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Chemical Oxygen Demand Characterization of Wastewaters Containing Mixed Effluents

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Abstract

This paper presents the results of a wastewater characterisation study that was conducted at Darvill wastewater treatment works (WWTW) in KwaZulu-Natal, South Africa. The wastewater characterization was conducted in order to determine chemical oxygen demand (COD) fractions that can be used for the optimization and modelling of the biological treatment process at the Darvill wastewater treatment works to maintain compliance with the legal discharge limits by Department of Water and Sanitation DWS to the Msunduzi River. The characterisation was determined using the respirometry method. The results of the study showed the COD fractions to be, biodegradable COD (bCOD) = 70.5% and non-biodegradable COD (iCOD) = 29.5% of total COD. The bCOD and iCOD were further characterized into the readily biodegradable soluble fraction (Ss) = 75%, slowly degradable (Xs) = 25%, particulate non-biodegradable (X_I) = 50.8% and the non-biodegradable soluble S_I =49.2%. It has been documented in various studies that industrial effluents contain less bCOD (43%) compared to domestic wastewater. Domestic wastewater is reported to have the following average compositions: X_I = 4–20 %, Xs = 24.5–65 %, S_I = 3 –14.3 % and Ss = 14–57 %. Darvill wastewater characteristics was found to be similar to typical domestic wastewater effluents however the iCOD does also show that it contains industrial effluent as the X_I and S_I fraction is higher than typical domestic.

Keywords: Wastewater modelling, Activated sludge models, Industrial effluents, COD fractions, Domestic effluents

INTRODUCTION

There has been a widespread use of activated sludge models (ASM) in wastewater treatment plant (WWTP) simulations. Currently, the optimization and design of WWTPs is built on simulation studies based on various mathematical models (Pasztor et al. 2008, Płuciennik-Koropczuk et al. 2013). Existing ASM focus primarily on the microbiology, chemical oxygen demand (COD) and often assume constant temperature for the associated coefficients of wastewater treatment simulations (Makinia et al. 2005). Wastewater treatment is a critical chain in the urban water cycle. The increase in urbanization due to population growth and the scarcity of water resources has enhanced the need for the proper design, optimization considerations and treatment methods and use of ASM to maintain and exceed the quality of the existing and affected water bodies.

The activated-sludge reactor (ASR) is one of the WWTP process units that assist with the biological nutrient removal (BNR) and COD removal processes. These processes occur as pollutants are used as substrate by various types of microorganisms. The ASR is a complex physical-chemical biological system with internal interactions between process variables and dynamic changes in influent wastewater flowrate, concentration, and composition. It has therefore, become an established treatment technology in wastewater treatment practice to control eutrophication (Hul et al. 2012).

Data availability

In cases where wastewater samples are not available for

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characterization in new WWTP design, the level of ASM calibration is often low. In these cases, only default values, literature data and assumptions can provide the base information needed to set biokinetic parameters and influent characteristics (Vanrolleghem et al. 2003). Pasztor et al. (2008) infers that, the assumed influent COD, P (orthophosphate, total phosphorous), N (ammonium, nitrate, total nitrogen) fractions can significantly influence the results of simulation-based design such as activated-sludge reactor (ASR) volume, effluent quality, solids residence time, oxygen demand, sludge production, recirculation rates, etc. Usually, influent N and P fractions are easily determined as they form part of routine monitoring in every WWTP. Furthermore, detailed characterization of N and P fractions is not as critical as COD characterization since the most part of the influent nitrogen is present in ammonia and most of the phosphorous occurs in orthophosphate form.

Traditionally, the complexity associated with implementing biological nutrient removal in WWTPs has been seen primarily in terms of balancing competing requirements for N and P removal, particularly with respect to the use of influent readily biodegradable chemical oxygen demand (Ss) which is a fraction of the total influent COD. COD is the measure of the amount of oxygen required to oxidise the oxidisable fraction of organic carbon contained in the effluent. This is measured in mgO_2/l and is sometimes referred to as the organic strength of the wastewater (Mnguni, 2010). According to Henze et al. (2008) the theoretical COD of a given substance can be calculated from an oxidation equation as presented in **Error! Reference source not found.**. In the case of ethanol as an example, the COD can be calculated using the following equation:

$$C_2H_6O + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad (1)$$

Which means, 46 g of ethanol requires 96 g of oxygen for the full oxidation to carbon dioxide and water. The theoretical COD of ethanol is therefore 96/46 = 2.09.

For ASMs, the wastewater COD needs to be characterised in terms of its biodegradability. Biodegradability is one of the imperative characteristics for wastewater treatability (Wu et al. 2014). COD can be characterized into the four fractions i.e. readily biodegradable COD (Ss), slowly biodegradable COD (Xs), soluble inert COD (S_I), and particulate inert COD (X_I) (Wentzel, 1999) as shown in Figure 1.

