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Sustainable Circular Economy Approach to Optimize Biological Nutrient Removal Using Glycerol (Bio-Diesel byproduct) as a Carbon Substrate

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Outline

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- Sustainable Circular Economy Approach to Optimize Biological Nutrient Removal Using Glycerol (Bio-Diesel by-product) as a Carbon Substrate
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sustainable approach for VFAs production, this study apply circular

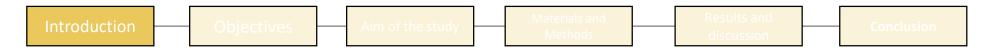
economy theories by using Biodiesel by-product (mainly glycerol) as an

alternative carbon source in biological phosphorus and nitrogen removal in

waste water treatment. This also in line with the Saudi "Vision 2030" of

achieving environmental sustainability, since about 50% of all waste in Saudi

Arabia is organic waste that has a great potential to be used to produce Biodiesel.

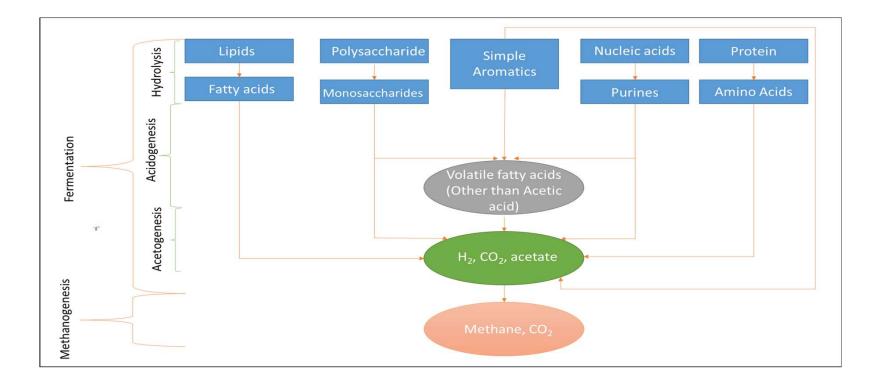


- Biological nutrient removal (BNR)(EBPR and Denitrification) require a carbon source to be carried out.
- VFAs:
 - Are the major carbon source in wastewater That can drive EBPR.
 - Concentration and composition significantly affect efficiency .
 - Can be produced through fermentation or external substrate fermentation.
 - production of VFAs for full-scale use is cost prohibitive.

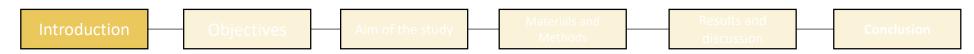
(Chen, Randall, & McCue, 2004; Shen & Zhou, 2016; Wu, Peng, Li, & Wang, 2010)

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Fermentation

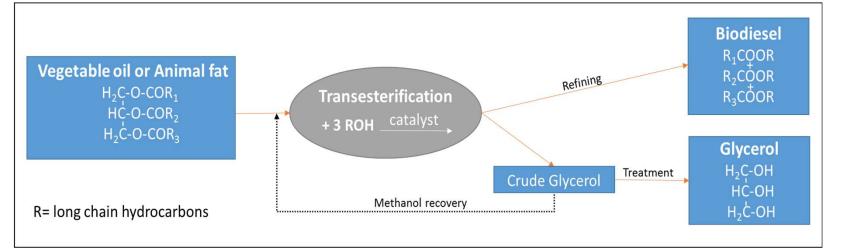


(Metcalf & Eddy, 2014)



Biodiesel

- Is a fuel produced from vegetable oils or animal fats (in the presence of a catalyst) through a transesterification reaction
- Results in glycerol as a by-product.
- Typical biodiesel waste mixtures contain 56% to 60% crude glycerol



(Correa & Arbilla, 2008; Demirbas, 2008; Eguchi, Kagawa, & Okamoto, 2015; Hoekman & Robbins, 2012; Leoneti, Aragao-Leoneti, & De Oliveira, 2012; Usta et al., 2005).

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Literature Review:

- Glycerol can be fermented to VFAs (Yin, Yu, Wang, & Shen, 2016).
- Prefermenter production of VFAs can be optimized by manipulating the mixing intensity (Banister & Pretorius, 1998; Danesh & Oleszkiewicz, 1997).
- Propionic acid was found to be more effective for BNR systems

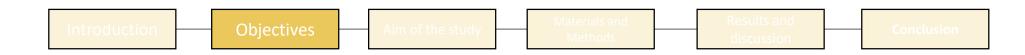
(Chen et al., 2004; Shen & Zhou, 2016; Wu et al., 2010).

