5
Treatment of Pharmaceutical Wastes

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5.1 INTRODUCTION

The pharmaceutical industry manufactures biological products, medicinal chemicals, botanical products, and the pharmaceutical products covered by Standard Industrial Classification Code Numbers 2831, 2833, and 2834, as well as other commodities. The industry is characterized by a diversity of products, processes, plant sizes, as well as wastewater quantity and quality. In fact, the pharmaceutical industry represents a range of industries with operations and processes as diverse as its products. Hence, it is almost impossible to describe a “typical” pharmaceutical effluent because of such diversity. The growth of pharmaceutical plants was greatly accelerated during World War II by the enormous demands of the armed forces for life-saving products. Manufacture of the new products, particularly the antibiotics that were developed during World War II and later periods, exacerbated the wastewater treatment problems resulting from this industry. Industrialization in the last few decades has given rise to the discharge of liquid, solid, and gaseous emissions into natural systems and consequent degradation of the environment [1]. This in turn has led to an increase in various kinds of diseases, which has necessitated the production of a wide array of pharmaceuticals in many countries. Wastewater treatment and disposal problems have also increased as a result. From 1999 to 2000, the U.S. Geological Survey conducted the first nationwide reconnaissance of the occurrence of pharmaceuticals, hormones, and other organic wastewater contaminants (OWC) in a network of 139 streams across 30 states. The study concluded that OWC were present in 80% of the streams sampled. The most frequently detected compounds were basically of pharmaceutical origin, that is, coprostanol (fecal steroid), cholesterol (plant and animal steroids), N,N-diethyltoluamide (insect repellant), caffeine (stimulant), triclosan (antimicrobial disinfectant), and so on [2].

5.2 CATEGORIZATION OF THE PHARMACEUTICAL INDUSTRY

Bulk pharmaceuticals are manufactured using a variety of processes including chemical synthesis, fermentation, extraction, and other complex methods. Moreover, the pharmaceutical industry produces many products using different kinds of raw material as well as processes;
hence it is difficult to generalize its classification. In spite of extreme varieties of processes, raw materials, final products, and uniqueness of plants, a first cut has been made to divide the industry into categories having roughly similar processes, waste disposal problems, and treatment methods. Based on the processes involved in manufacturing, pharmaceutical industries can be subdivided into the following five major subcategories:

1. Fermentation plants;
2. Synthesized organic chemicals plants;
3. Fermentation/synthesized organic chemicals plants (generally moderate to large plants);
4. Biological production plants (production of vaccines–antitoxins);
5. Drug mixing, formulation, and preparation plants (tablets, capsules, solutions, etc.).

Fermentation plants employ fermentation processes to produce medicinal chemicals (fine chemicals). In contrast, synthesized organic chemical plants produce medicinal chemicals by organic synthesis processes. Most plants are actually combinations of these two processes, yielding a third subcategory of fermentation/synthesized organic chemicals plants. Biological production plants produce vaccines and antitoxins. The fifth category comprises drug mixing, formulation, and preparation plants, which produce pharmaceutical preparations in a final form such as tablets, capsules, ointments, and so on.

Another attempt was made to classify the industry based on production of final product. The Kline Guide in 1974 defined the various classes of bulk pharmaceutical final products. Based on that, the NFIC–Denever (recently renamed NEIC, National Enforcement Investigation Center), Washington, D.C., classified the pharmaceutical industry into three major categories as depicted in Table 1 [3].

### 5.3 PROCESS DESCRIPTION AND WASTE CHARACTERISTICS

Pharmaceutical waste is one of the major complex and toxic industrial wastes [4]. As mentioned earlier, the pharmaceutical industry employs various processes and a wide variety of raw materials, final products, and uniqueness of plants, a first cut has been made to divide the industry into categories having roughly similar processes, waste disposal problems, and treatment methods. Based on the processes involved in manufacturing, pharmaceutical industries can be subdivided into the following five major subcategories:

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materials to produce an array of final products needed to fulfill national demands. As a result, a number of waste streams with different characteristics and volume are generated, which vary by plant, time, and even season, in order to fulfill the demands of some specific drugs. It has been reported that because of the seasonal use of many products, production within a given pharmaceutical plant often varies throughout the year, which changes the characteristics of wastewater by season [5]. Hence, it is difficult to generalize the characteristics of the effluent discharged from these industries.

Fermentation plants generally produce extremely strong and highly organic wastes, whereas synthetic organic chemical plants produce wastes that are strong, difficult to treat, and frequently inhibitory to biological systems. The production of antitoxins and vaccines by biological plants generates wastewater containing very high BOD (biochemical oxygen demand), COD (chemical oxygen demand), TS (total solids), colloidal solids, toxicity, and odor. The waste load from drug formulating processes is very low compared to the subcategory 1, 2, 3, bulk pharmaceutical manufacturing plants [3]. Characteristics of the waste produced and the process description of various types of pharmaceutical industries are described in the following sections.

5.3.1 Fermentation Plants

These plants use fermentation techniques to produce various pharmaceuticals. A detailed description of the fermentation process including formulation of typical broths, fermentation chemistry, and manufacturing steps of various medicines are given in the NEIC report [6]. Major unit operations involved in the fermentation process are generally comprised of seed production, fermentation (growth), and chemical adjustment of broths, evaporation, filtration, and drying. The waste generated in this process is called spent fermentation broth, which represents the leftover contents of the fermentation tank after the active pharmaceutical ingredients have been extracted. This broth may contain considerable levels of solvents and mycelium, which is the filamentous or vegetative mass of fungi or bacteria responsible for fermentation. One commercial ketone solvent has been reported as having a BOD of approximately 2 kg/L or some 9000 times stronger than untreated domestic sewage. One thousand gallons of this solvent was calculated as equivalent in BOD to the sewage coming from a city of 77,000 people. Similarly, amyl acetate, another common solvent, is reported as having a BOD of about 1 kg/L and acetone shows a BOD of about 400,000 mg/L [7–9]. The nature and composition of a typical spent fermentation broth are depicted in Table 2 [3].

5.3.2 Synthetic Organic Chemical Plants

These plants use the synthesis of various organic chemicals (raw materials) for the production of a wide array of pharmaceuticals. Major unit operations in synthesized organic chemical plants generally include chemical reactions in vessels, solvent extraction, crystallization, filtration, and drying. The waste streams generated from these plants typically consist of cooling waters, condensed steam still bottoms, mother liquors, crystal end product washes, and solvents resulting from the process [10]. The waste produced in this process is strong, difficult to treat, and frequently inhibitory to biological systems. They also contain a wide array of various chemical components prevailing at relatively high concentration produced from the production of chemical intermediates within the plant. Bioassay results on the composite waste from a plant in India approximated 0.3% when expressed as a 48 hour TLm. A typical example of untreated synthetic organic chemical waste for a pharmaceutical plant located in India is given in Table 3.
Various types of waste streams were generated from this plant depending upon the manufacturing process. Waste was segregated into various waste streams such as strong process waste, dilute process waste, service water, and composite waste [12]. The strength and magnitude of various waste streams generated at the Squibb, Inc. synthetic penicillin and antifungal plant in Humaco, Puerto Rico, are given in Table 4.

Many other researchers have segregated the waste generated from a synthetic organic chemical pharmaceutical plant located in Hyderabad, India, into different wastewater streams such as floor washing, also known as condensate waste, acid waste, and alkaline waste [13–15]. This plant is one of the largest of its kind in Asia and is involved in the production of various drugs, such as antipyretics, antitubercular drugs (isonicotinic acid hydrazide), antihelminthic, sulfa drugs, vitamins, and so on. Tables 5 to 8 present the characteristics of each waste stream generated from a synthetic drug plant at Hyderabad, along with the characteristics of the combined waste streams. Wastewater from this plant exhibited considerable BOD variation among the various waste streams generated from the plant. The BOD of the condensate waste

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration range (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-amino phenol, $p$-nitrophenolate, $p$-nitrochlorobenzene</td>
<td>150–200</td>
</tr>
<tr>
<td>Amino-nitrozo, amino-benzene, antipyrene sulfate</td>
<td>170–200</td>
</tr>
<tr>
<td>Chlorinated solvents</td>
<td>600–700</td>
</tr>
<tr>
<td>Various alcohols</td>
<td>2,500–3,000</td>
</tr>
<tr>
<td>Benzene, toluene</td>
<td>400–700</td>
</tr>
<tr>
<td>Sulfanilic acid</td>
<td>800–1,000</td>
</tr>
<tr>
<td>Sulfa drugs</td>
<td>400–700</td>
</tr>
<tr>
<td>Analogous substances</td>
<td>150–200</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>600–700</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>1,500–2,500</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>15,000–20,000</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>800–21,000</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>800–10,000</td>
</tr>
</tbody>
</table>

BOD, biochemical oxygen demand.
was found to be very low compared to other wastes. Acidic waste contributed 50% of the total waste flow at 600 m³/day and had a pH of 0.6. The combined waste had a pH of 0.8 (including acidic waste stream), whereas the pH of the waste without acidic waste stream was 9.3. The BOD to COD ratio of alkaline, condensate and combined wastewater was around 0.5–0.6, while for the acidic waste alone it was around 0.4, indicating that all these wastewaters are biologically treatable. The combined wastewater had average TOC, COD, and BOD values of 2109 mg/L, 4377 mg/L, and 2221 mg/L. Heavy metal concentration of the wastewater was found to be well below the limits according to IS-3306 (1974). Most of the solids present were in a dissolved form, with practically no suspended solids. The wastewater contained sufficient nitrogen, but was lacking in phosphorus, which is an essential nutrient for biological treatment. The 48-hour TLₘ values for alkaline and condensate wastes showed 0.73–2.1% (v/v) and 0.9% (v/v),

Table 4  Characteristics of Synthetic Organic Chemicals, Wastewater at Squibb, Inc., Humaco [12]

<table>
<thead>
<tr>
<th>Waste</th>
<th>Flow, g/day</th>
<th>BOD (mg/L)</th>
<th>COD (mg/L)</th>
<th>BOD load (lb/day)</th>
<th>COD load (lb/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong process</td>
<td>11,800</td>
<td>17,400</td>
<td>480,000</td>
<td>687,000</td>
<td>47,300</td>
</tr>
<tr>
<td>Dilute process</td>
<td>33,800</td>
<td>37,400</td>
<td>640</td>
<td>890</td>
<td>180</td>
</tr>
<tr>
<td>Service water</td>
<td>35,300</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Composite</td>
<td>80,900</td>
<td>–</td>
<td>70,365</td>
<td>109,585</td>
<td>47,500</td>
</tr>
</tbody>
</table>

BOD, biochemical oxygen demand; COD, chemical oxygen demand.

