

Improvements in Wastewater Treatment Technology

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Abstract: There have been several new improvements in the wastewater treatment field in the last years. Alternatives have presented themselves for classical and conventional wastewater treatment systems. Advanced wastewater treatments have become an area of global focus as individuals, communities, industries and nations strive for ways to keep essential resources available and suitable for use. Advanced wastewater treatment technology, coupled with wastewater reduction and water recycling initiatives, offer hope of slowing, and perhaps halting, the inevitable loss of usable water. Chemical oxidation processes for removal of color and oxygen demand from textile mill effluent, sequential anaerobic/aerobic biological treatment recalcitrant and inhibitory organic compounds in ammunition plant wastewaters, separation and recovery of organic solvents from mixed industrial waste streams, remediation of contaminated subsurface waters, membrane treatment of effluents from secondary biological wastewater treatment plants, and integrated bio-membrane treatment of industrial and municipal wastewaters. This paper covers all advanced methods of wastewater treatments and reuse.

Key words: Wastewater, primary treatment, secondary treatment, advanced water treatment, anaerobic/aerobic sequenced bio-processes, membrane processes, chemical oxidation, water treatment for reuse

Introduction

Outside of the laboratory there is no such thing as "pure" water. Even rain water, for example, will take on gases, solid particles and other "impurities" as it falls through the air to the earth. As water strikes the ground and flows across or through the surface of the earth, as would be expected, it takes on the characteristics of the materials it has encountered. For example, minerals are dissolved and contribute to the dissolved salts that are normally found in waters. At the same time organic matter from decomposed vegetation or from the soil, will also dissolve or be carried along within the water. Thus, waters will have many natural impurities. Generally these impurities do not detract from utilization of the water, e.g., drinking, washing, etc. Our main concern will be with waters that have been used by man and then discarded. While such waters have in the past been commonly referred to as sewage, over the more recent years they have come to be called "Wastewaters". The discharge of wastewater without treatment may cause microorganisms, in rivers, lakes and even seas to which they send, consumes the dissolved oxygen and cause depletion of the oxygen concentration in them.

Wastewater is about 99.94 percent water, with only 0.06 percent of the wastewater dissolved and suspended solid material. The cloudiness of wastewater is caused by suspended particles which in untreated wastewater ranges from 100 to 350 mg/l. A measure of the strength of the wastewater is biochemical oxygen demand, or

BOD₅. The BOD₅ measures the amount of oxygen microorganisms require in five days to break down wastewater. Untreated wastewater has a BOD₅ ranging from 100 mg/l to 300 mg/l. Pathogens or disease-causing organisms are present in wastewater. Coliform bacteria are used as an indicator of disease-causing organisms. Wastewater also contains nutrients (such as ammonia and phosphorus), minerals, and metals. Ammonia can range from 12 to 50 mg/l and phosphorus can range from 6 to 20 mg/l in untreated wastewater (Karen Mancl, 1996; Metcalf and Eddy, 2003).

Wastewater may be classified into four categories:

1. domestic: wastewater discharged from residences and commercial institutions and similar facilities.
2. industrial: wastewater in which industrial waste predominates.
3. infiltration/inflow: extraneous water that enters the sewer system through indirect and direct means such as through leaking joints, cracks, or porous walls. Inflow is storm water that enters the sewer system from storm drain connections, roof headers, foundation and basement drains or through manhole covers.
4. storm water: runoff resulting from flooding due to rainfall.

Wastewater treatment is a multi-stage process to renovate wastewater before it reenters a body of water, is applied to the land or is reused. The goal is to reduce or remove organic matter, solids, nutrients, disease-