• H₂ could inhibit Acetogenesis if H₂ exceeds 10⁻⁴ atm (Fukuzaki, Nishio,

Shobayashi, & Nagai, 1990; Metcalf&Eddy, 2014).

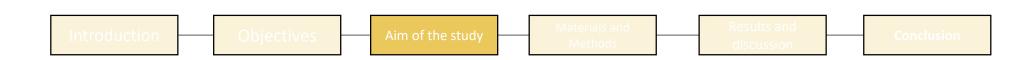
Objective:

 Is to apply circular economy theory to optimize activated sludge system nutrient removal using fermented and direct addition of glycerol (biodiesel byproduct) in a pilot scale A²O experiment.



Aim of the study:

- Compare the biological nutrient removal with and without prefermentation.
- Study the effect of glycerol adding location on the overall biological nutrient removal.
- Study the effect of prefermenter mixing intensity on the production of VFAs.





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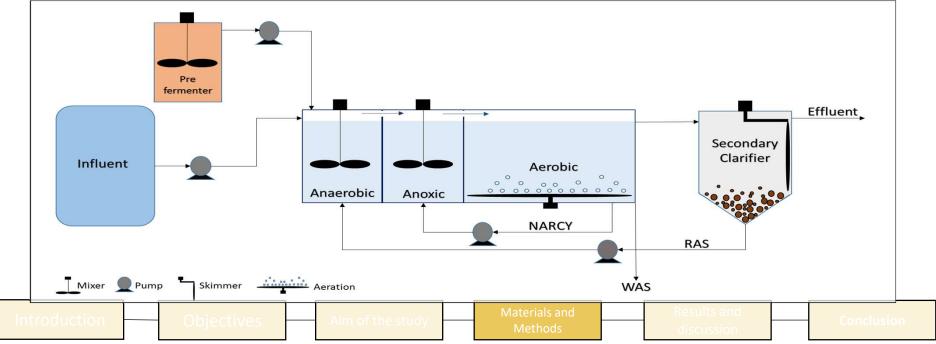
Conclusion

Materials and Methods:

- Two A₂O BNR system
- Real wastewater
- SRT = 10 days

Reactor	Volume (L)	Diameter (inches)	Liquid Height (inches)		
Anaerobic	3.59	4.00	17.43		
Anoxic	5.90	4.00	28.65		
Aerobic	17.95	8.00	21.79		

- Glycerol dose 68.5 (phase1) and 78.8 (phase 2) mg-COD/L influent
- All comparisons were tested statistically using paired sample t-test



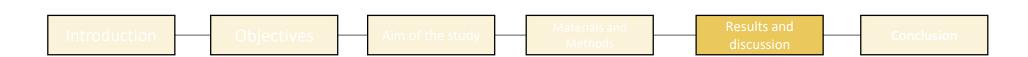
Average Influent characteristics for all phases (both receive same influent)

		Flowr ate	TN	TN NH3		SOP	TSS	s-COD	TCOD		DO
		L/day	mg/l as N	mg/l as N	mg/l as P	mg/l as P	mg/L	mg/L	mg/L	PH	mg/ L
Pre- Phase	Train A, B	54.1	39.2	37.8	5.0	5.0	74.4	193.2	319.1	7.6	0.2
Phase One	Train A, B	54.2	41.5	29.6	5.3	3.6	64.3	153.0	247.6	7.5	0.1
Phase two	Train A, B	51.7	52.3	33.9	4.4	3.4	52.8	120.5	208.8	7.7	0.1

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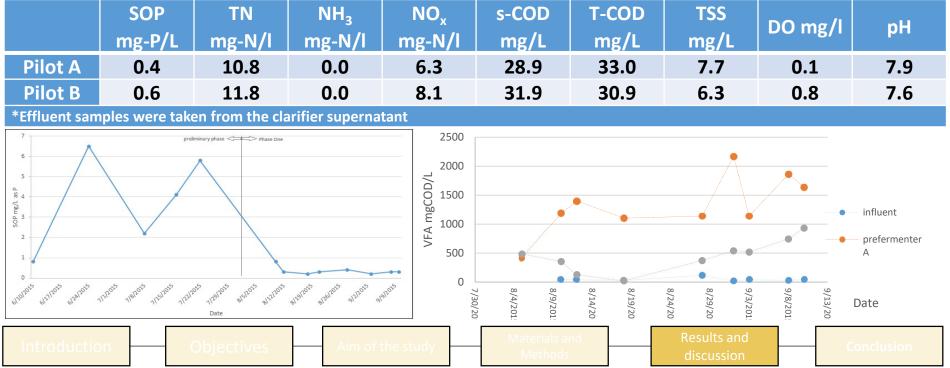
Results and discussion: Acclimation of the biomass (preliminary Phase)

