and color were determined by the methods of the Chinese NEPA standard (National Environment Protection Agency, China). The method of dehydrogenase (DHA) identification was conducted as the procedures described by Chen and Gu (2005).

1.5 Definitions of biodegradation ability

The Zahn-Wellens Test was carried out according to the protocol of Directive 88/302/EEC. The unadapted activated sludge obtained from a sewage treatment plant was used as inoculums. The raw activated sludge was preliminary treated as the procedure depicted by Lapertot et al. (2006). Besides, the control substrate of deithylene glycol (DEG) and the test water were added into separated vessels to perform the degradation. The required concentration of inoculums (C_I, mg wet sludge/L) is calculated using Eq. (2):

$$C_I = (3/0.09) \times \text{TOC} \tag{2}$$

The degradation process was monitored by determining the evolution of TOC values at regular time interval of 24 hr. In practical operation, TOC was always determined 3 hr later after beginning the test to avoid the adsorption of test material by the activated sludge. The operation was conducted for 28 days. The volume of the bio-reactors is kept constant during the long-term operation by adding
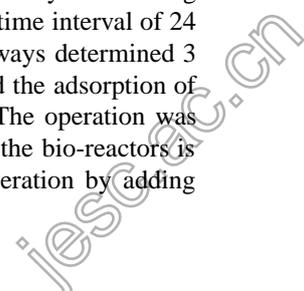
distilled water. The biodegradation percentage can be expressed as Eq. (3):

$$D_t = (1 - \frac{C_t - C_B}{C_A - C_{BA}}) \times 100\% \qquad (3)$$

where, D_t (%) is biodegradation percentage at time t, C_A (mg/L), and C_t (mg/L) are TOC values in the test mixture measured at 3rd hr after starting the test, and at time t, respectively, C_{BA} (mg/L) and C_B (mg/L) are TOC values of the blank measured at 3rd hr after test beginning, and at time t, respectively.

The ratio of the eliminated TOC after each interval to the value measured at 3rd hr after the start was expressed as percentage biodegradation which served as the measurement of degradation extent at the time (Wang et al., 2008). Substances $D_t > 70\%$ are considered biodegradable.

2 Results and discussion

2.1 Fenton oxidation and parameters optimization

2.1.1 Effect of initial pH

The wastewater sample for jar test of Fenton oxidation was characterized as: TOC 140 mg/L; RB4 8 mg/L; pH 7.3; and COD$_{Cr}$ 240 mg/L. Figure 4 shows the relationship between TOC removal percentage and pH under the initial condition of Fe^{2+} 1.7 mmol/L and H$_2$O$_2$ 17 mmol/L. The TOC removal ratio obtained after 35 min were 25.5%, 42.3%, 37.4% and 31.6% for an initial pH value of 1.5, 3.0, 5.0 and 6.0, respectively. High pH results in a decrease of free iron species in the mixed solution, which impedes the further reaction of Fe^{2+} with H$_2$O$_2$ and the regeneration of Fe^{2+} from Fe^{3+} (Lin and Lo, 1997). On the other hand, the low TOC removal efficiency at pH 1.5 is due to the formation of the complex species (Fe^{2+}(H$_2$O)$_6$)$^{2+}$ which reacts more slowly with H$_2$O$_2$ than (Fe^{2+}(OH)(H$_2$O)$_5$)$^+$ (Xu et al., 2004). In addition, the scavenging effect of ·OH by H$^+$ becomes more prominent at a relatively low pH level, which hinders the oxidation as well (Tang and Huang, 1996; Feng et al., 2003)

It can be seen that the TOC removal ratio is similar at initial pH 3.0 and 5.0. However, at pH 3.0, the dosage cost
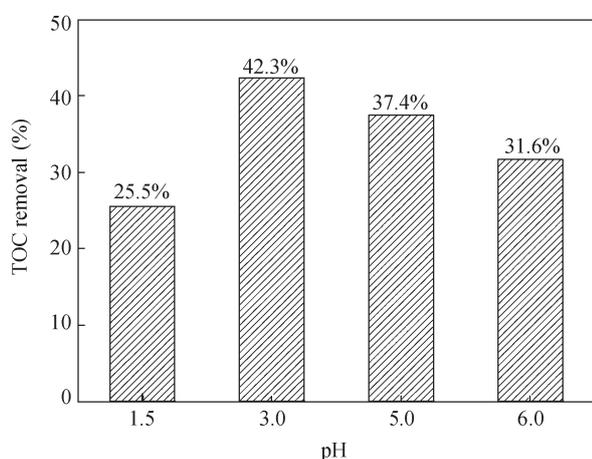
for pH regulation is much more than that at pH 5.0. Hence, the initial pH 5.0 is more reasonable and economic for the subsequent tests.