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Table 1: Quality of raw wastewater and primary effluent at selected treatment plants in California

| Quality Parameters, mg/l | City of Davis | | San Diego | | Los Angeles County joint plant | |
|--------------------------------|-----------------|------------------|-----------------|------------------|--------------------------------|------------------|
| | Raw waste-water | Primary effluent | Raw waste-water | Primary effluent | Raw waste-water | Primary effluent |
| BOD ⁵ | 112 | 73 | 184 | 134 | - | 204 |
| TOC | 63.8 | 40.6 | 64.8 | 52.3 | - | - |
| SS | 185 | 72 | 200 | 109 | - | 219 |
| Total nitrogen | 43.4 | 34.7 | - | - | - | - |
| NH ₃ -N | 35.6 | 26.2 | 21.0 | 20.0 | - | 39.5 |
| NO-N | 0 | 0 | - | - | - | - |
| Org-N | 7.8 | 8.5 | - | - | - | 14.9 |
| Total phosphorus | - | 7.5 | - | 10.2 | - | 11.2 |
| pH (unit) | 7.7 | - | 7.3 | 7.3 | - | - |
| Ca | - | - | - | - | 78.8 | - |
| K | - | - | - | - | 19 | 19 |
| Na | - | - | - | - | 357 | 359 |
| TDS | - | - | 829 | 821 | 1404 | 1406 |
| SO ₄ | - | - | 160 | - | 270 | - |
| Cl | - | - | 120 | - | 397 | - |
| Boron (B) - | - | - | - | - | 1.68 | 1.5 |
| Alkalinity(CaCO ₃) | - | - | - | - | 322 | 332 |
| Hardness (CaCO ₃) | - | - | - | - | 265 | - |

Source: International Desalination Association (IDA, 1987).

causing organisms and other pollutants from wastewater.

Conventional wastewater treatment processes:

Conventional wastewater treatment consists of a combination of physical, chemical, and biological processes and operations to remove solids, organic matter and, sometimes, nutrients from wastewater. General terms used to describe different degrees of treatment, in order of increasing treatment level, are preliminary, primary, secondary, and tertiary and/or advanced wastewater treatment. After these treatments municipal wastewater is usually disinfected using chlorine (or other disinfecting compounds, or occasionally ozone or ultraviolet light).

Preliminary treatment: Preliminary treatment to screen out, grind up, or separate debris is the first step in wastewater treatment. Sticks, rags, large food particles, sand, gravel, toys, etc., are removed at this stage to protect the pumping and other equipment in the treatment plant. Treatment equipment such as bar screens, comminutors (a large version of a garbage disposal), and grit chambers are used as the wastewater first enters a treatment plant. The collected debris is usually disposed of in a landfill.

Primary treatment: The objective of primary treatment is the removal of settle able organic and inorganic solids by sedimentation, and the removal of materials that will float (scum) by skimming. Approximately 25 to 50% of the incoming biochemical oxygen demand (BOD₅), 50 to 70% of the total suspended solids (SS), and 65% of the oil and grease are removed during

primary treatment. Some organic nitrogen, organic phosphorus, and heavy metals associated with solids are also removed during primary sedimentation but colloidal and dissolved constituents are not affected. The effluent from primary sedimentation units is referred to as primary effluent. Table 1 provides information on primary effluent from three sewage treatment plants in California along with data on the raw wastewaters.

Secondary treatment: The objective of secondary treatment is the further treatment of the effluent from primary treatment to remove the residual organic and suspended solids. In most cases, secondary treatment follows primary treatment and involves the removal of biodegradable dissolved and colloidal organic matter using aerobic biological treatment processes. Aerobic biological treatment is performed in the presence of oxygen by aerobic microorganisms (principally bacteria) that metabolize the organic matter in the wastewater, thereby producing more microorganisms and inorganic end-products (principally CO₂, NH₃, and H₂O). Several aerobic biological processes are used for secondary treatment differing primarily in the manner in which oxygen is supplied to the microorganisms and in the rate at which organisms metabolize the organic matter.

Improvements in wastewater treatment processes:

Primary and secondary treatment removes the majority of BOD and suspended solids found in wastewaters. However, in an increasing number of cases this level of treatment has proved to be insufficient to protect the receiving waters or to provide reusable water for industrial and/or domestic recycling. Thus, additional treatment steps have been added to wastewater

Table 2: Membrane pore size characteristics and target contaminants

| Membrane Process | Average Membrane Pore Size (nm) | Target Contaminants |
|------------------|---------------------------------|--|
| MF | 200 | Suspended solids, turbidity, and pathogens (Cryptosporidium, Giardia, bacteria). |
| UF | 2-50 | Macromolecules, viruses, colloids, and proteins. |
| NF | <2 | Color, organic, pesticides, and metals. |
| RO | <1 | Dissolved solids, nitrates, and radionuclides. |

MF= Microfiltration; UF= Ultrafiltration; NF= Nanofiltration; and, RO= Reverse Osmosis

treatment plants to provide for further organic and solids removals or to provide for removal of nutrients and/or toxic materials.

