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Biological COD reduction and inorganic suspended solids accumulation in a pilot-scale membrane bioreactor for traditional Chinese medicine wastewater treatment

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ABSTRACT

A pilot-scale test was conducted in a membrane bioreactor (MBR) for 452 days to treat high-strength traditional Chinese medicine (TCM) wastewater from two-phase anaerobic digest effluent. This study focuses on the chemical oxygen demand (COD) reduction and inorganic suspended solid (ISS) accumulation. The wastewater was high in COD, varying daily between 259 and 12,776 mg L^{-1}. Almost all the COD was removed by the MBR system, leaving a COD of <50 mg L^{-1} in the MBR effluent. This indicated a great potential of the MBR in TCM wastewater reuse. ISS produced in the bioreactor by metabolism of microorganism increased from 265 to 4912 g h^{-1}, which showed that there were large numbers of ISS accumulation in the bioreactor. Two models, built on the material balances of COD and ISS, were developed for the simulation of MBR system performance in the biodegradation of TCM wastewater. Consequently, the kinetic constants including the maximum substrate specific biodegradation rate (V_{max}), the half-saturation coefficient (K_s) and the inorganic suspended solids growth rate (k) were calculated as V_{max}, 3.64, 3.82, 4.39 d^{-1}, K_s, 56.4, 225, 394 mg L^{-1} and k, 265, 888, 4912 mg L^{-1} d^{-1} using the operational data at different hydraulic retention times (HRTs). The models well fitted the pilot-scale experimental data, and were able to simulate the COD reduction and ISS accumulation.

1. Introduction

The membrane bioreactor (MBR) is a system that combines biological treatment with membrane filtration into a single process. MBR technology is a promising method for water and wastewater treatment because of its ability to produce high-quality effluent that meets increasingly stringent water quality regulations [1–4]. Recently, most of the studies about MBR are focused on the operational stability and treatment of various wastewaters, such as landfill leachates [5–7] and drinking water treatment [8] and for several types of wastewaters, including oily wastewaters [9–12] and wastewaters from the food industry [13–15] and tanneries [16–19] and pharmaceutical wastewater [20,21] and olive mill wastewater [22]. However, up until the present, no laboratory or pilot-scale experiments have been reported exploiting processes based on the MBR technology to remediate high-strength traditional Chinese medicine (TCM) wastewaters. TCM products are health care supplements used on the basis of empirical data accumulated over many centuries in China. Raw TCM wastewaters are characterized by a high COD (6000–19,000 mg L^{-1}) and a low BOD_5/COD ratio (approximately 20%). Raw TCM wastewaters are usually mainly composed of glucide (amylose), protein, lignin, organic acid, resin, alkaloid, amino acid, hydroxybenzene and suspended solids. Application of MBR processes to the treatment of TCM wastewaters remains scarce, to authors' knowledge.

Previously, some studies reported the effects of operational parameters on MBR, including COD loading rates [23–27], hydraulic retention time [28–30] and solid retention time [16,31] and so on; the others investigated the kinetic properties of the MBR process [32–45]. However, previous investigators reported their results about reliable predictive models for COD, nitrogen (N), phosphorus (P) and the organic (volatile) suspended solids (VSS) concentration in the activated sludge (AS) system reactors, e.g. the steady-state

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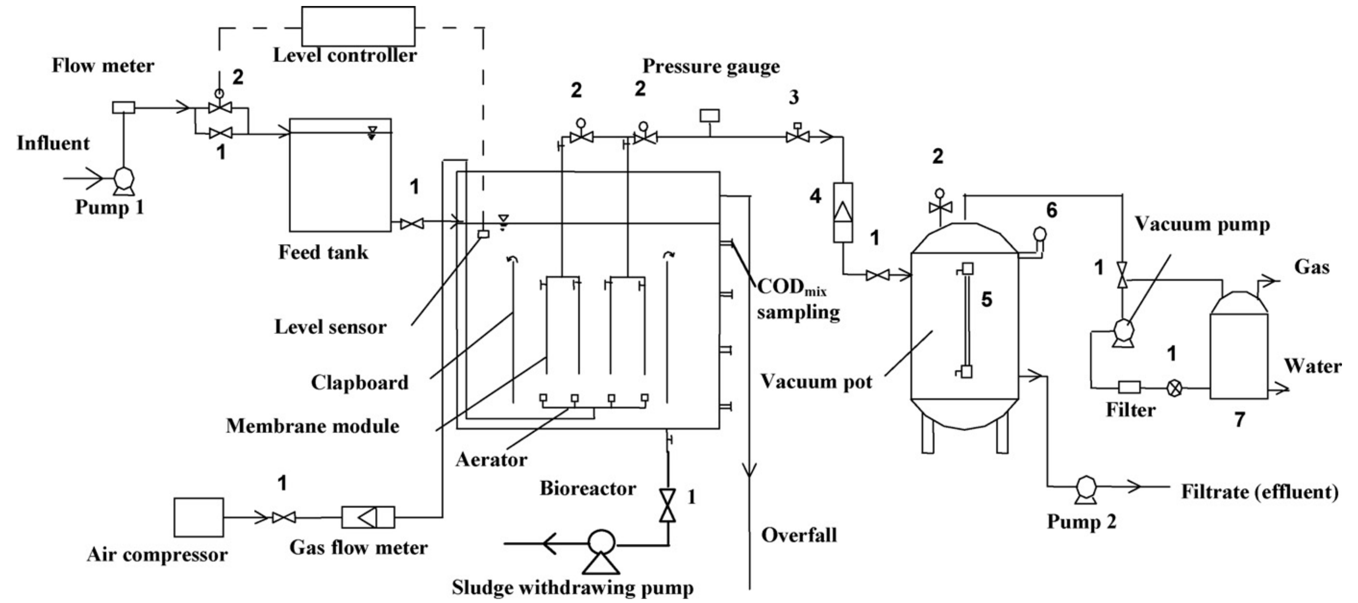

