# Wastewater Infrastructure & Control
# EPA Overview Report

for

**February 2021**

## BACKGROUND & OBJECTIVE

Merck Millipore Carrigtwohill (Merck) is a Life Science facility with a wide range of production processes. Wastewater arising from these processes (namely manufacture of membrane and chromatography media) is treated at an onsite effluent treatment plant prior to discharge to the adjacent Irish Water sewer. The facility holds an Industrial Emissions Licence from the EPA to carry out this activity.

Merck engaged with Castlegale from October 2020 to provide technical consulting services on their wastewater treatment process. Particular emphasis was on the treatment of current wastewater streams, best technologies required to treat these and the optimisation of the onsite treatment plant so that medium and long-term plans can be put in place.

This report is intended as a high-level summary overview for the purpose of discussion and open communication with the EPA. Review of key performance indicators (KPI's) and adjusted recommendations is also outlined within.

## EFFLUENT DISCHARGE LICENCE

Merck hold an Industrial Emissions Licence from the EPA, registered number P0571-04, issued in October 2017. Treated Effluent is discharged to Cork County Council sewer and onwards to Carrigtwohill Municipal wastewater plant for further treatment.

The Effluent discharge limits at the main point of discharge from Merck are as follows:

| **Parameter** | **Limit** | **Frequency** |
|---|---|---|
| Flow | 600 $m^3$/day ; 25 $m^3$/hr | Continuous |
| pH | 6.0 – 9.0 | Continuous |
| Temperature | 35$^{O}$C | Continuous |
| BOD | 1,150 mg/l ; 690 Kg/day | Weekly |
| COD | 2,600 mg/l ; 1560 Kg/day | Daily |
| Suspended Solids | 450 mg/l ; 270 Kg/day | Daily |
| Total Nitrogen | 300 mg/l | Weekly |
| Sulphates | 250 mg/l | Quarterly |
| Chlorides | 900 mg/l ; 267 Kg/day | Annual |
| Total Heavy Metals | 1 mg/l | Annual |
| Oils, Fats & Grease (OFG) | 30 mg/l | Quarterly |
| Acrylates | < 1 mg/l | Quarterly |
| VOC | 1 mg/l | Quarterly |
| Toxicity | 10 TU | As required |

## OVERVIEW OF WASTEWATER ARISING

Wastewater at the facility arises from the following sources:

- IC2
- Aircast (A/C) incorporating MW2
- IC1/SMF
- Chromatography (Media)

The average flow of wastewater from each area over a selected 3-month period from Sept-Nov 2020 are as follows:

| Flow from IC2 (m3/hr) | Flow from IC1/SMF (m3/hr) | Flow from MW2 & A/C (m3/hr) | Flow from media (M3/hr) | Total Flow from production (m3/hr) |
|---|---|---|---|---|
| | | | | |
| **4.62** | **4.35** | **1.85** | **0.41** | **11.24** |

The overall philosophy for wastes arising is that concentrated wastes are diverted to IBCs or waste tanks for offsite disposal or onsite solvent recovery. Aqueous washings containing the residues of chemicals used in the various processes are diverted to the onsite wastewater treatment plant for contaminant reduction prior to discharge to sewer.