2.1.2 Effects of initial Fe^{2+} dosage
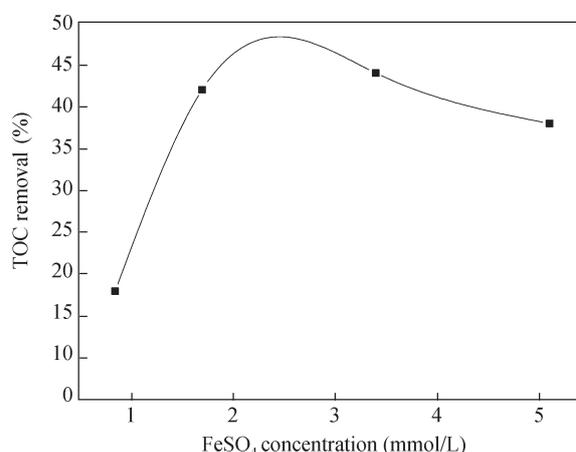
The effect of FeSO$_4$ concentration in Fenton's reagents on TOC removal was investigated. Figure 5 depicts the result of TOC removal ratios under different dosages of Fe^{2+}. With increasing Fe^{2+} concentration from 0.85 to 3.4 mmol/L, the corresponding TOC removal ratio increases from 18.3% to 44.2%. The result indicated that the TOC reduction is remarkably dependent on the initial Fe^{2+} concentration. Hence, it can be explained that higher ferrous concentration causes the generation of ·OH and accelerate the redox reaction. However, it should be pointed out that 5.1 mmol/L Fe^{2+} did not help to improve the TOC removal ratio, on the contrary, the high Fe^{2+} concentration slightly reduced the removal ratio to 38.3%. The result revealed that the overdose of Fe^{2+} led to the self-scavenging of ·OH and induced the decrease of degradation efficiency (Reaction (4)) (Chen and Pignatello, 1997)

$$·OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \qquad (4)$$

Considering the above results and the cost of dosage, optimal Fe^{2+} was selected to be 1.7 mmol/L.

2.1.3 Effects of H$_2$O$_2$ initial dosages

Experiments were carried out at H$_2$O$_2$ concentrations 8.5, 17, 34 and 51 mmol/L for duration of 35 min. As shown in Fig. 6, the TOC removal ratio was 23.3%, 43.3%, 48.6% and 50.2% for the corresponding initial H$_2$O$_2$ concentration of 8.5, 17, 34 and 51 mmol/L, respectively. It is apparent that more dosage of H$_2$O$_2$ in a suitable range could generate more ·OH available and preferential to crack the molecules of organic substrates containing in the wastewater. However, with continuous increasing dose of H$_2$O$_2$, the degradation rate changed slightly. This is due to the fact that the reactive ·OH could be consumed by H$_2$O$_2$, and resulted in the generation of less reactive ·OOH

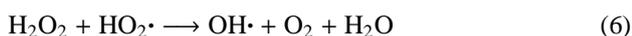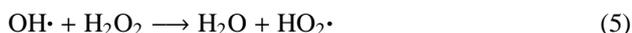**Fig. 4** Variation of TOC removal under different initial pH value (Fe^{2+}: 1.7 mmol/L, H$_2$O$_2$: 17 mmol/L, temperature: 20°C).

Fig. 5 TOC removal under different Fe^{2+} concentrations (H$_2$O$_2$: 17 mmol/L, temperature: 20°C, pH: 5).
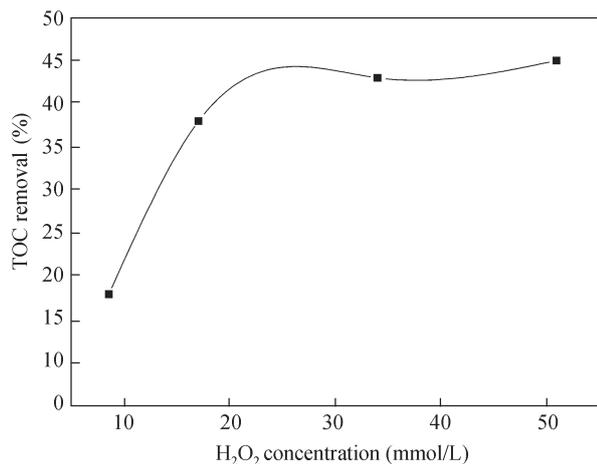
Fig. 6 TOC removal under different H_2O_2 dosages (Fe^{2+}: 1.7 mmol/L, pH: 5, temperature: 20°C, TOC concentration of EI: 140 mL/L).