Table 5  Characteristics of Alkaline Waste Stream of a Synthetic Drug Plant at Hyderabad [13,15]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (m³/day)</td>
<td>1,400–1,920 (1.710)</td>
<td>1,710</td>
</tr>
<tr>
<td>pH</td>
<td>4.1–7.5</td>
<td>2.3–11.2</td>
</tr>
<tr>
<td>Total alkalinity as CaCO₃</td>
<td>1,279–2,140</td>
<td>624–5630</td>
</tr>
<tr>
<td>Total solids</td>
<td>1.29–2.55%</td>
<td>11825–23265 mg/L</td>
</tr>
<tr>
<td>Total volatile solids</td>
<td>13.1–32.6% of TS</td>
<td>1,457–2,389 mg/L</td>
</tr>
<tr>
<td>Total nitrogen (mg/L)</td>
<td>284–1,036 (TKN)</td>
<td>266–669</td>
</tr>
<tr>
<td>Total phosphorus (mg/L)</td>
<td>14–42</td>
<td>10–64.8</td>
</tr>
<tr>
<td>BOD₅ at 20°C (mg/L)</td>
<td>2,874–4,300</td>
<td>2,980–3,780</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>5,426–7,848</td>
<td>5,480–7,465</td>
</tr>
<tr>
<td>BOD : COD</td>
<td>–</td>
<td>0.506–0.587</td>
</tr>
<tr>
<td>BOD : N : P</td>
<td>–</td>
<td>100 : (8.9–17.7) : (0.265–1.82)</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>–</td>
<td>11–126</td>
</tr>
<tr>
<td>Chlorides as Cl⁻ (mg/L)</td>
<td>–</td>
<td>2,900–4,500</td>
</tr>
</tbody>
</table>

TS, total solids; TKN, total Kjeldhal nitrogen; BOD, biochemical oxygen demand; COD, chemical oxygen demand.
respectively. Table 9 gives the characteristics of a typical pharmaceutical industry wastewater located at Bombay producing various types of allopathic medicines [16].

### 5.3.3 Fermentation/Synthetic Organic Chemical Plants

These plants employ fermentation techniques as well as synthesis of organic chemicals in the manufacturing of various pharmaceuticals. Typically, they are operated on a batch basis via fermentation and organic synthesis, depending upon specific requirements of

#### Table 6 Characteristics of Condensate Waste Stream of a Synthetic Drug Plant at Hyderabad [13,15]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (m³/day)</td>
<td>1,570–2,225 (1,990)</td>
<td>1,570–2,225 (1,990)</td>
</tr>
<tr>
<td>pH</td>
<td>2.1–7.3</td>
<td>7–7.8</td>
</tr>
<tr>
<td>Total alkalinity as CaCO₃</td>
<td>498–603</td>
<td>424–520</td>
</tr>
<tr>
<td>Total solids</td>
<td>0.31–1.22%</td>
<td>2,742–4,150 mg/L</td>
</tr>
<tr>
<td>Total volatile solids</td>
<td>13.6–37.2% of TS</td>
<td>363–800 mg/L</td>
</tr>
<tr>
<td>Total nitrogen (mg/L)</td>
<td>120–240 (TKN)</td>
<td>120–131</td>
</tr>
<tr>
<td>Total phosphorus (mg/L)</td>
<td>2.8–5</td>
<td>3.1–28.8</td>
</tr>
<tr>
<td>BOD₅ at 20°C (mg/L)</td>
<td>1,275–1,600</td>
<td>754–1,385</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>2,530–3,809</td>
<td>1,604–2,500</td>
</tr>
<tr>
<td>BOD : COD</td>
<td></td>
<td>0.4–0.688</td>
</tr>
<tr>
<td>BOD : N : P</td>
<td>– 100 : (10.9–16.71) : (0.28–3.82)</td>
<td></td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>– 39–200</td>
<td></td>
</tr>
<tr>
<td>Chlorides as Cl⁻ (mg/L)</td>
<td>– 700–790</td>
<td></td>
</tr>
</tbody>
</table>

TS, total solids; TKN, total Kjeldhal nitrogen; BOD, biochemical oxygen demand; COD, chemical oxygen demand.

#### Table 7 Characteristics of an Acid Waste Stream of a Synthetic Drug Plant at Hyderabad [13]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ranges (max. to min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (m³/day)</td>
<td>435</td>
</tr>
<tr>
<td>pH</td>
<td>0.4–0.65</td>
</tr>
<tr>
<td>BOD₅ at 20°C (mg/L)</td>
<td>2,920–3,260</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>7,190–9,674</td>
</tr>
<tr>
<td>BOD/COD ratio</td>
<td>0.34–0.41</td>
</tr>
<tr>
<td>Total solids (mg/L)</td>
<td>18,650–23,880</td>
</tr>
<tr>
<td>Total volatile solids (mg/L)</td>
<td>15,767–20,891</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>Traces</td>
</tr>
<tr>
<td>Total nitrogen (mg/L)</td>
<td>352</td>
</tr>
<tr>
<td>Total phosphorus (mg/L)</td>
<td>9.4</td>
</tr>
<tr>
<td>Total acidity as CaCO₃</td>
<td>29,850–48,050</td>
</tr>
<tr>
<td>Chlorides as Cl⁻ (mg/L)</td>
<td>6,500</td>
</tr>
<tr>
<td>Sulfate as SO₄²⁻ (mg/L)</td>
<td>15,000</td>
</tr>
</tbody>
</table>

BOD, biochemical oxygen demand; COD, chemical oxygen demand.
various pharmaceuticals. Characteristics of the waste generated vary greatly depending upon the manufacturing process and raw materials used in the production of various medicines.

### 5.3.4 Biological Production Plants

These plants are mainly involved in the production of antitoxins, antisera, vaccines, serums, toxoids, and antigens. The production of antitoxins, antisera, and vaccines generates wastewaters containing animal manure, animal organs, baby fluid, blood, fats, egg fluid and egg shells, spent grains, biological culture, media, feathers, solvents, antiseptic agents, herbicidal components, sanitary loads, and equipment and floor washings. Overall, 180,000 G/day of waste is generated by biological production plants [17]. The various types of waste generated mainly include:

- waste from test animals;
- pathogenic-infectious waste from laboratory research on animal disease;
- toxic chemical wastes from laboratory research on bacteriological, botanical, and zoological problems;
- waste from antisera/antitoxins production;
- sanitary wastes.

Table 10 gives the characteristics of liquid waste arising in liver and beef extract production from a biological production pharmaceutical plant [18]. These wastes can be very high in BOD, COD, TS, colloidal solids, toxicity, color, and odor. The BOD/COD ratio of the

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### Table 8 Characteristics of Combined Wastewater\(^a\) of a Synthetic Drug Plant at Hyderabad [15]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.9–7.6</td>
<td>–</td>
</tr>
<tr>
<td>BOD(_3) at 20(°)C (mg/L)</td>
<td>1,840–2,835</td>
<td>2.221 ± 301</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>4,000–5,194</td>
<td>4.377 ± 338</td>
</tr>
<tr>
<td>BOD/COD ratio</td>
<td>0.46–0.54</td>
<td>–</td>
</tr>
<tr>
<td>Total organic carbon (C) (mg/L)</td>
<td>1,965–2,190</td>
<td>2,109 ± 73</td>
</tr>
<tr>
<td>BOD exertion rate ((k)) constant(^b)</td>
<td>0.24–0.36</td>
<td>0.28 ± 0.02</td>
</tr>
</tbody>
</table>

\(^a\)Alkaline and condensate wastewater mixed in 1:1 ratio.

\(^b\)BOD, biochemical oxygen demand; COD, chemical oxygen demand.

### Table 9 Characteristics of Pharmaceutical Industry Wastewater Producing Allopathic Medicines [16]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range of concentration</th>
<th>Average concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5–7.0</td>
<td>7</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>1,200–1,700</td>
<td>1,500</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>2,000–3,000</td>
<td>2,700</td>
</tr>
<tr>
<td>BOD/COD ratio</td>
<td>0.57–0.6</td>
<td>0.55</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>300–400</td>
<td>400</td>
</tr>
<tr>
<td>Volatile acids (mg/L)</td>
<td>50–80</td>
<td>60</td>
</tr>
<tr>
<td>Alkalinity as CaCO(_3) (mg/L)</td>
<td>50–100</td>
<td>60</td>
</tr>
<tr>
<td>Phenols (mg/L)</td>
<td>65–72</td>
<td>65</td>
</tr>
</tbody>
</table>
waste is around 0.66. The waste contains volatile matter as 95% of TS present in the waste, containing easily degradable biopolymers such as fats and proteins. Table 11 presents the characteristics of spent streams generated from a typical biological production plant, Eli Lilly and Co., at Greenfield, IN [19,20].