The major chemicals used at the manufacturing facility include

- Simple organic solvents
- Complex organic solvents
- Acids & Alkalis

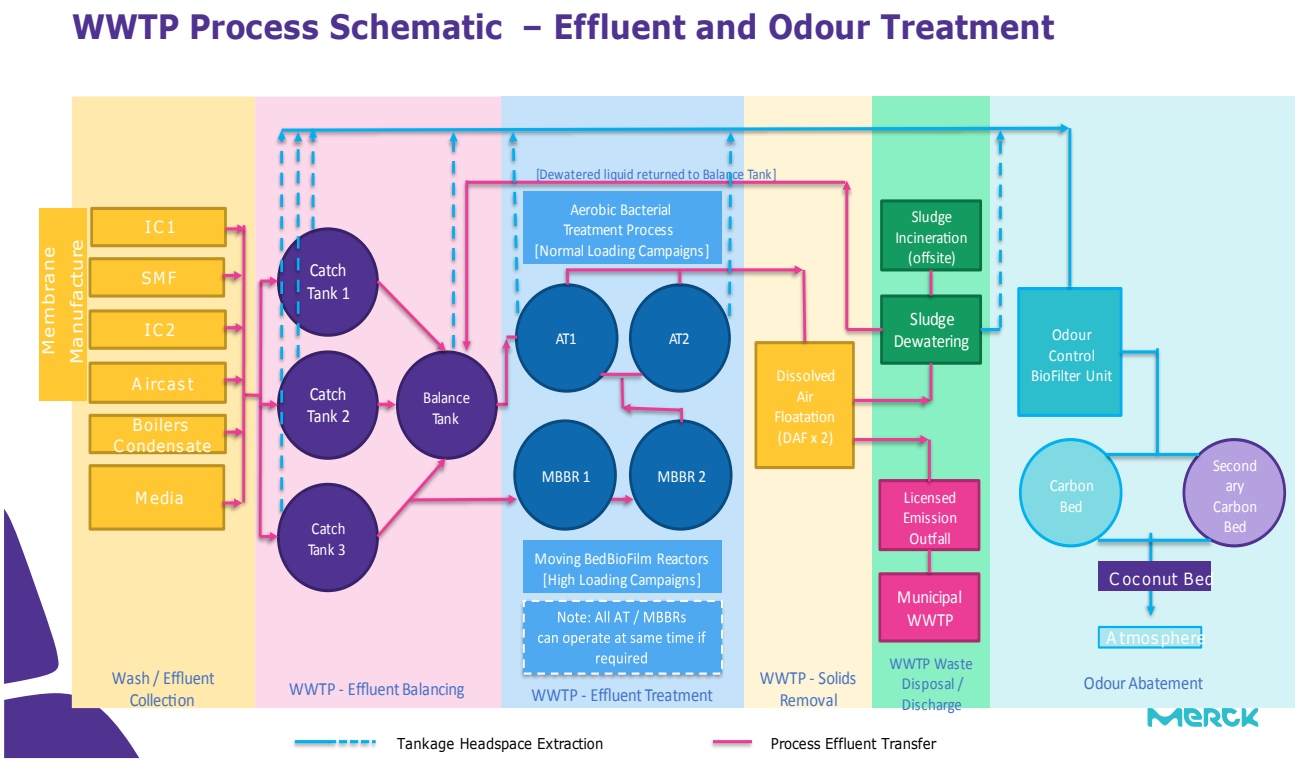
Aqueous process effluent for the most part is readily treatable by aeration/aerobic stages of the WWTP, however some components require extended retention and nutrient support

## OVERVIEW OF ONSITE WASTEWATER TREATMENT

Effluent from each area is pumped to one of three 'Catch Tanks' initially.
From there it can be directed to the Balance Tank, or to one of two Moving-Bed Bioreactor (MBBR) tanks which provide biological pre-treatment.
Effluent from the MBBR tanks and Balance Tank is sent on to two aeration tanks for further biological treatment.
Solids are separated at the two Dissolved Air Flotation (DAF) tanks and final effluent is discharged from there.