radical (Kang et al., 2002; Aravindhan et al., 2006).

$$OH\cdot + H_2O_2 \longrightarrow H_2O + HO_2\cdot \tag{5}$$

$$H_2O_2 + HO_2\cdot \longrightarrow OH\cdot + O_2 + H_2O \tag{6}$$

$$HO_2\cdot + OH\cdot \longrightarrow O_2 + H_2O \tag{7}$$

$$H_2O + \cdot OH \longrightarrow \cdot OOH + H_2O \tag{8}$$

Considering the cost and efficiency, the optimal concentration of H_2O_2 should be 17 mmol/L. Therefore, based on the selected conditions, 35 min of Fenton oxidation with dosage of 17 mmol/L H_2O_2 and 1.7 mmol/L Fe^{2+} would be sufficient to oxidize TOC from 140 to 84 mg/L.

2.2 RB4 degradation and color removal

Fenton process is effective to destroy the complicated molecular structure and de-color. The Fenton process can be divided into two stages for the color removal. One is the oxidation effect, and the other is coagulation and adsorption effect caused by gelatinous suspension of $Fe(OH)_2$ and $Fe(OH)_3$. Table 2 gives an overview of RB4 degradation and color removal rate of EI water achieved by Fenton process. By considering the efficiency and cost factors, H_2O_2 dose of 17 mmol/L and Fe^{2+} dose of 1.7 mmol/L were the optimal choices, which resulted in 98.9% RB4 degradation and 76% color removal respectively. During Fenton process, the generated $OH\cdot$ radicals react rapidly with RB4 and lead to a rapid breaking of chromophore of anthraquinone group. The almost vanished absorbance at λ_{max} 599 nm represents the absolutely destruction of RB4 molecule. It should be pointed out that Fenton oxidation can not mineralize RB4 completely and some

**Table 2** RB4 degradation and color removal by Fenton process

Test	Fe^{2+} (mmol/L)	H_2O_2 (mmol/L)	Initial pH	RB4 degradation (%)	Color removal (%)
1	1.7	8.5	5	83.5	56
2	1.7	17	5	98.9	76
3	0.85	17	5	76.5	52

intermediates and byproducts, such as 1,2-diacetylenzene, 2,5-diritrobenzoic acid and phthalic acid, are still exist in the mixed solution (Xu et al., 2008).

2.3 Biodegradability evaluation

EI wastewater (TOC 85 mg/L), Fenton treated wastewater (hereafter refers as FT water) (TOC 85 mg/L), pure RB4 solution (concentration 10 mg/L) and the control DEG solution (TOC 85 mg/L) were submitted to Zaha-Welllens test to investigate the potential of aerobic biodegradation. Figure 7 shows the evolutions of biodegradability of the four different substrates. DEG, a completely biodegradable standard, achieved 91% biodegradation in just 6 days, indicating that the used activated sludge is active and the test is valid. Therefore, the result demonstrated that RB4 was of non-biodegradable nature due to its poor biodegradation of 5% in the lag time of 28 days. That is the reason why the effluent of IDWTP still contains the residual RB4. Similarly, EI water was also proved to be sluggish to the action of microorganisms present in the test. Compared with the EI water and FT water, the increased biodegradability of FT water was apparent, although it took 16 days to mineralize about 70% of the residual organic carbon. It can be concluded that Fenton oxidation is effective to render the EI solution relatively easy biodegradable.

