

## Modeling the impact of membrane filtration on organic carbon removal by the activated sludge process for tannery wastewater

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### ABSTRACT

The study emphasized a new approach for modeling the activated sludge process with a membrane separation (MASM) for organic carbon removal of tannery wastewaters. The new model, differing from the commonly used activated sludge models 1, relied on a modified chemical oxygen demand (COD) fractionation considering the particle size distribution of the organic matter. A new COD fraction, entrapped COD, was included into the model related to the effective filtration size of the membrane module. Modeling studies were conducted for high rate; conventional and extended aeration activated sludge systems operated at sludge age levels of 4, 8–12, and 15–18 d, respectively. Model simulations were carried out for parallel systems both with gravity settling and membrane filtration. Comparative evaluation reflected a better effluent quality for the activated sludge systems with membrane separation at all sludge ages when both systems were designed for the same reactor volume. At a high rate operation, the effluent soluble COD level was estimated as 198 mg/L for membrane separation, below the threshold of 200 mg/L and 63% lower than the conventional scheme. Even for conventional and extended type of operation, the effluent COD remained around 170 mg/L, where it fluctuated between 300–350 mg/L including the particulate COD in the supernatant for the conventional scheme.

**Keywords:** Tannery wastewater; MASM, new model for membrane activated sludge; MAS, membrane activated sludge; Particle size distribution; Modified COD fractionation; Captured COD fractions

### 1. Introduction

Leather tanning involves a complicated sequence of different processes, each relying on an array of chemicals; consequently, it produces one of the most complex wastewaters that can be faced among industrial activities: Tannery effluent is a strong wastewater with a total chemical oxygen demand (COD) content of more than 3,000–4,000 mg/L and an equally high total nitrogen concentration of 150–250 mg/L, both significantly exceeding the levels generally encountered in domestic sewage [1,2]. It also includes

compound like chromium, sulfide, chloride, and number of chemicals likely to exert inhibitory and toxic effects on selected activated sludge configurations to remove COD and nitrogen [3–5]. Therefore, extensive research effort has been so far devoted to define an effective pre-treatment scheme [6–9].

Tannery effluent is well-studied in the literature [10], optimum treatment options have been studied and recommended both for effective COD and nitrogen removal [11–13]. They were conventional activated sludge system with gravity settling. They mostly suffered from periods of

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bulking and foaming conditions, which completely upset system performance. Occasional leakage of inhibitors from the pretreatment units and imbalance of wastewater composition disturbed settling properties of biomass and/or created conditions for selective growth of filamentous bacteria [14]. Tannery effluents usually contain lipids, fats, and proteins, which are known to enhance filamentous bulking and preferentially utilized by filamentous microorganisms such as *Microthrix parvicella* [15]. Extensive studies conducted on the microbial ecology of activated sludge in the treatment system of an Organized Leather Tanning District in Turkey indicated that (i) a periodic fluctuation of the sludge volume index from 50 mL/g to above 200 mL/g was observed every 40 d; (ii) substantial deterioration of effluent quality was associated with these periods, where effluent total COD increased from 100–150 mg/L to 350–735 mg/L; total suspended solids from 10–30 mg/L to 200–390 mg/L and total non-oxidized nitrogen (TKN) from 1.8–50 N mg/L to 8–236 N mg/L; (iii) bulking and foaming periods were always coupled with excessive growth of filamentous microorganisms such as *Nocardia*, *Nostocoida limicola* II, and *M. parvicella* [16].

The transition from gravity settling to membrane filtration should be recognized as a major milestone that shaped the future of the activated sludge process [17]. Essentially, the new activated sludge configuration, membrane activated sludge system (MAS), has been a significant breakthrough enabling total control of biomass in the reactor with no escape to the effluent. This possibility practically removed the limitations imposed by gravity settling on biomass concentrations in the reactor, leading to system operation with much higher biomass levels in the aeration tank at excessively high sludge ages without facing settling problems. In fact, the evolution of the activated sludge process with a membrane module started with sludge age levels of over 50 d and sustaining mixed liquor suspended solids (MLSS) concentrations as high as 30,000 mg/L [18], gradually decreasing to a sludge age range of 10–15 d, with MLSS levels around 10,000 mg/L [19,20]. This operation scheme would be perfectly suitable for strong wastewater such as tannery effluents because it would also eliminate all problems associated with filamentous microbial growth.

