Application of Respirometric Techniques to Determine COD Fractionation and Biokinetic Parameters of Sieved Wastewater

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INTRODUCTION

The implementation of COD fractions and kinetic coefficients improves the effectiveness of a model to describe and predict the fate of the COD fractions throughout activated sludge processes [Tas et al., 2009]. The Activated Sludge Model (ASM) is the most widely used model for design, operation, control, troubleshooting, upgrading, modelling, and optimization of biological wastewater treatment processes [Spanjers and Vanrolleghem, 1995; Gernaey et al., 2001; Gori et al., 2011].

Respirometry is one of the oldest tools that has been used to determine COD fractionation and kinetic parameters. In a respirometry test, measurements of the oxygen uptake rate (OUR) are used to delineate these characteristics since the oxygen consumption is directly associated with COD removal and the biomass generated [Vanrolleghem, 2002]. Among the biokinetic parameters, biomass yield coefficient (Y_H), maximum specific growth rate (μ_{max}), decay coefficient (b_H), and substrate half-saturation coefficient (K_S), associated with ordinary heterotrophic organisms (OHOs), have been identified to be the most *influential* parameters for model calibration [Liwarska-Bizukojc and Biernacki, 2010]. The Y_H has been reported in the literature to range between 0.58-0.67 mg cell COD/mg COD removed, whereas μ_{max} ranges from

1 to 6 d^{-1} [Orhon et al., 1995; Henze et al., 2000]. The b$_H$ is reported to range between 0.2-0.6 d^{-1} [Henze et al., 2000]. Municipal wastewaters can be fractionated into biodegradable and non-biodegradable components, where each of these fractions occur in soluble and particulate forms. Readily biodegradable COD (S$_S$), rapidly hydrolysable COD (S$_H$), and soluble inert COD (S$_I$) are associated with the soluble fraction, while the slowly biodegradable COD (X$_S$), heterotrophic biomass (X$_H$), and particulate inert COD (X$_I$) are associated with the particulate fraction. Typically, the S$_S$ fraction in municipal wastewater can range from 10% to 45% of the TCOD [Orhon et al., 1994; Ubay-Cokgor et al., 1998]. S$_I$ ranges from 2% to 7% of the TCOD, and the remaining soluble fraction is the S$_H$ [Ubay-Cokgor et al., 1998; Tas et al., 2009]. Within the particulate fraction, X$_S$ constitutes the majority ranging from 23% to 62% of the TCOD, whereas the X$_H$ accounts for 8%-20% of the TCOD [Ubay-Cokgor et al., 1998; Yu et al., 2010]. The X$_I$ ranges from 7% to 29% of the TCOD [Orhon et al., 1994; Tas et al., 2009].

Medium and high-strength wastewaters usually undergo primary treatment that affects the various COD fractions with different biodegradation characteristics, which eventually affects the performance of biological processes downstream [Gori et al., 2011]. The rotating belt filter (RBF), has emerged as a viable primary treatment alternative to primary clarification (PC). The RBF removes suspended solids by microsieving and the performance of the RBF depends on the particle size distribution in the influent wastewater as well as the mesh pore size, and flow rate [Lema and Martinez, 2017]. Furthermore, the RBF technology is reported to enhance cellulose (originating from toilet-paper use) removal from wastewater [Ruiken et al., 2013]. While the COD fractionation of primary clarification effluents is widely reported in the literature [Henze et al., 2000], the fractionation of RBF effluent COD has not been reported with only few sparse studies that examined its denitrification kinetics [Razafimanantsoa et al., 2014a;

Razafimanantsoa et al., 2014b].   Therefore, it is imperative to characterize the RBF effluent beyond the conventional macroscopic parameters in order to understand the implications of integrating RBF as well as predict overall performance. The concentration of organic carbon and its biodegradability in the influent to the biological process significantly impacts the overall nutrient removal efficiency, especially for biological phosphorous removal and nitrogen removal by pre-denitrification [Tas et al., 2009; Rusten et al., 2017].

In this context, the main objective of this study was to investigate the impact of RBF primary treatment technologies in terms of conventional parameters as well as the assessment of the fractionation of different COD components and the biokinetic parameters that are used for model simulations, to better understand the implication of using RBF for primary treatment. Two wastewaters, that is, raw wastewater and RBF effluent, were characterized using respirometric techniques.