Fig. 1. Scheme of the pilot-scaled MBR. (1) Valve; (2) electron-magnetic valve; (3) pressure control valve; (4) flow meter; (5) level sensor; 6. vacuum meter; 7. gas–water separator.

design models [46,47] and the International Water Association (IWA) Activated Sludge Simulation Model (ASM) 1 [48] for fully aerobic and anoxic–aerobic nitrification–denitrification systems, and the steady-state design model [49] and IWA ASM2 [50] and 2d [51] for anaerobic–anoxic–aerobic biological excess phosphorus removal (BEPR) systems. The steady-state models are largely stoichiometric materials mass balance-based models, which serve as aids for the selection of optimum design parameters for activated sludge systems, with measured (or assumed) influent wastewater flows and material concentrations as inputs. The simulation models are based additionally on biological transformation kinetic processes and also require the system design parameters (reactor volumes, recycle flows, etc.) as input which are generally obtained from the steady-state models. In contrast to the organic models above, predictive models for the reactor inorganic suspended solids (ISSs), and hence the total suspended solids (TSS = VSS + ISS) concentrations have not received the same attention or general acceptance. Reasonably accurate estimates of the ISS concentration are important for the design and operation of MBRs.

The aim of this work was double. Firstly, an effort was made to investigate the suitability of using this type of system for the treatment of TCM wastewaters. Therefore, a pilot-scale experiment using MBR technology was conducted. In this case, the TCM wastewater effluent was treated in a two-phase anaerobic digester and the effluent from the digester used to feed the MBR. The second aim of this work, to simulate and manage the operation of MBR, consisted of suggesting a model for the MBR process of degrading the digested TCM effluent, taking into account the biological COD degradation and ISS accumulation based on material balance. At the same time, the data from pilot-scale MBR was used to examine the applicability of the models.

2. Materials and methods

2.1. Experimental apparatus

A schematic of the MBR, which had a working volume of approximately 3.2 m^3, in which the membrane module was directly submerged, is shown in Fig. 1. The dissolved oxygen concentration (DO) was maintained at 2–4 $mg\,L^{-1}$ respectively by adjusting the air flow to between 5 and 20 $m^3\,h^{-1}$. The water level in the bioreactor was controlled with a level controller and a level sensor. The concentration of the mixed liquor suspended solids (MLSS) was 2140 $mg\,L^{-1}$. The sludge was withdrawn continuously with a pump set at different solid retention times (SRTs). HRT was controlled at 8.0, 5.0 and 3.2 h by a rotary flow meter under the operational condition of invariable membrane flux, i.e. respectively 8.0, 12.8 and 20.0 $L\,m^{-2}\,h^{-1}$. The influent was fed from a tank to the bioreactor by a peristaltic pump (Fig. 1, Pump 1). The effluent of the bioreactor was connected to an automatic vacuum effluent system directly by a rotary flow meter. The automatic vacuum effluent system consisted of vacuum reservoir, vacuum pump, gas–water segregator, level sensor, Pump 2, electron-magnetic valve and power control device (Fig. 1). When the vacuum pump started, part of the gas in the vacuum reservoir was pumped out to create a negative pressure, and then the wastewater in the bioreactor was drained out through the membrane module and entered into the vacuum reservoir. When the liquid surface in the vacuum reservoir reached 80% of its height, Pump 2 started up, and the effluent stored in the reservoir was drained out. Pump 2 and vacuum pump periodically run in the automatic vacuum effluent system. However vacuum level was kept constant at all the time in the vacuum reservoir whether Pump 2 and the vacuum pump were operating or not. Therefore, wastewater continuously entered the bioreactor through the vacuum reservoir and flowed into the submerged membrane module. Thus MBR effluent was continuously produced.

The experiments, carried out for 452 days, comprised three stages; the operating conditions of the MBR are shown in Table 1.

Table 1
Operating conditions of MBR.

Items	Stage 1	Stage 2	Stage 3
Duration (day)	1–155	160–307	312–452
SRT (h)	1200	2400	2400
HRT (h)	8.0	5.0	3.2
pH	7.9–8.5	7.9–8.5	7.9–8.5
Dissolved oxygen (DO) ($mg\,L^{-1}$)	2–4	2–4	2–4
Membrane flux ($L/m^2\,h$)	8.0	12.8	20.0
Effluent flux ($L\,h^{-1}$)	400	640	1000

