State-of-the-art Treatment Technology for Challenging Wastewaters Generated from Processing Opportunity Crudes

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Introduction

Wastewater treatment is sometimes one of the least attended areas of a petroleum refinery. However, improper performance of a treatment plant can potentially degrade treated effluent quality and adversely affect the smooth functioning of a refinery, as a whole. Wastewater treatment comprises of a combination of physicochemical and biochemical processes and is fundamentally different from the mainstream refining processes. A good understanding of wastewater treatment by refinery operators, engineers and managers will ensure its smooth operation, and hence an uninterrupted of the entire facility. This is even more necessary given the widespread trend of the use of "opportunity crudes" as raw materials, and the challenges posed by them in both refining and wastewater treatment processes.

Refinery Wastewater Treatment Process

Crude is a mixture of hydrocarbons. Refined crude is a valuable source of energy and chemicals. Crudes contain many impurities that can impede the refining process. Desalters are the first equipment to handle and process crudes. They make intimate contact between crude and water by thorough mixing at 105 to 150 °C to:

a) Transfer inorganic salts and solids from crude to water as a brine stream as much as possible, and
b) Separate crude and water in two layers, with an emulsion layer (rag layer) in between.

Formation of emulsion is undesirable. A thick emulsion layer indicates poor oil-water separation leading to:

- Large concentration of water in oil phase and oil in water phase;

- Excessive water in desalted crude causing high energy consumption in heating and pumping, and potential corrosion by dissolved salts; and
- Excessive oil under-carry in brine leads to large oil and grease (O&G) and large COD loads to wastewater treatment.

Desalter brine forms a major part of the overall wastewater stream in a refinery that needs treatment for safe disposal. It is mixed with wastewater from other sources in an equalization tank. Combined wastewater stream from equalization tank is fed to API separators for primary oil-water separation and suspended solids removal. This is followed by a secondary separation of oil & gas and solids by dissolved (or induced) air or gas separator. As the wastewater stream becomes significantly free from bulk of the free phase and emulsified organic compounds present as oil & grease in a typical refinery wastewater, it is fed to the biological treatment process to remove the residual organic compounds and associated chemical oxygen demand (COD). Microbes present in the reactor carry out biochemical oxidation reactions by oxygen supplied externally, typically in the form of air, to form benign end products water and carbon dioxide. A part of the organic substrate is utilized to grow new microbial cells. The reactor exit stream leaves with biomass in suspension (mixed liquor), which is introduced to a secondary clarifier for solid-liquid separation by gravity settling. Clarified effluent fulfills the regulatory requirements for safe discharge to the environment. A tertiary filtration step may be added if the discharge requirements call for higher quality effluent of low levels (< 10 mg/L) of BOD and TSS each. A typical wastewater treatment train is depicted as Figure 1.

