WRF 4973 Fact Sheet: ID 1310

Strategy: Chemical Addition

External Carbon Sources

Chemical Methanol Storage.
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Carbon Delivery Tanker.
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Carbon can be added to enhance denitrification and to improve enhanced biological phosphorus removal (EBPR) by supplementing the carbon (biochemical oxygen demand [BOD]) in raw wastewater.

Readily biodegradable carbon compounds, such as methanol, acetic acid, proprietary chemicals, and some industrial wastes, can be used to improve denitrification in biological nitrogen removal (BNR). The carbon is typically added in first or second anoxic zones of a BNR process or at a denitrification filter following the BNR process. Carbon addition can be used on a consistent basis to increase denitrification to reduce effluent nitrate or used intermittently as a carbon supplement to maintain stable effluent nitrogen (N) discharge.

Many carbon sources are available to increase denitrification, but the biological pathways are different. Acetate is readily used by heterotrophic bacteria for denitrification and cell growth. However, methanol requires special methylotrophic organisms for denitrification. These organisms are not present in large numbers in a BNR treating typical wastewater and must be grown in the biomass if methanol is added. This means that methanol is not well suited for intermittent application but is well suited if added continuously. Waste streams from some industries such as breweries, food processing, and fruit drinks contain sugars and volatile fatty acids (VFAs) that are well suited for denitrification. More complex waste, such as dairy waste, contains fats, oils, and other more complex organics that can be readily fermented in biological processes and then used in the activated sludge process, but at slower kinetics.

Biological phosphorus (P) removal can also be improved and stabilized with carbon addition to the anaerobic zone. The anaerobic zone environment fosters fermentation of more complex organic compounds to produce VFAs that are rapidly stored by polyphosphate-accumulating organisms (PAOs) in anaerobic environments. PAOs can then use the stored carbon in a subsequent aerobic phase to produce energy in order to bioaccumulate phosphorus, thereby biologically removing soluble phosphorus from the wastewater. The more complex carbon sources can thus be used to improve the available carbon for EBPR.

Carbon use for denitrification and EBPR can be optimized by using online instruments for dose control. In addition to conventional chemical dose design for a well-mixed injection point, avoiding dissolved oxygen (DO) entering the anaerobic and anoxic zones, limiting mixing intensity to limit reaeration, and eliminating short circuiting the anaerobic and anoxic zones can optimize the denitrification and EPBR efficiency.

See the Additional Information section below for more information.

Fact Sheet Application Checklist

R = fact sheet relevant to item
PR = fact sheet is potentially relevant to item depending on application, existing conditions, etc.

Category		Intensification
	R	Chemical addition
	PR	Carbon management
		I&C strategies
		Sidestream mgmt.
		Energy savings
		Chemical savings
		Operational savings
		Other means of NutRem
Nutrient		Ammonia
	R	NOx
	R	TN
	PR	Ortho-P
	PR	TP
Scale (design flow)	R	Small (<1 mgd)
	R	Medium (1–10 mgd)
	R	Large (>10 mgd)

Goal	R	Improve reliability
	R	Reduce nutrient
		Reduce O&M cost
Group	R	Optimize existing CNR
	R	Optimize existing TNR
		NutRem in secondary plant
Process		Small
		Pond
	R	Fixed film (secondary)
		Conventional act. sludge (CAS)
		Nitrifying act. sludge (NAS)
	R	Conventional NutRem (CNR)
	R	Tertiary NutRem (TNR)
	R	Other

CAS = conventional activated sludge (BOD only)
NAS = nitrifying activated sludge (without denitrification)
CNR = conventional nutrient removal no chemical/no filter, etc.
TNR = tertiary nutrient removal with chemical, filter, etc.