- No experimental variable
- No glycerol or prefermenters
- Does not have sufficient carbon source to drive biological nutrient removal
- Used as an acclimation period for the biomas



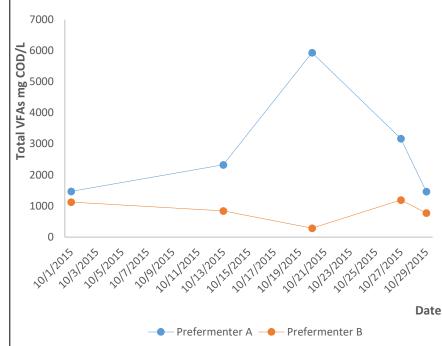
Results and discussion: Location of the Glycerol Dose (Phase 1)

- A produced 2.4 more total VFAs than prefermenter B
- EBPR functions showed a considerable improvement in phosphorus removal after attaching the prefermenters
- SOP removal efficiency for train A and B were 92.2% and 85.6% respectively
- both trains removed 100% ammonia



Results and discussion: Mixing Intensity (Phase 2)

- PF-A (7rpm) & PF-B (50rpm)
- VFA production had an inverse correlation with mixing intensity similar to a lab scale testing [12]
- Reducing the PF mixing to 7 rpm resulted in about 250% increase in the VFAs production and increased the propionic to acetic acid ratio about 50%.
- Better VFA production was observed with lower mixing intensity



L	SOP mg-P/L	TN mg-N/I	NH ₃ mg-N/l	NO _x mg-N/l	s-COD mg/L	T-COD mg/L	TSS mg/L	DO mg/l	рН			
Pilot A	0.7	10.8	1.5	5.7	30.2	30.7	9.3	0.4	7.8			
Pilot B	0.4	8.4	1.1	7.1	31.6	36.3	10.0	0.7	7.8			
*Effluent samples were taken from the clarifier supernatant												
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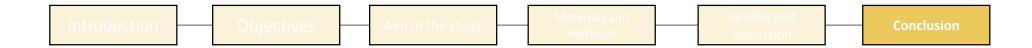
Conclusion:

- Both location of glycerol addition had beneficial effects on the A₂O with no significant difference in the effluent quality with respect to both P and N.
- 1.4 hour anaerobic HRT was enough to ferment the glycerol and make it available for EBPR.
- Direct addition of glycerol to the anaerobic zone in PP2, resulted in the lowest Y_{obs} in the whole study.
- Co-fermentation of glycerol and primary sludge resulted in a significant VFAs increase even beyond the theoretical estimated additional VFAs from the glycerol addition.

Conclusion

Conclusion (continued**):**

- Lower prefermenter mixing increased the VFAs production significantly (especially propionic acid) but did not correlate with superior EBPR effluent quality.
- In general, adding prefermentation reactor with glycerol dosage at low mixing energy should maximize the efficiency of the activated sludge system.
- Preliminary economic screening suggest that appling this optimization could save up to 20% of the BNR operational costs.



Questions & Comments

All welcome!



1. Metcalf&Eddy, *Wastewater engineering: treatment and resource recovery*. 2014, New York: McGraw-Hill Education.

2. Oehmen, A., et al., *Anaerobic metabolism of propionate by polyphosphate-accumulating organisms in enhanced biological phosphorus removal systems*. Biotechnology and Bioengineering, 2005. **91**(1): p. 43-53.

3. Bodík, I., et al., *Biodiesel waste as source of organic carbon for municipal WWTP denitrification*. Bioresource Technology, 2009. **100**(8): p. 2452-2456.

4. Barbirato, F., D. Chedaille, and A. Bories, *Propionic acid fermentation from glycerol: comparison with conventional substrates.* Applied Microbiology and Biotechnology, 1997. **47**(4): p. 441-446.