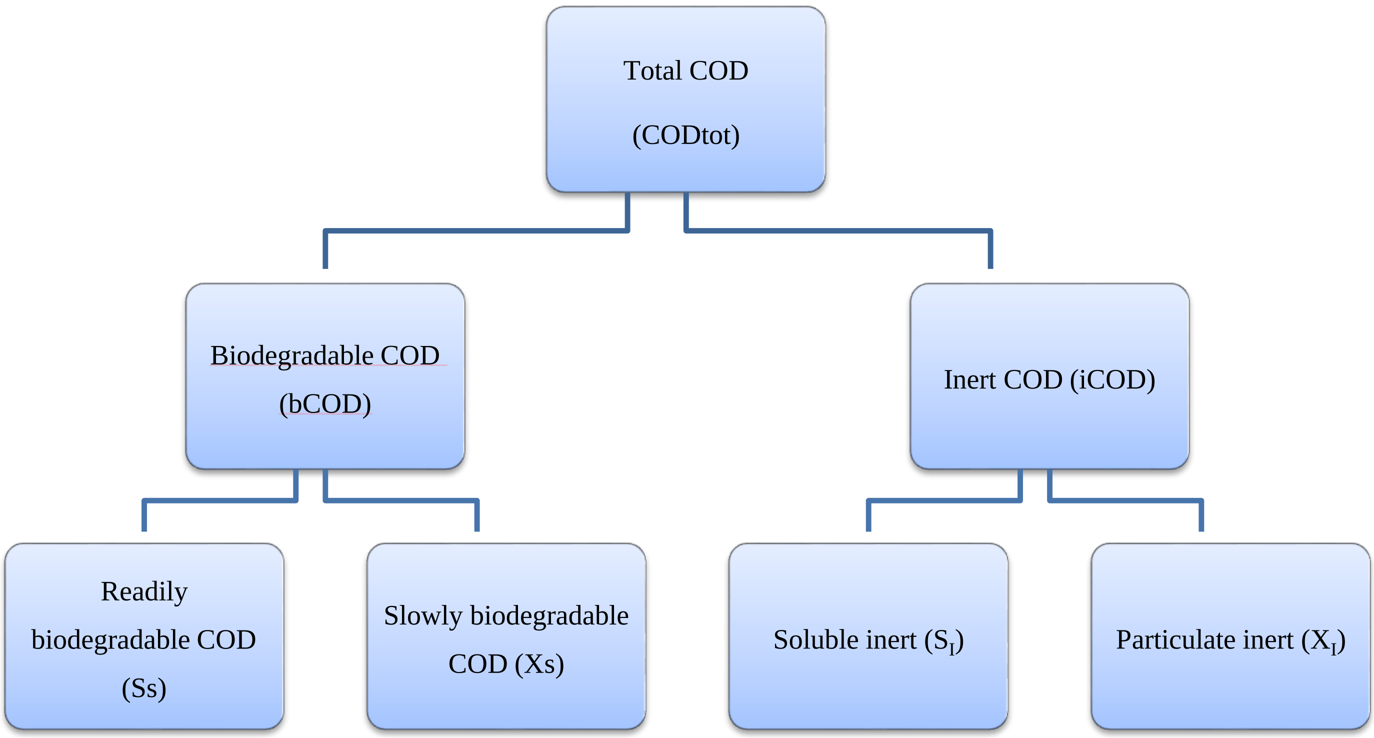

Figure 1. Distribution of the COD fractions

Typical concentrations of degradability of medium concentrated domestic wastewater influent adopted from Henze et al. (2008) are shown in Figure 2.