### Table 10 Characteristics of Liquid Waste Arising in Liver and Beef Extract Production from a Biological Production Pharmaceutical Wastewater [18]

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Range</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5–6.3</td>
<td>5.8</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>26.5–30</td>
<td>28</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>11,400–16,100</td>
<td>14,200</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>17,100–24,200</td>
<td>21,200</td>
</tr>
<tr>
<td>BOD/COD ratio</td>
<td>0.66–0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Total solids (TS) (mg/L)</td>
<td>16,500–21,600</td>
<td>20,000</td>
</tr>
<tr>
<td>Volatile solids (VS) (mg/L)</td>
<td>15,900–19,600</td>
<td>19,200</td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td>2,160–2,340</td>
<td>2,200</td>
</tr>
<tr>
<td>Crude fat (mg/L)</td>
<td>3,800–4,350</td>
<td>4,200</td>
</tr>
<tr>
<td>Volatile fatty acids (VFA) (mg/L)</td>
<td>1,060–1,680</td>
<td>1,460</td>
</tr>
</tbody>
</table>

BOD, biochemical oxygen demand; COD, chemical oxygen demand; TKN, total Kjeldhal nitrogen.

### Table 11 Characteristics of Typical Spent Stream of Biologicals Production Plant at Greenfield, IN [20]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (G/day)</td>
<td>15,000</td>
</tr>
<tr>
<td>pH</td>
<td>7.3–7.6</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>1,000–1,700</td>
</tr>
<tr>
<td>Total solids (TS) (mg/L)</td>
<td>4,000–8,500</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>200–800</td>
</tr>
<tr>
<td>Percentage suspended solids</td>
<td>5–10</td>
</tr>
</tbody>
</table>

BOD, biochemical oxygen demand.

5.3.5 Drug Mixing, Formulation, and Preparation Plants

Drug formulating processes consist of mixing (liquids or solids), palletizing, encapsulating, and packaging. Raw materials utilized by a drug formulator and packager may include ingredients such as sugar, corn syrup, cocoa, lactose, calcium, gelatin, talc, diatomaceous earth, alcohol, wine, glycerin, aspirin, penicillin, and so on. These plants are mainly engaged in the production of pharmaceuticals primarily of a nonprescription type, including medications for arthritis, coughs, colds, hay fever, sinus and bacterial infections, sedatives, digestive aids, and skin sunscreens. Wastewater characteristics of such plants vary by season, depending upon the production of medicines to meet seasonal demands. However, the waste can be characterized as being slightly acidic, of high organic strength (BOD, 750–2000 mg/L), relatively low in suspended solids (200–400 mg/L), and exhibiting a degree of toxicity. During the period when cough and cold medications are prepared, the waste may contain high concentrations of mono- and disaccharides and may be deficient in nitrogen [5]. A drug formulation plant usually operates a single shift, five days a week. Since drug formulating is labor-intensive, sanitary waste
constitutes a larger part of total wastes generated, therefore waste loads generated from such plants are very low compared to other subcategories of bulk pharmaceutical manufacturing plants.

5.4 SIGNIFICANT PARAMETERS IN PHARMACEUTICAL WASTEWATER TREATMENT

Significant parameters to be considered in designing a treatment and disposal facility for pharmaceutical wastewater are given in Table 12. Biochemical oxygen demand measurements of the waste have been reported to increase greatly with dilution, indicating the presence of toxic or inhibitory substances in some pharmaceutical effluents. The toxicity impact upon various biological treatments by various antibiotics, bactericidal-type compounds, and other pharmaceuticals has been described in the literature [21–24].

Discharge permits for pharmaceutical manufacturing plants place greater attention on high concentrations of ammonia and organic nitrogen in the waste. Considerable amounts of TKN (total Kjeldahl nitrogen) have been found to still remain in the effluent even after undergoing a high level of conventional biological treatment. It has also been reported that the nitrogen load of treated effluent may sometimes exceed even the BOD load. This generates an oxygen demand, increased chlorine demand, and formation of chloramines during chlorination, which may be toxic to fish life and create other suspected health problems. The regulatory authorities have limited the concentration of unoxidized ammonia nitrogen to 0.02 mg/L in treated effluent.

Certain pharmaceutical waste may be quite resistant to biodegradation by conventional biological treatment. For example, various nitroanilines have been used in synthesized production of sulfanilamide and phenol mercury wastes and show resistance against biological attack. Both ortho and meta nitroaniline were not satisfactorily degraded even after a period of many months [25]. Other priority pollutants such as tri-chloro-methyl-propional (TCMP) and toluene must be given attention in the treatment of pharmaceutical wastewater. With careful controls, \( p \)-nitroaniline can be biologically degraded, although the reaction requires many days for acclimatization [25,26].

<table>
<thead>
<tr>
<th>Table 12</th>
<th>Parameters of Significance for the Pharmaceutical Industry Wastewater [3]</th>
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</thead>
<tbody>
<tr>
<td>pH</td>
<td>Fecal coliform</td>
</tr>
<tr>
<td>Temperature</td>
<td>Manganese</td>
</tr>
<tr>
<td>BOD₅, BODUlt</td>
<td>Phenolics</td>
</tr>
<tr>
<td>COD</td>
<td>Chromium</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>Aluminum</td>
</tr>
<tr>
<td>TOC</td>
<td>Cyanides</td>
</tr>
<tr>
<td>Solids (suspended and dissolved)</td>
<td>Zinc</td>
</tr>
<tr>
<td>Oil and Grease</td>
<td>Lead</td>
</tr>
<tr>
<td>Nitrogen, (NH₄ and organic-N)</td>
<td>Copper</td>
</tr>
<tr>
<td>Sulfides</td>
<td>Mercury</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Iron</td>
</tr>
</tbody>
</table>

BOD, biochemical oxygen demand; COD, chemical oxygen demand; TOC, total organic carbon.
5.5 WASTE RECOVERY AND CONTROL

Production processes used in the pharmaceutical/fine chemical, cosmetic, textile, rubber, and other industries result in wastewaters containing significant levels of aliphatic solvents. It has been reported that of the 1000 tons per year of EC-defined toxic wastes generated in Ireland, organic solvents contribute 66% of the waste [27]. A survey of the constituents of pharmaceutical wastewater in Ireland has reported that aliphatic solvents contribute a significant proportion of the BOD/COD content of pharmaceutical effluents. Organic solvents are flammable, malodorous, and potentially toxic to aquatic organisms and thus require complete elimination by wastewater treatment systems.

Pretreatment and recovery of various useful byproducts such as solvents, acids, sodium sulfate, fermentation solids, and fermentation beers comprise a very important waste control strategy for pharmaceutical plants. Such an approach not only makes expensive biological treatment unnecessary, but also gives economic returns in recovery of valuable byproducts [19,21,28–33].

In fermentation plants, the spent fermentation broth contains considerable levels of solvents and mycelium. As mentioned earlier, these solvents exhibit very high BOD strength and also some of the solvents are not biologically degradable; hence, if not removed/recovered, the latter places a burden on the biological treatment of the waste and destroys the performance efficiency of biological treatment. Intense recovery of these solvents in fermentation processes is thus recommended as a viable option to reduce flow into pharmaceutical effluents. The mycelium, which poses several operational problems during treatment, can be recovered for use as animal feed supplements. Separate filtration, drying, and recovery of mycelium has been recommended as the best method for its use as animal feed or supplements. Moreover, spent fermentation broth contains high levels of nutrients and protein, which attains a high value when incorporated into animal feeds. Large-scale fermentation solids recovery is practiced at Abbott Labs, North Chicago, IL, and has been conducted at Upjohn Co., Kalamazoo, Michigan, and at Abbott Labs, Barceloneta, Puerto Rico [3].

Spent beers contain a substance toxic to the biological system and exhibit considerable organic strength; hence, it needs to be removed/recovered to avoid the extra burden on the biological treatment. Large-scale recovery of antibiotic spent beers by triple-effect evaporators was carried out at Upjohn Co., Kalamazoo, Michigan, in the 1950s. Biochemical oxygen demand reduction with the triple-effect evaporation system was reported to be 96 to 98% for four different types of antibiotic spent beers. A similar practice had been adopted by pharmaceutical plants Pfizer (Terre Haute, IN) and Lederle Labs (Pearl River, NY) for the recovery of spent beers in the 1950s and 1960s, but these practices have been discontinued due to changing products or other conditions.

From 1972 to 1973, Abbott Labs in North Chicago, IL, recovered beers with a BOD5 (five-day biological oxygen demand) load potential of 20,000 lb/day or greater. In the process, the spent beers were concentrated by multiple effect evaporators to 30% solids and the resulting syrup sold as a poultry feed additive. Any excess was incinerated in the main plant boilers. Abbott Labs reported that an average overall BOD reduction efficiency of the system up to 96% or more could be achieved.

Recovery of valuable products from penicillin, riboflavin, streptomycin, and vitamin B12 fermentation has been recommended as a viable waste control strategy when incorporated into animal feeds or supplements. Penicillin wastes, when recovered for animal feed, are reported to contain valuable growth factors, mycelium, and likewise evaporated spray-dried soluble matter [31,32,34].