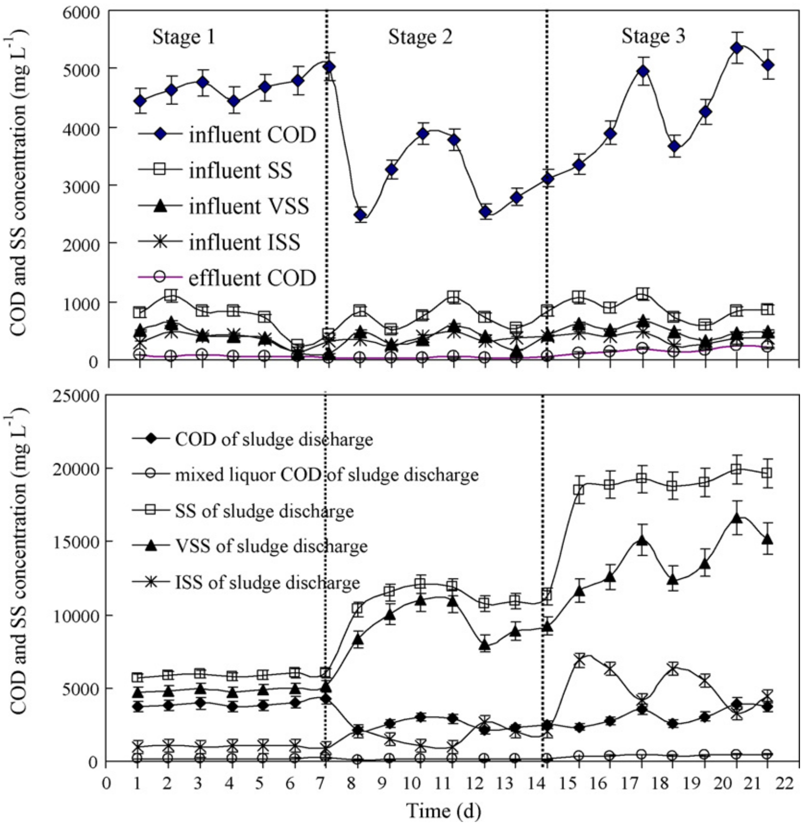

Fig. 2. The variations of COD and sludge concentration for materiel balances stage 1: SRT = 1200 h; HRT = 8 h; Q_i (influent flux) = 402 L h^{-1}; Q_e (effluent flux) = 400 L h^{-1}; Q_s (sludge discharge flux) = 2.67 L h^{-1}; stage 2: SRT = 2400 h; HRT = 5 h; Q_i = 641.33 L h^{-1}; Q_e = 640 L h^{-1}; Q_s = 1.33 L h^{-1}; stage 3: SRT = 2400 h; HRT = 3.2 h; Q_i = 1001.33 L h^{-1}; Q_e = 1000 L h^{-1}; Q_s = 1.33 L h^{-1}.

2.2. Membrane characteristics

In this pilot-plant test, a hollow-fiber PVDF microfiltration (MF) membrane (supplied Tianjin Motian Membrane Engineering and Technology Co. Ltd. in China.) was used with pore size of 0.22 μm and the effective surface area of a MF membrane module at 12.5 m^2. Four MF membrane modules were used in this study. Membrane flux was between 8.0 and 20.0 L m^{-2} h^{-1}.

2.3. Wastewater characteristics

The wastewater used in the study was from a Harbin traditional Chinese medicine company. An effluent from a two-phase anaerobic reactor, which was the in-house system for treating the company wastewater, was used. The major features of the digester effluent were: COD, 259–12,776 mg L^{-1}; BOD$_5$/COD ratio of approximately 20%; total nitrogen, 7–11 mg L^{-1}; total phosphorus 5–9 mg L^{-1}; and suspended solids, 1000–1600 mg L^{-1}.

2.4. Analytical methods

Standard methods (APHA, 1995) [52] were used to measure the value of SS, VSS, COD, BOD$_5$ and DO. Electro-pressure meter measured vacuum values. Rotor flowmeter measured influent flux (Q). Membrane flux was calculated by Eq. (1):

$$J = \frac{Q}{A} \tag{1}$$

with J the membrane flux (L m^{-2} h^{-1}), Q the influent flux (L h^{-1}), A the membrane area (m^2).

In order to investigate the membrane filtration effect, the mixed liquid COD (COD$_{\text{mix}}$) inside the reactor and the filtrate COD (COD$_{\text{fit}}$) were determined separately. We measured COD$_{\text{mix}}$ with a 0.45 μm filter after centrifugating the activated sludge out of mixed liquid. ISS was the difference of total suspended solids (SS) and volatile suspended solids (VSS). The calculational methods of average values were introduced for materiel balances to consider the well-regulated periods of TCM wastewater variations. The concrete modus operandi was that TCM wastewater was sampled and measured everyday during a week when MBR was in a steady-state. The average values of a week data were considered as input and output of MBR system. Models of COD removal and ISS formation were established based on based upon theoretical inference, experimental data analysis and regression of traditional mathematical model using the mathematical software program MATLAB, which from the literature does not appear to have been used previously for modeling MBR.

3. Results and discussion

3.1. Biological COD removal and ISS accumulation

The variations of COD and sludge concentration with time for materiel balances during stages 1–3 are illustrated in Fig. 2. The effluent COD was <100 mg L^{-1} although the influent COD fluctuated from 4000 to 5000 mg L^{-1} at stage 1. The lowest COD of effluent (on the 7th day) was only 38.4 mg L^{-1}. The effluent COD was <50 mg L^{-1} although the influent COD fluctuated from 2400 to 4000 mg L^{-1} at stage 2. The average COD of effluent was only 35.3 mg L^{-1}, which can still meet the reused water quality standard in China. Taking all the COD data into account at stage 3, 100% of the effluent

COD were >100 mg L^{-1} and the average of effluent COD was about 172 mg L^{-1}, which cannot meet the discharge water quality standard in China.