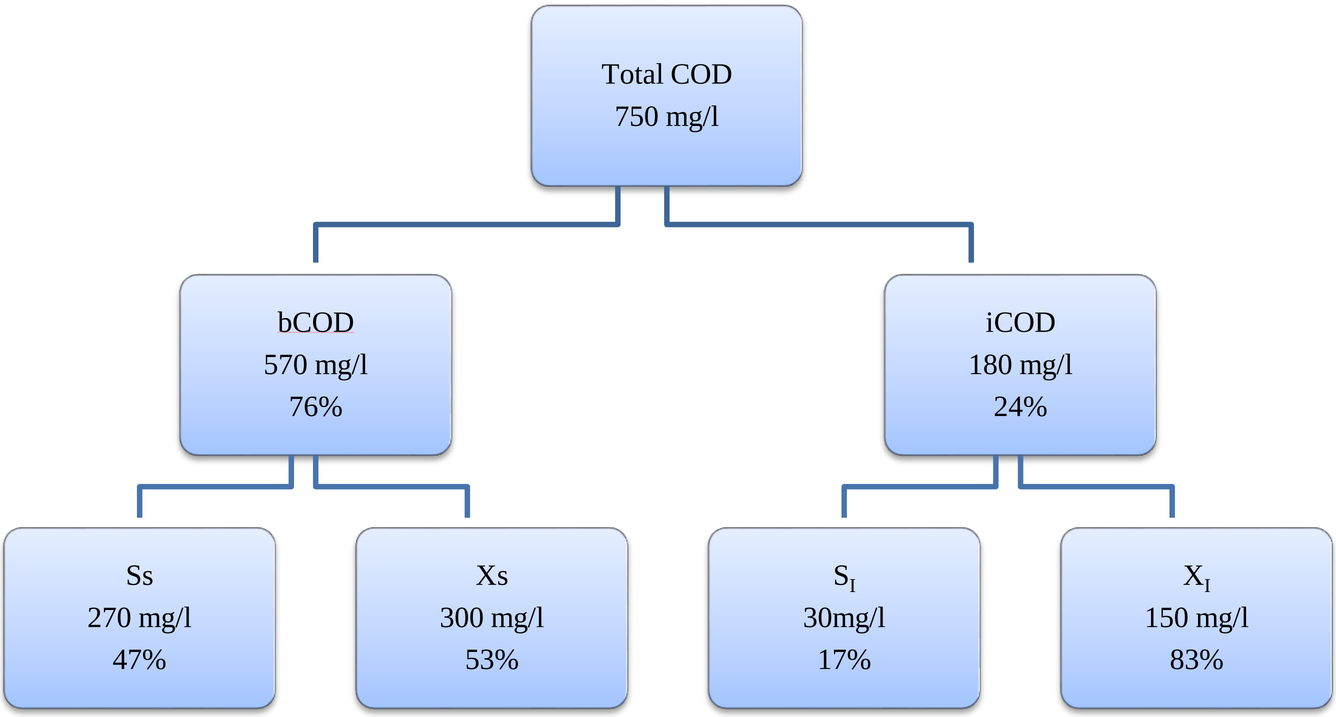

Figure 2. Degradability of medium concentrated domestic wastewater influent adopted from Henze et al. (2008)

The aim of this study is to characterize, the chemical oxygen demand (COD) from the primary treatment stage of the Darvill WWTP to provide the ASR - biological treatment optimization and modelling parameters. The Ss, Xs, S_I and X_I fractions were determined using the respirometry method. The respirometric characterization method is based on the measurement of the microbial response during substrate degradation in a batch type reactor The recorded consumption rate of the dissolved oxygen in the batch test is closely related to the quality and quantity of available substrate in the system.

METHODS

The study focuses on Darvill WWTP which is situated in Pietermaritzburg in the KwaZulu-Natal Province of South Africa and owned by Umgeni Water. The WWTP collects and treats domestic wastewater and effluent from nearby industries. The industries that discharge into the Darvill WWTP are largely Oil and Dairy. Acceptable WWTP final effluent quality should be devoid of excess organics- COD, ammonia (NH_3), nitrogen (N) and phosphorous (P) nutrients (Ying Xin Wu, 2015). Therefore, operation of Darvill WWW is subject to comply with the national legislative requirements of the Department of Water and Sanitation (DWS).

Table 1. Darvill WWTP discharge limits as per discharge license by DWS

Determinants	**Units**	**Value**
Chemical Oxygen Demand (COD)	mg O_2 /l	75
Ammonia (NH_3)	mg N/l	6
Nitrates (NO_3)	mg N/l	15
Soluble Reactive Phosphorus (SRP)	ug P/l	1000
Suspended Solids (SS)	mg SS/l	25

Experimental Method

In the research approach adopted for this study, a respirometer was used to conduct the experiments. The percentage fractions of the COD i.e. the bCOD and Ss were determined and thereafter the fractions of bCOD and the iCOD were determined using a set of equations and mass balance (equations 2-12). The bCOD can be fractionated into Ss and Xs whereas the iCOD is fractionated into X_I and S_I.

The respirometry principle is based on the oxygen uptake rate (OUR) by the microorganisms contained in the activated sludge in a biological reactor of the treatment plant to biodegrade a carbonaceous substrate. It works on a closed circuit batch mode. The sludge inoculum was collected at the end of the aerobic reactor since there is a low risk of having residual bCOD. The collected sludge was aerated for a minimum of 24 hours before use. This allowed it to reach the endogenous phase (the oxygen consumption rate in the absence of substrate from external sources). The sample was then filtered to remove larger particles present. A litre of the filtered sludge was used in the respirometer. The test was done in 3 stages.

Stage 1: Determination of the heterotrophic yield using Acetate.

The heterotrophic yield determines both the mass of electron acceptor utilized and the new cell biomass produced in the aerobic reactor. A solution of 400 mg of sodium acetate in 1 litre of distilled water was prepared. For this solution, a COD value (CODac ≈ 300 mg/l) was obtained from the lab using standard methods. The respirometric tests are carried out in order to determine the consumed oxygen (CO) due to the breakdown of acetate by the use of a 50 ml sample of acetate reacting with the 1 litre endogenous activated sludge. Once the respirometer has finalized we consider that the whole acetate has been broken-down.

CO: Consumed oxygen = ΔO_2 (mg/l)

$$Y_{H,\,COD} = 1 - COac / CODac \quad (2)$$

Where:

$Y_{H,\,COD}$ - Heterotrophic yield coefficient (mg O_2/mg COD).

Stage 2: The determination of bCOD by the addition of the 50 ml 24h composite sample.

An auto sampler was programmed to take samples of primary effluent at hourly intervals for 24hrs. The composite sample (50 ml) was used as substrate and its total COD concentration was determined using standard methods. 1-Allyl-2-Thiourea was used at a ratio of 2:1 to sludge MLSS to inhibit nitrification so that only the carbonaceous oxygen consumption is ascertained. The mixture of the sludge and samples were continuously aerated with dissolved oxygen measured every 2 seconds until the process was observed to be completed. The dissolved oxygen concentration decreased as the amount of consumed oxygen increased. The consumed oxygen becomes a resultant effect of the microorganisms' respiration in the activated sludge, from the biological oxidation of substrate (organic or ammonium) and from its own survival consumption (endogenous respiration). The test was observed to be complete when the amount of initial dissolved oxygen (DO) was equal to the final DO. Each batch runs as long as there is still consumed oxygen (approx. 50 min).