5. Himmi, E., et al., *Propionic acid fermentation of glycerol and glucose by Propionibacterium acidipropionici and Propionibacterium freudenreichii ssp. shermanii.* Applied Microbiology and Biotechnology, 2000. **53**(4): p. 435-440.

6. Zhang, A. and S.-T. Yang, *Propionic acid production from glycerol by metabolically engineered Propionibacterium acidipropionici*. Process Biochemistry, 2009. **44**(12): p. 1346-1351.

7. Yuan, Q., R. Sparling, and J. Oleszkiewicz, *VFA generation from waste activated sludge: Effect of temperature and mixing.* Chemosphere, 2011. **82**(4): p. 603-607.

8. Wu, C.-Y., et al., *Effect of carbon source on biological nitrogen and phosphorus removal in an anaerobic-anoxic-oxic (A2 O) process.* Journal of Environmental Engineering, 2010. **136**(11): p. 1248-1254.

9. Mu'azu, N.D., et al., *Food waste management current practices and sustainable future approaches: a Saudi Arabian perspectives.* Journal of Material Cycles and Waste Management, 2019. **21**(3): p. 678-690.

10. Rehan, M., et al., *Waste to biodiesel: A preliminary assessment for Saudi Arabia.* Bioresource Technology, 2018. **250**: p. 17-25.

11. Waqas, M., et al., *Optimizing the process of food waste compost and valorizing its applications: A case study of Saudi Arabia.* Journal of Cleaner Production, 2018. **176**: p. 426-438.

12. Ghasemi, M., *Use of glycerol/biodiesel waste via prefermentation for enhanced biological phosphorus removal in advanced wastewater treatment*. 2015, University of Central Florida: College of Engineering and Computer Science.

- Bernat, K., Kulikowska, D., & Godlewski, M. 2016. Crude glycerol as a carbon source at a low COD/N ratio provides efficient and stable denitritation. *Desalination and Water Treatment*, 57(42): 19632-19641.
- Bodík, I., Blšťáková, A., Sedláček, S., & Hutňan, M. 2009. Biodiesel waste as source of organic carbon for municipal WWTP denitrification. *Bioresource Technology*, 100(8): 2452-2456.
- Chen, Y., Randall, A. A., & McCue, T. 2004. The efficiency of enhanced biological phosphorus removal from real wastewater affected by different ratios of acetic to propionic acid. *Water Research*, 38(1): 27-36.
- Coats, E. R., Dobroth, Z. T., & Brinkman, C. K. 2015. EBPR using crude glycerol: assessing process resiliency and exploring metabolic anomalies. *Water Environment Research*, 87(1): 68-79.
- Correa, S. M., & Arbilla, G. 2008. Carbonyl emissions in diesel and biodiesel exhaust. *Atmospheric Environment*, 42(4): 769-775.
- Demirbas, A. 2008. Biodiesel. London, UK: Springer.
- Eguchi, S., Kagawa, S., & Okamoto, S. 2015. Environmental and economic performance of a biodiesel plant using waste cooking oil. *Journal of Cleaner Production*, 101: 245-250.
- Grabińska-ńoniewska, A., Słomczyński, T., & Kańska, Z. 1985. Denitrification studies with glycerol as a carbon source. *Water Research*, 19(12): 1471-1477.
- Guerrero, J., Guisasola, A., & Baeza, J. A. 2015. Controlled crude glycerol dosage to prevent EBPR failures in C/N/P removal WWTPs. *Chemical Engineering Journal*, 271: 114-127.
- Guerrero, J., Tayà, C., Guisasola, A., & Baeza, J. A. 2012. Glycerol as a sole carbon source for enhanced biological phosphorus removal. *Water Research*, 46(9): 2983-2991.
- Hoekman, S. K., & Robbins, C. 2012. Review of the effects of biodiesel on NOx emissions. *Fuel Processing Technology*, 96: 237-249.