Recovery of sodium sulfate from waste is an important waste control strategy within synthetic organic pharmaceutical plants. A sodium sulfate waste recovery system was employed
in the Hoffmann–La Roche (Belvidere, NJ) plant, which manufactured synthetic organic pharmaceuticals. In 1972, the company reported 80 tons/day of sodium sulfate recovery [3]. The recovery and subsequent sale of sodium sulfate not only gave an economic return, but also reduced the influent sulfate concentration that may otherwise cause sulfide toxicity in anaerobic treatment of the pharmaceutical effluents.

To use water efficiently, the cooling and jacketing tower water must be segregated from the main waste streams and should be recycled and reused in cooling towers. Scavenging and recovery of high-level ammonia waste streams is recommended as a viable option of ammonia recovery for waste streams containing high concentrations of ammonia nitrogen.

The recovery of alcohol by distillation, concentration of organics, and use of waste activated sludge as a soil conditioner and fertilizer has also been reported [35].

Based on extensive experience in wastewater reduction and recovery experience at Bristol Labs (Syracuse, NY) and at the Upjohn Company (Kalamzoo, Michigan), the following practices have been recommended for waste control and recovery of byproducts in pharmaceutical industries [8,9,36,37]:

1. Install stripping towers for solvent removal (recover solvents wherever possible);
2. Conduct a program of sampling and testing solvents on wastewater flows;
3. Collect and incinerate nonreusable combustible solvents and residues;
4. Remove all mycelium;
5. Carefully program dumping of contaminated or spoiled fermentation batches;
6. Eliminate all possible leakage of process materials;
7. Separate clean waters from contaminated wastewaters;
8. Collect and haul selected high organic wastes to land disposal or equivalent;
9. Recycle seal waters on a vacuumed pump system;
10. Improve housekeeping procedures.

5.6 TREATMENT OF PHARMACEUTICAL WASTEWATER

The pharmaceutical industry employs a wide array of wastewater treatment and disposal methods [3]. Wastes generated from these industries vary not only in composition but also in magnitude (volume) by plant, season, and even time, depending on the raw materials and the processes used in manufacturing of various pharmaceuticals. Hence it is very difficult to specify a particular treatment system for such a diversified pharmaceutical industry. Many alternative treatment processes are available to deal with the wide array of waste produced from this industry, but they are specific to the type of industry and associated wastes. Available treatment processes include the activated sludge process, trickling filtration, the powdered activated carbon-fed activated sludge process, and the anaerobic hybrid reactor. An incomplete listing of other treatments includes incineration, anaerobic filters, spray irrigation, oxidation ponds, sludge stabilization, and deep well injection. Based upon extensive experience with waste treatment across the industry, a listing of the available treatments and disposals is summarized as follows [3]:

- Separate filtration of mycelium, drying and recovery of fermentation broth and mycelium for use as animal feed supplements.
- Solvent recovery at centralized facilities or at individual sectors, reuse and/or incineration of collected solvents.
- Special recovery and subsequent sale of sodium sulfate.
- Cooling towers for reuse of cooling and jacketing waters.
Scavenging and recovery of high-level ammonia waste streams.

Elimination of barometric condensers.

Extensive holding and equalization of wastewater prior to main treatment.

Extensive neutralization and pH adjustment.

The activated sludge process including multiple-stage, extended aeration, the Unox pure oxygen system, aerated ponds, and other variations.

The trickling filter process, including conventional rate filters, multiple-stage, high-rate systems, and bio-oxidation roughing towers.

Treatment of selected waste streams by activated carbon, ion exchange, electromembranes, chemical coagulation, sand, and dual and multimedia filtration.

Spray irrigation of fermentation beers and other pharmaceutical wastes.

Collection of biological, synthetic organic, and pathogenic waste for incineration or disposal by separate means such as steam cooking and sterilization of pathogenic wastes.

Multiple effects evaporation–steam and/or oil, multiple hearth and rotary kiln incineration, and other special thermal oxidation systems.

Incineration of mycelium and excess biological sludge. Incineration system may also receive pathogenic wastes, unrecoverable solvents, fermentation broths or syrups, semi-solid and solid wastes, and so on. The system can be further integrated with the burning of odorous air streams.

Acid cracking at low pH.

Excess biological sludge can be handled by flotation, thickening, vacuum filtration, centrifugation, degasification, aerobic and/or anaerobic digestion, lagooning, drying, converting to useable product, incineration, land spreading, crop irrigation, composting, or land filling.

Chlorination, pasteurization, and other equivalent means of disinfecting final effluents. Disinfection is generally utilized inside vaccine-antitoxins production facilities, and in some cases dechlorination may be required.

Extensive air stream cleaning and treatment systems.

Municipal waste treatment.

The treatment options cited above are very specific to the type of waste. To have a clear understanding of the various unit operations used in the treatment and disposal of various types of wastes produced in the pharmaceutical industry, the treatment processes can be divided into the following three categories and subcategories:

1. physicochemical treatment process;
2. biological treatment process:
   (i) aerobic treatment,
   (ii) anaerobic treatment,
   (iii) two-stage biological treatment,
   (iv) combined treatment with other waste;
3. integrated treatment and disposal facility for a particular plant wastewater.

5.6.1 Physicochemical Treatment

Physicochemical treatment of pharmaceutical wastewater includes screening, equalization, neutralization/pH adjustment, coagulation/flocculation, sedimentation, adsorption, and ozone and hydrogen peroxide treatment. Detailed descriptions of the various physicochemical treatment processes are described in the following sections.
Extensive Holding and Equalization of Waste

As explained earlier, waste produced from the pharmaceutical industry varies in composition and magnitude depending upon various factors, that is, raw materials, manufacturing processes, process modifications, specific demand of seasonal medicines, and so on. Such variation in the quality and quantity of the wastewater may cause shock as well as underloading to the various treatment systems, which leads to malfunctioning or even failure of treatment processes, particularly biological treatment. To avoid these operational problems, extensive holding and equalization of wastewater is extremely important. Use of an equalization basin has been reported effectively to control shock loading on further treatment units treating the pharmaceutical waste [5]. The retention time and capacity of the holding tank in such cases is designed based on the degree of variability in composition and magnitude of the wastewater.

Neutralization/pH Adjustment

Wastewater generated from the pharmaceutical industry varies greatly in pH, ranging from acidic to alkaline. For example, the pH of an alkaline waste stream from a synthetic organic pharmaceutical plant ranges from 9 to 10, whereas a pH of 0.8 has been reported for acidic waste streams [13,15]. Nevertheless, almost all types of waste streams produced from the pharmaceutical industry are either alkaline or acidic, and require neutralization before biological treatment. Thus, neutralization/pH adjustment of the waste prior to the biological system is a very important treatment unit for the biological treatment of pharmaceutical wastewater. The pH of the wastewater in this unit is adjusted by adding alkali or acid depending upon the requirement of the raw wastewater.

Coagulation/Flocculation

Coagulation and flocculation of the wastewater are carried out for the removal of suspended and colloidal impurities. The application of such treatment units greatly depends upon the suspended and colloidal impurities present in the raw wastewater. Coagulation and flocculation of pharmaceutical wastewater have been reported to be less effective at a pharmaceutical plant in Bombay that produces allopathic medicines [16]. The effects of various coagulants such as FeSO₄, FeCl₃, and alum on suspended solids and COD removal efficiency were evaluated. The wastewater used in the study contained an average BOD of 1500 mg/L; COD, 2700 mg/L; phenol, 65 mg/L, and SS (suspended solids), 400 mg/L (Table 9). It was found that at the optimum doses of FeSO₄ (500 mg/L), FeCl₃, (500 mg/L), and alum (250 mg/L), the COD and SS removal efficiency was 24–28% and 70%, respectively. The study indicates that high doses of the coagulants were required, but the COD removal efficiency was marginal. Based on the above results, it was concluded that physicochemical treatment of effluent from this type of plant prior to biological treatment is neither effective nor economical [16]. A similar observation was made in a coagulation study of wastewater from the Alexandria Company for Pharmaceuticals and Chemical Industries (ACPCI) [38].

Air Stripping

Air stripping of pharmaceutical wastewater is a partial treatment used in particular for the removal of volatile organics from wastewater. M/S Hindustan Dorr Oliver, Bombay, in 1977 studied the effect of air stripping on the treatment of pharmaceutical wastewater and reported that a COD removal efficiency up to 30–45% can be achieved by air stripping. It was found that adding caustic soda did not appreciably increase the air stripping efficiency.
Ozone/Hydrogen Peroxide Treatment

Pharmaceutical wastewater contains various kinds of recalcitrant organics such as toluene, phenols, nitrophenols, nitroaniline, trichloromethyl propanol (TCMP), and other pollutants that exhibit resistance against biodegradation. Since these pollutants cannot be easily removed by biological treatment, biologically treated effluent exhibits a considerable oxygen demand, that is, BOD and COD, in the effluent. It has also been reported that activated carbon adsorption may not always be successful in removing such recalcitrant organics [39,40]. Economic constraints may also prohibit the treatment of pharmaceutical wastewater by activated carbon adsorption [41]. In such cases, ozone/hydrogen peroxide treatment may appear to be a proven technology for treating such pollutants from pharmaceutical wastewater.

The removal of organic 1,1,1-trichloro-2-methyl-2-propanol (TCMP), a common preservative found in pharmaceutical effluent, by ozone and hydrogen peroxide treatment has been studied [39]. Oxidation of TCMP was quite effective when it was contained in pure aqueous solutions, but almost nil when the same quantity of TCMP was present in pharmaceutical wastewater. Competitive ozonation of other organic solutes present inhibits the degradation of TCMP in pharmaceutical wastewater. Hence it has been concluded that for effective removal of TCMP by ozone/hydrogen peroxide, biological pretreatment of the wastewater for the removal of other biodegradable organics is crucial. It has been concluded that biological pretreatment of pharmaceutical wastewater before ozonation/hydrogen peroxide treatment should be utilized in order to increase the level of treatment.