Technology Summary Evaluation

Footprint	3	Compared to conventional (1 = much smaller; 3 = conventional; 5 = much larger)
Development status*	5	Technology ranking based (LIFT) see below*
Energy efficiency	3–5	Scale 1–5: 1 = use much less; 3 = use similar to conventional; 5 = use much more
O&M impact	3–5	Scale 1–5: 1 = cost much less; 3 = cost similar to conventional; 5 = cost much more
Material/consumables	1	Scale 1–3: minimal = 1; some = 2; significant = 3 (e.g., UV lamps/membranes)
Chemical use	2–3	Scale 1–3: minimal/none = 1; some = 2; significant = 3 (e.g., chemical process)

* Technology ranking based on Leaders Innovation Forum for Technology (LIFT) Water Research Foundation (WRF) Technology Development Level (TDL) definitions:
1 = bench research and development
2 = small-scale pilot
3 = full-scale pilot (demonstration)
4 = pioneer stage (production and implementation)
5 = conventional

Descriptions/Evaluation

Strategy	Carbon addition to aid nitrogen and biological phosphorus removal
Description	Soluble carbon sources are added to a BNR process to improve either N and/or P removal. External carbon sources include “pure” chemicals (methanol, acetate, etc.), proprietary chemicals (MicroC®, etc.), and industrial waste organic compounds (brewery waste, sugar water from bottling company, etc.).
Application	External carbon is added to achieve the following: • Supplement carbon for a wastewater deficient in readily biodegradable carbon • Improve N removal efficiency by increasing denitrification • Improve P removal efficiency by increasing PAO growth • Stabilize carbon availability to improve process reliability • Improve EBPR by removing nitrate from return activated sludge (RAS)
Constituents removed	Nitrogen and/or phosphorus
Development status*	Well established (TDL 5). New chemicals should be field-tested for effectiveness.
O&M considerations	Chemical addition increases operation cost both directly, through the chemical purchase, and indirectly by generating additional solids. Aeration requirements may also change because of the addition of external carbon. In tertiary applications, overdosing can result in permit violations on BOD. Online dosage control can be used to optimize chemical usage.
Benefits	Increased reliability compared to biological treatment alone. With carbon supplementation low effluent N and P levels can be achieved reliably. Compared to the use of a fermenter or primary effluent bypasses, dosing external supplemental carbon is better suited to match the actual BOD demand, thus minimizing the risk of over- or under-dosing.
Limitations	Carbon addition to a BNR process will increase mixed liquor suspended solids (MLSS) and thus impact secondary clarifier operation. Methanol is not used by ordinary heterotrophic organisms for denitrification. Consequently, a methylotrophic population of denitrifiers is required and must be maintained when using methanol to denitrify.

Design considerations	Carbon dose points need to be well mixed, but not excessively to limit oxygen entrainment into liquid. Some carbon sources like methanol or ethanol are highly flammable.
Potential fatal flaws	None on external carbon addition broadly. Exception: Methanol cannot be used intermittently and requires that the methylotrophic population be maintained.
Footprint requirements	Minor—limited to tanks and containment areas
Residuals	Some of the added carbon is converted to biomass, thus increasing WAS production.
Cost considerations	Varies—the two main cost components are the direct cost of purchasing chemicals and the indirect cost of generating additional solids.
Past experience	Many applications including Hampton Roads Sanitation District (HRSD) Virginia Initiative Plant (VIP) water resource recovery facility (WRRF) (Virginia), HRSD York River WRRF (Virginia), Truckee Meadows Water Reclamation Plant (Nevada), and City of Raleigh (North Carolina).
Publications	Graham, J., L. Mueller, S. Trujillo, and K. Brischke. 2012. "Beer: It Is Not Just for Drinking Anymore—Brewery Waste as a Supplemental Carbon Source for Biological Nutrient Removal." WEFTEC 2012. Gu, A.Z. and A. Onnis-Hayden. 2010. "Protocol to Evaluate Alternative External Carbon Sources for Denitrification at Full-Scale Wastewater Treatment Plants." WERF Nutrient Removal Challenge Report NUTR1R06b. Johnson, G.R., C.J. Wall, R. Terpstra, T. Minigh, and M. Saunders. 2013. "The Westside Regional WRF (City of Daytona Beach, Florida) Utilizes a Supplemental Carbon Source (glycerol) in a Unique Application to Enhance Biological Phosphorous Removal." WEFTEC 2013. Mehrdad, M., S. Ledwell, R. Coleman. 2021. "Glycerol Driven EBPR Correlated with Tetrasphaera Enrichment." WEFTEC 2021. Rohrbacher, J., K. Bilyk, T. Bruton, P. Pitt, and R. Latimer. 2009. "Evaluation of Alternative Supplemental Carbon Sources at Four BNR Facilities." WEF's 82nd Annual Technical Exhibition and Conference. Orlando, FL.: WEFTEC 2009. Sigmon, C. and S. Weirich. 2014. "The Best Carbon for the Job: Using the 2010 WERF Protocol to Choose an External Carbon Alternative for Enhanced Nitrate Removal." WEFTEC 2014. WRF (The Water Research Foundation). 2019. "Carbon Augmentation for Biological Nitrogen Removal" from the Nutrient Removal Challenge. https://www.waterrf.org/sites/default/files/file/2021-07/Carbon-Augmentation-BNR.pdf.
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Note