Therefore, advanced wastewater treatment is defined as: any process designed to produce an effluent of higher quality than normally achieved by secondary treatment processes or containing unit operations not normally found in secondary treatment. The above definition is intentionally very broad and encompasses almost all unit operations not commonly found in wastewater treatment today.

Advanced wastewater treatment: Advanced wastewater treatment may be divided into three major categories by the type of process flow scheme utilized:

1. Tertiary treatment
2. Physicochemical treatment
3. Combined biological-physical treatment

Tertiary treatment may be defined as any treatment process in which unit operations are added to the flow scheme following conventional secondary treatment. Additions to conventional secondary treatment could be as simple as the addition of a filter for suspended solids removal or as complex as the addition of many unit processes for organic, suspended solids, nitrogen and phosphorous removal. Physicochemical treatment is defined as a treatment process in which bio-logical and physical-chemical processes are intermixed to achieve the desired effluent. Combined biological-physical-chemical treatment is differentiated from tertiary treatment in that in tertiary treatment any unit processes are added after conventional biological treatment, while in combined treatment, biological and physicochemical treatments are mixed.

Another way to classify advanced wastewater treatment is to differentiate on the basis of desired treatment goals. Advanced wastewater treatment is used for:

1. additional organic and suspended solids removal
2. removal of nitrogenous oxygen demand(NOD)
3. nutrient removal
4. removal of toxic materials

In many, if not most instances today, conventional secondary treatment gives adequate BOD and suspended solids removals. But advanced wastewater treatment is necessary because advanced wastewater treatment plant effluents may be recycled directly or indirectly to increase the available domestic water supply.

Advanced wastewater treatment effluents maybe used for industrial process or cooling water supplies. Some receiving waters are not capable of withstanding the pollutional loads from the discharge of secondary effluents. Secondary treatment does not remove as much of the organic pollution in wastewater as may be assumed. The performance of secondary treatment plants is almost always measured in terms of BOD and SS removal. A well-designed and operated secondary plant will remove from 85% to 95% of the influent BOD and SS. However, the BOD test does not measure all of the organic material present in the wastewater. An average secondary effluent may have a BOD of 20 mg/L and a COD of 60 to 100 mg/L. The average secondary plant removes approximately 65% of the influent COD. Thus, when high-quality effluents are required, additional organic removal must be accomplished. In addition to the organic materials remaining in most secondary effluents, there is an additional oxygen demand resulting from the nitrogen present in the wastewater.

Chemical oxidation: Routine treatment of organic contaminants by chemical oxidation is frequently less economic than biological treatment. Systems involving latter have inherent advantages in that treatment is fueled by energy derived from the target substrates, while chemical oxidation systems rely on inputs of energy in the form of chemical oxidants, leading to increased operating costs. Under circumstances, however, chemical oxidation systems can be used cost effectively to treat organic chemicals that are normally toxic or refractory to microorganisms, in effect serving either as detoxification or refractory organic "softening" pretreatment steps for biological processes or as self-contained processes for transformation of organic or inorganic contaminants to environmentally acceptable oxidation /reduction products. Large quantities of suspended or dissolved solids quickly consume chemical oxidants, so waters targeted for such treatment should have relatively low concentrations of oxidizable background material, in the range of no more than a few hundred mg/L of total organic carbon.