For the index of BOD_5/COD_{Cr} ratio, FT water was achieved an increase from 0.1 (original EI water: BOD_5 24 mg/L, COD_{Cr} 232 mg/L) to about 0.44 (BOD_5 74 mg/L, COD_{Cr} 168 mg/L) due to the application of Fenton oxidation. It was observed that the increase of BOD_5 and decline of COD_{Cr} value. It should be pointed out that the long-term Zahn-Welllens Test can characterize the biodegradability of the treated solution more reliable for the closer operating conditions to the sludge biological reactors (Coelho et al., 2009). On the other hand, BOD_5/COD_{Cr} ratio was obtained through a relatively short-term test period and the result was highly influenced by the amount of organic matter and its oxidation state (Guhl and Steber, 2006).
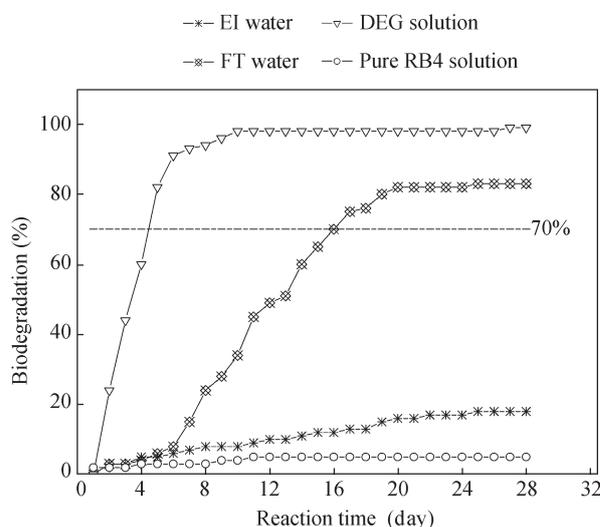
Fig. 7 Bio-degradability evolutions in Zahn-Wellens Test.

2.4 Performance of MBR system

2.4.1 Acclimation

The acclimation step is of importance and makes the microorganisms possessing the enzymatic material necessary to degrade the FT water and obtain an adequate population (Xiong et al., 1998). Stabilization of the reactor was assessed by measuring TOC reduction and DHA concentration. The bioreactor was originally seeded with sludge collected from the secondary sedimentation tank of IDWTP. Initially, the operational parameters such as the inoculated MLSS concentration, DO, HRT and influent TOC concentration of FT water were maintained approximately 4500 mg/L, 2–3 mg/L, 20 hr and 85 mg/L, respectively. Figure 8 depicts the evolution of influent and effluent TOC concentration and the variation of DHA during the acclimation stage. It can be seen that the bioreactor came into a stable state after 20 days with a considerable TOC reduction ratio of about 80%. Moreover, the slightly variation of DHA (20–30 μg TF/(mg MLSS·hr)) during the acclimation stage indicated the microorganism was of good activity and strong adaptation.

2.4.2 TOC and TN removal

After the acclimation, MBR system was studied in terms of TOC and TN reduction at different HRT. The fixed operation parameters of DO, MLSS and sludge retention time (SRT) were 2 mg/L, 6000 mg/L and 30 days, respectively. The average time elapsed for each HRT (10, 18, 25 hr) was about 24 days (stable state). An average food to microorganism ratio (F/M) of each run was 0.035, 0.018 and 0.007 kg TOC/(kg MLSS·day), which corresponded to the HRT of 10, 18 and 25 hr, respectively. The results of TOC evolutions are shown in Fig. 9. It can be seen that MBR system attained similar average TOC removal ratios of 79.1% and 81.4% in corresponding HRT of 18 and 25 hr, but under the reduction condition with HRT of 10 hr the TOC removal ratio was to only 69.9%. It is apparent that HRT 10 hr is not enough for full utilization of the substrate by microorganisms. On the contrary, compared with the result of HRT 18 hr, prolonged HRT of 25 hr contributed almost the same TOC removal ratio. It can be deduced
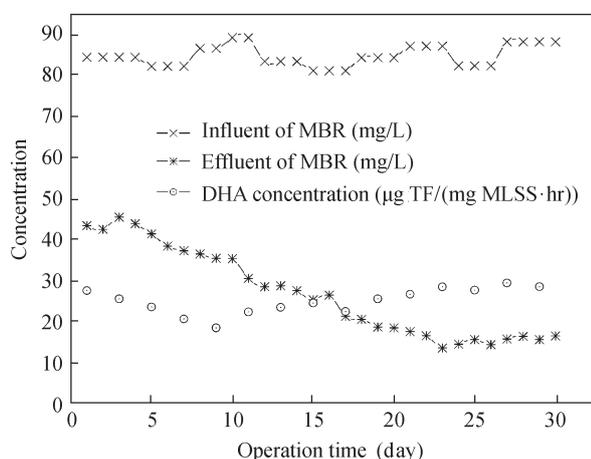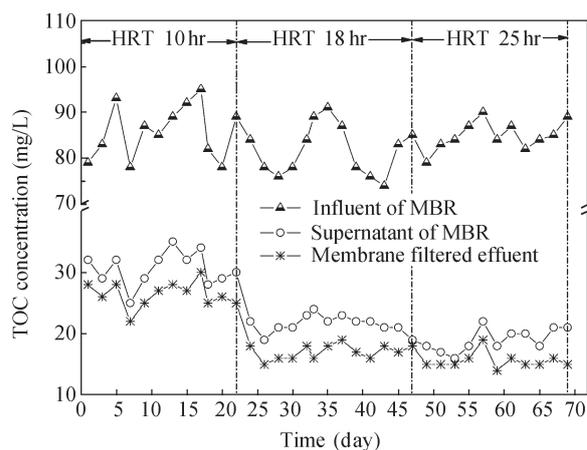