- Leoneti, A. B., Aragao-Leoneti, V., & De Oliveira, S. V. W. B. 2012. Glycerol as a by-product of biodiesel production in Brazil: Alternatives for the use of unrefined glycerol. *Renewable Energy*, 45: 138-145.
- Lu, H., & Chandran, K. 2010. Diagnosis and quantification of glycerol assimilating denitrifying bacteria in an integrated fixed-film activated sludge reactor via 13C DNA stable-isotope probing. *Environmental science & technology*, 44(23): 8943-8949.
- Merzouki, M., Bernet, N., Delgenès, J. P., & Benlemlih, M. 2005. Effect of prefermentation on denitrifying phosphorus removal in slaughterhouse wastewater. *Bioresource Technology*, 96(12): 1317-1322.
- Metcalf&Eddy. 2014. *Wastewater engineering: treatment and resource recovery*. New York: McGraw-Hill Education.
- Shen, N., & Zhou, Y. 2016. Enhanced biological phosphorus removal with different carbon sources. *Applied microbiology and biotechnology*, 100(11): 4735-4745.
- Torà, J. A., Baeza, J. A., Carrera, J., & Oleszkiewicz, J. A. 2011. Denitritation of a high-strength nitrite wastewater in a sequencing batch reactor using different organic carbon sources. *Chemical Engineering Journal*, 172(2–3): 994-998.
- Usta, N., Öztürk, E., Can, Ö., Conkur, E., Nas, S., Con, A., Can, A., & Topcu, M. 2005. Combustion of biodiesel fuel produced from hazelnut soapstock/waste sunflower oil mixture in a diesel engine. *Energy Conversion and Management*, 46(5): 741-755.
- Walsh, B. 2012. Preventing eutrophication: scientific support for dual nutrient criteria: US Environmental Protection Agency.
- Wanielista, M., Baldassari, T., Ryan, P., Rivera, B., Shah, T., & Stuart, E. 2008. Feasibility study of waste tire use in pollution control for stormwater management, drainfields and water conservation in florida, *Seminole County Florida and State DEP*.

- Wu, C.-Y., Peng, Y.-Z., Li, X.-L., & Wang, S.-Y. 2010. Effect of carbon source on biological nitrogen and phosphorus removal in an anaerobic-anoxic-oxic (A2 O) process. *Journal of Environmental Engineering*, 136(11): 1248-1254.
- Xuan, Z., Chang, N.-B., Daranpob, A., & Wanielista, M. 2009. Initial test of a subsurface constructed wetland with green sorption media for nutrient removal in on-site wastewater treatment systems. *Water Quality, Exposure and Health*, 1(3-4): 159-169.
- Yin, J., Yu, X., Wang, K., & Shen, D. 2016. Acidogenic fermentation of the main substrates of food waste to produce volatile fatty acids. *International Journal of Hydrogen Energy*, 41(46): 21713-21720.
- Yuan, Q., Sparling, R., Lagasse, P., Lee, Y. M., Taniguchi, D., & Oleszkiewicz, J. A. 2010. Enhancing biological phosphorus removal with glycerol. *Water Science and Technology*, 61(7): 1837-1843.
- Emanon Photography, The background picture was retrieved from http://emanonphoto.blogspot.com/2011/03/ucfknight_27.html



- High nutrient concentration in municipal wastewater could cause significant environmental problems and health risks if discharged to receiving water without proper treatment (Walsh, 2012; Wanielista et al., 2008; Xuan, Chang, Daranpob, & Wanielista, 2009).
- Wastewater Nutrient can be removed chemically through precipitation or biologically through biological nutrient removal (BNR) (Metcalf&Eddy, 2014).
- A²O, University of Cape Town (UCT), and 5-stage BardenphoTM (Metcalf&Eddy, 2014).
- Biological Nutrient removal is the nitrogen removal and enhanced biological phosphorus removal (EBPR).

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Biological Nitrogen Removal (Nitrification/Denitrification) <u>Nitrification</u>

Carried out by chemoautotrophic bacteria known as nitrifying bacteria in a two step process.

$$2NH_{4}^{+} + 3O_{2} \rightarrow 2NO_{2}^{-} + 4H^{+} + 2H_{2}O \quad \text{Nitrosomonas Europea}$$

$$2NO_{2}^{-} + 2O_{2} \rightarrow 2NO_{3}^{-} \qquad \text{Nitrobacter}$$

$$NH_{4}^{+} + 2O_{2} \rightarrow NO_{3}^{-} + 2H^{+} + H_{2}O \qquad \text{Net equation}$$

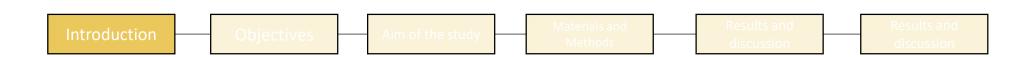
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Biological Nitrogen Removal (Nitrification/Denitrification)