Recent advances in oxidation processes have focused primarily on reaction rates, since it is this aspect of such processes that generally governs the performance of otherwise thermodynamically favorable reactions of strong oxidants with target contaminants. Common

Table 3: Biological and physicochemical treatment process for advanced water treatment

| Target Contaminants | AN/A Bio | Bio-M | COX | GAC | Poly | MF-UF | RO |
|---------------------|----------|-------|-----|-----|------|-------|----|
| Diss solids | | | ⊕ | | | | ⊕ |
| Susp solids | ⊕ | ⊕ | | | | ⊕ | |
| BOD | ⊕ | ⊕ | | ⊕ | | ⊕ | ⊕ |
| Pathogens | | | ⊕ | | | ⊕ | ⊕ |
| Non VOCs | ⊕ | ⊕ | | ⊕ | ⊕ | | ⊕ |
| VOCs | ⊕ | ⊕ | ⊕ | ⊕ | ⊕ | | ⊕ |
| Metals | ⊕ | | | | | | ⊕ |

AN/A Bio = Anaerobic/Aerobic Bio-Processes; Bio-M = Bio-Membranes; COX = Chemical Oxidation; GAC = Granular Activated Carbon Adsorption; POLY = Synthetic Polymer Adsorption; MF-UF = Microfiltration and Ultrafiltration; RO = Reverse Osmosis

oxidants include hydrogen peroxide, ozone, potassium permanganate, and chlorine dioxide. Each of these oxidants has unique properties and reactivity characteristics which influence its suitability and mode of use for different applications.

Hydrogen peroxide (H₂O₂), for example, is most reactive in the pH range from 3.0 to 4.0. adjustments in pH to enhance the oxidation effectiveness of this reagent are normally accomplished through use of one or more catalysts, the most common being ferrous sulfate (FeSO₄), in so-called Fenton reagent reactions in the pH region of ~3.5 (Bowers, 1990).

Recent use of Fenton reagent reactions have focused on color removal from biologically recalcitrant textile mill dyes, and destruction of toxic or refractory organic occurring in low concentrations in contaminated groundwater system.

Sequenced anaerobic/aerobic bio-processes:

Numerous advances in biological treatment have occurred over the past ten years, fueled largely by increasingly strict regulations on discharges of BOD, organic phosphorus, nitrogen, and toxic organic chemicals from both industrial and municipal facilities. Aerobic treatment processes have traditionally been employed for reduction of BOD, but concurrent reductions of other contaminants often proves infeasible without coupling aerobic treatment with anaerobic or anoxic pretreatment. Anoxic and anaerobic treatments have been found to provide opportunities for transformation of biological phosphorus, nitrogen, and many organic chemicals that are toxic to aerobic systems (Zitomer and Speece, 1993). Although complete mineralization of toxic organic is not normally accomplished by anaerobic treatment, the ability of these systems to biologically transform toxic organic chemicals to forms more easily degraded in aerobic environments greatly expands the capabilities of biological systems for treatment of organic wastes.

While anaerobic systems are often beneficial in reducing the toxicity of refractory organic as a pretreatment step for subsequent aerobic treatment, a number of difficulties can be encountered with this

process. Problems include sensitivity to shock or variable substrate loadings, and the need to retain naturally slow-growing anaerobic cell populations for longer periods of time; i.e., slow-growing anaerobic systems cannot afford losses of cell mass common to fast-growing aerobic systems. Shock loading problems in large systems can usually be overcome by using mass equalization basins. More innovative methods may be required for low flow systems that experience widely varying substrate loadings. One such method is the use of granular activated carbon (GAC) adsorption columns in the recycle loops of recycling anaerobic bioreactors to control concentrations of inhibitory compounds in the reaction chambers (Fox and Suidan, 1996).

Enhancing the residence time of sludge biomass can be accomplished by use of reactors providing appropriate means for cell attachment, such as sand, GAC, or polymeric membranes. GAC is particularly advantageous for treatment of refractory and/or toxic organic wastes because of its ability to attenuate large concentration swings in chemical feed streams, thereby allowing for enhanced process performance.

Adsorption: Adsorption is a widely used method for the treatment of industrial wastewater containing color, heavy metals and other inorganic and organic impurities. The advantages of adsorption process are for its simplicity in operation, inexpensive (compared to other separation processes) and without sludge formation.

Activated carbon has been widely used as adsorbents in various industrial applications, such as purification of water in sewage facilities and filtration of air in toxicity-treating factories (Bansal *et al.*, 1998). Numerous attempts have been made to change chemical and physical properties of activated carbon for improving its adsorb ability so far (Domingo-Garcl'a *et al.*, 2000).