During the pilot experiment the SRT varied from 1200 to 2400 h and HRT, from 8.0, 5.0 to 3.2 h, but the average removal rate of COD remained at 98% or even higher at stage 2. It can be concluded that the removal rate of organic pollutants was high and stable when SRT = 2400 h and HRT = 5.0 h. This indicated a great potential of the MBR in TCM wastewater reuse. The formation of sludge during the experiment is also shown in Fig. 2. SS, VSS and ISS were in existence of influent. The average values of influent SS, VSS and ISS were 700, 350, 350 mg L^{-1} respectively. An increasing trend of sludge concentration (SS, VSS and ISS) with time resulted mainly from the prolongation of SRT and decrease of HRT from stages 1 to 3 (Fig. 2). The relationship between the measured and predicted results are analyzed and discussed later.

Based on the data in Fig. 2, the materiel balance results of COD were listed in Table 2. As shown, taking all the COD data into account at stages 1–3, 98.1%, 98.7%, 95.5% of the COD were adsorbed and biodegraded by microorganism, 0.55%, 0.17%, 0.1% of the COD were in existence of discharged sludge, 1.31%, 1.13%, 3.95% of the COD were in existence of the effluent, from stages 1 to 3 respectively. This indicated that COD removal was mainly obtained by the metabolism of microorganism, the percent of influent COD translated into excess sludge reduced from 0.55% to 0.17% and to 0.1% with the SRT from 1200 to 2400 h and HRT from 8.0, 5.0 to 3.2 h. However the percent of influent COD discharged out of system by other approaches increased from 98.1% to 98.7% at first and reduced from 98.7% to 95.5% subsequently with the variations of HRT and SRT.

The materiel balance of inorganic suspended solids (ISSs) was also shown in Table 2. In this paper, the authors assume that ISS was inert and drop out of various reactions. But ISS came to being in the bioreactor potentially. The all and one of the ISS were remained in the bioreactor by membrane module. So one and only outlet of ISS was sludge withdraw. The experimental results of ISS material balance showed that all the errors were negative, which indicated that ISS was produced in the bioreactor during stages 1–3 by the metabolism of microorganism. Thus, ISS included influent ISS and produced ISS in the bioreactor. We can also see from Table 2 that ISS produced in the bioreactor by metabolism of microorganism increased from 265 g h^{-1} at stage 1 to 4913 g h^{-1} at stage 3, which showed that there were large numbers of ISS accumulation in the bioreactor.

3.2. Kinetic aspects of the COD reduction and ISS accumulation

The mathematical models have been found by Monod and Lawrence–McCarty in order to get the statistically best description of the microorganism growth and substrate biodegradation [53–55]. These models describe relatively well the substrate biodegradation and microorganism growth rate in the presence of microbial populations. The assimilation of the substrate may be described very simply using these models which take into account (i) the synthesis of new elements (synthesis of new cells, synthesis of substances in reserve), which bring about an increase in the weight of the biomass present (anabolism), and (ii) the freeing of biologically useable energy which makes it possible to uphold and maintain these cells (catabolism). Substrate is at the same time an inhibitor of the metabolism of this microbial population that is pure or heterogeneous (mixed). Even at low concentrations, substrate had a substantial inhibitory effect on the microorganism specific growth rate (u). The microorganism specific growth rate tends to increase with the substrate, but u rises to a peak and finally decreases due to the inhibitory effect of C as its concentration is increased. The substrate biodegradation rate in the bioreactor can be well described by the Lawrence–McCarty model shown as Eq. (2) which is derived from the Monod equation [53–55].

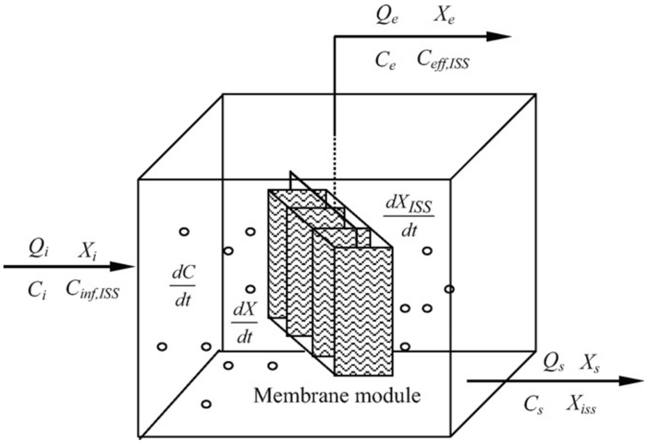

Fig. 3. Scheme of the COD and SS mass balance Q_i, Q_e, Q_s were the flux of influent, effluent, surplus sludge discharging (L h^{-1}) respectively, C_i, C_e, C_s, C were the substrate of influent, effluent, sludge supernatant discharging, the bioreactor (mg L^{-1}) respectively, X_i, X_e, X_s, X were the total SS of influent, effluent, surplus sludge discharging, the bioreactor (mg L^{-1}), $C_{\text{inf,iss}}$, $C_{\text{eff,iss}}$, X_{iss}, X_{iss} were the ISS of influent, effluent, surplus sludge discharging, the bioreactor (mg L^{-1}) and t the time (d).

$$\nu = \frac{V_{\max} C}{K_s + C} \tag{2}$$

with ν the substrate specific biodegradation rate (h^{-1}), $V_{\max}$ the maximum substrate specific biodegradation rate (h^{-1}), C the concentration of substrate in the bioreactor (mg L^{-1}), K_s the half-saturation coefficient or the substrate affinity constant (mg L^{-1}).