In this context, the objective of the study was to evaluate the positive attributes of the activated sludge process with a membrane filtration on the treatment of tannery effluents. For this purpose, the structure of a novel activated sludge model with a membrane module, MASM, requiring modified COD fractionation based on effective filtration size was defined and implemented.

## 2. Materials and methods

### 2.1. Conceptual approach

The relationship between biodegradation of organic carbon (BOD/COD) and particle size was first explored in 1936, based on limited experimental methods available at the time [21]. Recently, this interest has been revived by the introduction of a procedure for particle size distribution (PSD) analysis by means of sequential filtration/ultrafiltration from 1,600 nm all the way down to 2 nm,

which provided a specific size of fingerprint for selected parameters such as COD, total organic carbon (TOC), color, etc. [22,23]. Lately, PSD analysis was used together with the assessment of COD fractionation by respirometry for a better understanding of biodegradation characteristics [24]. A similar evaluation was also carried out for tannery wastewaters, where the filtrates of each sequential size fractions between 450–2 nm and <2 nm were subjected to respirometry and evaluated by model calibration of respective oxygen uptake rate (OUR) profiles, offering a new perspective on the fate of soluble COD fractions, information of vital importance for evaluating the effect of the membrane module on activated sludge modeling [25].

Existing activated sludge models simply overlooked PSD, except a single size threshold of 450 nm, which simply differentiated particulate and soluble matter. For activated sludge configurations supplemented with a membrane separation unit (MASs), the performance restrictions of gravity settling, and the concept of soluble fractions determined on the basis of 450 nm size threshold become obsolete, because the membrane module involves a much lower separation size. The membrane bioreactor creates a capture/entrapment particle size lower than the actual pore size of the membrane unit, due to additional cake filtration effect induced by biofilm formation on the surface of the membrane; many studies investigated the effective filtration size under different experimental conditions and suggested a size range of 8–13 nm that could be adopted as a default range for model evaluation [26,27].

In this context, the membrane module coupled to an activated sludge configuration induces a radical change for the size threshold of 450 nm implemented for differentiating COD fractions, bringing it down to the effective filtration size, which was adopted as 8 nm in the model simulation of the study. While this value was supported by reported findings of different experimental work, it would always be advisable to determine this parameter for specific case studies.

### 2.2. Model structure

This study utilized a novel model specifically designed for membrane activated sludge, MASM [28]. The model basically involved a modified COD fractionation accounting for fractions that would be entrapped by the membrane as a compulsory refinement for the existing ASMs, for providing an accurate assessment of the fate and biodegradation of soluble COD. In this context, the overall soluble hydrolyzable COD,  $S_{HT}$  was accounted for as two different fractions, namely,  $S_{HC}$ , the fraction that would be captured and returned into the reactor, and  $S_{HE}$ , the remaining fraction after biodegradation that would by-pass the membrane and exit the system with the effluent stream. The same differentiation was also made for the total soluble inert COD,  $S_{IT}$ , which was equally split into  $S_{IC}$ , the entrapped fraction, and  $S_{IE}$ , the other fraction that would escape with the effluent stream. Furthermore, on the basis of experimental results of PSD analyses [28], the model included a similar differentiation for the overall particulate slowly biodegradable COD fraction,  $X_{SPT}$ , identifying the settleable fraction,  $X_{SS}$  from the remaining part,  $X_{S}$ , both undergoing hydrolysis. While the

hydrolysis of  $X_s$  would directly generate  $S_s$ , as assumed in the ASMs, the hydrolysis of  $X_{ss}$  would follow a two-step reaction with an initial hydrolysis and conversion into  $S_{HC}$ .

Consequently, MASM was structured over the basic template of all ASM models defined for organic carbon removal, previously implemented in many studies [30]. In this study, the adopted template is the one defining activated sludge models 1 (ASM1), modified for endogenous decay [31,32], it basically adopted the modified COD fractionation in the wastewater including the entrapped fractions as model components, together with soluble and particulate residual microbial products,  $S_p$  and  $X_p$ , accounted for as part of endogenous respiration with the simplifying assumption of a decay associated generation process [33]. The template also included active heterotrophic biomass concentration,  $X_H$ , and finally, dissolved oxygen concentration. So, the basic parameter for the evaluation of the OUR profiles. Obviously, the  $X_{ss}$  component will not be considered in the modeling of the activated sludge configurations operated with a primary settler. Related rate expressions and basic stoichiometry were defined in a way compatible with ASM1 and presented in the usual matrix format in Table 1.