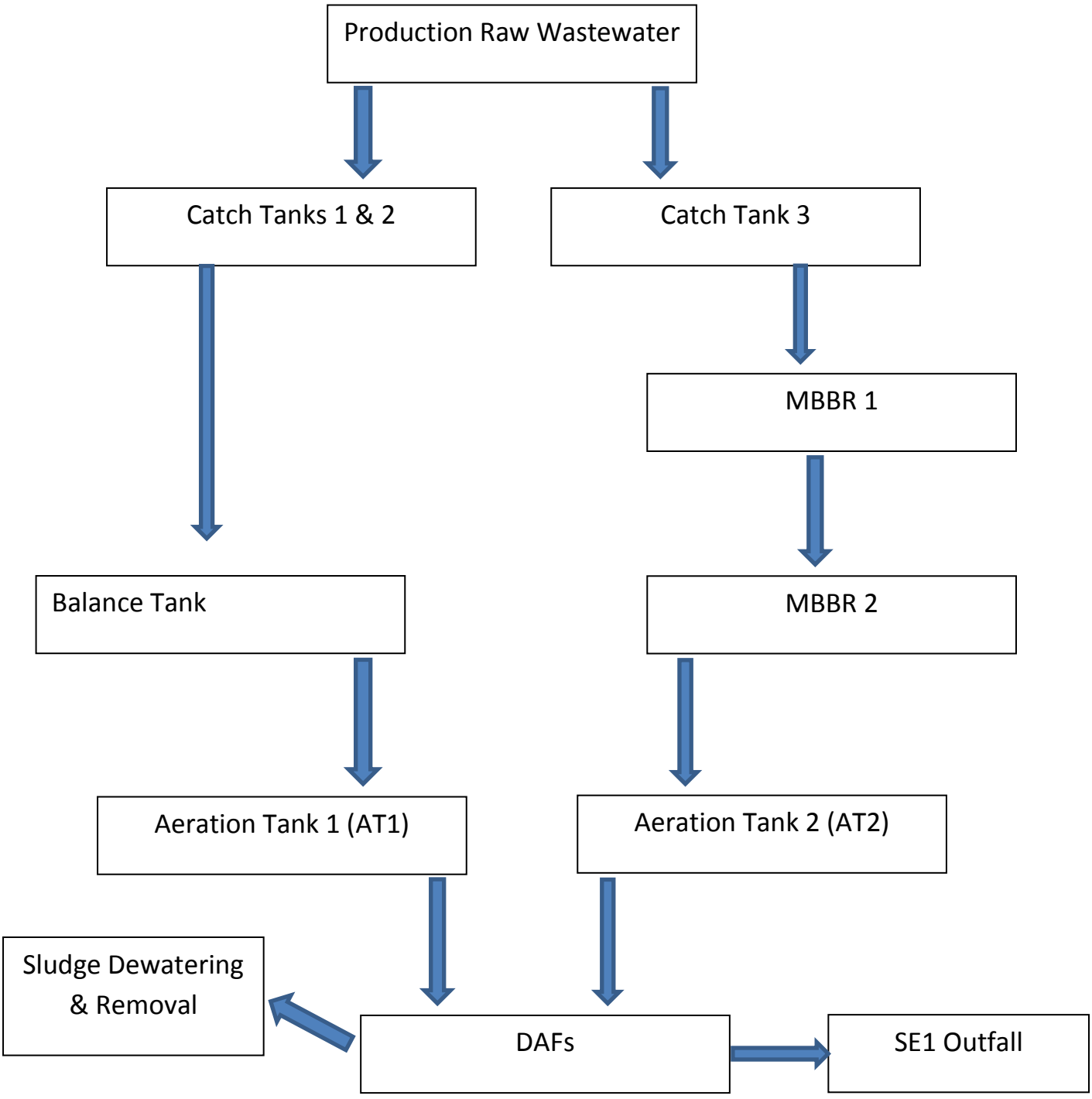
The wastewater treatment process is almost completely reliant on biological treatment and solids removal.

The onsite wastewater treatment plant is represented in the following schematic:



And in the following Process Flow sketch:

**Merck WWTP Process Flow**



The main WWTP infrastructure is as follows:

- **Catch & Release Tanks x 3** – T-901, T-902, T-903 – 200 $m^3$ capacity each
    - The purpose of these tanks is to provide balancing and holding capacity for the high-strength aqueous effluents from production

- **Balance Tank** – T-904 – 1,000 $m^3$ capacity
    - The purpose of this tank is to provide sufficient balancing volume for raw effluent, such that the effluent is as consistent as possible for onward treatment. pH is also controlled in this tank

- **MBBR Tanks x 2** – MBBR-2901, MBBR-2902 – 400 $m^3$ capacity each
    - These are Moving-Bed Bioreactors. Their purpose is to break down organic compounds using fixed film biomass, specifically to reduce the COD/BOD loading from high strength effluent

- **Aeration Tanks x 2** (AT1/AT2) – T-905, T-906 – 1,000 $m^3$ capacity each
    - The purpose of these tanks is to contain activated sludge micro-organisms to reduce COD/BOD by breaking down organic compounds

- **DAF Tanks x 2** – T-909, T-910 – 100 $m^3$ capacity each
    - The purpose of these tanks is to separate the biological solids from the treated effluent

- **Sludge Holding Tank** – T-915 – 200 $m^3$ capacity
    - The purpose of this tank is to contain waste biological sludge before it is dewatered through centrifuges and removed offsite

## FEATURES OF BIOLOGICAL WASTEWATER TREATMENT

As outlined above the wastewater treatment process as Merck is largely dependent on a biological system. The MBBR tanks contain micro-organisms in a 'fixed-film' arrangement, whereby the biomass is attached to small discs which are kept in suspension in the wastewater. The Aeration Tanks contain a suspension of micro-organisms in a conventional activated sludge biomass.