Substrate biodegradation rate in a MBR may be also modeled by the following equation:

$$\nu = -\frac{1}{X_\nu} \times \gamma_s = \frac{\mathrm{d}(C_i - C_e)}{X_\nu dt} \tag{3}$$

with X_ν the concentration of mixed liquor volatile suspended solids (mg L^{-1}), γ_s the substrate comsuming rate (mg COD L^{-1} h^{-1}), C_i the influent substrate (mg L^{-1}), C_e the effluent substrate (mg L^{-1}) and t the time (d).

Rearranging expressions Eqs. (2) and (3), and substituting C_{sup} for C in a completely mixed flow bioreactor, thereafter the substrate comsuming rate γ_s can be solved:

$$-\gamma_s = \frac{V_{\max} X_\nu C_{\text{sup}}}{K_s + C_{\text{sup}}} \tag{4}$$

with C_{sup} the mixed liquor substrate concentration in the bioreactor of a MBR (mg L^{-1}).

Fig. 3 describes the material balance chart of the bioreactor in the MBR system, from which the substrate (COD) and inorganic suspended solids (ISSs) balance equations can be easily written as below,

$$\begin{cases} Q_i C_i + V\gamma_s - Q_s C_s - Q_e C_e = V\dfrac{dC}{dt} \\ Q_i C_i - Q_s X_{\text{iss}} - Q_e C_{\text{eff,iss}} = -V\dfrac{dX_{\text{iss}}}{dt} \end{cases} \tag{5}$$

with Q_i the influent flow flux (L h^{-1}), Q_s the surplus sludge discharging rate (L h^{-1}), Q_e the effluent flow flux (L h^{-1}), V the volume of the bioreactor (m^3), C_s the substrate concentration of sludge supernatant discharging (mg L^{-1}), X the total suspended solids concentration (mg L^{-1}), with $C_{\text{inf,iss}}$ the inorganic suspended solids concentration of influent (mg L^{-1}), $C_{\text{eff,iss}}$ the inorganic suspended

Table 2
The materiel balance results of COD and ISS.

Item	Stage	Input			Output				Balance		
		Influent (g h^{-1})	Input (%)	Sludge discharge (g h^{-1})	Output (%)	Effluent (g h^{-1})	Output (%)	Others (g h^{-1})	Output (%)	ΣTotal	% Input
COD	I	1887	100	10.4	0.55	24.7	1.31	1852	98.1	0	–
	II	2003	100	3.33	0.17	22.5	1.13	1977	98.7	0	–
	III	4372	100	4.17	0.10	172	3.95	4195	95.9	0	–
ISS	I	137	100	2.67	1.9	0	-	400	291	−265	−192
	II	237	100	2.34	1.0	0	-	1124	472	−888	−373
	III	367	100	7.01	1.9	0	-	5273	1436	−4912	−1338

Values of Table 2 were determined by mathematical calculation as follows: influent COD = $Q_i \times C_i$; sludge discharge COD = $Q_s \times C_s$; effluent COD = $Q_e \times C_e$; influent ISS = $Q_i \times C_{\mathrm{inf,ISS}}$; sludge discharge ISS = $Q_s \times X_{\mathrm{iss}}$; effluent ISS = $Q_e \times C_{\mathrm{eff,ISS}}$; others = $(Q_i \times Q_s) \times X_{iss}$.

solids concentration of effluent (mg L^{-1}) and X_{iss} the inorganic suspended solids concentration in the bioreactor (mg L^{-1}).

If the system is operating in a steady-state, the following expressions can be obtained conclusively:

$$\begin{cases} \dfrac{dC}{dt} = 0 \\ C_s = C_{\mathrm{sup}} + X_v \dfrac{C_i - C_{\mathrm{sup}}}{X} \\ \dfrac{V}{Q_e} = \mathrm{HRT} \\ \dfrac{V}{Q_s} = \mathrm{SRT} \\ Q_i = Q_s + Q_e \\ C_{\mathrm{eff,iss}} = 0 \\ \dfrac{dX_{\mathrm{iss}}}{dt} = k \end{cases} \tag{6}$$

with HRT, the hydraulic retention time (h), SRT the sludge retention time (h), k the inorganic suspended solids growth rate (mg L^{-1} d^{-1}).

As shown in Table 2, k was 265, 888, 4912 mg L^{-1} d^{-1} at HRT of 8.0, 5.0, 3.2 h from stages 1 to 3, respectively. Therefore, k was the function of HRT. Eq. (7) by regression was expressed as:

$$k = \frac{179{,}652}{\mathrm{HRT}^{3.17}} \tag{7}$$

Rearranging expressions Eqs. (5)–(7), thereafter Eq. (8) can be obtained:

$$\begin{cases} C_e = C_i - \mathrm{HRT}\dfrac{V_{\max} C_{\mathrm{sup}}}{K_S + C_{\mathrm{sup}}} X_v + \dfrac{\mathrm{HRT}}{\mathrm{SRT}}(C_i - C_s) \\ X_{\mathrm{iss}} = X - X_v = \left(\dfrac{\mathrm{SRT}}{\mathrm{HRT}} + 1\right) C_{\mathrm{inf,iss}} + \mathrm{SRT} \cdot k \end{cases} \tag{8}$$

From Eq. (8), it can be seen that the sludge concentration X_v and effluent COD C_e in the MBR bioreactor is not only related to influent COD C_i, HRT, SRT, etc. but also related to C_s and C_{sup} in the bioreactor. From Eq. (8), it can be also seen that X_v and X_{iss} are inverse and direct proportion with SRT. That is X_v decreased and X_{iss} increased with the increase of SRT. According to Eq. (8), proportion of X_{iss} and X increased. Accumulative X_{iss} affect the operation of MBR by all means. Therefore, surplus sludge must be discharged in a MBR, which disprove the opinion of zero sludge discharging. Eq. (8) is the kinetic models of COD removal and ISS formation in a MBR.