In this study, the activated sludge configuration for modeling was created using the SUMO program [34]. The configuration involved three CSTRs that were linked to each other and at the end of the process a point separator acted as membrane for MAS. From point separator, the return activated sludge was linked to the first CSTR compartment and the waste activated sludge undergoes to dewatering process. The flowrate of the system defined as 10,000 m<sup>3</sup>/d where the volume and returned activated sludge (RAS) rate were changed for different runs. Fig. 1 displays the process configuration used in modeling.

### 2.3. Model components and process kinetics

Characterization of modified COD fractionation for tannery wastewaters was performed using the information in the experimental studies reporting results of respirometric evaluation together with PSD analysis [25]. COD fractions were selected to also serve as model components in the model. This approach was necessary for providing an accurate and reliable information concerning the fractions for soluble COD components that would be entrapped and captured in the reactor by means of membrane filtration. The modified COD fractionation is listed in Table 2. This table also includes corresponding information for domestic sewage and textile wastewater, mainly for the purpose of comparison.

A literature survey was carried out for the kinetic coefficients defining COD utilization for the tannery wastewater, as outlined in Table 3. The heterotrophic yield coefficient,  $Y_H$ , an important stoichiometric parameter for model assessment was selected as 0.64 mg cell COD/mg COD for domestic sewage and tannery wastewater [17]. Soluble and particulate residues of endogenous respiration,  $f_s$  and  $f_x$  were selected as 0.05 and 0.10, respectively [35].

Kinetic parameters provide a specific biodegradation fingerprint for wastewaters and obviously they are different for each wastewater. Detailed information on this issue is provided in Orhon et al. [36]. To better reflect this aspect,

Table 3 is expanded to also include kinetic information on sewage and a few industrial effluents [28].

## 3. Modeling results and discussion

### 3.1. Evaluation rationale

System behavior for MAS was tested with the proposed model, MASM, while the parallel traditional activated sludge system with gravity settling (AS) was evaluated by means of ASM1, modified for endogenous decay. Model assessment of both systems was adjusted to visualize the impact of two key parameters, that is, the sludge age,  $q_X$ , and the hydraulic retention time (HRT),  $q_H$ ; it was carried out for a set of different operating conditions: (i) in the first step, modeling involved different footprints, that is, different  $q_H$  values for the two systems (mixed liquor suspended concentrations (MLSS) of around 10,000 mg/L for MAS and 4,000 mg/L for AS) but the same  $q_X$ ; this parameter was varied in different runs to designate various applicable activated sludge configurations, that is, super-fast; high rate; conventional, etc., (ii) in the second step, models were implemented using the same  $q_H$  value, that is, the same reactor volume and MLSS level (around 5,000 mg/L) for the two systems. A wastewater flow rate,  $Q$ , of 10,000 m<sup>3</sup>/d was adopted for the entire model evaluation sets.

### 3.2. Fate of soluble hydrolysable COD

The specific characteristics of the tannery wastewater used for model simulation in the study is defined in terms of the adopted COD fractionation and kinetic and stoichiometric coefficients as outlined in the preceding sections. The selected wastewater characteristics for tannery effluent indicate that the COD fraction, which controls the organic carbon removal in the activated sludge process is the magnitude of the total influent soluble hydrolyzable COD,  $S_{HTI}$ . In fact, it amounts to around 50% of the total soluble COD in the wastewater and about twice as high as the readily biodegradable COD,  $S_{SI}$ , the other biodegradable COD component in the soluble range (Table 1). The significance of  $S_H$  may better be visualized in comparison with particulate COD, which will be retained in the reactor, and with the readily biodegradable COD, which will be fully utilized under all operating conditions.

One of the major benefits associated with MAS, is suggested as the much smaller footprint, that is, reactor volume, achieved with this process configuration, due to the possibility of maintaining significant higher MLSS levels in the reactor. Accordingly, this phase of modeling was carried out by adopting this principle, which differentiated the respective footprint of traditional activated sludge system with gravity settling (AS) and MAS:MLSS levels were selected around 4,000–4,400 mg/L and 10,250–10,500 mg/L for AS and MAS respectively. As expected, selected design levels for MLSS yielded more than twice lower HRT values for MAS systems and consequently, a much smaller footprint.