These biological processes utilise microorganisms to convert organic, and certain inorganic, matter from wastewater into cell mass. The activated sludge is then separated from the liquid by clarification (using the DAFs in Merck). The separated sludge is either returned (RAS) or wasted (WAS).

Biological processes are commonly used in wastewater treatment process because they are effective and versatile and capable of a high degree of treatment. The principal role micro-organisms have in the activated sludge process is to convert dissolved and particulate organic matter, measured as biochemical oxygen demand (BOD), into cell mass. In a conventional activated sludge process, microorganisms use oxygen to break down organic matter (food) for their growth and survival. Over time, and as wastewater moves through the process, food (BOD) decreases with a resultant increase in cell mass (MLSS concentration).

The biological treatment processes must operate under proper environmental conditions to support a healthy, growing population of micro-organisms. The process must be tailored to ensure the right environmental conditions are being provided for the microorganisms. Efficient wastewater treatment plant performance will then be achieved.

Some factors affecting biological performance include:

- Feed quantity & complexity
- Flow rate
- Dissolved Oxygen
- Temperature
- pH
- Nutrients
- Toxicity

***Feed quantity & complexity***

Incoming wastewater to a treatment plant provides the food that micro-organisms need for their growth and reproduction. This food is mostly organic material. The more soluble the organic material is, the more easily microorganisms can use it. Since the amount and type of organic loading in the treatment plant affects the growth of the microorganisms, influent BOD and COD are important indicators of the amount and type of incoming food for the microorganisms. The ratio of food (F) to micro-organisms (M) or F:M ratio is an important factor also.

### *Flow Rate*

Incoming wastewater must flow through a treatment plant at a rate that allows micro-organisms sufficient time to consume the incoming food and to separate properly. High flows can shorten the time necessary for the full treatment of wastewater. Extremely high flows can wash microorganisms out of the plant through the DAF.

### *Dissolved Oxygen*

Conventional activated sludge is an aerobic process. Many bacteria in the activated sludge process need free oxygen (O2) to convert food into energy for their growth. For optimal performance, it is very important to be sure enough oxygen is being provided in the aeration tanks for the microorganisms (typically 0.5 - 1.5 mg/L). Aeration basin dissolved oxygen concentrations (milligrams per litre) is measured continuously to ensure adequate oxygen is available. Noted previous KPI of >0.3 is too low and it is recommended to run in this range of 0.5-1.5 mg/L.

### *Temperature*

All biological and chemical reactions are affected by temperature. Microorganisms growth and reaction rates are slow at cold temperatures and much faster at warmer temperatures. Most microorganisms do best under moderate temperatures (10-25 $^{O}$C), although consistency is more important than absolute values. Aeration basin temperatures should be routinely measured and recorded.

### *pH*

Biological and chemical reactions are affected by pH. Most microorganisms do well in a pH environment between 6.0-9.0, ideally 7.2 – 8.4. Acidic (low pH) or alkaline (high pH) conditions can adversely affect microorganism growth and survival. Both influent pH and aeration basin pH is measured to ensure proper plant pH conditions.

### *Nutrients*

Microorganisms need trace nutrients such as Nitrogen, Phosphorus and some trace elements for their metabolism. Most incoming wastewater to a treatment plant, especially domestic sewage, contains an abundance of these trace nutrients. The ratio of BOD5 to nitrogen (N) to phosphorus (P) should be at least 100:5:1. Influent wastewater can be measured to determine this nutrient ratio and effluent concentrations will indicate if there is sufficient bio-available nutrient.