5.6.2 Biological Treatment

The biological treatment of pharmaceutical wastewater includes both aerobic and anaerobic treatment systems. Aerobic treatment systems have traditionally been employed, including the activated sludge process, extended aeration activated sludge process, activated sludge process with granular activated carbon, or natural or genetically engineered microorganisms and aerobic fixed growth system, such as trickling filters and rotating biological contactors. Anaerobic treatment includes membrane reactors, continuously stirred tank reactors (anaerobic digestion), upflow filters (anaerobic filters), fluidized bed reactors, and upflow anaerobic sludge blanket reactors. Anaerobic hybrid reactors, which are a combination of suspended growth and attached growth systems, have recently become popular. Pharmaceutical/fine chemical wastewater presents difficult substrates for biological treatment due to their varying content of a wide range of organic chemicals, both natural and xenobiotic, which may not be readily metabolized by the microbial associations present in the bioreactors. Various processes dealing with the biological treatment of pharmaceutical wastewater are summarized in subsequent sections.

Activated Sludge Process

The activated sludge process has been found to be the most efficient treatment for various categories of pharmaceutical wastewater [14,15,19,42–46]. It has also been reported that this process can be successfully employed for the removal of tert-butanol, a common solvent in pharmaceutical wastewater that cannot be degraded by anaerobic treatment [44]. At a volumetric loading rate of 1.05 kg COD/m³ day, HRT (hydraulic retention time) of 17 hours, and mixed liquor dissolved oxygen concentration of 1 mg/dm³, the tert-butanol can be completely removed by the activated sludge process.

The activated sludge process has been successfully employed for the treatment of a wide variety of pharmaceutical wastewaters. The American Cynamid Company operated an activated sludge treatment plant to treat wastewater generated from the manufacture of a large variety of
The activated sludge process has also been successfully employed for the treatment of wastewater in the chemical and pharmaceutical industries [42]. M/S Hindustan Dorr Oliver of Bombay studied the performance of the activated sludge process for the treatment of wastewater from its plant in 1977, and concluded that at an MLSS (mixed liquor suspended solids) concentration of 1800–2200 mg/L and aeration period of 24 hours, a COD removal efficiency of 50–83% can be achieved.

The performance of the activated sludge process for the treatment of wastewater from a synthetic drug factory, has been reported [14,15,45]. One of the biggest plants of its kind in Asia, M/S Indian Drugs and Pharmaceutical Ltd., Hyderabad, went into production in 1966 to make sulfa drugs such as sulfanilamides: antipyretics (phenacetin), B-group vitamins, antitubercular drugs (isonicotinic acid hydrazide) and anthelminthics, and so on.

When the performance of the activated sludge process was first studied for the treatment of simulated pharmaceutical wastewater, it was found that the wastewater was biologically treatable and that this process can be successfully employed for treating wastewater from pharmaceutical plants [45]. Based on Mohanrao’s [14] recommendation, the performance of the activated sludge process for the treatment of actual waste streams generated from this plant, that is, alkaline waste, condensate waste, and a mixture of the two along with domestic sewage (1 : 2 : 1) as evaluated. Characteristics of various types of wastes used in the study are depicted in Table 13. The study demonstrated that condensate waste, as well as mixture, could be treated successfully, yielding an effluent BOD of less than 10 mg/L. However, the BOD removal efficiency of the system for the alkaline waste alone was found to be only 70%. The settleability of the activated sludge in all three units was found to be excellent, yielding a sludge volume index 23 and 45. The study indicated that biological treatability of the waste remained the same, although the actual waste was about 10 times diluted compared with the synthetic waste.

In 1984, the performance of a completely mixed activated sludge process for the treatment of combined wastewater was again evaluated. It was found that the activated sludge process was amenable for the treatment of combined wastewater from the plant, concluding that segregation and giving separate treatment for various waste streams of the plant would not be beneficial. The study was conducted at various sludge loading rates (0.14–0.16, 0.17–0.19, and 0.20–0.26 kg BOD/kg MLVSS (mixed liquor volatile suspended solids) per day and indicated that for the lower two loadings, effluent BOD was less than 50 mg/L, while for the other two higher loading

<table>
<thead>
<tr>
<th>Table 13</th>
<th>Characteristics of Alkaline and Condensate Wastes Generated from a Synthetic Drug Plant at Hyderabad [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>Alkaline waste</td>
</tr>
<tr>
<td>pH</td>
<td>Min. 8.6</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>1025</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>2475</td>
</tr>
<tr>
<td>COD/BOD</td>
<td>2.41</td>
</tr>
<tr>
<td>Total solids (%)</td>
<td>0.53</td>
</tr>
<tr>
<td>Volatile solids (% of TS)</td>
<td>29.3</td>
</tr>
<tr>
<td>Total nitrogen (mg/L)</td>
<td>–</td>
</tr>
<tr>
<td>Total phosphorus (mg/L)</td>
<td>–</td>
</tr>
</tbody>
</table>

TS, total solids; BOD, biochemical oxygen demand; COD, chemical oxygen demand.
effluents BOD was less than 100 mg/L. The average TOC, COD, and BOD reductions were around 80, 80, and 99% respectively. The settleability of the activated sludge was found to be excellent with an SVI of 65–72 [15].

A similar study was conducted at Merck & Co. (Stonewall Plant, Elkton, Virginia) to assess the feasibility of the activated sludge process for treating wastewater generated from this plant. This plant is one of the six Merck Chemical Manufacturing Division facilities operated on a batch basis for fermentation and organic synthesis and has been in operation since 1941. A bench-scale study revealed that a food to microorganism (F/M) ratio from 0.15 to 0.25, MLVSS of 3500 mg/L, HRT 4 days, and minimum DO (dissolved oxygen) concentration of 3 mg/L were essential for meeting the proposed effluent limits and maintaining a viable and good settling sludge in the activated sludge process [46]. Based on these design criteria, a pilot plant and full-scale system were designed and studied. The old treatment plant consisted of an equalization basin, neutralization, primary sedimentation, roughing biofilter, activated sludge system, and rock trickling filter with final clarifiers. In the proposed study, the old activated sludge system, rock filter, and final clarifier were replaced with a new single-stage, nitrification-activated sludge system. A schematic diagram of the pilot plant is presented in Figure 1. The study demonstrated that BOD₅ removal efficiencies of the pilot and bench-scale plant were 94 and 98%, respectively. The TKN and NH₄-N removal were found to be 65 and 59%, respectively. It has also been observed that system operation was stable and efficient at F/M ratios ranging from 0.19 to 0.30, but prolonged operation at an F/M ratio less than 0.15 led to an episode of filamentous bulking.

The performance of the activated sludge process has been evaluated for the treatment of ACPCI (Alexandria Company for Pharmaceutical and Chemical Industry) effluent. These drug formulation and preparation-type plants are mainly involved in the production of a wide variety of pharmaceuticals, including analgesics, anthelmintics, antibiotics, cardiacs, chemotherapeutics, urologics, and vitamins. A study indicated that significant dispersed biosolids were found in the treated effluent when applying aeration for 6 hours. However, extending the aeration to 9–12 hours and maintaining the MLSS at levels higher than 2500 mg/L improved sludge
settling and produced effluent with low SS. The study concluded that the activated sludge process is capable of producing effluent with BOD and SS values within the limits of the Egyptian standards. However, sand filtration was needed for polishing the treated effluent [38].

**Powdered Activated Carbon Activated Sludge Process**

Various researchers [47,48] have investigated the effect of powdered activated carbon (PAC) on the performance of the activated sludge process for the treatment of pharmaceutical wastewater. Various treatment units such as the activated sludge process (ASP), PAC-ASP, granular activated carbon (GAC), and a resin column were studied and compared in removing priority pollutants from a pharmaceutical plant’s wastewater [47]. The wastewater generated from the plant contained 0-nitroaniline (0-NA), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 1,1,2-trichloroethane (TCE), 1,1-dichloroethylene (DCE), phenol, various metals, and other organics. Characteristics of the wastewater collected from the holding pond are given in Table 14. The study concluded that there are treatment processes available that can successfully remove the priority pollutants from pharmaceutical wastewater. The treatment systems, ASP, PAC-ASP, and GAC, were all quite efficient in removing phenol, 2-NP, and 4-NP, while the resin column was found unable to treat phenol. However, 2-NP and 4-NP can be treated to a certain extent (72 and 65%, respectively). The author further concluded that 1,1,2-dichloroethane and 1,1-dichloroethylene can be treated successfully by all four treatment systems, but the efficiency of the resin column and GAC exceeded the other two systems. In terms of TOC removal, ASP and PAC-ASP were found to be more efficient than either GAC or the resin column. However, the performance of the PAC-fed ASP was found to be most efficient. In terms of color removal, PAC, GAC, and the resin process were more efficient than ASP, whereas in terms of arsenic removal, GAC and resin column were found most efficient. The performance summary of various treatment systems is given in Table 15. In general, it may be concluded that the addition of PAC in the ASP produced a better effluent than the ASP.