* Technology ranking based on LIFT WRF TDL definitions:

1 = bench research and development
2 = small-scale pilot
3 = full-scale pilot (demonstration)
4 = pioneer stage (production and implementation)
5 = Conventional (https://www.waterrf.org/sites/default/files/file/2019-07/LIFT%20Scan%20Application-LIFT%20Link%2BHub_0.pdf: accessed September 2020)

Additional Information

Table 1 and Table 2 contain the chemical characteristics for the commonly used carbon sources.

Table 3 contains a comparison of the advantages and disadvantages when using various carbon sources.

Table 1. Carbon Sources.

Carbon Source	Design Dose	COD	Specific Weight	COD Load	Formula
	lb COD/lb N	g COD/g Source	-	lb COD/gal	
Ethanol	5.1	2.09	0.79	13.8	C_2H_5OH
Acetate	5.1	1.08	1.05	9.4	CH_3COOH
Glycerol	6.09	1.22	1.26	12.8	$C_3H_8O_3$
MicroC® 2000	6.09	0.9	1.23	9.17	N/A
MicroC® 1000	6.09	0.55	1.23	5.52	N/A
Methanol	4.3	1.50	0.79	9.9	CH_3OH

Table 2. Carbon Sources.

Carbon Source	COD	Denitrification Potential [a]	Formula
	mg/L	g COD/g N	
Methanol	1,188,000	3.57–4.80	CH_3OH
Ethanol	1,647,000	N/A	C_2H_5OH
Na-acetate	1,131,700	3.5–5.7	$NaCH_3COO$
Acetic acid	1,121,000	4	CH_3COOH
Butyric acid	1,740,000	N/A	$CH_3CH_2CH_2CO_2H$
Propionic acid	1,070,000	N/A	$CH_3CH_2CO_2H$
Formic acid	440,000	N/A	CH_2O_2
Glucose	1,490,000	8.9	$C_6H_{12}O_6$
Hydrolyzed/fermented sludge	N/A	4.5–6.9	N/A
Fermented municipal solid waste	N/A	1.6–2.4	N/A
Hydrolyzed molasses	N/A	4.3–5.8	N/A
Corn syrup	N/A	4.5–7.9	N/A
Sugar solution	N/A	10.2	N/A
Olive oil mill	N/A	4.6–5.4	N/A
Dairy waste	N/A	3.6–4.7	N/A
Winery waste	N/A	3.4	N/A
Distillery fuel oils	N/A	2.22	N/A
Pea blanch water	N/A	5.71	N/A
Wine sludge concentration	N/A	7.3	N/A
Methanol still bottoms	N/A	3.66	N/A
National starch	N/A	3.26	N/A
Tomato sludge	N/A	2.54	N/A
Distillers' fusel oils	N/A	5.32	N/A
Organic acid waste	N/A	5.14	N/A
Methanol heads	N/A	2.45	N/A
Acetic acid waste	N/A	1.71	N/A
Fibers glycol waste	N/A	5.98	N/A
Waste dextrose	N/A	8.19	N/A
Formaldehyde waste	N/A	6.21	N/A
Brewery waste	N/A	3.0–6.2	N/A
Biodiesel byproduct	N/A	N/A	N/A
MicroC™	663,000	6.4	N/A
Beet-sugar waste	N/A	3.4	N/A
Methane	N/A	4.0–5.9	CH_4

a. Listed denitrification potentials were experimentally determined.