MATERIALS AND METHODS

Sample collection: Raw wastewater (RWW) (screened and degritted) and return activated sludge (RAS; used as inoculum) were collected from the Greenway Wastewater Treatment Plant in London, ON (Canada). RBF effluent (RBFE) was collected from a full-scale RBF pilot (Salsnes Filter 2000 equipped with 350 µm microsieve) operated at a high hydraulic loading rate to avert cake formation. The 350 µm microsieve simultaneously optimizes filter capacity and solids retention. This pore size also corresponds to the most widely used microsieve in full-scale applications [Rusten et al., 2017]. The wastewater samples were stored at 4 °C until use within

10 days of collection. The unfiltered wastewater samples were used the same day of collection. Filtered wastewater was filtered the same day of collection prior to storing at 4 $^{\circ}$C.

Respirometry set-up: Oxygen uptake (OU) was measured using an 8-cell Challenge Respirometer (Respirometer Systems and Application, Fayetteville, Arkansas, USA) equipped with 0.5 L batch bottles completely mixed with magnetic stirrers (Fig. 1). The OUR measurements were used to determine the biomass yield coefficient (Y_H), readily biodegradable COD (S_S), maximum growth rate (μ_{max}), heterotrophic biomass (X_H), and endogenous decay (b_H), using the methods described by Xu et al. [2006]. The tests were set an at initial substrate-to-biomass ratio of 4 mg COD/mg VSS [Xu et al., 2006] and allylthiourea (ATU) was added (20 mg/L) to the test bottles to inhibit nitrification. The assessment of the S_I was determined using the method developed by Orhon et al. [1994] using sequential batch reactors (SBR) fed with glucose, filtered, and unfiltered wastewater; with the same initial COD as the filtered wastewater reactor (Fig. 1). The SBRs (1 L working volume) were operated at a SRT of infinity, fill ratio of 0.5, and one cycle per day (5 min feeding, 22.75 h react, 1 h settling followed by 10 min decanting). The remaining soluble fraction (readily hydrolysable COD, S_H), as well as the remaining particulate fractions (slowly biodegradable COD, X_S; particulate inert COD, X_I) were calculated based on the COD mass balance. The respirometer and the SBRs were conducted at room temperature (20-22 $^{\circ}$C). Respirometry tests were conducted on the filtered and unfiltered wastewater samples of RWW and RBFE. The respirometry test was run for a duration of 3-5 days until the OU plateaued, and the SBRs were operated until a stable COD was reached in the decanted effluent. Three respirometric runs (Sep 2017, Dec 2017, and Jan 2018) were conducted to validate the results as well as report the range in parameters since wastewater characteristics vary from day-to-day.
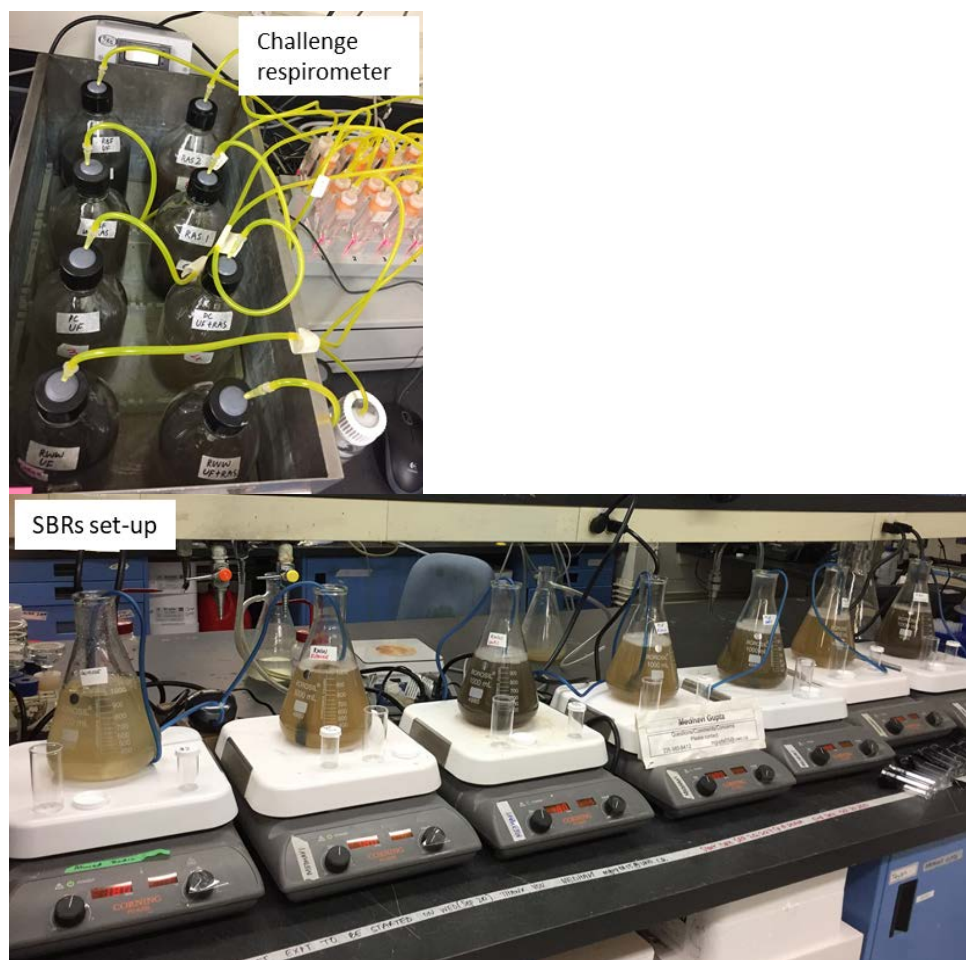
Figure 1. Respirometry setup