3.3. Kinetic constants V_{max} and K_s evaluation

According to the basic theory of activated sludge, the two constants $V_{\max}$ and K_s are generally adopted to describe the dynamic behaviors. $V_{\max}$ and K_s refer to substrate degradation. These kinetic constants are significant in guiding scientific research and engineering design. The actual values of the two constants were investigated for the MBR system applied to TCM wastewater treatment.

Table 3
Experimental data and solution of V_{max} and K_s during stages 1–3.

Item	Time (d)	SRT (h)	HRT (h)	X_v (mg VSS L^{-1})	$C_i - C_s$ (mg L^{-1})	$C_i - C_e$ (mg L^{-1})	C_{sup} (mg L^{-1})	$C_{sup} - C_e$ (mg L^{-1})	$K_s/V_{\max}$	$1/V_{\max}$	$V_{\max}$ (d^{-1})	K_s (mg L^{-1})	$V_{\max}/K_s$
Stage 1	1	1200	8.0	4745	717.7	4365.9	177.3	93.6	15.4	0.27	3.64	56.4	0.065
	2	1200	8.0	4824	797	4570.4	184.4	122					
	3	1200	8.0	4987	795.9	4678.6	196.4	119.8					
	4	1200	8.0	4707	725.2	4398.6	180.2	124.1					
	5	1200	8.0	4884	850.2	4622.8	188.7	135.2					
	6	1200	8.0	4965	765.8	4739.9	212.9	150.6					
	7	1200	8.0	5120	725.3	4996.6	233.6	195.2					
Stage 2	8	2400	5.0	8354	373.4	2464.23	130.4	104.8	58.8	0.26	3.82	225	0.017
	9	2400	5.0	10,025	703	3231.6	153.2	120.1					
	10	2400	5.0	11,044	864.2	3845.6	173.5	137.1					
	11	2400	5.0	10,949	589.1	3723	166.6	125.4					
	12	2400	5.0	8041	429.4	2518.2	148.8	118.3					
	13	2400	5.0	8858	499.7	2758.7	150.2	110.5					
	14	2400	5.0	9244	598.7	3078	152.4	111.8					
Stage 3	15	2400	3.2	11,647	1024.1	3240.7	357.9	241.4	89.8	0.23	4.4	394	0.011
	16	2400	3.2	12,591	1119.3	3749.9	394	250.3					
	17	2400	3.2	15,097	1393.2	4759.1	452.7	254.5					
	18	2400	3.2	12,497	1072.4	3534.9	376.6	242.8					
	19	2400	3.2	13,544	1190.8	4079.4	413.3	242.9					
	20	2400	3.2	16,646	1440	5124.1	480.1	237					
	21	2400	3.2	15,237	1361.2	4870	463.2	261.5					
Average values	–	–	–	–	–	–	–	–	51.6	0.26	3.95	225	0.031

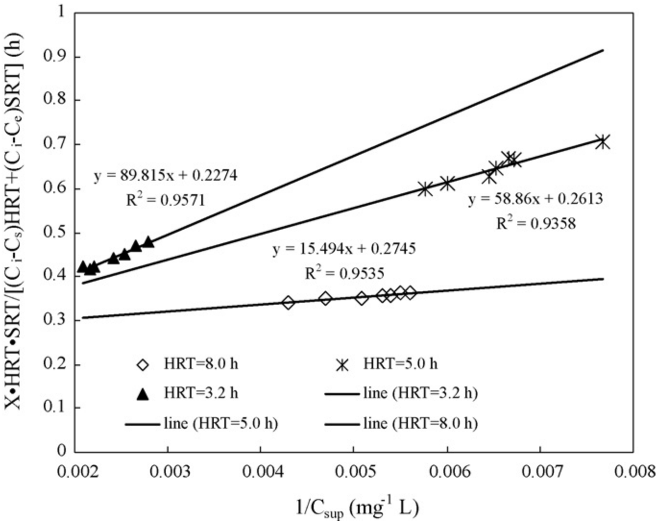

Fig. 4. Solution of V_{max} and K_s at stages 1–3.

The X_v, $C_i - C_s$, $C_i - C_e$, $C_{\text{sup}} - C_e$ in different SRTs and HRTs (Table 3) were calculated using the operation data of the MBR system during the steady-state shown in Fig. 2. In this study, the $C_{\text{sup}} - C_e$ stands for the contribution of the membrane module to COD removal. Since this part of COD removal was not achieved through the metabolic activity of microorganisms, there was no corresponding degree of sludge increase. Therefore, the membrane module in the MBR functions not only as an ideal settling tank but also removes a small part of the COD by mechanical interception and separation.