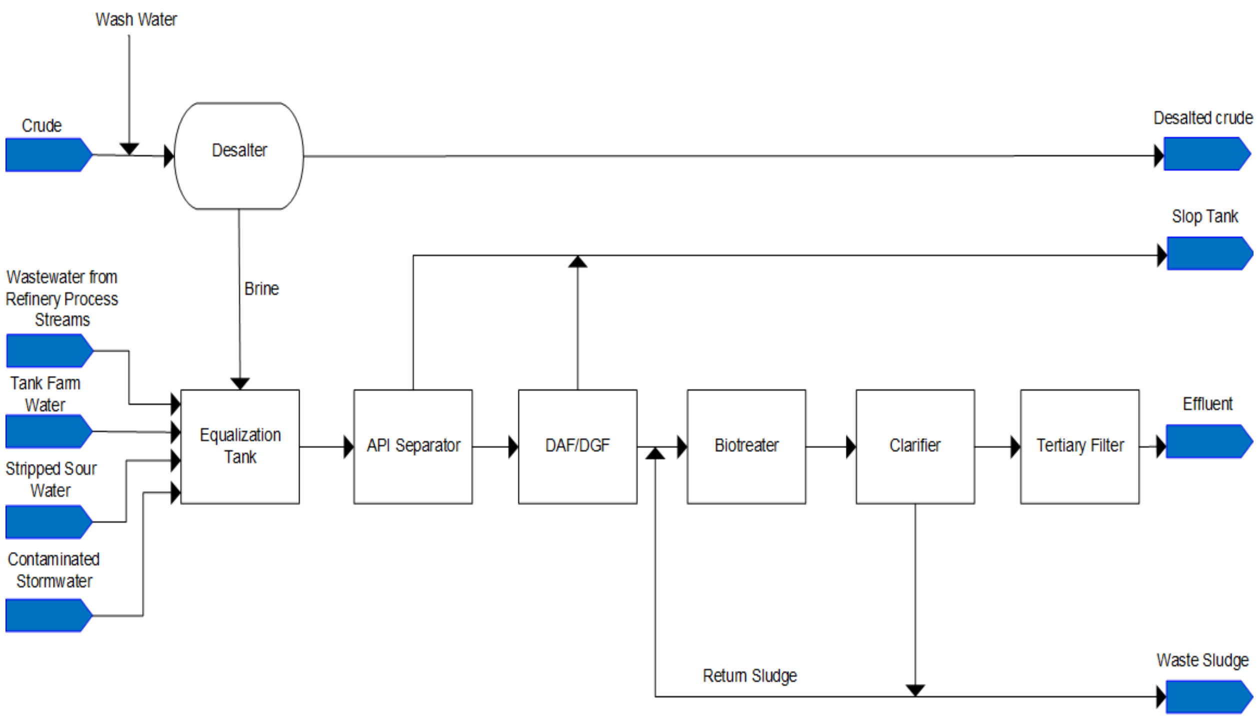

Figure 1: A Typical Wastewater Treatment Train

As regulations become increasingly stringent globally, effluent ammonia and total nitrogen limits are frequently being encountered by refiners. Typically, in a refinery wastewater stream nitrogen is present as ammonia and organic nitrogen compounds. A large part of the organic nitrogen compounds is broken down to ammonia by the microorganisms in the treatment plant. Refineries that are required to comply with ammonia limits are designed and operated to convert ammonia to nitrate to make the effluent suitable for discharge. This requires a significantly larger volume of reactor basin, and also a larger quantity of air than that needed to remove only COD and BOD. However, if the regulation calls for a discharge limit on total nitrogen then the treatment process needs to go one step further by converting nitrate to nitrogen, which can leave the system as a gas. This step is conducted by reacting the nitrate with a COD rich stream, typically the raw influent. However, if that is not sufficient, additional COD is sourced from external supply of chemicals, e.g. methanol.

<u>Opportunity Crudes and their Impacts on Wastewater Treatment Process</u>

Opportunity crudes are those that were not traditionally used in the past in large quantities. However, refiners have been increasingly using such crudes over the past decade as those are abundant, available at lower than benchmark prices, and offer significant opportunities for margin enhancement. Such an advantage comes with some challenges associated with the processing these crudes and the wastewater treatment operation at refineries. They disturb desalter and downstream refining processes due to constituents that refineries are not typically designed to process. Wastewater streams generated from processing such crudes also present formidable challenges to ETP.

- Some examples of opportunity crudes and their sources:
  - Heavy crudes from Canadian Rockies
  - Doba crude from West Africa
  - Light tight oil (LTO) from North American shale plays.

- Characteristics of concern:
  - High and low API gravities outside desirable range
  - High viscosity, leading to high energy for liquid pumping and mixing
  - Naphthenic acids content causing equipment corrosion and challenge to biotreatment of wastewater
  - Metals concentrations, especially Ca and Fe, resulting in scaling and catalyst fouling
  - High filterable solids (FS) that deposit in process and wastewater treatment equipment, resulting in reduction in retention time and incomplete reactions
  - High amines concentrations that adversely impact desalter operation and biological wastewater treatment process.

Several of the above characteristics, particularly naphthenic acids, high FS and high amines concentrations can lead to potential permit violations and impact the overall operation of a

refinery. It is also difficult to predict and be prepared for such occurrences as those spikes are associated with the types of crude slates and therefore, unpredictable. Refiners have tried blending these crudes with traditional ones to balance their properties, but sometimes these crudes are not compatible with each other and leads to formation of solid or semi-solid asphalt materials that precipitate in desalter and upset its operation.
The most vulnerable part in the wastewater treatment plant is the biological treatment. Moving Bed Bioreactor (MBBR) is an innovative and state-of-the-art technology to overcome challenges posed by characteristics of concern associated with opportunity crudes.

