EFFECTIVE PRETREATMENT
FOR HYDROCARBON / VOC REMOVAL

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A paper presented at the WEF Industrial Wastes Technical Conference, Nashville, TN, 1998

ABSTRACT

Pretreatment of industrial wastewater to remove hydrocarbons is often required so that the hydrocarbons will not cause VOC emissions from Publicly Owned Treatment Plants (POTWs) to exceed regulatory limits. A discussion of hydrocarbons in wastewater and several methods of pretreatment are included as well as examples of pretreatment systems and recommended criteria for choosing a pretreatment system.

KEYWORDS

VOC, industrial wastewater, pretreatment, water, separation, hydrocarbon removal, oil

INTRODUCTION

Hydrocarbons in industrial wastewater can be troublesome both to publicly owned treatment works (POTW) and to the plant originating the waste. Some hydrocarbons are volatile and would contribute to VOC emissions from a POTW. In addition to being a VOC problem, too much hydrocarbon content in the incoming water would be detrimental to the health of the microbes in the sanitary plant.

The basic law covering discharges is the Clean Water Act. It was originally enacted as the Federal Water Pollution Control Act of 1972, but was amended extensively in 1977. The 1977 amendments, in conjunction with the earlier legislation, became known as the Clean Water Act. Under the terms of this Act, amended Section 402 created the National Pollutant Discharge Elimination System (NPDES) permit system. Permits for point sources including POTWs under this system are granted by the Environmental Protection Agency (EPA) or by states with EPA approved programs.

Often, the choice of pretreatment methods is dictated by the requirements of regulatory agencies. In the case of the oil reclaiming company discussed below, the necessity for low VOC emissions at the local POTW caused a requirement for less than 2 mg/l effluent from the reclaiming plant that mandated the use of absorbents. In one installation in Ontario, Canada, it was required that the effluent from a groundwater remediation facility be treated to drinking water standards before being discharged to a POTW.

HYDROCARBONS IN WATER

The hydrocarbons present in industrial wastewater can exist in one or more of several conditions. These are shown below, arranged generally in order of difficulty of removal:

- Free oil - large droplets or sheets that rise freely to the surface. This oil is easily removed in simple gravity separators.

- Mechanically dispersed oil - fine droplets ranging from a few microns up to a few millimeters. The oil found in droplets is usually the result of some mechanical mixing of oil and water such as is found in pumping or in turbulent flow through a pipe. The oil droplets can be found in a "bell curve" of droplet sizes with some small, some large and a predominance of average size droplets. The average size will vary dependent on the amount of mixing the two liquids have undergone as well as the presence or absence of emulsion causing surfactant chemicals such as soaps or detergents. These dispersions may be removed by the use of an enhanced gravity or coalescing cartridge system.

- Chemically stabilized emulsions - droplet dispersions similar to mechanically dispersed oil, but with droplets stabilized by surface-active agents (surfactants). More surfactants or more mixing will cause a smaller average droplet size. The average droplet size is important because many separation devices are designed to capture droplets by gravity or enhanced gravity separation and if the average droplet size is smaller, the separator will have to be larger and consequently more expensive. Coalescing cartridges which rely on surface properties of the media will not be effective in removing these dispersions.

- Oil adhering to solid particles. Can be removed by filtration or by enhanced gravity separation if the combined specific gravity is different from the water.

- Dissolved oil - either truly dissolved oil or finely dispersed droplets so small (less than 5 microns) that removal by normal physical means is impossible. This oil must be removed by biological treatment, absorbents, distillation, or other non-gravity means.

In many industrial systems, the majority of the oil will be present as either free oil or mechanical dispersions of oil. These may be treated readily by enhanced gravity systems for removal of the hydrocarbons.

Most hydrocarbon removal systems depend on gravity or enhanced gravity separation, taking advantage of the buoyancy of the droplets.

The rising of hydrocarbon droplets in a separator is governed by Stokes's Law. This function, simply stated is shown in the following equation:

$$Vp = \frac{G}{(18x\mu)} x(d_p - d_c) x D^2$$

Where: V_p = droplet settling velocity, cm/sec
G = gravitational constant, 980 cm/sec^2
μ = absolute viscosity of continuous fluid(water), poise
d_p = density of particle (droplet), gm/cm^3
d_c = density of continuous fluid, gm/cm^3
D = diameter of particle, cm

From the above it may be seen that the important variables are the viscosity of the water, the difference in specific gravity of the water and hydrocarbons, and the hydrocarbon droplet size. After these are known, the droplet rise velocity and therefore the size of separator that is required may be calculated. Stokes's Law is only valid for spherical particles or droplets and only in a laminar flow range. Laminar flow may be defined using several different Reynolds numbers, but a Reynolds Number of 500 or less is generally considered to indicate laminar flow.