Applications of sorption technologies in water treatment have grown from the original, and still widely-employed, use of GAC as a broad-spectrum sorbent for removal of assortments of organic chemicals and heavy metals over wide concentration ranges (Isabel and Wayne,

2005), to the development and application of more specialized polymeric adsorbents having chemical compositions and forms engineered for targeted solute removal and/or recovery.

Polymeric adsorbents take one of two general forms; carbonaceous and non-carbonaceous. The carbonaceous forms perform in a manner similar to GAC, except that they are often more selective for specific organic chemicals at lower solute concentrations, and less easily fouled by dissolved organic matter. Non-carbonaceous polymeric sorbents, which have enjoyed long and widespread use as ion exchange resins, are more recently being evaluated for selective removal and concentration (or subsequent reuse) of organic solutes in industrial operations (Gusler *et al.*, 1993). Industrial process waste streams often contain a number of components of varying chemical characteristics, some of which may be reusable if recovered in relatively pure form. The broad-spectrum properties of activated carbon that provide such an advantage for water recovery and reuse in many mixed contaminant situations may not be desirable for targeted solute recovery and reuse.

Membrane processes: A number of pressure-driven membrane processes are finding increased use for advanced water treatment, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Table 2 summarizes the increasingly limiting membrane pore size (and thus increasing permselectivity) and associated target contaminants for these respective pressure-driven separation processes. Other membrane processes driven by forces other than mechanical pressure (e.g. osmosis and electrodialysis) also have environmental applications, but these are more limited and will not be discussed here.

While fouling and member life continue to be problematic in many applications, recent advances in polymer technology have led to membranes having improved contaminant rejection capabilities, lower pressure requirements, and greater durability. In reverse osmosis, for example, these developments have led to two-fold increases in membrane performance over that of conventional cellulose acetate membranes (Matsuura, 1993). Such achievements have been realized primarily by the use of chemically resistive layers of poly (amide)-based or poly (ether)-based materials placed on top of cellulose acetate membranes; i.e., composite membranes. For RO applications, these composites provide a very thin layer having either a positive or negative surface charge, resulting in higher water fluxes due to higher salt rejections originating from ion-ion repulsion.

Reverse osmosis (RO) membranes have been widely used for water and wastewater treatment facilities, but the prevention of membrane fouling is important to maintain stable operation. Membrane fouling causes the

decrease of water flux (the increase of the applied pressure) and the decrease of solute rejection properties. Membrane fouling is mainly affected by the composition of feed solution and the physicochemical properties of the membranes. For the application of membrane filtration for water and wastewater treatments, the development of technology to alleviate and/or prevent fouling has been an important target, which includes operational conditions and membrane cleaning methods (Neofotistou and Demadis, 2004).

Membrane fouling is caused by a wide range of materials, and the effects of fouling vary with fouling materials. Fouling materials are generally classified into the following types: scaling or salt precipitation (Sheikholeslami, 2004), particulate or colloidal fouling (Ning *et al.*, 2005), organic fouling (Chan and Chen, 2004), biofouling (Vrouwenvelder *et al.*, 2000), and complex fouling (Marshall *et al.*, 2003). Some fouling materials may be removed by pre-treatment prior to the membrane process; however, it is difficult to remove the ionic components which are precipitated by enrichment with the membrane. In some cases, pH adjustment of the feed solution and/or the addition of antiscalants are used to prevent fouling (Maartens *et al.*, 2002).

Another interesting area of development in membrane treatment technology is that of so-called biomembrane processes. Such processes may take one of three general system forms: extraction systems (Livingston, 1994); fixed-film systems (Illias and Schimmel, 1995); and filtration systems (Urbain, 1996). In each case, the membrane serves as a barrier to facilitate selective solute transport, enhance biofilm attachment, and/or restrict microorganism access to downstream permeate.