Addition of PAC to the activated sludge process increases the soluble chemical oxygen demand (SCOD) removal from the pharmaceutical wastewater but no measurable effect in terms

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average</th>
<th>Ranges (min.–max.)</th>
</tr>
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<tbody>
<tr>
<td>Color</td>
<td>4,648</td>
<td>1,800–6,600</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>234</td>
<td>47–2,700</td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>152</td>
<td>17–1,910</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>387</td>
<td>205–630</td>
</tr>
<tr>
<td>Arsenic (mg/L)</td>
<td>5.82</td>
<td>4–12</td>
</tr>
<tr>
<td>o-Nitraniline (ONA) (μg/L)</td>
<td>12,427</td>
<td>3,200–30,500</td>
</tr>
<tr>
<td>Phenol (μg/L)</td>
<td>1.034</td>
<td>&lt;10 to 3,700</td>
</tr>
<tr>
<td>2-NP (μg/L)</td>
<td>1.271</td>
<td>&lt;10 to 2,900</td>
</tr>
<tr>
<td>4-NP (μg/L)</td>
<td>635</td>
<td>&lt;10 to 2,300</td>
</tr>
<tr>
<td>TCE (μg/L)</td>
<td>4,080</td>
<td>620–6,550</td>
</tr>
<tr>
<td>DCE (μg/L)</td>
<td>291</td>
<td>&lt;10 to 1,060</td>
</tr>
</tbody>
</table>

TSS, total suspended solids; VSS, volatile suspended solids; 4-NP, 4-nitrophenol; 2-NP, 2-nitrophenol; TCE, 1,1,2-trichloroethane; DCE, 1,1-dichloroethylene; TOC, total organic carbon.
of soluble-carbonaceous biochemical oxygen demand (S-CBOD) was observed [48]. Moreover, addition of PAC increased the sludge settleability, but the MLSS settling rate remained at a very low level (0.01 to 0.05 cm/min) and resulted in a viscous floating MLSS layer at the surface of the activated sludge unit and clarifier. This study concluded that a PAC-fed ASP cannot be recommended as a viable option for this plant wastewater until the cause of the viscous floating MLSS layer is identified and adequate safeguards against its occurrence are demonstrated. The relationship to estimate the dose of activated carbon required for producing a desired quality of the effluent is given in Eq. (1).

$$\frac{X}{M} = 3.7 \times 10^{-7} C_e^{2.1}$$  

(1)

where $X$ is the amount of SCOD removal attributed to the PAC (mg/L), $M$ is the PAC dose to the influent (mg/L), and $C_e$ is the equilibrium effluent SCOD concentration (mg/L).

### Extended Aeration

The performance of the ASP has been found to be more efficient when operating on an extended aeration basis. The design parameters of the process were evaluated for the treatment of combined wastewater from a pharmaceutical and chemical company in North Cairo that produced drugs, diuretics, laboratory chemicals, and so on [49]. The study revealed that at an extended aeration period of 20 hours, COD and BOD removal efficiency ranges of 89–95% and 88–98%, respectively, can be achieved. The COD and BOD values of the treated effluent were found to be 74 mg/L and 43 mg/L, respectively.

In contrast, the performance of an extended aeration system for the treatment of pharmaceutical wastewater at Lincoln, Nebraska, was poor. At an organic loading of 30 kg BOD/day and a detention period of 25 hours, the percentage BOD reduction ranged from 30 to 70%. The degree of treatment provided was quite variable and insufficient to produce a satisfactory effluent. The pilot plant study performed at various feeding rates of 1.5, 2.4, 3.0, 3.6, and 4.8 L/12 hours indicated that at feeding rate of 4.8 L/12 hours, the sludge volume index was 645 and suspended solids were being carried over in the effluent.
Oxidation Ditch
The performance of an oxidation ditch for treating pharmaceutical wastewater has been evaluated and described by many researchers [16,50]. Treatability of wastewater from a typical pharmaceutical industry at Bombay producing various types of allopathic medicines was studied in an oxidation ditch at HRTs ranging from 1 to 3 days, corresponding to an SRT (solid retention time) of 8–16 days. The average MLVSS concentration in the reactor varied from 3000 to 4800 mg/L during the investigation period. The study indicated that on average about 86–91% of influent COD and 50% of phenols could be removed by this process [16].

A pilot-scale oxidation ditch was evaluated for the treatment of pharmaceutical wastewater at a Baroda unit. The treatment system was comprised of neutralization followed by clarifier and oxidation ditch. Primary treatment of the wastewater using neutralization with lime followed by sedimentation in a clarifier demonstrated SS and BOD removal of 30–41% and 28–57%, respectively. The effluent from the clarifier was further treated in an oxidation ditch operating on an extended aeration basis. It was found that at loading of 0.1–0.5 lb BOD/lb MLSS/day, an MLSS concentration of 3000–4000 mg/L, and aeration period of 22 hours, a BOD removal up to 70–80% could be achieved. The high COD of treated effluent indicated the presence of organic constituents resistant to biodegradation. Considering the high COD/BOD ratio of the wastewater, it has been suggested that the biological treatment should be supplemented with chemical treatment for this type of plant wastewater [50].

Aerated Lagoon
The performance studies of aerated lagoons carried out by many researchers [14,51] have demonstrated that lagoons are capable of successfully treating wastewater containing diversified fine chemicals and pharmaceutical intermediates.

A laboratory-scale study of alkaline and condensate waste streams from a synthetic drug factory at Hyderabad demonstrated that an aerated lagoon is capable of treating the wastewater from this industry [14]. The BOD removal rate $K$ of the system was found to be 0.18/day and 0.155/day based on the soluble and total BOD, respectively. Based on the laboratory studies, a flow sheet (Fig. 2) for the treatment of waste was developed and recommended to the factory.

Trickling Filter
The performance of a trickling filter has been studied by many researchers [14,38,49,51–53] and it was found that a high-rate trickling filter was capable of treating wastewater containing diversified fine chemicals and pharmaceutical intermediates to a level of effluent BOD less than 100 mg/L [51]. A similar conclusion was made in the performance study of a trickling filter for the treatment of wastewater from chemical and pharmaceutical units [53].

It has also been reported that wastewater from a pharmaceutical plant manufacturing antibiotics, vitamins, and sulfa drugs can be treated by using a trickling filter [52]. One study evaluated the efficiency of a sand bed filter for the treatment of acidic waste streams from a synthetic organic pharmaceutical plant at Hyderabad. The acidic waste stream was neutralized to a pH of 7.0 and treated separately through a sand bed filter. The sand bed filter was efficient in treating the acidic waste stream to a level proposed for its discharge to municipal sewer [14].

The efficiency of the biological filter (trickling filter) for treatment of combined wastewater from a pharmaceutical and chemical company in North Cairo has been evaluated. The treatment system consisted of a biological filter followed by sedimentation. The degree of treatment was found quite variable. The COD and BOD removal efficiencies of the trickling filter at an average OLR (organic loading rate) of 26.8 g BOD/m² day were found to be 43–88%.
Figure 2  Flow sheet for treatment of synthetic drug waste.
and 58–87%, respectively. The study revealed that a biological filter alone was unable to produce effluents to a level complying with the national standards regulating wastewater disposal into the surface water [49].

Similar conclusions were made in the treatment of ACPCI effluent using a biofilter. The low performance efficiency and presence of dispersed biosolids in the effluent have made the trickling filter unsuitable for the treatment of this plant wastewater [38].

Anaerobic Filter

The anaerobic filter has been reported to be a promising technology for the treatment of wide varieties of pharmaceutical wastewater [4,10,54–59]. The performance of the anaerobic filter was first studied at a pharmaceutical plant in Springfield, Missouri [54]. The characteristics of the waste fed into the reactor are given in Table 16. The treatability study revealed that at an HRT of two days, an OLR ranging from 0.37 to 3.52 kg COD/m³ day, and influent COD concentration ranging from 1000 to 16,000 mg/L, COD removal efficiencies of 93.7 to 97.8% can be achieved. Moreover, the problem of sludge recycling and sludge disposal in the case of the anaerobic filter can be reduced to a great extent due to the much smaller biomass yield, that is, 0.027 g VSS (volatile suspended solids)/g COD removed. The shock loading study revealed that shock increase in organic loading did not result in a failure of the capability of the filter to treat the waste. This is a distinct feature of anaerobic filters, especially when dealing with pharmaceutical wastewater, which is supposed to cause shock loading due to frequent variation in composition as well as in magnitude of the waste load. In contrast, it has been reported that the

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.5–10.1</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>15,950–16,130</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>28–32</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>432–565</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>412–540</td>
</tr>
<tr>
<td>Nitrogen (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>0–11.8</td>
</tr>
<tr>
<td>Organic</td>
<td>33.3–34.2</td>
</tr>
<tr>
<td>Phosphorus (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Ortho</td>
<td>0.4–0.5</td>
</tr>
<tr>
<td>Total</td>
<td>0.9–0.95</td>
</tr>
<tr>
<td>Heavy metals (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>0.005–0.007</td>
</tr>
<tr>
<td>Copper</td>
<td>0.140</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.018–0.11</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.020–0.22</td>
</tr>
<tr>
<td>Iron</td>
<td>0.05–0.56</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.020–0.01</td>
</tr>
<tr>
<td>Calcium</td>
<td>9.7–58.7</td>
</tr>
<tr>
<td>Magnesium</td>
<td>7.5–14.7</td>
</tr>
</tbody>
</table>

COD, chemical oxygen demand; SS, suspended solids; TS, total solids.

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anaerobic filter fed with pharmaceutical wastewater containing high ammonia nitrogen could not withstand a three-fold increase in OLR [55]. It has been further concluded that the amber color of the untreated waste can be removed through treatment, but due to poor degradability of the odor-producing toluene, the effluent maintained the tell-tale odor of toluene, indicating that it passed through the filter with little or no treatment.