Fig. 9 TOC variation in MBR system under different HRT.

that the bio-degradable organic substrate was consumed absolutely by microbes in 18 hr. Besides, due to the insufficient nutrients and low F/M ratio, microorganisms may come into a state of endogenous respiration and even self-decomposition. The dead microorganisms may dissolve in the mixed solution and affect the quality of effluent. On the other hand, TOC reduction rate (r_{TOC}, kg TOC/(m³·day)) of each run was 0.153, 0.078 and 0.067 kg TOC/(m³·day), which corresponded to the HRT of 10, 18 and 25 hr, respectively. Based on the relatively fixed influent quality (TOC 80–95 mg/L) and the close TOC reduction ratio (69.9%–81.4%), the highest r_{TOC} of 0.153 kg TOC/(m³·day) indicated that the microorganisms could sustain the reasonable bio-activity under high F/M ratio. The results also indicated that parameters of F/M ratio, r_{TOC} and TOC removal ratio were interrelated and interact on each other.

It should be pointed out that the total TOC removal of MBR system is attributable to two factors, one is biological removal by microorganisms and the other is physical interception by membrane and the cake layer attached on the membrane surface (Wang et al., 2005). The both guarantee the performance of interception of particles and macromolecular substances during the filtration process (Tian et al., 2008). The physical interception contributed approximately 4%–5.5% of the total TOC removal. Therefore, HRT 18 hr was the best for TOC removal.

Figure 10 depicts the variations of TN concentration under the three different HRT. The average TN removals were 47.4%, 52.4% and 55.2%, corresponding to HRT 10, 18 and 25 hr, respectively. It can be seen that the TN removal ratio was relatively low. This could be partially attributed to the low TOC/TN ratio of 3.4–5.1 in the influent. The denitrification process was severely hindered due to the lack of carbon source which acts as the electron donor (Modin et al., 2007). Another important factor which may affect the TN removal ratio was the sole aerobic condition. It should be pointed out that the denitrification was occurred in the anoxic conditions formed in the activated sludge flocs at high sludge concentrations of the MBR system. Similarly, the physical interception of
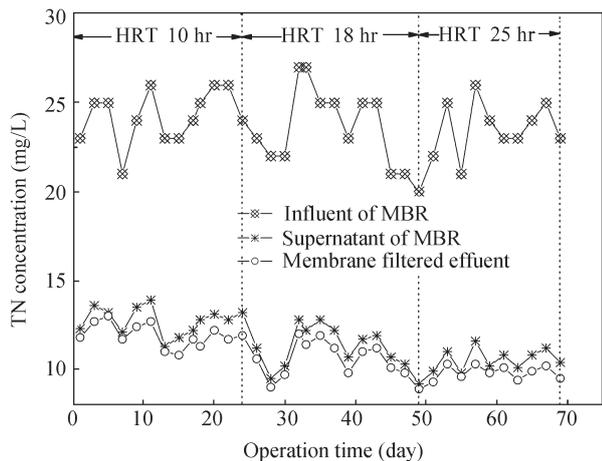

Fig. 8 Variation of TOC and DHA during the acclimation stage.

Fig. 10 TN variation of MBR system under different HRT.

membrane contributed approximately 2.9%–3.4% to the total TN removal. Due to the high efficiency of aerobic bio-treatment and the low background concentration, the NH_4^+-N concentration of MBR effluent was in the range of 0.5–2 mg/L indicating the efficient nitrification.