Through this experiment one was able to calculate the amount of bCOD in the sample using the amount of the consumed oxygen.

$$bCOD = CO_{bCOD} / (1 - Y_{H,\,COD)} = mg/l \quad (3)$$

where:

CO_{bCOD} - Consumed oxygen due to the breakdown of the 24 hr composite sample

From the amount of bCOD determined a percentage could thereafter be derived from the total COD concentration of the 24hr composite sample that was analysed in the lab using standard methods.

$$\%bCOD = (bCOD/COD_{COMP}) *100 \quad (4)$$

It is from here that the iCOD was deduced from the CODtot and bCOD concentration

Where

$$iCOD = COD_{COMP} - bCOD \quad \text{and} \quad (5)$$

$$\%iCOD = 100 - \%bCOD \quad (6)$$

Stage 3: Determination of Ss by the addition of the filtered 24h composite

The stage 2 procedure was followed to determine the Ss concentration and a 50 ml filtered (0.45 µm filter) composite sample was used as substrate.

The experiment yields a consumed oxygen concentration through the breakdown of the filtered sample. It is from this concentration that the concentration of Ss was determined:

$$Ss = CO_{rbCOD} / (1 - Y_{H,\,COD}) \quad (7)$$

where:

CO_{rbCOD} - Consumed oxygen due to the breakdown of the 24 hr filtered composite sample

The bCOD concentration (stage 2) and the Ss concentration are used to determined Ss percentage (%Ss)

$$\%Ss = (Ss/bCOD) *100 \quad (8)$$

It is from here that the Xs was deduced from the bCOD and Ss concentration as:

$$Xs = Ss - bCOD \quad (9)$$

Resulting in a %Xs = 100 - %Ss (10)

Stage 4: X_I and S_I fractions are deduced through mathematical reduction from all the experimentally/lab determined fractions

$$S_I = COD_{TS} - Ss \quad (11)$$

Where:

COD_{TS} – The total soluble COD in the composite sample as per lab analysis using standard methods

$$X_I = iCOD - S_I \quad (12)$$

Where:

iCOD – The inert COD fraction deduced through mass balance using the total COD of the composite less the bCOD.

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RESULTS AND DISCUSSION

Data from a COD fractionation experiment are shown in Table 2

Table 2. Sample of experimental results of study

CODcomp (mg/l)	440	COD_{TS} (mg/l)	205
	Consumed Oxygen (mgO/l)	**COD Concentration (mg/l)**	**Percentage fraction (%)**
Y_H,acetate	117.71	320	63
bCOD	97.9	266.2	60.5
iCOD		173.8	39.5
Ss	62.63	170.26	63.96
Xs		173.8	36.04
S_I		34.74	20
X_I		139.06	80

The heterotrophic yield is used as basis for all experimental calculations on the endogenous sludge sample (Table 2) for finding the COD fractions as the heterotrophic yield denotes the biomass available in the reactor used for the experiment.

RESULTS: Oxygen consumption response

Stage 1: The heterotrophic yield using Acetate

Acetate, which is a readily biodegradable substrate, was used as a reference for assessing the bioactivity of the endogenous sludge under aerobic conditions.

The typical heterotrophic response is presented in Figure 3 and Figure 4 respectively. Upon addition of acetate solution to the endogenous sludge, a rise in the consumption of oxygen is observed while a decline in dissolved oxygen is noted from about 82 s to about 1569 s. This is indicative of microbial breakdown on the added acetate. The oxygen utilization is triggered by the presence of acetate and/or the electron acceptor. Since no exogenous substrates other than acetate was added to the batch reactors, all responses were considered to be due to the utilization of endogenous products released by the bacterial cells attached to the sludge.

At about 1685 s there is a notable steady increase in the dissolved oxygen and at 2525 s the consumed oxygen curve becomes constant and no further changes in consumed oxygen are noted. This is indicative of the complete breakdown of acetate in the system and therefore from the experimental data a value of the amount of consumed oxygen due to the breakdown of acetate can be determined.

