Surfactant Testing and Treatment Plant Impacts November 8, 2022

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Foaming and mixed liquor suspended solids (MLSS) deflocculation are two possible sewer plant challenges that operators may attribute to surfactants that enter the facility. Biomonitoring may also be impacted.

Surfactants, by design are deflocculants. They are designed to spread-out oils and dirt and will do the same to MLSS. The non-ionic are reported to be the class of surfactants that impact the plants the most severely (Jenkins 2004). Tennessee plants have experienced effluent deterioration because of discharges from truck washes, a poultry hatchery, and a major bakery where discharges of quaternary ammonia inhibited ammonia removal and caused effluent deterioration. There are plant upsets that correlate with car wash discharges and "deep cleaning" of schools during 2020. Severe cases of sludge dewatering failure have been attributed to synthetic lubricants which can be surfactants.

Generally, there are three types of surfactants. (1) Anionic, negatively charged, make up the largest type manufactured and used and are quantified using the MBAS test. These are generally readily biodegradable. (2) The cationic, positively charged, surfactants that include the quaternary ammonia products. The CTAB test will quantify the "quats" which are known to be toxic to nitrifying bacteria at low levels (2.0 mg/L). (3) Non-ionic surfactants, quantified by the CTAS test, are reported to deflocculate MLSS and enhance foaming (Jenkins, 2004). Liwarska-Bizukojc et.al. (2008) reports that a non-ionic surfactant level of 50 mg/L is needed to "induce pinpoint flocs and decrease in wastewater treatment efficiency" and that the "no adverse effect" level was 5 mg/L. It must be noted that surfactant chemistry is very complex and diverse, and acclimation of the biomass is quite important, so a 24/7/365 discharge to the treatment plant is preferred. Slug loads of surfactants often cause severe foaming problems in addition to biomass impacts and effluent impacts. In 2010, Narayanan et.al. reported "Even very low concentrations of non-ionic surfactant deflocculated activated sludge flocs containing floc-bound norcardiaform organisms…." Influent surfactant levels range from 3-20 mg/L. Influent foaming is often the first indication of excess surfactant loading.

Treatment Plant Foaming, or Not

Over the years operators have graciously shared photographs from their plants, often when "bad" things are happening. Below are four pictures of treatment plant foaming situations. The upper-right hand photo is a small SBR plant. Months after denying any problems, the local industrial contact let it slip out that a drum of soap had been spilled and washed down the drain.

Such foaming situations get everyone's attention, though tracking down the true source can be difficult. Dr. Jenkins states that the really bad filamentous foaming situations that he has seen over the years are a combination of filaments and surfactants.

But some surfactants are “low foaming.” The non-ionic products are known for this property. Dishwashing detergents are based on the low foaming non-ionic compounds, and truck washing products commonly use non-ionics because of their low temperature degreasing properties.

MLSS Deflocculation or Effluent Deterioration

The toughest sewer plant troubleshooting situation I have experienced generally starts with the statement, “the effluent looks bad; it is cloudy and turbid.” Many times, there is still full permit compliance, but a significant deterioration of effluent quality. It is these situations that I generally begin with questions about surfactant sources and surfactant testing.

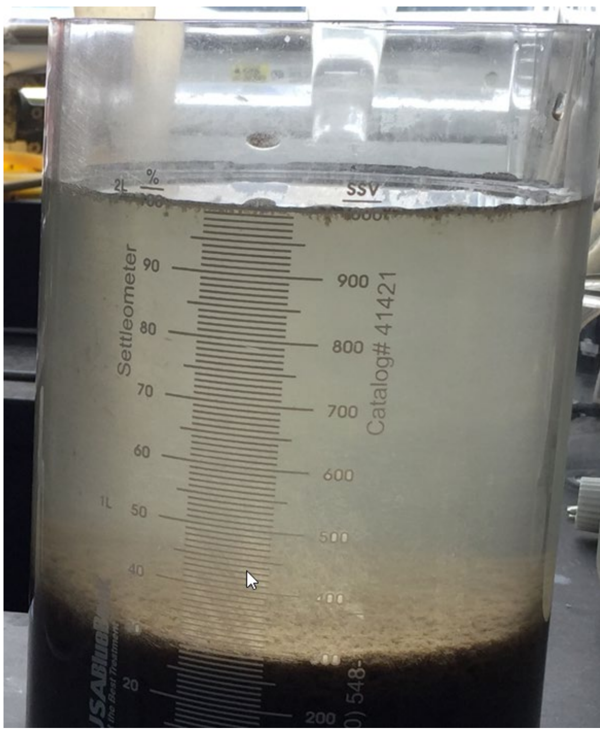
Visual Indicators

If there is foam, there are surfactants, that is compounds with surface acting properties. These could be natural surfactants or manmade. Add aeration and mixing or simply turbulence and the surface acting compounds will foam. Activated sludge naturally foams, in most plants this in not a problem. The normal “light crisp unstable” foam is different from the white-sudsy surfactant foam. Though plant “start up” conditions will often have white-sudsy foam simply because there is not enough MLSS to oxidize the normal surfactant levels. Excessive foaming may be an indication of an abnormal surfactant load. If foam is causing effluent violations or simply a deterioration of effluent quality, determining the cause highly recommended.