### *Toxicity*

Incoming wastewater to a treatment plant may at times contain materials or compounds that are inhibitory to micro-organisms, thus impairing the wastewater treatment plant efficiency.

## SUMMARY OF CURRENT TREATMENT EFFICIENCY & RESULTS

A review of the final effluent results from the WWTP over the period Sep-Nov 2020 shows the following:

| Summary - Merck SE1 Outfall Results Sep-Nov 2020 | | | | | | |
|---|---|---|---|---|---|---|
| Date | Flow SE1 (m3/day) | COD (mg/\l) | Suspended Solids (mg/L) | Total Nitrogen (mg/l) | pH | Temp (oC) |
| Limit | 600 | 2600 | 450 | 300 | 6 to 9 | 35 |
| Average | 280 | 1194 | 313 | 120 | 8.2 | 28 |
| Max | 415 | 2532 | 472 | 235 | 8.71 | 32.9 |

These results show that the discharge is largely compliant with SE1 Limits (Non-Conformances reported accordingly to EPA).

It has been noted that the performance of the WWTP can vary during the course of the year, and that is somewhat dependent on the particular production processes being carried out at any given time. This can lead to increases in COD and suspended solids in the outfall, although these are still in compliance.

Some of the measures proposed to counteract periods of lower performance include:

- Bio-augmentation of the activated sludge to maintain biological health
- Addition of alkalinity buffers to assist Nitrogen removal
- Addition of a wide range of chemical supplements to maintain biological health

## FACTORS THAT AFFECT PERFORMANCE

Looking at the factors affecting biological performance, as outlined earlier, let's look in detail at each and whether it may be a cause:

- **Feed quantity & complexity** –The F:M ratio over the period Sep-Nov 2020 was 0.10 average for AT1 and 0.09 average for AT2, which are in an acceptable range. However it was noted that BOD is not 'measured' daily but is typically calculated from the COD and compared to the weekly BOD result. This can be misleading as the ratio of COD:BOD varies widely in industrial wastewater. Simple organics break down much more easily than complex ones. So it appears that the feed quantity may be acceptable but there are questions regarding fluctuations in the complexity. Organics easily broken down are generally considered to be 'short, straight-chain' in nature. Looking at the organic chemicals used onsite you would expect that the likes of simple alcohols to be easily consumed, while the more complex structures are more difficult to break down.

- **Flow rate -** The flow rate of wastewater does not appear to be causing any hydraulic issue.

- **Dissolved Oxygen –** The dissolved oxygen in both AT1 & AT2 is maintained in the region of 0.5 – 1.5 mg/l. At times the MLSS is kept at a higher level by necessity to deal with higher COD loadings, which can affect oxygen transfer efficiency. Recommended KPI adjusted accordingly.

- **Temperature** – The temperature in the aeration basins is typically in the range of 30 – 35$^{O}$C

- **pH** – The pH fluctuates due to the nature of the incoming streams. However automatic pH control is in place in the balance tank and pH appears to be within acceptable limits in the biological system.

- **Nutrients** – Levels of Nitrogen can vary widely as seen from the results. Although the outfall level is typically acceptable internal high levels of Nitrogen may contribute to poor biological health at times.

## SAMPLING & ANALYSIS SURVEY

From the information gathered, data & background presented above, and site knowledge of past performance it appears that the main issues at the WWTP originate from wastewater from treatment of the higher COD Loading organics.

The scope of the evaluation was to;

1. Determine over a period of 4 weeks the consistency of COD, BOD, pH, Suspended solids, Total Nitrogen concentrations and the efficiency of the breakdown of the Higher COD streams.
2. Determine the efficacy of pre-treatment using Advanced Oxidation Process (AOP) in terms of improving breakdown efficiency
3. Assess via respirometry analysis and AOP conditioning technique of the process waste waters the improvements in the breakdown efficiency of the process waste waters with regards to further biological Activated Sludge treatment processing.
4. Quantify the improvement in specific substrate elimination rate of the activated sludge when fed with the higher COD aqueous waste waters at increased levels of AOP conditioning.

The first daily composite samples were collected on the 13$^{th}$ of October 2020 and continued for a four-week period to the 9$^{th}$ of November 2020.