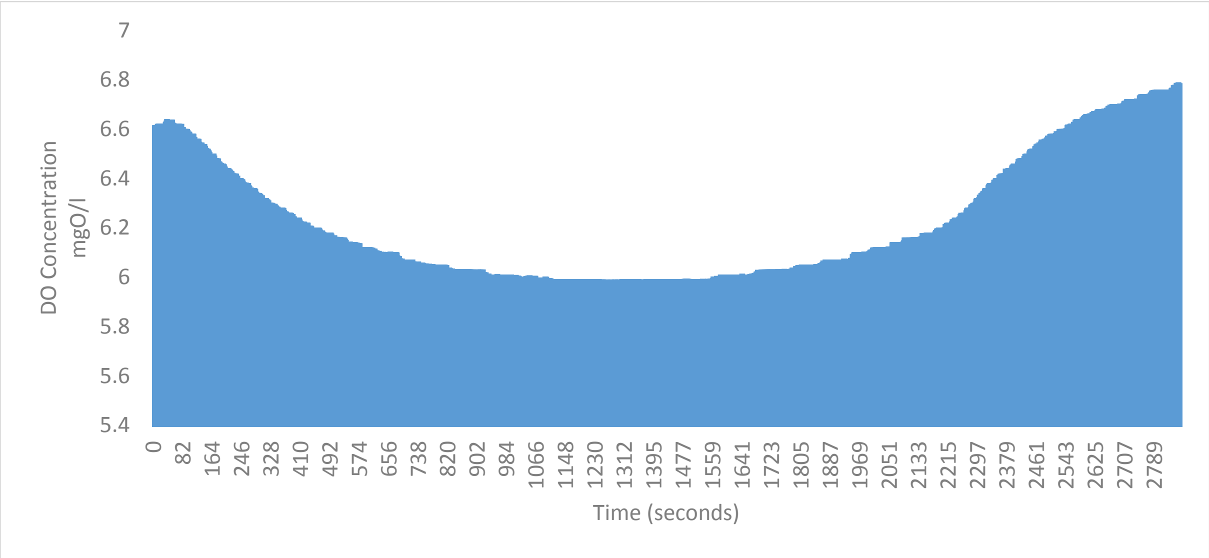

Figure 3. Dissolved oxygen response due to the addition of acetate

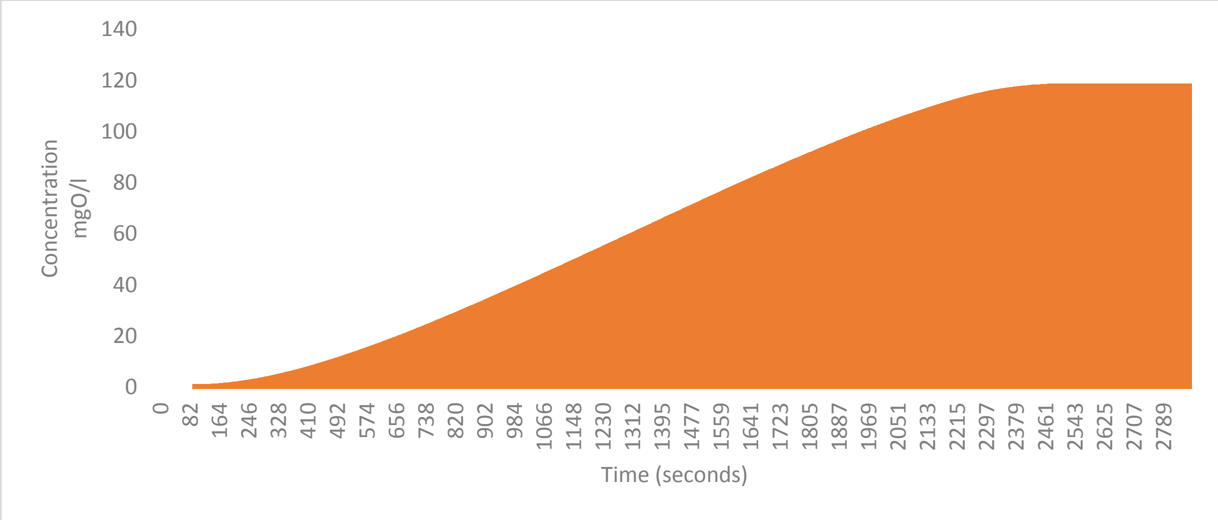

Figure 4. Consumed Oxygen response due to the addition of acetate

The extracted consumed oxygen of 117.71 mg/l and the lab analysed acetate COD concentration (320 mg/l) was used to determine the heterotrophic yield (see equation 2) which was found to be 0.63 mgCOD/mgCOD (see Table 2).

The accepted standard heterotrophic yield value of 0.67 mgCOD/mgCOD is used in ASMs and similar models (Muller et al. 2004) and the value of 0.63 mgO2/mgO2 is the yield coefficient suggested by Henze et al., (1995) for aerobic/anoxic reactions involving activated sludge. The experimental yield was found to be 0.63 mgCOD/mgCOD which is well within range and comparable to the expected literature values. High yield coefficients calculated are due to the presence of polyphosphate accumulating organisms which take up and store some of the available acetate. This is believed to be prevalent in biomass that has been growing under dynamic conditions (Naidoo, 1999).

Stage 2: Determination of the bCOD fraction

The response to the addition of the sample is similar to the response to the addition of acetate. There was a notable decrease in the amount of dissolved oxygen and a noted increase in amount of consumed oxygen. This is also due to the biodegradation of the COD present in the 24 hr composite sample. The added allyl thio urea inhibitor ensured that the response observed was solely due to the breakdown of the bCOD. The response curves to the addition of the 24 hr composite sample are noted Figure 5 and Figure 6.