Analytical methods: The collected wastewater samples were analyzed for total suspended solids (TSS), volatile suspended solids (VSS) following Standard Methods [APHA, 1998]. A 0.45 µm membrane filter was used to differentiate between soluble and particulate fractions. Accordingly, total chemical oxygen demand (TCOD) and soluble chemical oxygen demand (SCOD) were measured using HACH test kits (HACH, London, Ontario, Canada). Nitrates (NO_3-N) were measured using HACH test kits.

RESULTS AND DISCUSSION

Conventional characterization: Results of conventional/routine characterization of the two wastewaters sampled at three different times are presented in Table 1. TSS measurements indicates that the TSS removal efficiencies of the full-scale pilot RBF was 28±1%, and accordingly the TCOD removal efficiency was 17±2%. Measurements of the TCOD and SCOD indicated that 61±5% and 54±3% of the TCOD was particulate (XCOD) in nature for the RWW and RBFE, respectively. As expected, the SCOD in the two wastewaters was similar at 313±52 mg/L, and thus, RBF did not impact the SCOD fraction. The SCOD fraction in the two wastewaters followed a similar trend as that of the TSS removal efficiency, where the fraction of SCOD/TCOD fraction was the lower for RWW (39%), and higher for RBFE (46%). The observed VSS/TSS ratios of 0.78±0.03 and 0.74±0.05 for RWW and RBFE, respectively, were consistent with the typical ratio (0.6 to 0.8) observed in municipal wastewater [Tchobanoglous et al., 2003]. The XCOD/VSS ratio were observed to be 1.82±0.40 and 1.95±0.44 for RWW and RBFE, respectively, which are slightly higher than the typical ratio of 1.50 [Henze et al., 2008]. The differences observed in the VSS/TSS and XOCD/VSS ratios in the two wastewaters were statistically insignificant ($p>0.05$).

Table 1. Conventional characteristics of the two wastewaters at three different sampling days

Parameter	Unit	RWW					RBFE				
		#1	#2	#3	Avg	StDev	#1	#2	#3	Avg	StDev
TCOD (C_T)	mg/L	715	826	871	804	80	586	674	744	668	79
SCOD (S_T)	mg/L	271	289	389	316	63	269	296	368	311	51
XCOD (X_T)	mg/L	444	537	482	488	46	318	378	377	357	34
TSS	mg/L	266	381	419	356	80	193	270	309	258	59
VSS	mg/L	198	302	333	278	71	131	204	241	192	56
ISS	mg/L	69	80	86	78	9	62	67	69	66	3
TSS Removal	%	na	na	na	na	na	28	29	26	28%	1%
TCOD Removal	%	na	na	na	na	na	18	18	15	17%	2%
SCOD/TCOD		0.38	0.35	0.45	0.39	0.05	0.46	0.44	0.49	0.46	0.03
VSS/TSS		0.74	0.79	0.79	0.78	0.03	0.68	0.75	0.78	0.74	0.05
XCOD/VSS		2.25	1.78	1.45	1.82	0.40	2.42	1.85	1.56	1.95	0.44