2.4.3 Biomass production

The cell growth occurs concurrently with the utilization of organic compounds. The yield of activated sludge is a direct index describing the amount of excess sludge produced in the bio-treatment system (Pirbazari et al., 1996; Hsien and Lin, 2005). During the three runs of different HRT, concentration of suspended biomass and the TOC evolutions were recorded at regular intervals (the calculation of accumulated biomass concentration included the biomass for sampling). Figure 11 shows MLSS accumulation versus TOC utilization under three HRT. From the linear fitted equations, the different biomass yield coefficients were 0.15, 0.13 and 0.09 g MLSS/g TOC corresponding to HRT 10, 18 and 25 hr, respectively. The yield coefficients are distinctly lower than those observed in conventional aerobic active sludge systems (Artiga et al.,
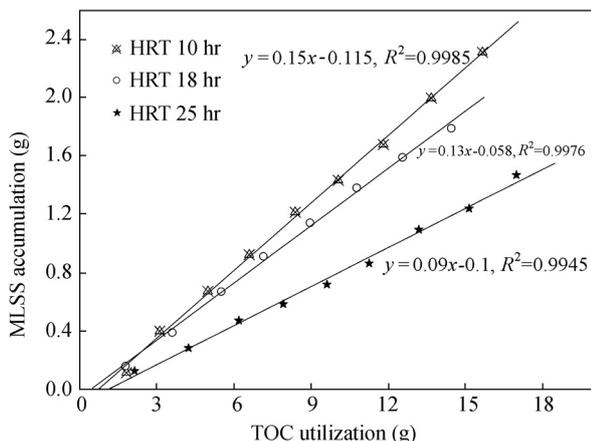
2005). Commonly, the substrate utilization of microorganisms is divided into three parts, substrate used for growth (ΔS_g), maintenance (ΔS_m) and energy spilling (ΔS_w) (Liu and Chen, 1997):

$$\Delta S = \Delta S_g + \Delta S_m + \Delta S_w \qquad (9)$$

In the MBR system, due to the relatively low F/M ratio, the substrates are entirely assimilated by the microorganisms and there is little tendency to synthesize new biomass. The energy obtained from the oxidation of organic substrates is mostly consumed for the cell maintenance in catabolism process (Heran et al., 2008). It implies that the substrate utilization is mostly contributed to the function of ΔS_m and ΔS_w. In addition, the prolonged SRT (30 days) of MBR system caused the low sludge production rate due to the dominative endogenous metabolism of microorganisms.

2.4.4 Membrane fouling evaluation

The MBR was continuously fed with the FT water to evaluate the membrane fouling at constant permeate of 7.5 L/(m²·hr). Operations were carried out under the conditions of HRT 18 hr, MLSS 6 g/L, SRT 30 days and DO 2–3 mg/L. Figure 12 depicts the evolution of TMP in 65 days. The evolution of TMP from 1 to 51 days was substantially in agreement with the two stages described by Cho and Fan (2002). The TMP evolution of stage 1 from day 1 to day 43 was a prolonged period of slow TMP rise, which was mainly ascribe to the accumulation of extracellular polymeric substances (EPS), biopolymers and the formation of cake layer. Stage 1 can be considered as a relatively equilibrium state with the moderate dTMP/dt ratio of 0.356 kPa/day. Stage 2 from day 44 to day 51 was observed a sudden and irreversible rise of TMP up to 35 kPa. In this case, the balance of fouling and self-cleaning was broken with high dTMP/dt ratio of 1.18 kPa/day. Similarly, some researchers (Zhang et al., 2006) also indicated a sudden TMP rise in stage 1 occurred in few hours after the beginning of the membrane filtration. This phenomenon was owed to the instantaneous pore blockage and closure. On day 51, chemical cleaning (Lebegue et al., 2008) was conducted to eliminate the membrane fouling. It can be seen that the TMP was recovered to normal level.
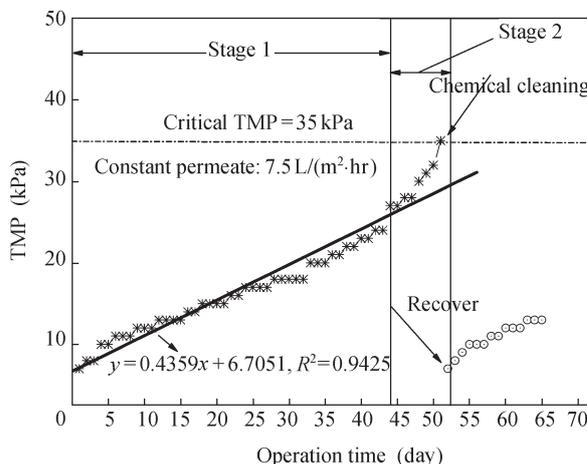

Fig. 11 Plot of MLSS accumulation versus TOC utilization.