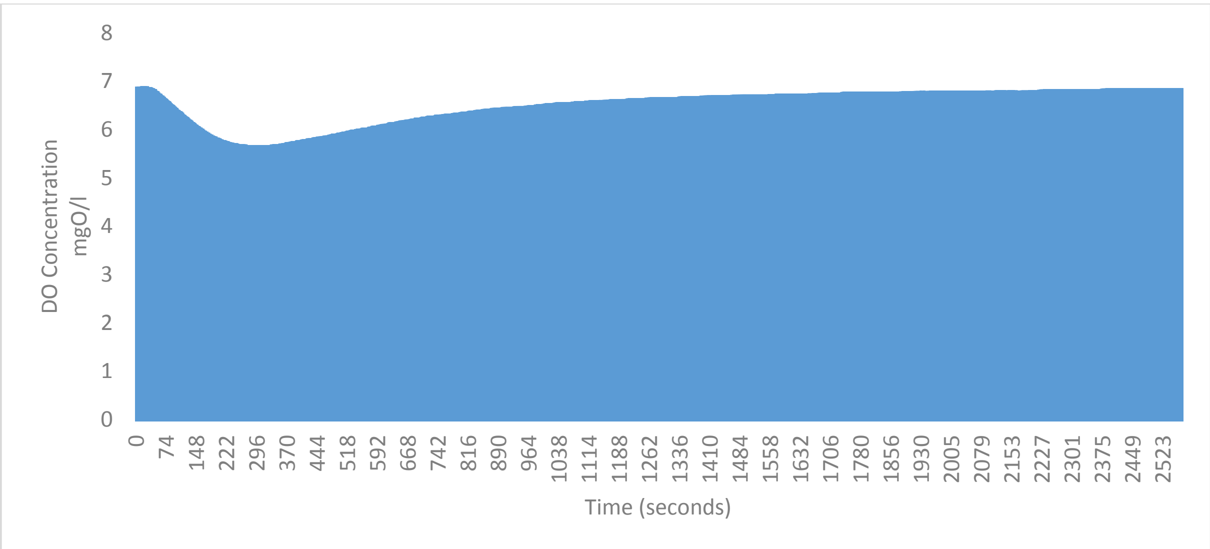

Figure 5. Dissolved oxygen response due to the addition of 24hr composite sample

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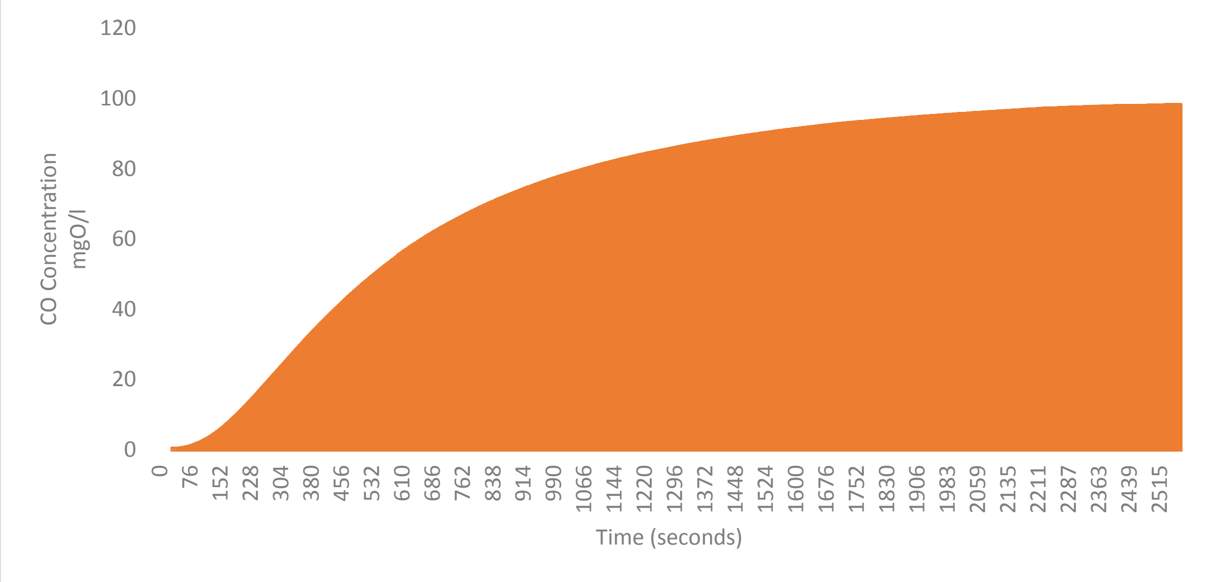

Figure 6. Consumed oxygen response due to addition of 24hr composite sample

The consumed oxygen due to the breakdown of the 24hr composite sample was found to be 97.92 mg/l. The bCOD concentration was found to be 266.2 mg/l (equation 3).

Stage 3: The determination of Ss COD

The response curves due to the addition of the filtered composite sample (Figure 7 and Figure 8) are similar to that of the acetate and the bCOD. There is an observed drop in the dissolved oxygen in the endogenous sludge from 102 s to 632 s where the lowest DO was observed (6.71 mgO/l). The DO steadily increases denoting the decreased concentration of the readily biodegradable COD in the system where at 1821 s the DO becomes constant which indicates a complete breakdown of Ss.