## DISCUSSION OF RESULTS

A summary of the findings is as follows:

- The samples from the higher COD streams contained a fine light solid. Over time these solids settled. Further work was carried out to coagulate and separate those solids for removal.
- The ratio of BOD:COD showed a large degree of variability
- The AOP process improved the BOD:COD ratio to > 66% in all cases
- The AOP process significantly improved the respiration rate of the tested materials
- The removal of the fine solids before AOP and Respirometry testing improved both the physical performance of the technologies and also the BOD:COD ratio

## OPTIONS FOR IMPROVED PLANT OPERATION

The fine solids from the higher COD processes are likely to be a root cause of less efficient breakdown of COD within the WWTP. The BOD:COD profile of the wastewater from the higher COD processes shows a large degree of variability.

We therefore recommend that technologies are installed to pre-treat the higher COD wastewater streams in order to remove solids and increase breakdown efficiency.

The technologies recommended for pre-treatment of the higher COD wastewater streams are:

- Coagulation/flocculation for liquid-solid separation
- DAF for solids removal
- Advanced Oxidation for increasing treatment performance and associated energy savings.

Coagulation/Flocculation & DAF

Coagulation in wastewater treatment is a process involving neutralisation of colloidal particles in an aqueous environment, allowing them to form a 'pin-floc' of solid material. This pin-floc often resembles 'dust' and would not settle or separate readily from its liquid surrounds. Flocculants, such as organic polyelectrolytes, are added to coalesce the pin-floc into a larger 'Floc' which can be removed by settlement clarifiers, DAFs or dewatering devices.

The process of coagulation usually requires a coagulant salt which 'attracts' the material you wish to remove. This is often followed by pH correction as the process usually operates best in a neutral pH environment. A solid or liquid polyelectrolyte may be added, via a dilution system, to give a larger floc. This allows for the separation of liquid from solid using a DAF

Equipment Required may include:

- Balance Tank (e.g. use of existing Catch tank)
- Flocculation chamber or pipe flocculator
- pH controller
- Chemical dosing pumps
- DAF
- Sludge holding tank
- Sludge dewatering Equipment
- Inline monitoring

Advanced Oxidation Process (AOP)

Advanced oxidation covers a range of technologies which utilise UV and Fenton's chemistry to break down complex organics.

The technology evaluated during the survey was that of Enviolet GmbH AOP which utilises the combination of UV and chemical manipulation to improve the efficiency of treating high COD loading.

The AOP technology is employed in over 600 installations worldwide, including several in Ireland (inc. IE Licenced facilities) as well as Merck Headquarters in Darmstadt, Germany.

The AOP technology is typically provided as a modular system, which can be added to for future upgrades. We recommend that a full scale proposal is sought for an installation suited to the needs of Merck. The results from the evaluation should be adequate to allow a budget proposal to be submitted without delay.

## PROPOSED PLANT CONFIGURATION OPTIONS

It appears that the existing biological treatment infrastructure can be enhanced with future plant upgrades. Furthermore it appears that the existing infrastructure is of sufficient scale to continue to treat the existing wastewater, and is well positioned to install the pre-treatment steps recommended.

Balancing capacity is more than adequate for the hydraulic flows and can provide 2 days or more of equalisation.

The existing biological treatment can maintain an F:M of ca. 0.1 and given that future pre-treatment could reduce the loading upstream then the capacity to treat onsite based on current production seems okay.

While there are times that the dissolved oxygen levels are more difficult to maintain due to the issues outlined above, it is always maintained at levels of > 0.3 mg/l and typically 0.5-1.5 mg/l, so again capacity in the existing air blower system seems adequate.

Further evaluation will be needed to establish what total enhanced treatment capacity the proposed upgraded facility would give Merck.