Working Principle of MBBR Technology

MBBR is a media based attached growth process where the biomass grows on the surfaces of plastic media. Fixed film on media surfaces provides a home for a large population of biomass in a limited volume. As opposed to the other fixed film processes, the media in a MBBR reactor is suspended and continuously in motion. Air is provided to the MBBR reactor for respiration and mixing. Air keeps the media continuously in suspension in the reactor. Biomass attached on the media surfaces carry out the treatment reactions. The attached growth of biomass on media surface is shown in Figure 2.

Figure 2: MBBR Media with Biofilm Attached on the Interior Surfaces

MBBR media are made of high-density polyethylene (HDPE), and occupy 30 to 60% of empty tank volume. Its specific gravity is 0.95 to 0.98 and float in water under quiescent condition. This is an important requirement as media made of materials heavier than water will sink to the bottom and be ineffective in areas of lower turbulence within the reactor. Also, large amount of air, and hence aeration energy, would be required to keep heavy media in suspension.

The media are designed to provide a large surface area/volume ratio for biomass growth and attachment in a limited volume. It is the protected surface area, which is the surface area inside the openings of the media, that supports the biomass attachment on it. The external surface is not available, and inactive for biomass growth as it is continuously subject to shearing action by the turbulence of the liquid and collision between each other. It is evident from Figure 1 that the biofilm is attached only on the internal surfaces of the media and absent on the external surface.

MBBR is a once through process. Excess growth sloughs off and leaves with effluent. Solids leaving MBBR effluent are lighter and slow settling compared to suspended growth process, and a dissolved air floatation (DAF) separator is better suited for solid-liquid separation.

Sludge from the DAF is wasted, and no biomass stream returns to the reactor. The process flow scheme is presented as Figure 3.

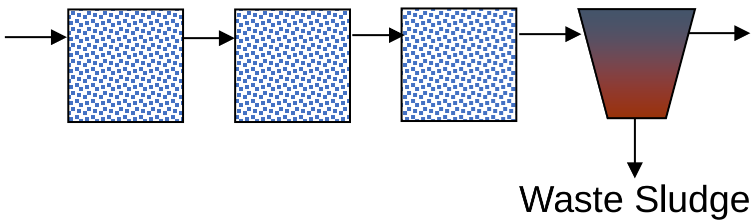

Figure 3: Typical MBBR Process Train

Unlike suspended growth reactors, the possibility of biomass washout and process failure due to toxic or shock loads, and/or hydraulic overloading, is minimal with MBBR. This is because, even if some outer layers of the attached biomass are lost due to such events there will still be a population left in the inner layers, which will provide the seed for regrowth of the films once such events are over. Moreover, the possibility of bulking sludge, which is very common in activated sludge reactors, is absent as the biomass is attached.

The treated effluent leaves MBBR reactor through multiple outlet lines that are connected externally into a common outlet header. A stainless-steel wedge wire screen of 8-mm opening is mounted on each outlet line to prevent escape of media with the effluent. Similarly, the reactor drain lines are also equipped with screens to prevent media drain out with water when the reactor is emptied out for maintenance. MBBR reactor inlet also passes through a screen of 6-mm opening size to prevent the passage of large and coarse objects into the reactor.

In summary, the advantages of MBBR over other types of processes, especially activated sludge process are as follows.

Advantages

- Resistant to toxic and bio-refractory chemicals which are very common to refinery wastewaters, in general, particularly those that use blends of opportunity crudes from different parts of the world
- Resilient to peak flows and shock loads
- Suitable for treating high flows and loads with limited available footprint.
- Simple, hands free operation as there is no return activated sludge (RAS) and waste activated sludge (WAS) streams to monitor and control, and no need to control F:M ratio.

Summary and Conclusions

Headworks develops high rate biological wastewater process for difficult treatable refinery wastewater

Refinery wastewater streams contain chemicals associated with the crude. Some of these may be difficult to treat biologically by the traditional activated sludge process. This is especially the case with certain constituents of "opportunity crudes". Presence of such chemicals can upset the health of the microbial population. Moreover, escape of such chemicals with the treated effluent can be toxic to the aquatic life in the receiving body of water. MBBR is an innovative and state-of-the-art process that overcomes many challenges associated with refractory and toxic chemicals by promoting their breakdown by the action of microbial population present in the reactor in the form of fixed films.