Source: Table adapted from Gu, A.Z. and A. Onnis-Hayden. 2010. "Protocol to Evaluate Alternative External Carbon Sources for Denitrification at Full-Scale Wastewater Treatment Plants." WERF Nutrient Removal Challenge Report NUTR1R06b.

Table 3. Comparison of Carbon Source Use Considerations.

Source	Advantages	Disadvantages
Methanol	• Reasonable denitrification rate • Long-term experience at many WRRFs	• Handling and safety issues—it is flammable and must be stored in a special facility • Toxic • Long startup/acclimation period (2–3 weeks)
Ethanol	• Denitrification rates can be 3 times higher than that of methanol • Immediate response to denitrification • No acclimation required	• Handling and safety issues, similar to methanol; requires a special storage facility • High cost
Acetic acid	• High denitrification rates • Safer than ethanol and methanol • Non-toxic • Immediate response to denitrification	• High cost, depending on quality and source • Handling and safety requirements • State and local codes may prohibit storage at a site • 100% acetic acid may favor the proliferation of glycogen-accumulating organisms (GAOs), which compete with PAOs for VFAs
VFAs (fermentate)	• Low operating cost • High denitrification rate, usually greater than that of methanol and ethanol • Recycling approach (“green” technology)	• Ammonia may be present • Odor generation • Inconsistent VFA content • Capital cost involved with the addition of a fermenter
Glycerol	• Safe • Cost-effective • Locally available co-product • No apparent acclimation period	• Minimum data on effectiveness • Varying physical characteristics require pre-processing before feeding
MicroC® 2000	• Satisfactory denitrification rate • Cost-effective	• For P removal purposes, an acclimation period of 2–3 weeks has been observed
MicroC® 1000	• No handling or safety issues associated • Cost-effective • Environmentally sustainable • Satisfactory denitrification rate.	• Denitrification rate is lower than MicroC® 2000 and methanol
Unicarb-DN	• Safe • Non-toxic • Attractive cost • No apparent acclimation period	• Minimal data on product
Soft drink bottling waste sugar water	• Satisfactory denitrification • Can be no cost, depending on source; if the demand for sugar water waste increases, the price may be about $0.25/lb • Safe	• Contract with the soft drink bottling companies must established • Product is inconsistent; may require a backup carbon source to support denitrification • Soft drinking companies may be required to pretreat wastes
Hydrolyzed molasses	• Effective and economical	• Requires hydrolyzation • Optimum dosage is not known
Sodium acetate	• Satisfactory denitrification	• Requires handling facilities for dry chemical and mixing into solution • Capital cost for storage tank and mixer • Additional handling required
Industrial waste [a]	• Satisfactory denitrification • Previous history at BIWWTP	• Denitrification efficiencies are inferior to that of methanol • May impact BOD removal

a. Industrial carbon sources include brewery waste, sweet whey, acid whey, corn steep liquor, and soluble potato solids, among others.

Abbreviations

BNR	Biological nutrient removal
BOD	Biochemical oxygen demand
CAS	Conventional activated sludge: BOD removal only
CNR	Conventional nutrient removal
COD	Chemical oxygen demand
DO	Dissolved oxygen
EBPR	Enhanced biological phosphorus removal
g	Gram(s)
gal	Gallon(s)
GAO	Glycogen-accumulating organism
HRSD	Hampton Roads Sanitation District
I&C	Instrumentation and controls
L	Liter
lb	Pound(s)
LIFT	Leaders Innovation Forum for Technology (now RIC and RISE)
mg	Milligram(s)
mgd	Million gallons per day
MLSS	Mixed liquor suspended solids
N	Nitrogen
NAS	Nitrifying activated sludge
NO_x	Oxidized nitrogen (nitrate + nitrite)
NutRem	Nutrient removal
O&M	Operations and maintenance
P	Phosphorus
PAO	Polyphosphate-accumulating organism
RAS	Return activated sludge
RIC	Research & Innovation Committee
RISE	Research and Innovation for Strengthening Engagement
TDL	Technology Development Level
TN	Total nitrogen
TP	Total phosphorus
UV	Ultraviolet
VFA	Volatile fatty acid
VIP	Virginia Initiative Plant
WRF	The Water Research Foundation

WRRF	Water resource recovery facility