METHODS OF PRETREATMENT

Numerous methods are available to reduce the hydrocarbon content of wastewater. Some of the more common methods and some new ones are discussed below. These are:

- API Separators
- Chemical flocculation
- Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF)
- Coalescing Cartridge type separators
- Centrifugal devices
- Coalescing Plate Separators

API Separators

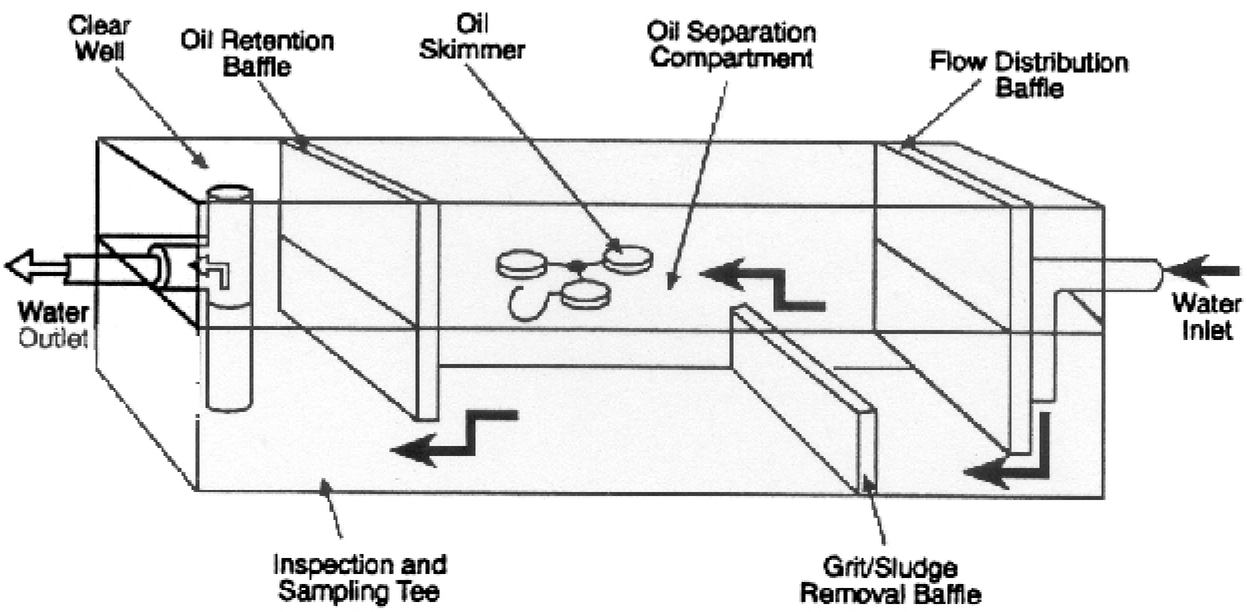
API (American Petroleum Institute) design separators may be used as pretreatment systems in situations where a large amount of oil may be expected to be present in the waste stream and it is desired to recover the oil as is particularly the case in systems treating the wastewater from petroleum refineries. API separators are designed to remove 150 micron and larger droplets and can generate effluent concentrations of oil down to about 150 mg/l (API, 1990). API separator design is based on a study done in 1948 at the Engineering Experiment Station at the University of Wisconsin.

Since it is generally accepted that a sheen will form on the surface of the water if oil concentrations are more than 15 mg/l, and oil sheen is not acceptable under the conditions of the Clean Water Act, these separators are generally not acceptable as final treatment systems. Litchfield (1993) discussed the use of a small refinery's API separator as a pre-treatment device in advance of a constructed wetland. Litchfield reports oil and grease discharge from the API separator of 143 kg/day (almost three times the NPDES limit) and from the downstream wetlands complex of 0.32 kg/day. Wastewater flow was approximately 2,000,000 L/day (530,000 gpd) through the API and a wetlands system of approximately 16 ha (41 acres).