A sludge age range of 4.0–18.0 d was selected for model evaluation which basically defined high rate, conventional and extended modes of system operation. Table 4 gives the model outputs summarizing the fate of  $S_H$  in the two

Table 1  
Matrix format of the MASM utilized for model evaluation

Model components →	$S_I$	$S_{IC}$	$X_I$	$S_S$	$S_H$	$X_S$	$S_O$	$X_P$	$S_P$	$X_{SS}$	$S_{HC}$	$X_H$	Process rate
Process ↓													
Growth of $X_H$				$-\frac{1}{Y_H}$			$-\frac{1-Y_H}{Y_H}$					1	$\hat{\mu}_H \frac{S_S}{K_S + S_S} X_H$
Hydrolysis of $S_H$				1	-1								$k_{hS} \frac{S_H / X_H}{K_{hS} + S_H / X_H} X_H$
Hydrolysis of $S_{HC}$				1							-1		$k_{hS} \frac{S_{HC} / X_H}{K_{hS} + S_{HC} / X_H} X_H$
Hydrolysis of $X_S$				1		-1							$k_{hX} \frac{X_S / X_H}{K_{hX} + X_S / X_H} X_H$
Hydrolysis of $X_{SS}$										-1	1		$k_{hX} \frac{X_{SS} / X_H}{K_{hX} + X_{SS} / X_H} X_H$
Decay Parameter	COD	COD	COD	COD	COD	COD	$-(1-f_s-f_x) O_2$	$f_x$ COD	$f_s$ COD	COD	COD	-1 Cell COD	$b_H X_H$

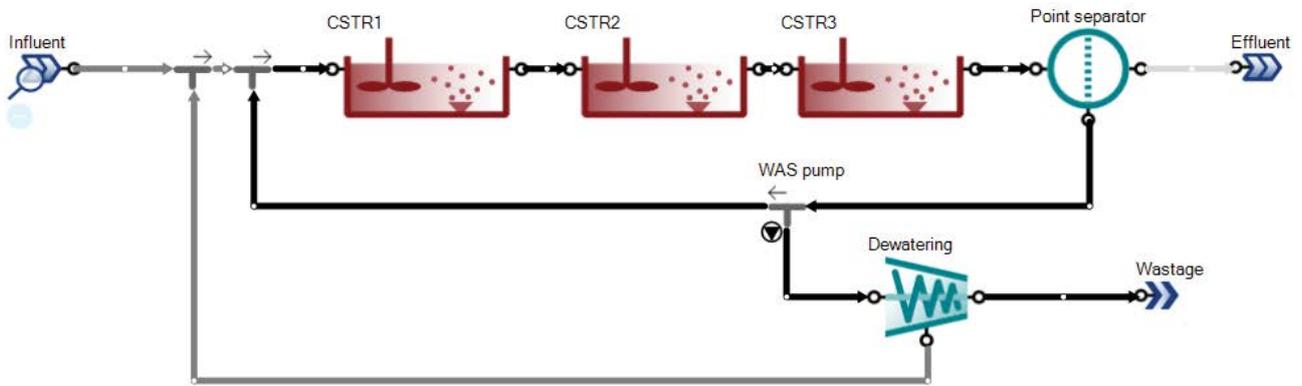


Fig. 1. SUMO configuration used in modeling (AS with gravity settling and MAS with membrane separation).

Table 2  
Modified COD fractionation for selected wastewaters

Wastewaters →	Tannery [27]	Textile [25]	Domestic [31]
Parameters ↓			
Total COD (mg/L), $C_{T1}$	2,284	1,340	415
Total soluble COD (mg/L), $S_{T1}$	1,297	965	120
Total particulate COD (mg/L), $X_{T1}$	987	375	295
Readily biodegradable COD (mg/L), $S_{S1}$	434	280	40
Total soluble hydrolysable COD (mg/L), $S_{HT1}$	649	460	62
Influent soluble hydrolysable COD (mg/L), $S_{H1}$	406	100	15
Captured soluble hydrolysable COD (mg/L), $S_{HC1}$	243	360	47
Total soluble inert COD (mg/L), $S_{IT1}$	214	225	18
Influent soluble inert COD (mg/L), $S_{I1}$	118	135	10
Captured soluble inert COD (mg/L), $S_{IC1}$	96	90	8
Total particulate hydrolysable COD (mg/L), $X_{ST1}$	720	360	253
Influent particulate hydrolysable COD (mg/L), $X_{S1}$	720	162	113
Settleable biodegradable COD (mg/L), $X_{SS1}$	0	198	140
Total particulate inert COD (mg/L), $X_{IT1}$	267	15	42
Influent particulate inert COD (mg/L), $X_{I1}$	120	7	19
Settleable inert COD (mg/L), $X_{IS1}$	147	8	23