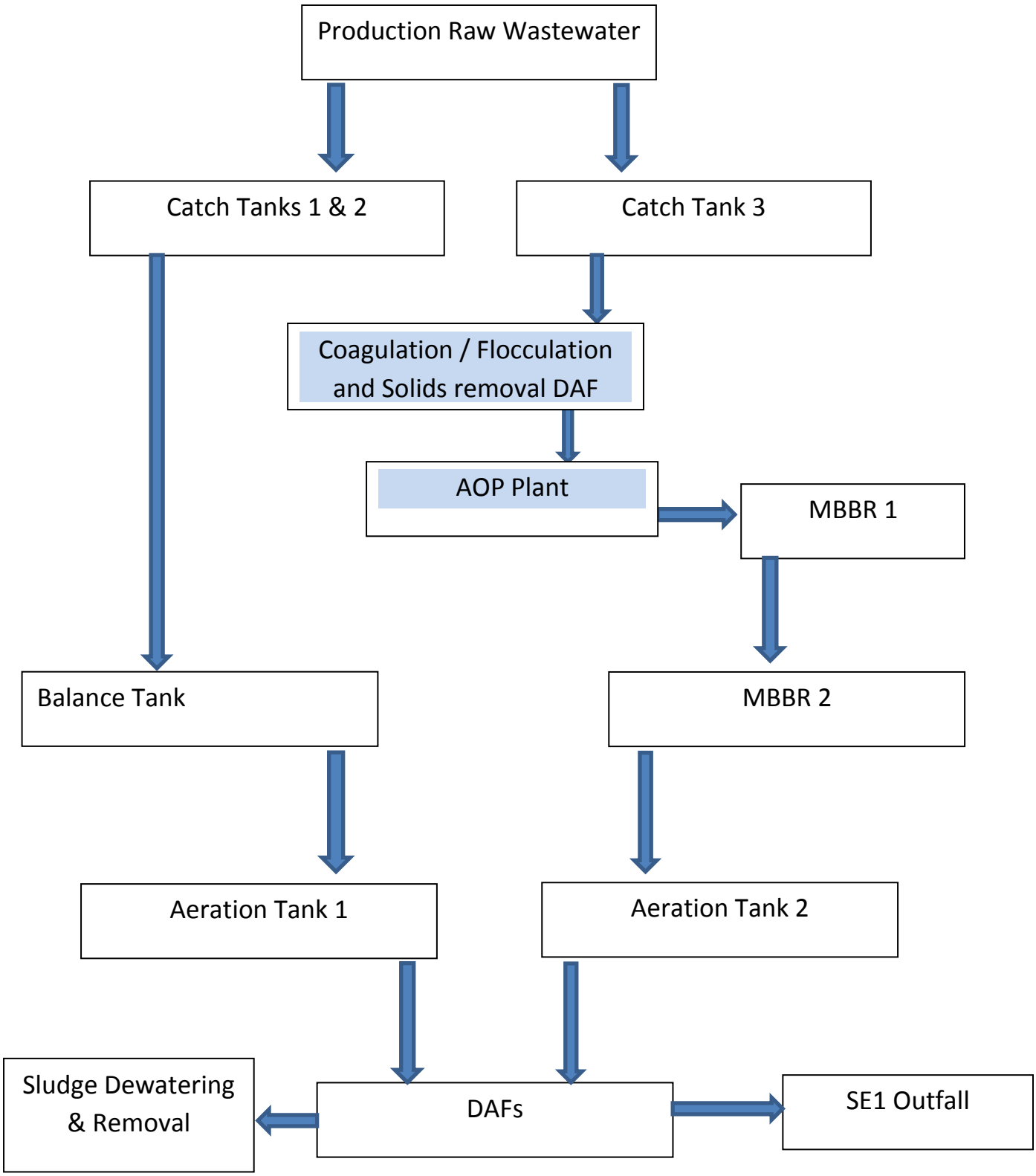
A future treatment regime which allows for pre-treatment of the high COD process streams is envisaged. This would likely involve a solids-separation step and an Advanced Oxidation Process step.

The wastewater from the high COD streams which has been thus pretreated would then be combined with the other wastewater and treated biologically in the existing plant.

We would encourage that valving and pipework arrangements be reviewed in order to give the optimum flexibility for moving flow between the different tanks. Improvements in the final liquid-solid separation may also be considered.

A general process flow of what is proposed is outlined below.