Rebhun and Galil (1994) reported oil removals by an API separator in an oil refinery to be about 70%, with effluent quality averaging about 75 mg/l, although it varied widely. Subsequent treatment with flocculation and a DAF unit reduced the concentration to about 20 mg/l. To make this separation, about 40 mg/l of alum was required and 300 m^3/day of sludge was produced.

In a survey done by the API in 1985 (API, 1990), fewer than half of the separators were generating effluent qualities less than 100 mg/l and approximately one third were more than 200 mg/l. Please see Figure 1 for a schematic of a typical API separator.

Figure 1
API Separator



Chemical Flocculation

Chemical flocculation may be used to agglomerate small oil droplets into larger ones that may be removed by flotation. Kalbfus(1986) discussed results of treatment of oil refinery effluent in European refineries and offers the example that in one refinery the n-$C_{16}H_{34}$ concentration exiting the API separator was 80 μ g/l, and chemical flocculation decreased this to about 0.4 μ g/l. Subsequent biological treatment decreased this to about 0.2 μ g/l and all hydrocarbons down to 0.5 μ g/l. Disadvantages of flocculation are the cost of flocculent chemicals and difficulties in removing any excess chemicals. Advantages are the low levels of hydrocarbons that may be attained by their use.

Torini (1997) discusses a system capable of removing colloidal dispersions. This system utilizes a proprietary food-grade coagulant that is said to easily remove, by flocculation, those colloidal suspensions that are difficult to remove utilizing conventional coagulants. This system is particularly useful in treating the wastes from cheese manufacturing as well as in car washing facilities.

Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF)

DAF or IAF are often used for removal of small hydrocarbon droplets that cannot be removed by API separators. DAF designs require compressed air be dissolved in the wastewater under pressure. When the pressure is released, very small air bubbles attach to the hydrocarbon droplets and lift them to the surface of the separator. The resulting foam or "float" is removed by a surface scraper and processed separately for recovery of the hydrocarbons. Alum or other chemicals are often used as well. Advantages of this system include effective removal of the hydrocarbons, even when present as very small droplets. DAF also removes some of the COD attributed to dissolved components by hydroperoxide reactions in the DAF tank (Prather, 1981). Disadvantages are system cost, operating cost for compressor utilities, chemical cost, and maintenance costs for the compressors and piping systems.

Chin and Wong (1981) reported approximately 20 mg/l of oil and grease in the effluent of a pilot DAF system processing palm oil refinery effluent operating at 4 bar of pressure and influent concentration of approximately 2900 mg/l. This was comparable to field data from an operating plant. Effluent from the downstream activated sludge unit was 10-12 mg/l.

Induced air floatation is similar to DAF except that the air is not actually dissolved in the water, but rather introduced in such a manner that small bubbles are produced, generating a "float" similar to that produced by DAF systems. DAF and IAF systems are considered to have high operating and maintenance costs due to air compression requirements.

Coalescing Cartridge Type Separators

Coalescing cartridges are often used as the second stage of a separator after a first stage of coalescing plates, although they are sometimes used as a primary coalescer. Coalescing cartridges are capable of producing effluent quality of 10 mg/l or less, and are suitable for use in systems where little or no solids are present. Disadvantages are plugging with solids, becoming disarmed or poisoned (becoming disabled) due to surfactants in the water stream, and expense of replacement. Generally, coalescer cartridges that have become disarmed due to surfactants must be replaced, as their efficiency cannot be recovered.

Centrifugal treatment

Shelly (1997) describes a system for handling refinery "slop oil" that utilizes a three-phase centrifuge that separates oil, solids, and oily water. The inlet water and oil mixture contained approximately 75% water, 20% oil, and 5% solids and was pretreated with heat and demulsifiers. The solids were a mixture of hydrocarbons, catalyst fines and iron sulfide particles. The centrifugal system then generated a water stream of 98% purity with 2% oil. No cost data is provided, but it would be expected that this would be an expensive system that would be only utilized where other, more economical, methods were not successful. It would still be necessary to treat the water to remove the remaining oil before biological treatment would be operable. In a centrifuge, the lighter oil phase collects near the vortex at the center of the centrifuge. This requires that the hydrocarbon removal system be designed to remove the small amount of oil at the centerline of the vortex. The maximum advantage of a centrifugal system occurs at the outer region, away from the oil. Effluent qualities of 50 to 75 mg/l of oil are reported. (Chereminisoff, 1993).