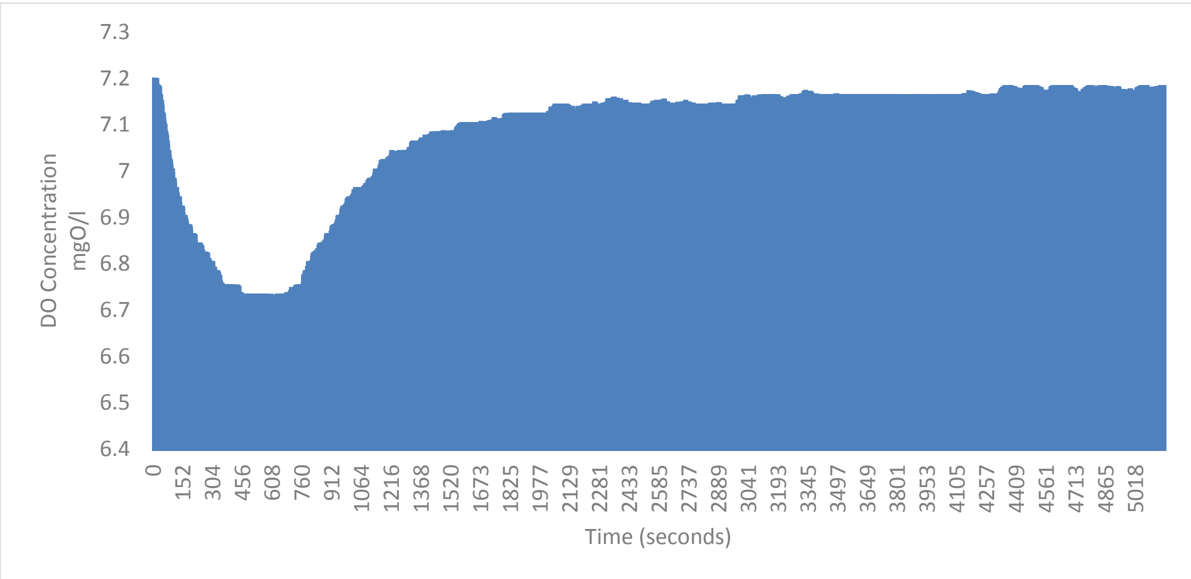

Figure 7. Dissolved oxygen response due to the addition of the 24hr filtered composite sample

The behaviour of consumed oxygen due to the addition of the 24hr filtered composite sample is observed in **Error! Reference source not found. Error! Reference source not found.**. It is seen that there is some activity two seconds after the addition of the sample and there is a measure of consumed oxygen. There is an increase from 14 s to 4763 s, after point

4763 s there is an observed constant consumption of oxygen. Once there is a constant trend, biodegradation is said to be complete as at this point the DO response curve is also seen to be constant (7.18 mgO/l).

The difference in the 3 experiments that have been performed are the times taken to run each experiment to completion. This is simply due to the nature of COD in the 3 instances. Acetate has a shorter carbon compared to the bCOD and readily biodegradable COD is a filtered sample (no particulate matter) and is a soluble readily biodegradable fraction of the bCOD.

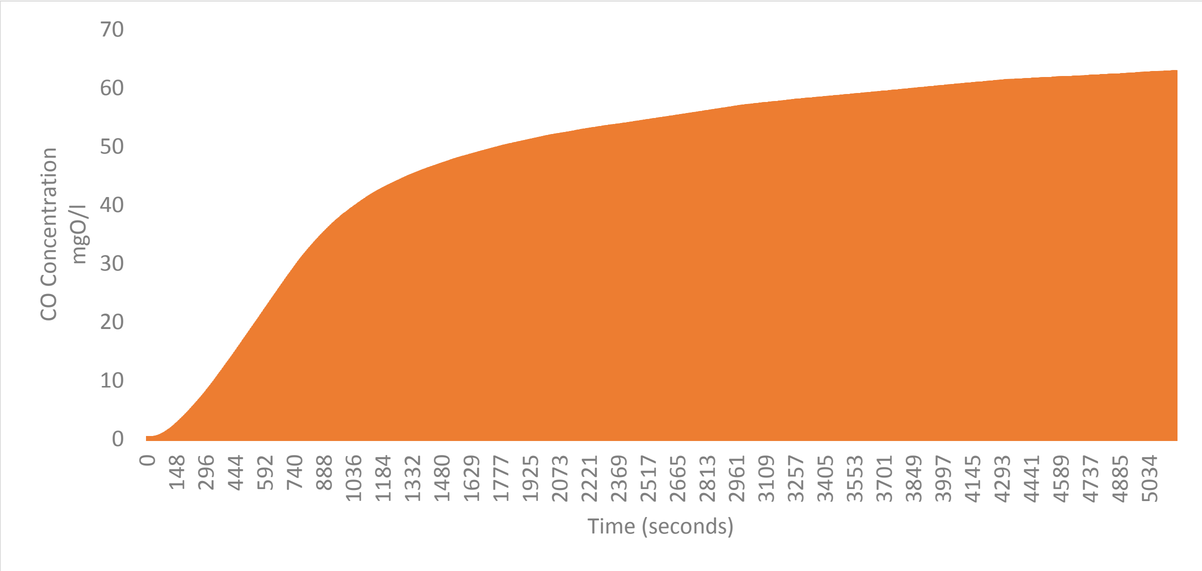

Figure 8. Consumed oxygen response due to the addition of 24hr filtered composite sample

The experiment yielded a consumed oxygen concentration of 62.63 mg/l through the breakdown of the filtered sample. The Ss concentration was found to be 170.26 mg/l (see equation 7). The Ss concentration is found to be the higher fraction of the bCOD and this is beneficial for the ASR. Choi et al. (2017) discussed that Ss is one of the most important components of COD as it is readily degraded by microbial metabolism. The %Ss in this instance is 63.96% (see Table 2) and is significantly higher than the 47% from Figure 2 of degradability of medium concentrated domestic wastewater influent adopted from Henze et al. (2008).

CHARACTERIZATION

On average the primary effluent bCOD was found to be higher than the iCOD and Ss was higher than Xs. The Ss is the most valued substrate as it is easier for the microorganisms to breakdown. This therefore means that Darvill primary effluent has sufficient substrate for the COD removal and the biological nutrient removal process. The primary effluent of Darvill WWTW is seen to be similar to domestic wastewater as the amount of bCOD was 70.5% and domestic wastewater was averaged by Henze et al. (2008) to be 75%; however, it is seen that the Ss fraction is significantly higher (75%) than the Xs fraction (25%). This can be directly linked to the industrial effluent coming into the plant. Oil (VFA) and Dairy have a high Ss content.