**Merck WWTP Future Possible Process Flow**



## RECOMMENDED KPI'S

Based on the work carried out to date we recommend that the following KPI's are tracked as a minimum:

**Catch Tanks**

| Parameter | Frequency | KPI | Control |
|---|---|---|---|
| pH | Continuous | 6-10 | pH controller |
| COD | Daily | < 50,000 mg/l | Flow control of forward feed to control loading |

**Balance Tank**

| Parameter | Frequency | KPI | Control |
|---|---|---|---|
| pH | Continuous | 6-10 | pH controller |
| COD | Daily | < 25,000 mg/l | Flow control of forward feed to control loading |

**MBBRs**

| Parameter | Frequency | KPI | Control |
|---|---|---|---|
| pH | Continuous | 6-10 | pH Controller |
| Dissolved Oxygen | Continuous | > 0.5 mg/l | DO meters and blowers |
| COD loading | Daily | 7,500 Kg/day | Flow control of forward feed to control loading |

**Aeration Tanks**

| Parameter | Frequency | KPI | Control |
|---|---|---|---|
| pH | Continuous | 6-10 | pH Controller |
| Dissolved Oxygen | Continuous | > 0.5 mg/l | DO meters and blowers |
| MLSS | Daily | < 16,000 mg/l | Feed quantity, wasting and Dewatering |
| COD loading | Daily | 5,000 Kg/day | Flow control of forward feed to control loading |
| F:M Ratio | Daily | 0.05-0.15 | Loading control and MLSS control as above |
| Nitrogen & Phosphorus | Twice weekly | Maintain excess of OrthoP and Kjeldahl N in outfall (below limits) for bio health | Nutrient dosing equipment |
| Microscopic evaluation | Twice weekly | Consistency in floc formation | Overall control of loading and biological health |

**DAFs**

| Parameter | Frequency | KPI | Control |
|---|---|---|---|
| pH | Continuous | 6-10 | pH controller |
| COD | Daily | < 2,600 mg/l<br>IC < 2,080 mg/l | DAF controls, polymer addition, Aeration controls |
| Suspended Solids | Daily | < 450 mg/l<br>IC < 360 mg/l | DAF controls, polymer addition, Aeration controls |

**Final Outfall** – All licence parameters as follows

| Parameter | Frequency | Licence Limit | Internal KPI |
|---|---|---|---|
| Flow | Continuous | 600 m3/day | 24 m3/hour |
| COD | Daily | 2,600 mg/l | 2,080 mg/l |
| COD Kg | Daily | 1,560 Kg | |
| BOD | Weekly | 1,150 mg/l | |
| BOD Kg | Weekly | 690 Kg | |
| Suspended Solids | Daily | 450 mg/l | 360 mg/l |
| Suspended Solids Kg | Daily | 270 Kg | |
| Total Nitrogen | Weekly | 300 mg/l | 240 mg/l |
| pH | Continuous | 6-9 | 6.5 – 8.5 |
| Temperature | Continuous | 35 degC | 32 degC |
| OFG | Quarterly | 30 mg/l | |
| Sulphates | Quarterly | 250 mg/l | |
| Acrylates | Quarterly | 1 mg/l | |
| VOC | Quarterly | 1 mg/l | |
| Chlorides | Annual | 900 mg/l , 267 Kg/d | |
| Total Heavy Metals | Annual | 1 mg/l | |

## CONCLUSION & TIMEFRAMES

Based on the information outlined above we recommend that a 2-phase approach is taken:

**Phase 1**

- A Trial Flocculation & solids-removal DAF system be specified and implemented asap
- Budget proposals are sought for an AOP plant
- Continued bioaugmentation of the existing biological plant as required to maintain a healthy biomass
- Continued chemical supplementation as required to maintain a healthy biomass and compliant discharge
- An overall project plan and team is put in place to manage the trial phases, specifications, plant upgrades needed and full scale project implementation

**Phase 2**

- Installation of a full-scale Flocculation & solids-removal DAF system
- Installation of a full-scale Advanced Oxidation plant
- Additional flexibility to be incorporated into the existing plant to allow flow diversion and treatment changes as required for different campaigns

A realistic timeframe would be as follows:

- Phase 1 – commence March 2021
- Phase 2 – conclude Q2 2022

Proposed technology upgrades at this stage are expected to be introduced under condition 1.4 of IE licence P0571-04

Castlegale will work with Merck in the interim to optimise the existing plant for compliance whilst any changes are being planned.

***E&OE***