Table 2. Summary of biokinetic parameters and COD fractionation of the two wastewaters

Parameter		Unit	RWW	RBFE
Biomass yield coefficient	Y_H	mg COD/mg COD	0.65±0.05	0.64±0.04
Decay coefficient	b_H	d^{-1}	0.40±0.04	
Maximum specific growth rate	μ_{max}	d^{-1}	2.30±0.80	2.48±0.67
Readily biodegradable COD	S_S	mg COD/L	239±29	222±18
		% of TCOD	30%±4%	34%±5%
		% of SCOD	76%±8%	73%±12%
Soluble inert COD	S_I	mg COD/L	13±3	14±3
		% of TCOD	2%±0.4%	2%±0.5%
		% of SCOD	4%±1%	5%±1%
Readily hydrolysable COD	S_H	mg COD/L	64±41	74±51
		% of TCOD	8%±4%	11%±6%
		% of SCOD	19%±9%	23%±13%
Heterotrophic biomass	X_H	mg COD/L	18±6	17±4
		% of TCOD	2%±0.6%	3%±0.4%
Slowly biodegradable COD	X_S	mg COD/L	250±20	180±16
		% of TCOD	31%±3%	27%±1%
		% of XCOD	51%	50%
Particulate inert COD	X_I	mg COD/L	219±21	161±15
		% of TCOD	27%±2%	24%±1%
		% of XCOD	45%	45%
Total inert COD	$S_I + X_I$	mg COD/L	233±23	175±17
		% of TCOD	29%±3%	26%±2%

COD fractionation: The detailed COD fractions of the two wastewaters are depicted in Table 2. Y_H was calculated to be 0.65±0.004 mg COD/mg COD by plotting net oxygen consumption simultaneously with SCOD consumption in the filtered wastewater respirometer bottles (Eq. 4.1). The Y_H determined agreed with the literature which reports a range of 0.63-0.67 mg COD/mg COD [Henze et al., 2000]. Readily biodegradable COD (S_S) was experimentally determined from the OUR profile of the filtered wastewater samples. During the consumption of S_S, the OUR remains approximately constant, however, the OUR drops to a lower level when the S_S is completely depleted. The oxygen consumed before this drop is used to estimate the S_S (Eq. 4.2), for instance, the OUR profiles from Run #1 are plotted in Fig. 2, where the S_S was depleted at ~47 h.

$$Y_H = 1 - \frac{\Delta O_2}{\Delta SCOD} \qquad \text{(Eq. 4.1)}$$

$$S_S = \frac{\Delta O_2}{1 - Y_H} \qquad \text{(Eq. 4.2)}$$

Accordingly, the S_S was determined to be 239 and 222 mg COD/L (average of 231±12 mg COD/L), accounting for 30% and 34% of the TCOD for RWW and RBFE, respectively. Moreover, since the SCOD in the two wastewaters was similar 313±52 mg/L, 75±3% of the SCOD was S_S. Soluble inert COD (S_I) was determined from the SBRs. The SCOD profiles of RWW (filtered and unfiltered) and glucose-fed SBR from Run #1 are depicted in Fig. 3. The S_I fraction is the difference in the residual SCOD of the filtered wastewater SBR and glucose SBR, and accordingly the S_I was determined to be 14±0.7 mg/L for the two wastewaters corresponding to 5% of the SCOD and 2% of the TCOD. The remaining soluble fraction, S_H, was calculated by using the mass balance on the soluble fractions (Eq. 4.3) as 64 and 74 mg/L, accounting for 19% and 23% of the SCOD for RWW and RBFE, respectively. The literature reports S_H to range anywhere from 13% to 39% of the TCOD [Orhon et al., 1999; Tas et al., 2009].