Table 3  
Kinetic coefficients for tannery effluents and selected wastewaters

Wastewater type	Kinetic coefficients							References
	$\hat{\mu}_H$	$K_S$	$b_H$	$k_{hs}$	$K_{hs}$	$k_{hx}$	$K_{hx}$	
Tannery	–	–	–	1.1	0.2	0.3	0.2	[8]
	1.8	12	0.08	1.8	0.01	1.7	0.05	[25]
	5.1	30–80	0.21	0.6	0.05	0.22	0.1	[29]
	2.1	30	0.15	0.4	0.2	0.28	0.1	[30]
	2.1	30	0.19	0.63	0.2	0.35	0.1	[31]
	<b>2.2</b>	<b>28</b>	<b>0.12</b>	<b>0.91</b>	<b>0.13</b>	<b>0.57</b>	<b>0.11</b>	<b>Selected for modeling</b>
Domestic	4.2	3	0.2	2.96	0.12	1.34	0.2	[28]
Textile	3.6	15	0.14	2.45	0.09	0.68	0.28	[28]
Leachate	4	3.5	0.2	2.43	0.08	0.88	0.05	[28]

Table 4  
 $S_{HE}$  removal in AS and MAS systems operated for different footprints (different HRTs)

Operational Conditions	ASM1				MASM		
	SRT (d)	HRT (h)	$S_{HE}$ (mg/L)	$S_H$ removal (%)	HRT (h)	$S_{HE}$ (mg/L)	$S_H$ removal (%)
High rate	4	18.7	83	87	6.5	152	77
Conventional	8	28.8	39	94	13	84	87
	12	42	19	97	18	59	90
Extended	15	47	15	98	22	48	93
	18	57.6	10	99	25	40	94

systems. Two observations displayed in this table deserve additional emphasis: (i) they showed consistently higher values for the remaining soluble hydrolyzable COD,  $S_{HE}$ , in the effluent of MAS configurations, despite the fact that a fraction of  $S_{HT1}$  was captured in the MAS reactor. The discrepancy between  $S_{HE}$  levels of the two systems was too steep for high-rate operation, gradually decreasing for higher sludge age values; (ii)  $S_H$  removal rates were always significantly lower for the AS systems, although it was evaluated as the total removal rate for ASM1 and as the removal of the  $S_H$  fraction which could escape entrapment by the membrane in MAS systems. These observations deserve to be further discussed in the next section.

In the next phase, modeling was performed for matching HRT and consequently, MLSS values in parallel systems for each of the SRT level tested. The results are summarized in Table 5: modeling  $S_H$  removal for tannery wastewaters practically indicated the same  $S_{HE}$  levels, all below 30 mg/L and even around 10 mg/L for extended aeration, except for the high rate operation where the MAS was able to reduce  $S_{HE}$  down to 59 mg/L, more than 25% lower than 80 mg/L obtained in system operation with gravity settling. Values in the table indicated similar removal rates for both systems.

### 3.3. Effluent quality

It should be noted that effluent quality in terms of COD removal does not entirely depend on the fate of soluble hydrolyzable COD,  $S_H$ ; capture of a fraction of the initial soluble inert COD also plays an important role. Furthermore, biomass escape to the effluent would cause significantly deterioration of effluent quality for wastewaters like tannery effluents, where settling properties of biomass may easily be worsened by adverse environmental

conditions. Model estimation of effluent quality both for ASM1 and MASM are summarized in Table 6. In order to set a basis for a comparative evaluation, values for likely effluent particulate COD,  $X_{TE}$  were also adopted in the range of 40–140 mg COD/L (30–100 mg VSS/L) for different system configurations, in accordance with observations on tannery wastewater treatment [16] and included in Table 6. Results displayed in this table indicated that the effluent soluble COD that could be provided by MAS was at least 10% lower when evaluated for original design footprint, with reactors volumes around 2.5 times smaller than the conventional activated sludge reactors. For the extended aeration type of operation (SRT > 18 d), the MAS could reduce the effluent soluble COD down to 200 mg/L. Considering the biomass escape from gravity settling, the performance of MAS was 65% better than their counterparts with conventional activated sludge operation.