Coalescing Plate Separators

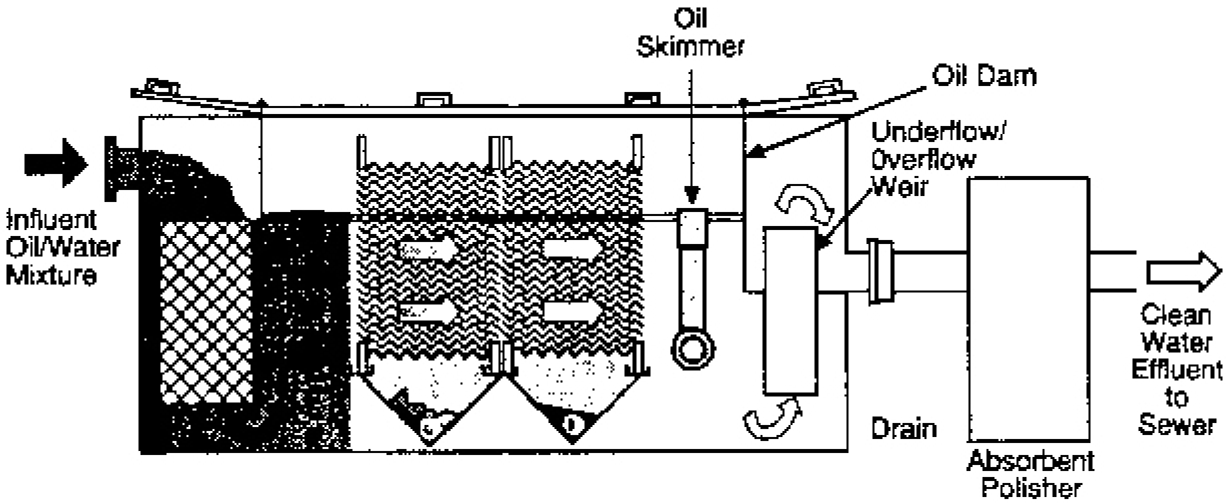
Coalescing plate separators were designed to overcome some of the disadvantages of API separators and provide separation of hydrocarbons from water streams in more compact and efficient systems. API separators are designed to remove 150 micron and larger droplets, and have effluent quality in the range of 150 mg/l, whereas coalescing plate separators may be designed to removed droplets down to 20 microns or less with effluent qualities down to 10 mg/l or less. Since oil is often present in a spectrum of small droplet sizes, the value of these separators may readily be seen as they produce relatively pure oil and do not require the use of absorbents which become waste when used. Several types of coalescing plate separators have been used, the latest being multiple angle separators. These separators combine the best features of highly efficient flat plate separators and solids tolerant tilted plate separators.

EXAMPLES OF PRETREATMENT SYSTEMS

Oil Reclaiming Facility

East Side Oil in St. Cloud, MN, is a reclaimer of used lubricating oil, processing approximately 750 m3/year (200,000 gal per year). They were required by local regulators to provide wastewater pretreatment down to 2 mg/l to meet VOC requirements as a precondition to obtaining an operating permit. The system installed utilizes a multiple angle separator with a wood pulp-based absorbent downstream. A schematic of the system is attached as Figure 2. The separator effluent is not tested, but exhibits no slick (which would indicate less than 15 mg/l). Effluent from the absorbent bed meets the requirements of the POTW. The system has successfully operated for several years, with flow rate depending on the plant throughput and water content of the inlet oil.