Some industries use a “shake test” before discharging industrial wastewater as a process control test to give them early indication of potential foaming at the treatment plant. This can be a simple glass or plastic bottle, generally less than ¼ to ½ full, that is shaken a specified number of times.   Also, Dr.

Jenkins has an Alka-Seltzer foam test. The Alka-Seltzer tablets create a standard amount of aeration or mixing.

Microscopic exams of MLSS or plant effluent also provide a visual indication of deflocculation, perhaps from surfactants or other compounds. The photos below show a deflocculated MLSS and the small treatment solids, or pin floc, in the effluent. If the visual indicators seem to indicate there are excessive surfactants, or other compounds present, locating the source and identifying the compounds is the next step.



Deflocculated MLSS

Turbid effluent at 100x

Operator Knowledge and Awareness

Even in the days of fully computerized, monitored and operated plants, operator knowledge and awareness are important. When a plant is producing pristine effluent and everything is going great, do some expanded influent and process control testing. This baseline data can be invaluable in a troubleshooting situation.

Data to consider include MLSS microscopic exam to document floc quality and condition when there is good performance. Another helpful process control is Oxygen Uptake Rate or Specific Oxygen Uptake Rate when the plant is performing well. If your city has an industrial pretreatment program you already have some expanded influent data, but other helpful tests include influent ammonia, TKN, phosphorus, Oil & Grease, MBAS, CTAS, CTAB, light metals such as calcium, magnesium, potassium, and sodium. Having baseline influent data can be very helpful when a plant is upset.

It is also helpful to have a general understanding of your customers, what they do send you, and what they may send you. Again, if you have an industrial pretreatment program, you know a little about the "significant industrial users" but what about other users. Do any users have large amounts of stored liquid chemicals which may spill into the sanitary sewer? What about warehouses? There are cases where spill in warehouses caused treatment plant problems. Fire Department hazardous material inventory information is a way of beginning this type of investigation. Specifically, this is the Emergency Planning Community Right-to-Know inventory. The Emergency Management Director or Fire Department may be able to assist you in getting access to this database. You would be looking for chemicals in volumes, that if spilled down the sanitary sewer, could interfere or pass-through the treatment plant.

A key operator skill that is often not greatly valued is one's skill in observing the collection system and plant. These are just plain "operator skills" that are rarely taught, encouraged, or valued. It starts in the collection system. What do you see, smell, and observe? All this information gives a "hint" of what the customers are sending down the pipe and what is happening within the collection system.

At the treatment plant the same is true. What you see, smell and observe within the influent and in each treatment unit can be helpful in running the plant and especially in a trouble shooting situation.

There have been deflocculation incidences that appear to be tied to car wash locations. One event in a small city suddenly improved after an inspection and discussion with the car wash owner. A second event appeared to correlate with warming weather, after a time of ice and snow, when "every car wash in town was lined up out into the street." This plant upset could have been surfactant related or caused or compounded by a time of high salt I/I from runoff from heavily salted streets and highways.

Surfactant Testing

For general surfactant testing there are three test methods, MBAS, CTAS, and CTAB that generally identify the three types of surfactants. Most commercial labs will do the MBAS analysis, the other two are more expensive and it is harder to locate labs that perform them. To properly evaluate the impact of surfactants all three need to be performed until such time as one or more are not needed. In industrial wastewater testing the MBAS is often the method that is dropped when little or no anionic surfactants are in the wastewater stream.

The Fourier-transform infrared spectroscopy, or IR scan, or "library" scan can be helpful. It may or may not tell you exactly what is in a sample, but it can be very helpful when comparing two samples and clearly identify that what is in one is also in the other. An example is tying an industrial discharge clearly to a wastewater plant pass-through.

Most commercial labs, when questioned, will more clearly identify individual surfactant products, if they have a sample of the pure surfactant with which to compare the wastewater sample. In an actual plant upset or troubleshooting situation this may not be possible.

Testing Interference

Numerous compounds interfere with surfactant testing including other types of surfactants. Before testing, even before ordering sample containers, have a discussion with your lab about steps that can be taken to lessen the various types of interference. This may involve multiple samples where different pretreatment steps are taken to lessen different types of interference.

Swisher (1970) reports that as much as 90% of surfactants are adsorbed by the MLSS quite quickly. For more accurate testing a desorption step or solid phase extraction may be needed. Ying (2005) states that 95% of cationic surfactants are adsorbed to the MLSS and the order of greatest adsorption is cationic > non-ionic > anionic. Below is a listing of various types of interference, the concentration and type of surfactant which caused the interference.