When both systems were designed for the same reactor volume (same HRT), the performance provided by membrane filtration was significantly enhanced as shown in Table 7: at high rate operation (SRT of 4.0 d), the effluent soluble COD level of the MAS system was computed as 198 mg/L, already below the threshold of 200 mg/L, and 63% lower than 314 mg/L calculated for the conventional scheme. It gradually tailored down to a plateau of around 170 mg/L, when the corresponding plateau for conventional AS units was approximately 260–265 mg/L; including the contribution of particulate COD, this plateau remained above 300 mg/L.

### 3.4. Evaluation of results

The results of the modeling study revealed a few issues that need to be further highlighted; one of them is the modification on the fate of the soluble hydrolyzable COD

Table 5  
 $S_H$  removal in AS and MAS systems operated at the same HRT values

Operational Conditions	ASM1				MASM	
	SRT (d)	HRT (h)	$S_{HE}$ (mg/L)	$S_H$ removal (%)	$S_{HE}$ (mg/L)	$S_H$ removal (%)
High rate	4	19.4	80	88	59	86
Conventional	8	32.4	32	96	30	93
	12	43.2	18	98	20	96
Extended	15	50.4	13	98	15	97
	18	57.6	10	99	12	97

Table 6  
Effluent COD fractionation for AS and MAS systems for different footprints

	$S_{S1}$	$S_{H1}$	$S_{I1}$	$S_P$	$S_{T1}$	$X_{T1}$	$C_{T1}$		$S_{S1}$	$S_{H1}$	$S_{I1}$	$S_P$	$S_{T1}$	$X_{T1}$	$C_{T1}$	
Influent COD (mg/L)	434	649	214	0	1,297	987	2,284		434	406	214	0	1,297	987	2,284	
	ASMI							MASM								
Effluent COD (mg/L)	$S_{SE}$	$S_{HE}$	$S_{IE}$	$S_{PE}$	$S_{TE}$	$X_{TE}$	$C_{TE}$		$S_{SE}$	$S_{HE}$	$S_{IE}$	$S_{PE}$	$S_{TE}$			
SRT (d)	HRT (h)								HRT (h)							
4	18.7	4	83	214	17	318	140	458	6.5	6	152	118	14	290		
8	28.8	2	39	214	25	280	70	350	13	3	84	118	26	231		
12	42	1.1	19	214	33	267	55	322	18	2.5	59	118	32	211.5		
15	47	1	15	214	35	265	40	305	22	2	48	118	35	203		
18	57.6	0.7	10	214	38	262	40	302	25	2	40	118	38	198		

Table 7  
Effluent COD fractionation for AS with gravity settling and MAS systems for the same footprint (same HRT)

	$S_{S1}$	$S_{H1}$	$S_{I1}$	$S_P$	$S_{T1}$	$X_{T1}$	$C_{T1}$		$S_{S1}$	$S_{H1}$	$S_{I1}$	$S_P$	$S_{T1}$	$X_{T1}$	$C_{T1}$	
Influent COD (mg/L)	434	649	214	0	1,297	987	2,284		434	406	214	0	1,297	987	2,284	
	ASMI							MASM								
Effluent COD (mg/L)	$S_{SE}$	$S_{HE}$	$S_{IE}$	$S_{PE}$	$S_{TE}$	$X_{TE}$	$C_{TE}$		$S_{SE}$	$S_{HE}$	$S_{IE}$	$S_{PE}$	$S_{TE}$			
SRT (d)	HRT (h)								HRT (h)							
4	19.4	4	80	214	16	314	140	454	4	59	118	17	198			
8	32.4	2	32	214	26	274	70	344	2.6	30	118	26	176.6			
12	43.2	1	18	214	33	266	55	321	2	20	118	32	172			
15	50.4	1	13	214	36	264	40	304	1.6	15	118	36	170.6			
18	57.6	0.7	10	214	38	263	40	303	1	12	118	38	169			

fraction,  $S_{H1}$  brought about by membrane activated sludge: The general mass balance for  $S_{H1}$  may be written as follows:

$$S_{H1} - S_{HE} + \frac{V}{Q} r_{SH} = 0 \tag{1}$$

where  $r_{SH}$  denotes the reaction rate for hydrolysis.