Fig. 12 TMP evolution of MBR at constant permeate of 7.5 L/(m²·hr).

It was proved that the membrane had a good potential of fouling resistance due to the low average TMP increase ratio of 0.44 kPa/day (from day 1 to day 52).

2.5 Overall evaluation of combined Fenton oxidation and MBR process

Table 3 summarizes the TOC and color (average value) evolution of Fenton and MBR process. According to the original EI water, the combined system achieved the average TOC and color removal ratio of 88.2% and 91.3% respectively. Of the TOC removal ratio, Fenton oxidation accounted for 39.3% while MBR made up the rest 48.9%. As for the contribution of color removal, the percentage of Fenton oxidation was 69.6% and MBR was 21.7%.

Table 3 TOC and color (average value) evolution of Fenton and MBR process

Item	EI water	FT water	MBR effluent	Overall removal ratio
TOC (mg/L)	142.6	86.5	16.8	88.2%
Color (time)	23	7	2	91.3%

The characteristics of the final MBR effluent and the criterion of GBT18920-2002 are summarized in Table 4. It can be seen that the MBR effluents can meet the standards of GBT18920-2002 of China, and can be used for toilet flushing, landscaping and sprinkling.

Table 4 Quality of final MBR effluent and GBT18920-2002

Parameter	GBT18920-2002	MBR effluent
COD_{Cr} (mg/L)	–	20–30
BOD_5 (mg/L)	10	2–5
TOC (mg/L)	–	10–20
NH_4^+-N (mg/L)	10–20	0.5–2.0
pH	6–9	7.2–7.5
Conductivity (μs/cm)	–	2300–2500

–: Undefined.

3 Conclusions

The combined Fenton oxidation and MBR process was efficient in the reduction of TOC and color of the EI water, reaching average values about 88.2% and 91.3%, respectively. The optimal Fenton operating parameters of initial pH, Fe^{2+} concentration and H_2O_2 concentration were 5, 1.7 and 17 mmol/L, respectively. Residual dyes of RB4 and some biorecalcitrant compounds in EI solution were degraded by Fenton oxidation, which resulted in an enhanced biodegradability of the solution. The result was fully confirmed by Zahn-Wallens Test. The final effluent of MBR can meet the Chinese standard of GBT18920-2002, which is a key success of the combined system.

Acknowledgments

References

Aravindhan R, Fathima N N, Rao J R, Nair B U, 2006. Wet oxidation of acid brown dye by hydrogen peroxide using heterogeneous catalyst Mn-salen-Y zeolite: A potential catalyst. *Journal of Hazardous Materials*, 138(1-2): 152–159.

Artiga P, Ficara E, Malpei F, Garrido J M, Mendez R, 2005. Treatment of two industrial wastewaters in a submerged membrane bioreactor. *Desalination*, 179(1-3): 161–169.

Bae W, Lee S H, Ko G B, 2004. Evaluation of predominant reaction mechanisms for the Fenton process in textile dying wastewater treatment. *Water Science and Technology*, 49(4): 91–96.

Brik M, Schoeberl P, Chamam B, Braun R, Fuchs W, 2006. Advanced treatment of textile wastewater towards reuse using a membrane bioreactor. *Process Biochemistry*, 41(8): 1751–1757.

Chen Y G, Gu G W, 2005. Preliminary studies on continuous chromium(VI) biological removal from wastewater by anaerobic-aerobic activated sludge process. *Bioresource Technology*, 96(15): 1713–1721

Coelho A D, Sans C, Aguera A, Gomez M J, Esplugas S, Dezotti M, 2009. Effects of ozone pre-treatment on diclofenac: Intermediates, biodegradability and toxicity assessment. *Science of the Total Environment*, 407(11): 3572–3578

Cho B D, Fan A G, 2002. Fouling transients in nominally sub-critical flux operation of a membrane bioreactor. *Journal of Membrane Science*, 209(2): 391–403

Chen R, Pignatello J J, 1997. Role of quinine intermediates as electron shuttles in Fenton and photo-assisted Fenton oxidation s of aromatic compounds. *Environment Science and Technology*, 31(8): 2399–2406.

Fan F, Zhou H, Husain H, 2006. Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor process. *Water Research*, 40(2): 205–212.