The suitability of the anaerobic filter for treatment of wastewater from a chemically synthesizing pharmaceutical industry has been studied [10]. Characteristics of the strong waste stream used in the study are given in Table 17. The study revealed that at an HRT of 48 hours and COD concentration of 1000 mg/L, waste can be treated at least to a level of treatment generally occurring when employing aerobic treatment. Moreover, methane-rich biogas is generated in this treatment, which can be utilized later as an energy source. Thus the use of an anaerobic filter system would be a net energy producer rather than an energy consumer as in the case of current aerobic systems. In addition, the effluent from this system was found to contain far less color than the effluent from the existing system.

The performance of an anaerobic mesophilic fixed film reactor (AMFFR) and an anaerobic thermophilic fixed film reactor (ATFFR) for the treatment of pharmaceutical wastewater of a typical pharmaceutical plant at Mumbai was studied and compared [56]. The study revealed that at an OLR of 0.51 kg/m³ day and HRT of 4.7 days, the COD removal efficiency of mesophilic was superior (97%) to the thermophilic reactor (89%). The effect of organic loading and reactor height on the performance of anaerobic mesophilic (30°C) and thermophilic (55°C) fixed film reactors have demonstrated that the AMFFR can take a load of several orders of magnitude higher, with higher removal efficiency compared to the ATFFR for pharmaceutical wastewater [56]. Wastewater used in the study was collected from an equalization tank of the pharmaceutical industry treatment plant at Bombay. The characteristics of the wastewater are given in Table 18. The start-up study has indicated that a starting-up period for the AMFFR (four months) was far less than the starting-up period for the ATFFR (six months). The gas production and methane percentage were also found to be higher in the AMFFR compared to the ATFFR. The effective height of the reactor was found to be in the range of 30–90 cm. Other researchers [10,54,55,58,59] have reported a similar effective height range of 15–90 cm. They have

**Table 17** Characteristics of a Concentrated Waste Stream of Synthesized Organic Chemicals—Type Pharmaceutical Industry [10]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sample 1 (28-02-76)</th>
<th>Sample 2 (20-04-76)</th>
<th>Sample 3 (10-10-76)</th>
<th>Sample 4 (20-11-76)</th>
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</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.6</td>
<td>3.5</td>
<td>2.2</td>
<td>1.6</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>Varies</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>514,900</td>
<td>533,000</td>
<td>89,000</td>
<td>62,530</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>37,740</td>
<td>38,520</td>
<td>13,090</td>
<td>5,190</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>37,650</td>
<td>38,420</td>
<td>13,030</td>
<td>5,180</td>
</tr>
<tr>
<td>TVSS (mg/L)</td>
<td>18,880</td>
<td>19,070</td>
<td>5,180</td>
<td>2,090</td>
</tr>
<tr>
<td>Dissolved volatile solids (mg/L)</td>
<td>18,800</td>
<td>18,980</td>
<td>5,120</td>
<td>2,080</td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td>19.3</td>
<td>25.8</td>
<td>23.0</td>
<td>33.6</td>
</tr>
<tr>
<td>NH₄⁻N (mg/L)</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>–</td>
<td>–</td>
<td>75.0</td>
<td>183</td>
</tr>
<tr>
<td>Total phosphorous (mg/L)</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>

BOD, biochemical oxygen demand; COD, chemical oxygen demand; TS, total solids; TDS, total dissolved solids; TVSS, total volatile suspended solids; TKN, total Kjeldhal nitrogen; BDL, below detectable limit.

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reported that rapid change in most of the characteristics occurs only in the lower portion of the reactor.

**Two-Stage Biological System**

The two-stage biological system generally provides a better quality of effluent than the single-stage biological system for the treatment of pharmaceutical wastewater. It has been reported that a single-stage biological system such as activated sludge process and trickling filter alone is not capable of treating the wastewater to the effluent limit proposed for its safe discharge to inland surface water [49]. However, the combined treatment using a two-stage aerobic treatment system is efficient in treating wastewater to a level complying with national regulatory standards. A performance study of a two-stage biological system for the treatment of pharmaceutical wastewater generated from Dorsey Laboratories Plant

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Concentration range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.5–9.2</td>
<td>7.2</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1,200–7,000</td>
<td>2,500</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>30–55</td>
<td>40</td>
</tr>
<tr>
<td>Total alkalinity as CaCO3 (mg/L)</td>
<td>70–1,500</td>
<td>750</td>
</tr>
<tr>
<td>TVA (mg/L)</td>
<td>70–2,000</td>
<td>750</td>
</tr>
<tr>
<td>NH4⁺-N (mg/L)</td>
<td>80–500</td>
<td>200</td>
</tr>
<tr>
<td>PO₄³⁻-P (mg/L)</td>
<td>3.5–35</td>
<td>16</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>100–700</td>
<td>300</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>500–1,200</td>
<td>900</td>
</tr>
<tr>
<td>Sulfide (mg/L)</td>
<td>2–8</td>
<td>5</td>
</tr>
<tr>
<td>Cobalt (mg/L)</td>
<td>0–0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Potassium (mg/L)</td>
<td>5–25</td>
<td>18</td>
</tr>
<tr>
<td>Lead (mg/L)</td>
<td>0.05–0.9</td>
<td>0.35</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
<td>0.2–0.9</td>
<td>0.45</td>
</tr>
<tr>
<td>Zinc (mg/L)</td>
<td>0.05–0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>Chromium (mg/L)</td>
<td>0.1–0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Mercury (mg/L)</td>
<td>0.15–0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>Copper (mg/L)</td>
<td>0–0.10</td>
<td>0.1</td>
</tr>
<tr>
<td>Cadmium (mg/L)</td>
<td>0.07–0.25</td>
<td>0.10</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>200–3,000</td>
<td>2,000</td>
</tr>
<tr>
<td>Manganese (mg/L)</td>
<td>0.1–0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Silicon (mg/L)</td>
<td>5–50</td>
<td>25</td>
</tr>
<tr>
<td>Magnesium (mg/L)</td>
<td>5–60</td>
<td>40</td>
</tr>
<tr>
<td>Tin (mg/L)</td>
<td>0.1–1.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Aluminum (mg/L)</td>
<td>0.05–0.20</td>
<td>0.10</td>
</tr>
<tr>
<td>Barium (mg/L)</td>
<td>0.1–0.3</td>
<td>0.16</td>
</tr>
<tr>
<td>Arsenic (mg/L)</td>
<td>0.1–0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>Bismuth (mg/L)</td>
<td>0.09–0.3</td>
<td>0.15</td>
</tr>
<tr>
<td>Antimony (mg/L)</td>
<td>0.50–3.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Selenium (mg/L)</td>
<td>0.1–0.95</td>
<td>0.38</td>
</tr>
</tbody>
</table>

TVA, total volatile acid; COD, chemical oxygen demand; TSS, total suspended solids.
drug mixing and formulation type plant) at Lincoln, Nebraska, was carried out and the following conclusions drawn:

- Shock organic and hydraulic loading created serious operational problems in the system. Bulking sludge and the inability to return solids from the clarifier to the aeration unit further complicated plant operation.
- Microscopic observations of the sludge flock showed the presence of filamentous organisms, *Sphaerotilus natans*, in high concentrations. The presence of these organisms was expected to be due to deficiency of the nitrogen in the wastewater.

To overcome the problem of sludge bulking, nitrogen was supplemented in the wastewater as ammonium sulfate, but operational problems continued even after nitrogen was added. Hence, to avoid shock loading on the treatment, the effluent treatment plant (ETP) was expanded. The expanded treatment system (Fig. 3) consists of a communicator, basket screen, equalization basin, biological tower, activated sludge process, disinfection, and filtration. The study indicated that the equalization basin and biological tower effectively controlled shock loading on the activated sludge process. Overall, BOD and COD removal of 96 and 88%, respectively, may be achieved by employing a two-stage biological system [5]. It has also been found that a two-stage biological system generally provides a high degree of treatment. However, bulking sludge causes severe operational problems in the extended aeration system and sand filter.

A two-stage biological treatment system consisting of anaerobic digestion followed by an activated sludge process was developed for the treatment of liquid waste arising from a liver and beef extract production plant. Being rich in proteins and fats, the waste had the following characteristics: pH, 5.8; COD, 21,200 mg/L; BOD, 14,200 mg/L; and TS, 20,000 mg/L. The treatability study of the waste in anaerobic digestion revealed that at an optimum organic loading rate of 0.7 kg COD/m^3^ day and an HRT of 30 days, a COD and BOD removal efficiency of 89 and 91% can be achieved [18]. The effluent from anaerobic digestion still contains a COD of 2300 mg/L and BOD of 1200 mg/L. The effluent from anaerobic digestion was settled in a primary settling tank. At an optimum retention time of 60 minutes in the settling tank, the percentage COD and BOD removal increased to 94 and 95%, respectively. The effluent from the settling tank was then subjected to the activated sludge process. At an optimum HRT of 4 days, the COD and BOD removal increased to 96 and 97%, respectively. The effluent from the activated sludge process was settled for 1 hour in a secondary settling tank, which gave an increase in COD and BOD removal to 98 and 99%, respectively. The study therefore revealed that the combination of anaerobic–aerobic treatment resulted in an overall COD and BOD reduction of 98 and 99%, respectively. The final effluent had a COD of 290 mg/L and BOD of 50 mg/L, meeting the effluent standard for land irrigation.

The performance of two-stage biological systems was examined for the treatment of wastewater from a pharmaceutical and chemical company in North Cairo. A combined treatment using an extended aeration system (20 hour aeration) or a fixed film reactor (trickling filter) followed by an activated sludge process (11 hour detention time) was found efficient in treating the wastewater to a level complying with national regulatory standards. From a construction cost point of view, the extended aeration system followed by activated sludge process would be more economical than the fixed film reactor followed by activated sludge process. The flow diagrams of the two recommended alternative treatment processes for the treatment of this plant wastewater are depicted in Figure 4 and Figure 5, respectively [49].