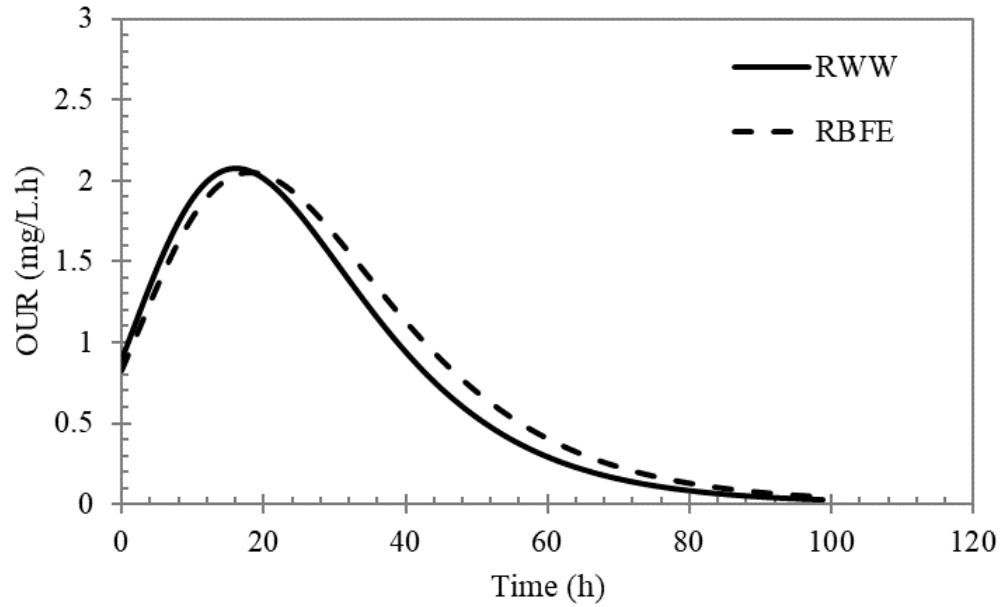$$S_H = S_T - S_S - S_I \qquad \text{(Eq. 4.3)}$$

Figure 2. Oxygen uptake rate profile for the filtered wastewaters for Run #1
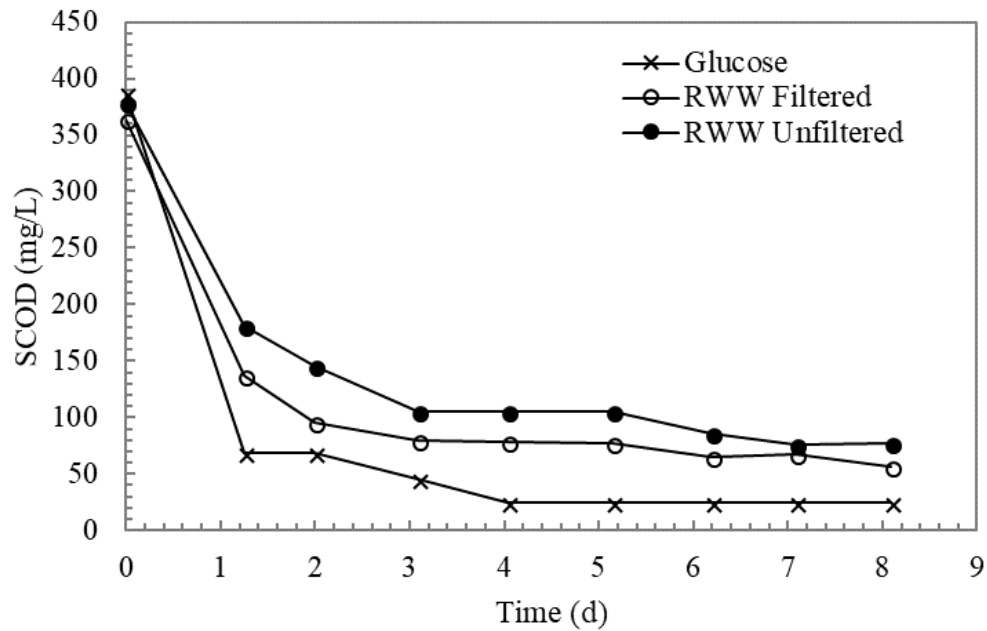