Figure 2
Oil Reclaiming Facility
Water Pretreatment



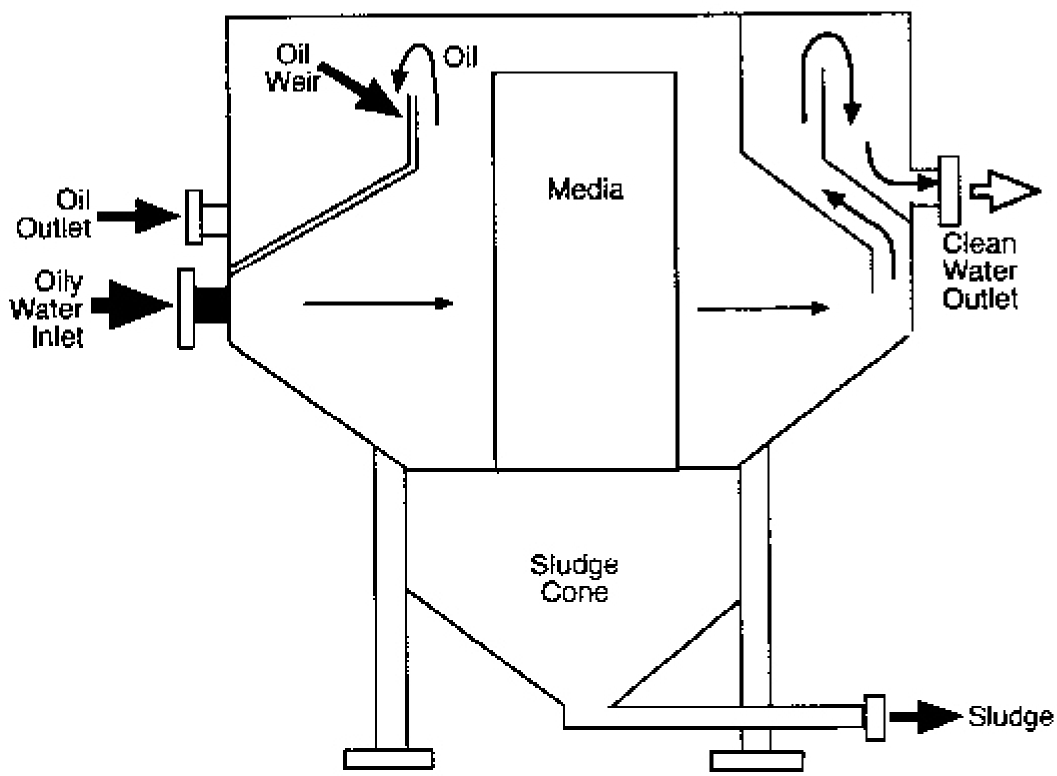
Pipe Manufacturing plant

Napa Pipe, located in Napa, CA, is a large established manufacturer of steel pipe. The process water from this facility contains oil that is washed off of the incoming steel strip as well as a great deal of mill scale type solids. Even though a large, cone bottom oil-water separator was installed, the effluent from the plant sometimes failed to meet the 50 mg/l criteria of the local POTW, often being between 75-125 mg/l of oil in the effluent water.

It was determined that the separator media in the oil-water separator was not sufficiently effective to meet the performance required. Furthermore, the media plugged with solids regularly and required removal for cleaning approximately weekly. This was both troublesome and expensive as it was necessary to shut down and empty the separator, use a crane to remove the media pack, and flush the pack using a fire hose. Maintenance required approximately 1 man-day per week.
It is likely that the pluggage contributed to the poor performance of the separator, although the irregularity of the media may have contributed to performance problems by providing clear flow paths through the separator so that some of the water was not processed properly. The inlet to the separator consisted of 19.3 - 28.4 m^3/hr (85-125 gpm) of water containing approximately 2000 mg/l of 0.9 SG hydraulic oil and 1400 mg/l of solid particles. Effluent from the separator was approximately 75-125 mg/l, significantly more than the 50 mg/l allowed by the POTW.

The media was replaced with more efficient multiple-angle media utilizing a design that readily sheds solid particles to the bottom of the separator. Please see Figure 3 for a schematic of this system. Cleaning is reduced to about 25% of previous requirements because of the self-cleaning nature of the media. The pack is flushed in place approximately weekly and removed for thorough cleaning approximately monthly. Current effluent analyses show 3-5 mg/l or less meeting the POTW requirements.