Sample Containers

If your plant is prone to mysterious interferences or you want to be prepared, just in case, keep sample containers on hand. In initial trouble shooting work you may not be able to comply strictly to all sampling and testing regulatory rules. But in these cases, of initial investigation, it is more important to collect timely samples for general identification and direction than following 40 CFR 136 to the letter. But as knowledge is gathered about a suspected discharge more strictly following the rules is advised. Several clean, one liter, plastic and glass containers are a start. Collect the samples and call your lab for guidance on preservation and holding times. Additionally, containers for metals, volatile organics, and semi-volatile organics can be helpful. If you suspect or have a history of foaming events or surfactants keep containers for the three surfactant tests also.

Plant Interferences.

Situation	Concentration	Surfactant	Reference
Influent Foam, low potential	< 4 mg/L	~ MBAS + CTAS	Lawrence KS (2005)
Influent Foam, medium potential	4-10 mg/L	~ MBAS + CTAS	Lawrence KS (2005)
Influent Foam, high potential	>10 mg/L	~MBAS + CTAS	Lawrence KS (2005)
Deflocculation	50 mg/L	Non-Ionic	Liwarska-Bizukojc et.al. (2008)
Floc Impacts	>25 mg/L	Anionic, MBDS	Mitru (2020)
Floc Impacts	>10 mg/L	Non-Ionic, PGN	Mitru (2020)
Floc Impacts	5 mg/L	Non-Ionic	Liwarska-Bizukojc et.al. (2008)
8% reduction in BOD removal	5 mg/L	Non-Ionic, AE	Liwarska-Bizukojc et.al. (2008)
12% reduction in BOD removal	5 mg/L	Non-Ionic, APE	Liwarska-Bizukojc et.al. (2008)
Heterotrophic Inhibition	10-40 mg/L	Cationic, BAC	Hora et. al. (2020)
27% Nitrification Inhibition	1 mg/L	Non-Ionic, NPE	Othman (2010)
Nitrification, IC 20	11.95 mg/L	Anionic, SDBS	Othman (2010)
Nitrification, IC 20	21.3 mg/L	Anionic, SDS	Othman (2010)
Nitrification Inhibition	1.5 mg/L	Cationic, BAC	Hora et. al. (2020)

Strongly Inhibit Nitrification	3 mg/L	Cationic	Boethling (1984)

Biomonitoring, Whole Effluent Toxicity (WET)

Toxicity Level	Concentration	Organism	Reference
Alcohol Ethoxylate			
EC20	0.124 mg/l	Daphnia magna (water flea)	Environment Canada (2013)
EC20	0.181 mg/L	Fathead minnow	Environment Canada (2013)
Mixed Anionic & Non-ionic			
Acute Toxicity	3.69 mg/L	Daphnia magna	Mitur (2020)
Anionic Surfactants			
EC50	3-250 mg/L	Water Flea	Yuan (2014)
Non-ionic			
EC50	42-48 mg/L	Water Flea	Yuan (2014)
Cationic			
EC50	82 mg/L	Water Flea	Yuan (2014)
Anionic, Alkylbenzene Sulfonate			
LC50	0.04-0.06 mg/L	Daphnia magna	Ostroumov (2005)
LC50	0.86-1.23 mg/L	Pinephales notatus	Ostroumov (2005)

Othman and Liwarska-Bizukojc both make note that toxicity is higher, it occurs at lower concentrations where the surfactant has a benzene ring present. These would be the names with benzene or phenol included.

Operational Response

Most surfactants are biodegradable. But the time needed may be longer than normal sewage BOD. Also, the treatment bacteria may need a longer acclimation time before biodegradation even begins. Generally speaking, an “oxidative pressure” in needed. Longer hydraulic detention time, higher levels of MLSS, more treatment basins, lower RAS rates, higher level of DO. Of course, locating the source and eliminating that source may be appropriate, or changing the discharge from a “slug load” to continuous feed can also be helpful. In extreme cases chemical aids may be needed to prevent plant violations. These may be chemical defoaming/anti foaming products or coagulation/flocculation aids.

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Abbreviations

AE	Alcohol Ethoxylate
APE	Alkylphenol Ethoxylate
BAC	Benzalkyl dimethylammonium compounds, a quaternary ammonia compound
EC20	Effect Concentration twenty percent. The concentration that effects 20% of the population
IC20	Inhibition Concentration twenty percent. The concentration that inhibits 20% of the population
LC50	Lethal Concentration fifty percent. The concentration that kills 50% of the population
MBDS	Methyl dodecyl benzene sulfonate
NPE	Nonylphenol ethoxylate
PGN	4 nonylphenol polyethylene glycol
SDBS	Sodium dodecyl benzene sulfonate
SDS	Sodium dodecyl sulfonate