Figure 3. SCOD profiles for the RWW SBRs from Run #1

The decay coefficient was calculated by plotting OUR with time of the respirometer test with sludge-only and devoid of substrate (Eq. 4.4).

$$\ln OUR = -b_H t \qquad\qquad \text{(Eq. 4.4)}$$

The decay coefficient (b_H) of the activated sludge from the three runs was determined to be 0.40±0.04 d^{-1} which was in accordance with Henze et al. [2000]. The maximum growth rate of heterotrophs (μ_{max}) was experimentally determined from the OUR data of the filtered wastewater samples according to Eq. 4.5:

$$\ln \frac{OUR}{OUR_{initial}} = (\mu_{max} - b_H)\, t \qquad\qquad \text{(Eq. 4.5)}$$

The average μ_{max} were calculated to be 2.30 and 2.48 d^{-1} for RWW and RBFE, respectively, consistent with the 2-6 d^{-1} reported by Henze et al. [2000].

As expected, the heterotrophic biomass (X_H) was calculated (Eq. 4.6) to be comparable for RWW (18 mg COD/L) and RBFE (17 mg/L), corresponding to the 2% to 3 % of the TCOD.

$$OUR_{initial} = \frac{1-Y_H}{Y_H}\mu_{max}X_H + (1 - f_e)\, b_H X_H \qquad\qquad \text{(Eq. 4.6)}$$

Where f_e is the inert COD produced from biomass decay and a value of 0.2 g COD/g COD was used [Tchobanoglous et al., 2003].

The slowly biodegradable COD (X_S) was determined by first calculating particulate BOD$_5$ (XBOD$_5$) which can be obtained from the OU data of the unfiltered wastewater and filtered wastewater (Eq. 4.7). Typically, the biodegradable COD to BOD$_5$ ratio is 1.6 [Tchobanoglous et al., 2003], therefore, based on the BOD$_5$ data, biodegradable XCOD was estimated and plotted against the VSS for all the three runs of the two wastewaters.

$$XBOD_5 = BOD_5 - SBOD_5 \qquad\qquad \text{(4.7)}$$

Using the abovementioned relationship and the average XCOD/VSS ratio for all wastewaters (Table 1, that is, 1.89), biodegradable XCOD was estimated to be 55% of the particulate COD. Accordingly, the X_S was calculated as per Eq. 4.8 and was determined to be 250±20 and 180±16, accounting for 31% and 27% of the TCOD for RWW and RBFE, respectively.

$$X_S = (0.55 \times X_T) - X_H \qquad (4.8)$$

The remaining X_I, was calculated by using the mass balance on the particulate fractions (Eq. 4.9) as 27% and 24% of the TCOD for RWW and RBFE, respectively.

$$X_I = X_T - X_S - X_H \qquad (4.9)$$

Although, typically biodegradable XCOD is ~80% of the XCOD, the ranges observed in this study are in line with the ones reported in the literature. The literature has reported wide ranges for X_S (23%-62%) and X_I (7%-29%) fractions [Orhon et al., 1994; Orhon et al., 1999; Ubay-Cokgor et al., 1998]. The wide range reported in the literature is because the composition of wastewater varies from day-to-day and from site-to-site. The need to collect site-specific data for COD fractionation and biokinetic parameters for better implementation of models has been emphasized by Gori et al. [2011].

CONCLUSIONS

Based on the experimental results obtained in this study, the following conclusions can be drawn:

- The RWW is predominantly biodegradable where 71% of the TCOD was observed to be biodegradable. RBF treatment increased the biodegradable fraction to 74%, by removing inert particulates by sieving.

- As expected, microsieving did not impact the soluble components in the wastewaters as reflected by the same readily biodegradable COD, soluble inert COD, and rapidly hydrolysable COD, for RWW and RBFE. The readily biodegradable COD accounted for 30% and 34% of the TCOD for RWW and RBFE, respectively.

- The fractionation of the particulate COD was comparable between the two wastewaters, where 55% of the particulate COD was biodegradable.

- The slowly biodegradable COD accounted for 31% and 27% of the TCOD, whereas the particulate inert COD accounted for 27% and 24% of the TCOD for RWW and RBFE, respectively.

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