Figure 3
Pipe Manufacturing Plant System

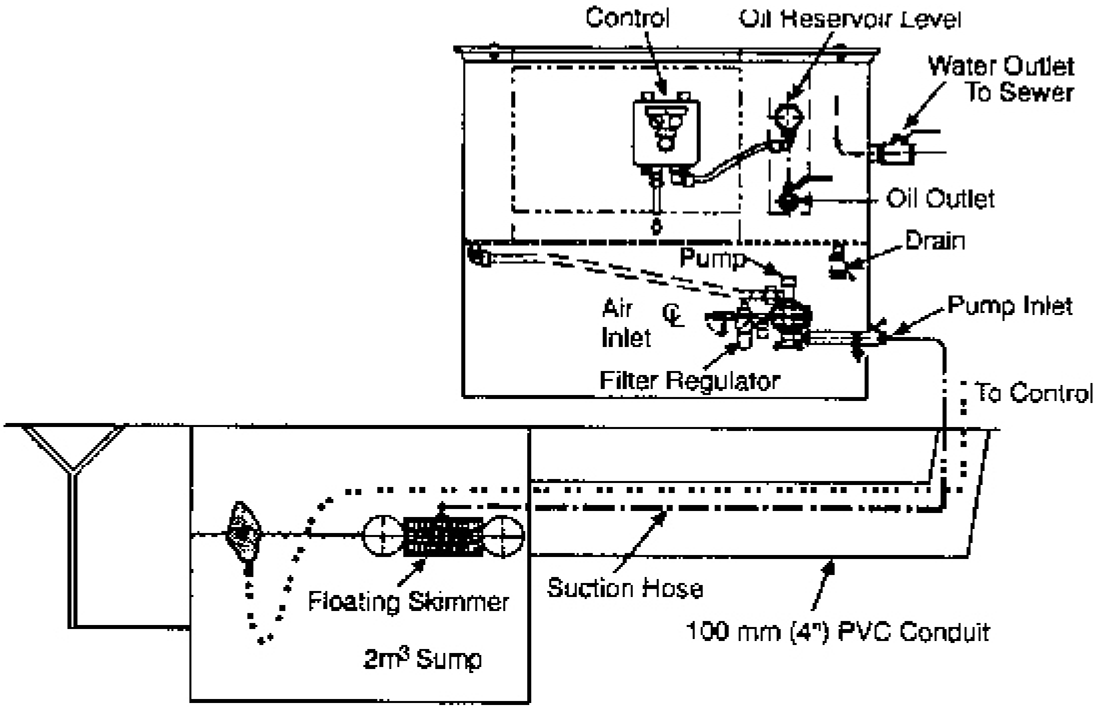


Auto Maintenance Floor Washing Water

A major US auto company was interested in developing a standard design for dealer maintenance shops that involved use of a thorough separation device to separate any oil that might be contained in floor washing water and ensure that it not be directed to the sanitary sewers in the community.

Since the flow was relatively low and a positive assurance against the oil being allowed into the sewers was desired, a system was designed consisting of a series of floor drains directed to a "dead end" sump of 2 m^3 (500 gal.) capacity. Please see Figure 4 for a schematic of this design.

Figure 4
Auto Maintenance
Floor Washing Water



The hydrocarbon removal is by a high efficiency multiple-angle type plate separator with a flow capacity of 6 l/min. (1.6 gpm) and is provided with an automatic operating/control system.

A level switch in the sump turns the system feed pump on and off as necessary. When the pump is operating, oil is automatically separated from the water and comes to the surface of the separator where it is skimmed off into an integral oil tank. An alarm system in the separator actuates a "service separator" light located remotely in the building to alert the operator to drain and recycle the collected oil. Cleaned effluent water from the system flows directly to the sewer by gravity.

Quick Lubrication Facility Water

A major U.S. company operating a chain of quick lubrication facilities wished to install a system for removal of hydrocarbons from the floor drain system of their facilities. The system was to be automatic, high efficiency, and meet the requirements of the local environmental authorities. The system designed is similar to that used at the auto dealership described above except that it is installed underground as part of the sewer system instead of being aboveground and pump fed. The system alarm is a light mounted in the service bay to alert the operator to empty the oil tank. Initial operations of the unit indicate that about 8 liters of oil were captured in the first three months of operation. Please note that this would be enough oil to cause a slick on about 500,000 liters of water.

CONCLUSIONS

Air emissions standards for evaporation of VOCs from wastewater treatment ponds and POTW are becoming more stringent. Many of the troublesome compounds are hydrocarbon in nature and their presence in the POTW is the result of inadequate pretreatment of industrial wastewater streams.

Numerous methods are available for pretreatment of industrial water streams; only a few of them are listed above. Generally the best treatment method for any wastewater stream must be chosen by review of the available options and costs.

Criteria for choice of options should be:

- Effectiveness of treatment
- Simplicity and reliability of operation
- Minimum consumable use
- Minimum production of sludges and used filter/absorbent cartridges
- Minimum energy use
- Governmental/regulatory requirements

The best and most cost effective method is usually the simplest and particularly the one that generates the least amount of waste in the pretreatment facility while still providing adequate pretreatment.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the support of Napa Pipe, and East Side Oil for allowing their installations to be described.

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