Illustrative case-oriented examples of bio-membrane process applications have been given by Livingston (Livingston, 1994), and by (Illias and Schimmel, 1995). For industrial waste streams originating from an organic synthesis process, the presence of high concentrations of inorganic materials such as acids, bases, salts, and left-over catalysts can adversely affect the ability of microorganisms to effectively degrade toxic organic compounds. The use of extraction bio-membrane systems can circumvent this problem by specifically targeting facilitated transport of organic through the membrane. (Livingston, 1994) describes the use of extractive membrane bioreactors (EMB) which employ silicone rubber and other organophilic polymers known to be permeable to volatile chlorinated hydrocarbons, but are impermeable to water and other polar and ionic compounds. For EMB systems similar to that shown in Fig. 1, this allows for better control of the composition medium to be biodegraded, effectively replicating similar conditions under which the biomedium culture was developed (Livingston, 1994).

Industrial or municipal wastewaters may also contain trace amounts or organic compounds at concentrations

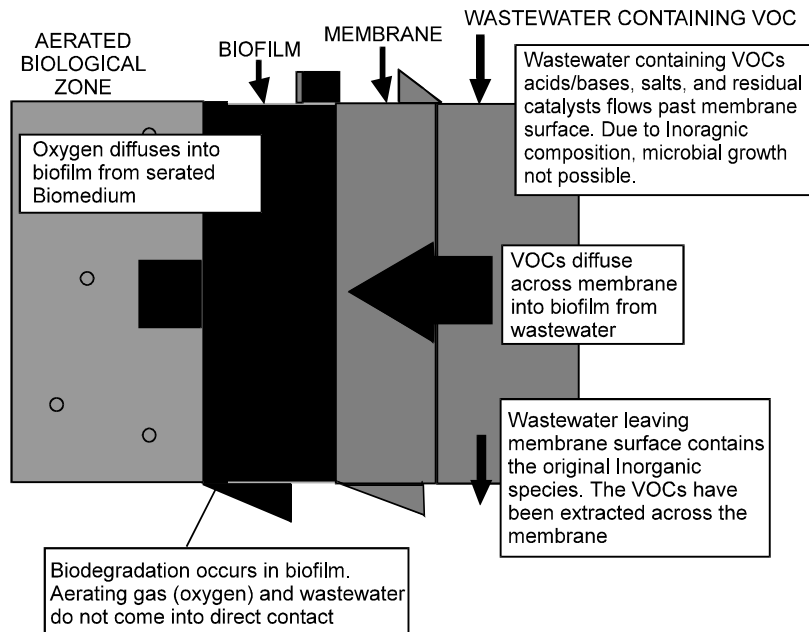


Fig. 1: Detoxifying chemical process wastewaters (Livingston, 1994).

too low to sustain biological populations in normal reactor systems. This problem may be resolved through the use of fixed-film bio-membranes permeable to organic on one side while supporting biofilm growth on the other side. This allows the growth of cell populations an order of magnitude greater than those achieved in suspended growth reactors (Illias and Schimmel, 1995).

Conclusions: The objectives originally sought in wastewater treatment include:

1. Protection and maintenance of sources for use as domestic water supplies.
2. Prevention of disease and spread of diseases.
3. Prevention of nuisance conditions.
4. Maintenance of clean waters for bathing and other recreational purposes.
5. Protection and maintenance of the environment. For example, maintaining natural waters for the propagation and survival of fish life.
6. Conservation and protection of water for industrial and agricultural uses.
7. Prevention of silting in navigable channels.

Water recycling has been recognized as a key approach to alleviate water shortage, which has now become a worldwide issue. While available advanced technologies such as membrane filtration, advanced oxidation, and carbon adsorption have been instrumental in propelling water recycling forward.

A wastewater treatment plant is designed to remove from the wastewater enough organic and inorganic solids so that it can be disposed of without contravening or affecting the objectives sought. Treatment devices merely localize and confine these processes to a

restricted, controlled, suitable area or environment and provide favorable conditions for the acceleration of the physical and biochemical reactions.

Wastewater treatment processes require careful management to ensure the protection of the water body that receives the discharge. Trained and certified treatment plant operator's measure and monitor the incoming sewage, the treatment process and the final effluent. The ultimate goal of wastewater treatment should be managing wastewater effectively, economically, and ecologically.

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