This equation applies to all activated sludge configurations and clearly shows that the magnitude of  $S_{HE}$  is controlled by the HRT, selected for system operation. Therefore, it explains why lower HRT values adopted to achieve smaller footprints for activated sludge configurations with membrane filtration may cause higher effluent COD, especially for high-rate system operation.

However, MAS systems differentiate two  $S_{H1}$  fractions:  $S_{HE}$ , the fraction that would by-pass the membrane and exit the system with the effluent stream, and the other fraction,  $S_{HC}$ , that would be captured and returned into the reactor, which would be expressed by means of a totally different mass balance equation:

$$QS_{HC1} - P_{SHC} + Vr_{SHC} = 0 \tag{2}$$

Eq. (2) clearly explains why  $S_{HC}$  that stays in the reactor, behaves just like slowly biodegradable particulate

matter,  $X_S$ . Therefore,  $S_{HC}$  basically becomes a part of sludge and it can be expressed as:

$$P_{SHC} = \frac{VS_{HC}}{\theta_x} \tag{3}$$

These equations provide clear indication that  $S_{HC}$  would be controlled by the sludge age, remaining, and accumulating in the reactor. A similar differentiation would be applicable and necessary for soluble residual COD fractions,  $S_I$  and  $S_P$ , in terms of prediction of system performance.

The other issue concerns the merit of MAS for the biological treatment of tannery effluents. This can only be visualized by the novel model structure provided by MASM, which offers an indispensable modeling approach, because (i)  $S_{H1}$  is the major soluble COD fraction in tannery effluents, accounting for 52% of the total soluble COD,  $S_{T1}$  level; (ii) the captured fraction  $S_{HC}$  is identified as 37% of  $S_{HT1}$ ; similarly, the captured fraction  $S_{IC}$  of the initial soluble inert COD  $S_{IT1}$  amounts to 45%, both being decisive COD components for effluent quality. Together with total entrapment of particulate matter, capture of larger size soluble COD portions should be recognized as the major asset for better performance of membrane activated sludge treatment of tannery effluents, as visualized in Fig. 2.

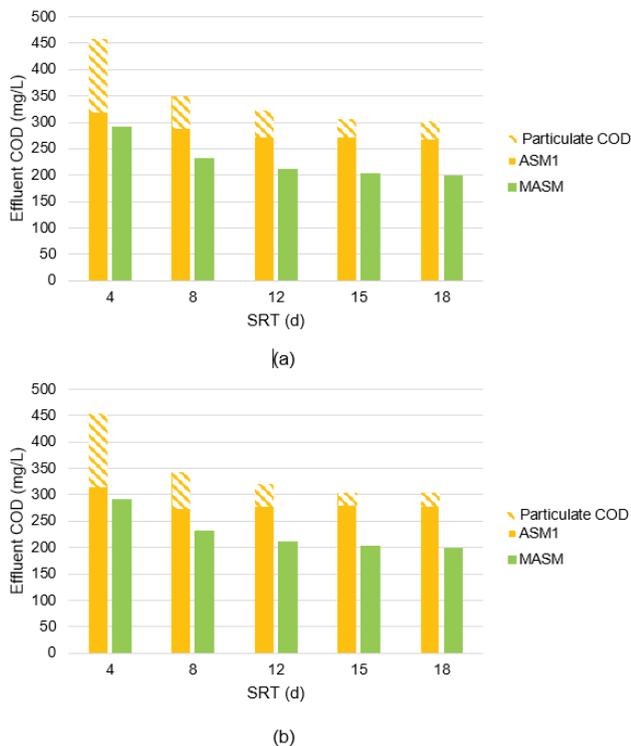


Fig. 2. Comparative performance evaluation for ASM1 and MASM: (a) at different HRTs (b) at same HRTs.

#### 4. Conclusion

Replacement of gravity settling by membrane filtration in membrane activated sludge configurations definitely requires a new modeling perspective for an accurate assessment of system behavior. This fact should be recognized as the main message of the study.

The novel model, MASM designed and tested for this purpose based on real data proved itself to satisfy this need, as its structural framework involving a modified COD fractionation that provided a reliable and accurate mechanistic interpretation of microbial mechanisms taking place in MASs. MASM successfully disclosed the shortcomings of existing ASM1 in predicting the performance of MAS configurations for the biological treatment of tannery effluents.

MASM introduced PSD analysis as a new experimental instrument and recommended it to be an integral complement of respirometry for an accurate description of COD fractions defining wastewater characteristics.

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