Particulate organic matter which is Xs was found to be 25%. The lower fraction is beneficial for the treatment process as this fraction is degraded slowly by a series of microbial actions, such as adsorption, hydrolysis, and metabolism. The S_I, was found to be 49.2% of the iCOD. The S_I, is quite refractory in biodegradation and is contained mostly in industrial effluent. Aromatic compounds which are used in various industries and are typical examples of S_I. It includes varieties of soluble compounds, which can pass through the microbial wall but cannot be degraded due to their refractory nature. As a result, the S_I leaves the activated sludge reactor unaltered in concentration and characteristics (Wu et al. 2014). Darvill WWTP S_I fraction is significantly higher than that of medium concentrated domestic wastewater influent adopted from Henze et al. (2008) which is 17% (Figure 2. **Degradability** of medium concentrated domestic wastewater influent adopted from Henze et al. (2008)). This shows that Darvill receives both industrial and domestic effluent.

Non-biodegradable Particulate COD (X_I) fraction was found to be 50.8%. This fraction becomes absorbed in the activated sludge and is removed by sludge wasting in a WWTP. The X_I significantly affects the volume of wasted sludge and forms part of considerations for WWTP reactor design (Choi et al. 2017). Both S_I and X_I cannot be biologically degraded further in a WWTP and therefore can pass through the activated sludge system unchanged.

Hence, precise COD characterization is important for the efficient operation of biological nutrient removal wastewater treatment process. Several methods have been developed for COD characterization, but the two most commonly used processes are the biological and physical-chemical characterizations. The COD characterization results are represented in Figure 9 below.

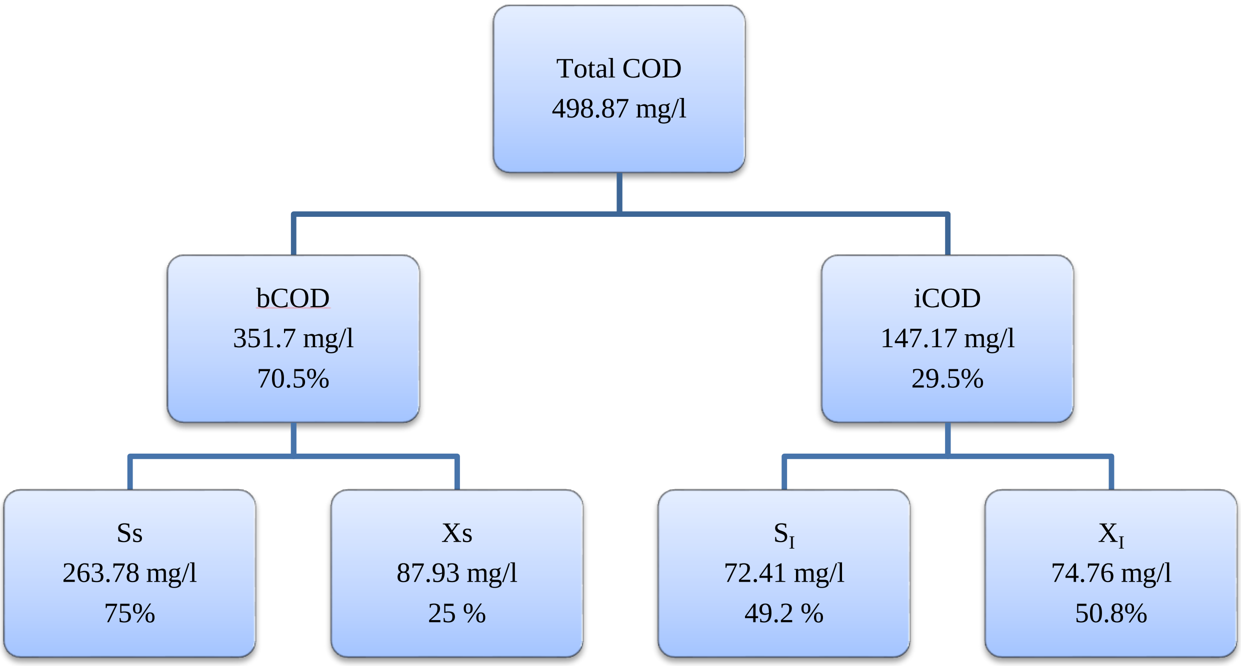

Figure 9. COD characterization results

CONCLUSION

Wastewater characteristics are unique to every treatment plant and cannot be predicted without comprehensive analysis especially in cases where the influent is made up of both industrial and domestic waste. The characteristics of Darvill primary effluent COD have now been understood. The plant receives process favorable COD fractions as there is a higher bCOD (70.5%) component and Ss (75%) component compared to the iCOD (29.5%).

Domestic wastewater is reported to have the following average compositions: X_I= 4–20%, slowly biodegradable COD) = 24.5–65%, S_I = 3 –14.3% and Ss = 14–57%. Darvill wastewater characteristics show more resemblance to domestic wastewater effluents in terms of the biodegradable fractions, however the non-biodegradable fractions do show that Darvill receive mixed effluents. The most important fractions in this study are the bCOD fractions and are significantly higher than the iCOD which means that the process microorganisms in the ASR have sufficient substrate for the current biological nutrient removal process and no chemical additions are required to supplement the process and COD fractions can serve as input for an ASM.

It is recommended that COD should be analyzed and characterized into its relative fractions on a routine basis for ease of process optimization through ASM.

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