Denitrification

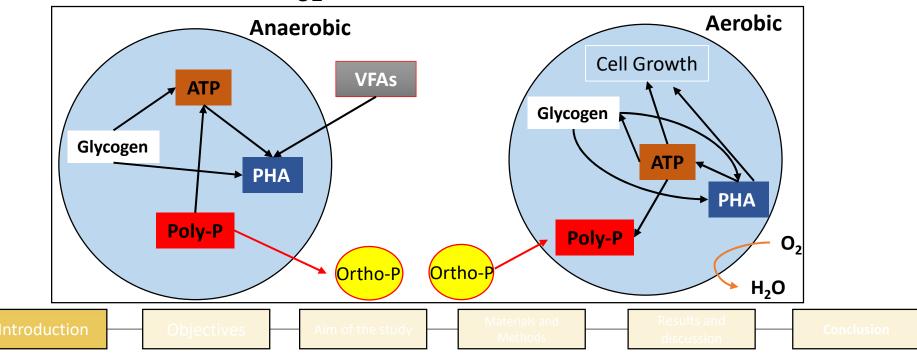
Denitrification is carried out as a dissimilation process by a broad range of heterotrophic groups of bacteria.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N$$



Enhanced Biological Phosphorus Removal (EBPR)

- Phosphorus removal from wastewater takes place in two main environments: anaerobic and aerobic.
- Anaerobic:
 - PAO + Poly-P + VFAs $\xrightarrow{\text{ATP}}$ Ortho-P + PHA
- Aerobic:
 - Ortho-P + PHA $\xrightarrow{\text{ATP}}$ PAOs+ CO₂ + H₂O



Composition of Crude Glycerol (w/w): 30% **glycerol**, 50% methanol, 13% soap, 2% moisture, approximately 2-3% salts (primarily sodium and potassium), and 2-3% other impurities

VFAs were measured using a Shimadzu (Columbia, Maryland) gas chromatograph equipped with a Supelco (St Louis, Missouri) Nukol column, and flame ionization detector (FID). The injection port and the detector were maintained at 220°C. Column initial temperature was 110°C and then ramped up at 5°C/min to reach a final temperature of 190°C which was held for 10 minutes. The carrier gas was helium at a flow rate of 20 cm/min, and a 10 mM volatile free acid mix was used to develop the standard curve

Table 6 Wastewater influent and side-stream prefermenters effluent characteristics

		Raw	Influent	Prefermenters						
		Phase one	Phase two	Phase	one	Phase two				
	~	г цазе оце	r hase two	PF1	PF2	PF3	PF4			
TN	ma	42.7±4.5	52.3±18	207±117	304±170	234±92	285±104			
NO _x	mg- N/L	0.28±0.1	*0.00	0.72±0.1	0.64±0.4	0.66±0.4	0.98±0.2			
NH3	IN/L	30.3±7.0	30.3±7.0 33.9±6.1 41.8±4.4 51.3±11		81.3±12	81.4±14				
TP	mg-	5.23±1.4	4.42±1.5	52.2±14	65.1±1.8	-	-			
SOP	P/L	3.70±1.2	3.40±0.9	18.30±2.9	22.9±4.6	29.1±6.2	28.8±6.0			
TSS		73.3±23	52.8±27	3465±1130	3985±4.6	3790±1898	5427±626			
s-COD	mg/L	155±35	121±23	1850±423	801±237	2737±88	1899±627			
TCOD	57.5	252±58	209±71	6517±1310	5814±637	7515±2325	8776±1055			
VFA	mg- COD/L	51.5±37	*0.00	1471±481	660±455	2875±1658	931±358			

- Phase one values are the average of 8 sampling events, and phase two is the average of 6 sampling events *below detection limit

+/-=1 standard deviation

- PF= prefermenter

Analytical Techniques

Samples were collected from the anaerobic, anoxic, aerobic, and secondary clarifier as well as influent and effluent reservoirs in two sample containers. One of the sample containers was filtered immediately on site with a glass fiber filter (Whatman[™], 1827-025, Pittsburgh, Pennsylvania) before transporting to the lab. The measurements of chemical oxygen demand (COD), e.g. TCOD and s-COD, ammonia (NH₃), nitrate (NO₃), nitrite (NO₂), total nitrogen (TN), total phosphorus (TP), soluble ortho-phosphate (SOP), total suspended solids (TSS), and volatile suspended solids (VSS) were performed according to the procedures published in Standard Methods (APHA, 2005).

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