$x = C_{\text{sup}}^{-1}$ and $y = X_v[(C_i - C_s)\text{SRT}^{-1} + (C_i - C_e)\text{HRT}^{-1}]^{-1}$ were selected as the abscissa and ordinate respectively based upon Eq. (8) and the data in Table 3, a linear regression of $X_v[(C_i - C_s)\text{SRT}^{-1} + (C_i - C_e)\text{HRT}^{-1}]^{-1}$ against C_{sup}^{-1} was carried out (Fig. 4).

The inter-relationship coefficient was $R^2 = 0.953$, 0.935 and 0.957 at stages 1–3 respectively and:

$$\frac{X}{(C_i - C_s)/\text{SRT} + (C_i - C_e)/\text{HRT}} = \frac{K_s}{V_{\max}} \times \frac{1}{C_{\text{sup}}} + \frac{1}{V_{\max}} = 15.4 \times \frac{1}{C_{\text{sup}}} + 0.27 \quad (\text{HRT} = 8.0\ \text{h}) \tag{9}$$

$$\frac{X}{(C_i - C_s)/\text{SRT} + (C_i - C_e)/\text{HRT}} = \frac{K_s}{V_{\max}} \times \frac{1}{C_{\text{sup}}} + \frac{1}{V_{\max}} = 58.8 \times \frac{1}{C_{\text{sup}}} + 0.26 \quad (\text{HRT} = 5.0\ \text{h}) \tag{10}$$

$$\frac{X}{(C_i - C_s)/\text{SRT} + (C_i - C_e)/\text{HRT}} = \frac{K_s}{V_{\max}} \times \frac{1}{C_{\text{sup}}} + \frac{1}{V_{\max}} = 89.8 \times \frac{1}{C_{\text{sup}}} + 0.23 \quad (\text{HRT} = 3.2\ \text{h}) \tag{11}$$

According to Eqs. (9)–(11),

$$V_{\max} = 3.64\,\text{d}^{-1},\ K_s = 56.4\,\text{mg}\,\text{L}^{-1} \quad (\text{HRT} = 8.0\,\text{h}) \tag{12}$$

$$V_{\max} = 3.82\,\text{d}^{-1}, K_s = 225\,\text{mg}\,\text{L}^{-1} \quad (\text{HRT} = 5.0\,\text{h}) \tag{13}$$

$$V_{\max} = 4.39\,\text{d}^{-1}, K_s = 394\,\text{mg}\,\text{L}^{-1} \quad (\text{HRT} = 3.2\,\text{h}) \tag{14}$$

From Eqs. (9)–(11), the value of $V_{\max}/K_s$ (Table 3) can be easily calculated using the experimental data in Fig. 4. The values of $V_{\max}/K_s$ ranged from 0.011 to 0.065 with an average of 0.031 in this paper. The values of $V_{\max}/K_s$ ranged from 0.08 to 0.24 (or 0.048) for the traditional activated sludge process for municipal and domestic wastewater treatment [56,57]. Thus the $V_{\max}/K_s$ value in the MBR is as a whole lower than that in the traditional activated sludge process. However, the $V_{\max}/K_s$ value in the MBR for TCM wastewater is as a whole higher than that in the MBR for urban wastewater [32]. The average values of $V_{\max}$ and K_s were $3.95\,\text{d}^{-1}$ and $225\,\text{mg}\,\text{L}^{-1}$ in this paper respectively. The values of $V_{\max}$ and K_s ranged from 6 to 8 d^{-1} and 25 to 100 $\text{mg}\,\text{L}^{-1}$ for the traditional activated sludge process for municipal wastewater treatment [57]. Thus the $V_{\max}$ value in the MBR is as a whole lower than that in the traditional activated sludge process. However, the K_s value in the MBR for TCM wastewater is as a whole higher than that in the traditional activated sludge process. This indicated that TCM wastewater was easy to be biodegraded, which was consistent with the results of material balance.

A linear Eq. (15) was considered to simulate the $K_s \cdot V_{\max}^{-1}$ and $V_{\max}^{-1}$ data of Table 3.

$$y = k_1 x + k_2 \tag{15}$$

with k_1 was $K_s \cdot V_{\max}^{-1}$ and k_2 was $V_{\max}^{-1}$. k_1 and k_2 were the functions of HRT.

$$\begin{cases} y_1 = 15.4x + 0.27,\ \text{HRT} = 8.0\ \text{h} \\ y_2 = 58.8x + 0.26,\ \text{HRT} = 5.0\ \text{h} \\ y_3 = 89.8x + 0.23,\ \text{HRT} = 3.2\ \text{h} \end{cases} \tag{16}$$

Unknown coefficients of k_1 and k_2 needed to be calculated by the equation group (17), where a matrix with three rows and two columns showed the coefficients.

$$\begin{bmatrix} k_{11} & k_{21} \\ k_{12} & k_{22} \\ k_{13} & k_{23} \end{bmatrix} = \begin{bmatrix} 15.4 & 0.27 \\ 58.8 & 0.26 \\ 89.8 & 0.23 \end{bmatrix} \tag{17}$$

Based on Eq. (17), Eqs. (18) and (19) could be obtained at different HRTs by linear regressive analysis.

$$\frac{K_s}{V_{\max}} = 137 - 15.3\ \text{HRT}(R^2 = 0.997) \tag{18}$$

$$\frac{1}{V_{\max}} = 0.18\ \text{HRT}^{0.2}(R^2 = 0.921) \tag{19}$$

Based on Eqs. (18) and (19), Eqs. (20) and (21) could be obtained.