Feng J, Hu X, Yue P L, Zhu H Y, Liu G Q, 2003. Degradation of azo-dye Orange II by a photo-assisted Fenton reaction using a novel composite of iron oxide and silicate nanoparticles as a catalyst. *Industrial and Engineering Chemistry Research*, 42(10): 2058–2066.

Guhl W, Steber J, 2006. The value of biodegradation screening test results for predicting the elimination of chemicals' organic carbon in waste water treatment plants. *Chemosphere*, 63(1): 9–16

Heran M, Wisniewski C, Orantes J, Grasmick A, 2008. Measurement of kinetic parameters in a submerged aerobic membrane bioreactor fed on acetate and operated without biomass discharge. *Biochemical Engineering Journal*, 38(1): 70–77.

Hsien T Y, Lin Y H, 2005. Biodegradation of phenolic wastewater in a fixed biofilm reactor. *Biochemical Engineering Journal*, 27(2): 95–103.

Kang N, Lee D S, Yoon J, 2002. Kinetic modeling of Fenton oxidation of phenol and monochlorophenols. *Chemosphere*, 47(9): 915–924.

Kritikos D E, Xekoukoulotakis N P, Psillakis E, Mantzavinos D, 2007. Photocatalytic degradation of Reactive Black 5 in aqueous solution: Effect of operating conditions and coupling with ultrasound irradiation. *Water Research*, 41(10): 2236–2246.

Lapertot M, Pulgrin C, Fernadez-lbanez P, Maldonado M, Pere-Rstrada L, Oller I et al., 2006. Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton.

Water Research, 40(5): 1086–1094.

Lebegue J, Heran M, Grasmick A, 2008. MBR functioning under steady and unsteady state conditions. Impact on performances and membrane fouling dynamics. *Desalination*, 231(1-3): 209–218.

Lin S H, Lo C C, 1997. Fenton process for treatment of desizing wastewater. *Water Research*, 31(8): 2050–2056.

Liu Y, Chen G H, 1997. Model of energy uncoupling for substrate-sufficient culture. *Biotechnology and Bioengineering*, 55(3): 571–576.

Modin O, Fukushi K, Yamamoto K, 2007. Denitrificatin with methane as external carbon source. *Water Research*, 41(12): 2726–2738.

NEPA (National Environment Protection Agency), 2002. Standard Methods for the Examination of Water and Wastewater (4th ed.). Beijing, China.

Pirbazari M, Ravinfran V, Badriyha B N, Kim S H, 1996. Hybrid membrane filtration process for leachate treatment. *Water Research*, 30(11): 2691–2706.

Ruppert G, Bauer R, Heister G, Novalic S, 1993. Mineralization of cyclic organic water contaminants by the photo-Fenton reaction–Influence of structure and substituents. *Chemosphere*, 27(8): 1139–1347.

Tang W Z, Huang C P, 1996. 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent. *Environmental Technology*, 17(12): 1371–1378.

Tian J Y, Liang H, Li X, You S J, Tian S, Li G B, 2008. Membrane coagulation bioreactor (MCBR) for drinking water treatment. *Water Research*, 42(14): 3910–3920.

Wang X J, Song Y, Mai J S, 2008. Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate. *Journal of Hazardous Materials*, 160(2-3): 344–348.

Wang Y, Huang X, Yuan Q P, 2005. Nitrogen and carbon removals from food processing wastewater by an anoxic/aerobic membrane bioreactor. *Process Biochemistry*, 40(5): 1733–1739.

Xiong X J, Hirata M, Takanashi H, Lee M G, Hano T, 1998. Analysis of acclimation behavior against nitrification inhibitors in activated sludge processes. *Journal of Fermentation and Bioengineering*, 86(2): 207–214.

Xu X R, Zhao Z Y, Li X Y, Gu J D, 2004. Chemical oxidative degradation of methyl tert-butyl ether in aqueous solution by Fenton's reagent. *Chemosphere*, 55(1): 73–79.

Xu H, Zhang D X, Xu W G, 2008. Monitoring of decolorization kinetics of Reactive Brilliant Blue X-BR by online spectrophotometric method in Fenton oxidation process. *Journal of Hazardous Materials*, 158(2-3): 445–453

Zhang J, Chua H C, Zhou J, Fane A G, 2006. Factors affecting the membrane performance in submerged membrane bioreactors. *Journal of Membrane Science*, 284(1-2): 54–66