$$V_{\max} = \frac{1}{a \cdot \text{HRT}^b} \tag{20}$$

$$K_s = \frac{c - d \cdot \text{HRT}}{\text{HRT}^b} \tag{21}$$

with a, b, c and d the constants. Substituting the value of $V_{\max}$ and K_s into Eq. (8) and rewriting:

$$C_e = C_i - \text{HRT}\frac{C_{\text{sup}}}{137 - 15.3\ \text{HRT} + 0.18\,\text{HRT}^{0.2}C_{\text{sup}}}X_v + \frac{\text{HRT}}{\text{SRT}}(C_i - C_s) \tag{22}$$

When the influent and operational conditions such as HRT and SRT are known, the growth trend of sludge in bioreactor and effluent COD can be predicted from Eq. (22). The predicted and measured values of sludge concentration and effluent COD for the experiments of this work are illustrated in Fig. 5. The predicted sludge and effluent COD concentrations were close to the measured values for most of the points which proved the applicability of the equations

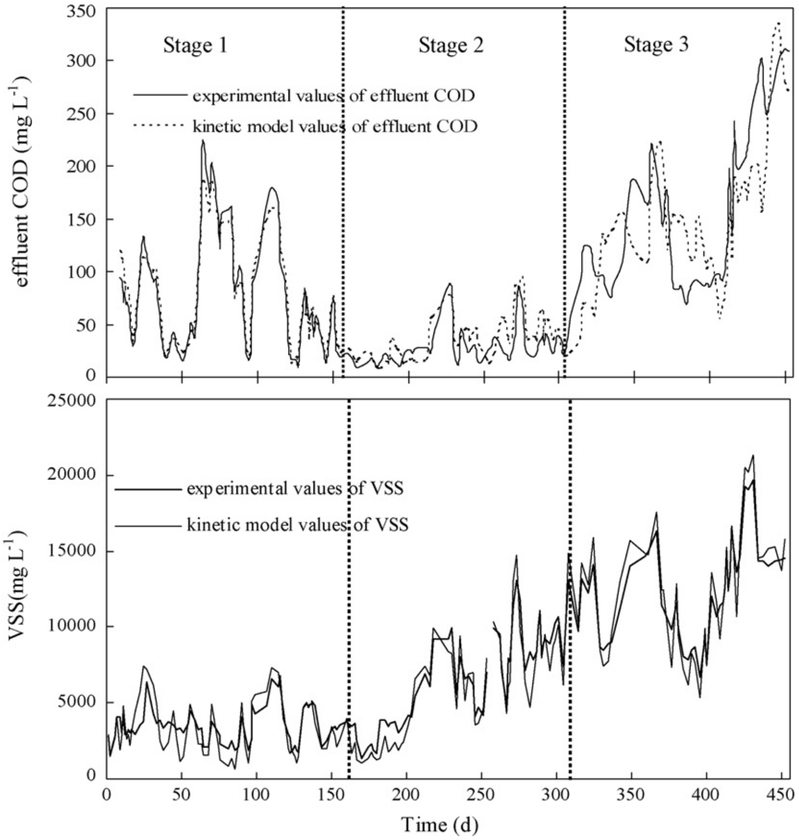

Fig. 5. Comparison between experimental and kinetic model values of effluent COD and VSS during stages 1–3.

for the calculation of the sludge and effluent COD concentration and those kinetic constants obtained. However, there exist a few predicted points that were lower or higher than the operation data. That is mainly because the growth or decay of microorganism in the bioreactor could not respond to a quick increase or decrease of influent concentration.

Kinetic models of COD removal and ISS formation based on the pilot experiment data and material balances could predict the operating manner and performance of the MBR, and especially were hydraulic retention time (HRT), sludge retention time (SRT) and influent COD concentration (C_i). According to the two models, in one hand, ISS concentration could be confirmed and the increasing trends of the ISS concentration could be predicted by the adjustment of operational parameters. The higher COD removal rate and better effluent COD could be obtained by controlling VSS, HRT and SRT in the bioreactor. On the other hand, we could simply control and manage the MBR operation by adjusting operating parameters HRT, SRT and C_i according to the models.

4. Conclusions

A novel MBR process was demonstrated on a pilot-scale for the treatment of TCM wastewater. The wastewater was high in COD, varying daily between 259 and 12,776 mg L^{-1}. Almost all the COD was removed by the MBR system, leaving a COD of <50 mg L^{-1} in the MBR effluent. This indicated a great potential of the MBR in TCM wastewater reuse. ISS produced in the bioreactor by metabolism of microorganism increased from 265 to 4912 g h^{-1}, which showed that there were large numbers of ISS accumulation in the bioreactor.

Two models to calculate the COD reduction and ISS accumulation in the MBR were successfully derived from the material balances of COD and ISS. Consequently, the kinetic constants including the maximum substrate specific biodegradation rate ($V_{\max}$), the half-saturation coefficient (K_s) and the inorganic suspended solids growth rate (k) were calculated as $V_{\max}$, 3.64, 3.82, 4.39 d^{-1}, K_s, 56.4, 225, 394 mg L^{-1} and k, 265, 888, 4912 mg L^{-1} d^{-1} using the operational data at different hydraulic retention times (HRTs). In addition, $V_{\max}$, K_s, k were the functions of HRT by regression. The models well fitted the pilot-scale experimental data, and was able to simulate the COD reduction and ISS accumulation. It follows that the simulation models are a feasible and practical means to simulate and predict the COD reduction and ISS accumulation by the MBR system.

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