Anaerobic treatment of high-strength wastewater containing high sulfate poses several unique problems. The conversion of sulfate to sulfide inhibits methanogenesis in anaerobic treatment processes and thus reduces the overall performance efficiency of the system. Treatment of high sulfate pharmaceutical wastewater via an anaerobic baffled reactor coupled
Figure 3  Flow diagram of wastewater treatment plant at Dorsey Laboratory.
Figure 4  Flow diagram for treatment process using activated sludge, extended aeration.
Figure 5  Flow diagram for treatment process using biological filters followed by activated sludge process.
with biological sulfide oxidation was carried out and evaluated. The schematic view of the combined treatment system is given in Fig. 6. The wastewater used in the study contained isopropyl acetate, sulfate, and cellular product. The COD and sulfate concentration of the wastewater were 40,000 mg/L and 5000 mg/L, respectively. Treatment of the wastewater using an anaerobic baffled reactor alone was found effective at 10% dilution but at higher concentration, sulfide inhibition reduced the efficiency of both COD conversion and sulfate conversion. To reduce sulfide inhibition, the treated effluent was subjected to a thin film sulfide oxidizing reactor to facilitate biological oxidation of sulfide into elemental sulfur. The study indicated that at an influent concentration of 40% and HRT of 1 day, COD removal efficiencies greater than 50% can be achieved. The conversion of influent sulfate was greater than 95% with effluent sulfide concentration less than 20 mg/L [60]. Coupled anaerobic/aerobic treatment of high sulfate-containing wastewater effectively alleviated the sulfide inhibition of both methanogenesis and sulfate reduction. A thin film sulfide oxidizing reactor was also effective in converting the sulfide to elemental sulfur without adding excess oxygen, which made recycling of treated anaerobic effluent through the sulfide oxidizing reactor feasible. This indicates that biological sulfide oxidation could provide an alternative method to remove sulfide produced during anaerobic treatment, thereby alleviating sulfide inhibition by removing sulfur from the wastewater stream.

**Anaerobic Hybrid Reactor**

The anaerobic hybrid reactor is generally a combination of suspended growth and attached growth systems. Recently, this technology has become popular in the treatment of industrial wastewater, in particular in cases of high-strength wastewater. It has been reported that this
reactor design presents a viable alternative to continuously stirred reactors, anaerobic filters, and anaerobic fluidized bed reactors for the high-rate treatment of pharmaceutical wastewater containing C₃ and C₄ aliphatic alcohol and other solvents [44]. The suitability of an anaerobic hybrid reactor for the treatment of synthetic pharmaceutical wastewater containing target solvents C₃ and C₄, tert-butanol, sec-butanol, and ethyl acetate was assessed at various organic loadings and varying influent concentrations. The study indicated that isopropanol, isobutanol, and sec-butanol can be almost fully degraded by using the anaerobic hybrid reactor. At OLR ranging from 3.5 to 4.5 kg COD/m³ day and HRT of 2 days, the reactor achieved total and soluble COD removal efficiencies of 97 and 99%, respectively. However, the reactor was unable to degrade the tert-butanol, resulting in a decrease in soluble COD removal efficiency to 58%. A bacterial enrichment study with the tert-butanol as a sole substrate indicated that this is poorly degradable in anaerobic conditions. The observed recalcitrance of the tert-butanol in the present case contrasts with the findings of earlier researchers, who have listed these solvents as being amenable to anaerobic digestion [61,62]. Degradation of tert-butanol in the activated sludge process has been evaluated, and it was found that aerobic posttreatment/polishing of the anaerobically treated effluent of pharmaceutical wastewater is essential for removing the residual solvent [43]. The addition of a trace metals cocktail in the feed did not affect steady-state reactor performance, but was found beneficial in handling the influent compositional changes. Moreover, the methanogenic activity of the granular sludge fed with trace metals was found significantly higher than the granular sludge of the reference anaerobic hybrid reactor.

Combined Waste Treatment with Other Industrial Waste

The possibility of treatment of pharmaceutical wastewater combined with other industrial waste has been explored and evaluated [63]. One study carried out nitrification of high-strength nitrogenous wastewater (a concentrated stream from a urea plant) in a continuously stirred tank reactor. Pharmaceutical wastewater was used as an organic carbon source to maintain a COD/TKN ratio of 1. The reactor was operated at an HRT of 1.5–2.1 days and solid retention time (SRT) ranging from 10–62.5 days. Characteristics of the wastewater from the urea plant, pharmaceutical wastewater, and combined wastewater are depicted in Table 19. The study concluded that pharmaceutical wastewater may be used as a co-substrate to supply energy for nitrification of high-strength nitrogenous wastewater. Such treatment alternatives establish the advantages of a dual mechanism of treatment, that is, nitrification as well as oxidation of organic pollutants.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Urea plant</th>
<th>Pharmaceutical plant</th>
<th>Combined wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11.0–12.5</td>
<td>5.0–8.0</td>
<td>7.0–9.0</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>3,520–4,850</td>
<td>1,100–5,500</td>
<td>1,010–1,290</td>
</tr>
<tr>
<td>Alkalinity as CaCO₃ (g/L)</td>
<td>1.005–1.010</td>
<td>0.30–2.0</td>
<td>4.4–5.45</td>
</tr>
<tr>
<td>PO₄³⁻-P (mg P/L)</td>
<td>0.7–1.0</td>
<td>2.8–14.4</td>
<td>22.8</td>
</tr>
<tr>
<td>NH₄⁻-N (mg N/L)</td>
<td>38,000–45,000</td>
<td>30–50</td>
<td>500–550</td>
</tr>
<tr>
<td>Urea-N (mg N/L)</td>
<td>1,860–2,380</td>
<td>–</td>
<td>500</td>
</tr>
</tbody>
</table>

COD, chemical oxygen demand.

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5.6.3 Integrated Treatment and Disposal Facilities for Specific Pharmaceutical Waste

The above-cited studies demonstrate the performance of a particular unit system for the treatment of specific type of waste stream. A particular unit system alone may not be able to treat the wastewater to a level of effluent standard prescribed for its safe disposal. Hence a number of pretreatments, such as screening, sedimentation, equalization, and neutralization, and post-treatment units such as secondary sedimentation, sludge thickening, digestion and disposal, disinfection, and so on, are extremely important for complete treatment. The effluent treatment and disposal facilities adopted by various types of pharmaceutical industries are described in the following sections.

Treatment of Synthetic Organic Bulk Pharmaceutical Waste

The Hoffman–La Roche plant in Belvedere, NJ, manufactures synthetic organic bulk pharmaceuticals, including dry vitamin powders, sulfa drugs, vitamin C, riboflavin, aromatics, and sodium sulfate salts. An integrated sodium sulfate recovery system was employed in this plant to recover sodium sulfate. The plant’s waste control and treatment system includes screening, preclarifier, equalization with aeration (1 day detention time), pH adjustment/neutralization, flocculator-clarifier, activated sludge process, secondary settler, two oxidation ponds in series, sludge thickening, aerobic sludge digestion, sludge drying beds, and final chlorination. The treatment plant was initially designed for a design flow of 1 MGD (million gallons per day) with BOD<sub>5</sub> and TSS removal efficiency of the system at 97.4 and 98%, respectively. Effluent from this plant had a BOD<sub>5</sub> of 50 mg/L and TSS of 20 mg/L. In 1973, the raw waste load at the plant increased from 1 MGD to 1.6 MGD with BOD load of 30,000 lb/day or more, together with 8400 lb/day of TSS. By late 1973, the effluent load was about twice the design specification. Although data on the performance of the treatment plant for the current waste loads (1973, 1974) were lacking, the author has indicated a typical removal of BOD, COD, and TSS of 97.5, 90, and 90%, respectively.

Treatment of Fermentation/Synthetic Organic Bulk Pharmaceutical Waste

Pfizer, Inc. (Terre Haute, IN) is a fermentation/synthesized organic bulk pharmaceutical type plant mainly involved in the manufacture of streptomycin, terramycin, two undefined antibiotics, fumaric acid, benzoic acid, and so on. This plant employs a five-stage biological system with a retention time of process waste varying from 45 to 65 days. The treatment plant consists of a primary clarifier, two extended aeration (activated sludge) basins in series (12 days detention), secondary settling tank, two clari-digesters in parallel, two standard rate trickling filters in parallel, a high-rate bio-oxidation tower, final clarifier, two aerated stabilization ponds in series, stabilization pond, chlorination, aerobic sludge digester, sludge stabilization pond, land/crop application of stabilized sludges, and holding pond for spent cooling waters (1 day detention). The plant was designed for combined waste of 1.3 MGD of process waste and 5 MGD of spent cooling water flow. In 1972, Pfizer reported average BOD and TSS removal of 98 and 97.5%, respectively. From 1973 to 1974, the BOD and TSS removal were reported to be 99.1 and 97.8%, respectively. The treated effluent contained a BOD of 10–15 mg/L and TSS of 20–30 mg/L. The Pfizer system was capable of giving 50% phosphorous reduction. The TKN, NH<sub>4</sub>-N, and organic nitrogen removal were reported to be 75, 67, and 81%, respectively.

A similar plant, Clinton Laboratories (Clinton, IN), is mainly involved in producing a cephalosporin-type antibiotic. Major products include monensin sodium, keflex, and kefzol. The waste generated in this plant includes mycelia, general trash, concentrated chemical wastes, diluted chemical wastes, water process waste, sanitary sewage, and a clear water stream.
The control and treatment system in this plant mainly relies on the chemical destruction of waste rather than biological processes. The plant generates a raw waste load as high as 400,000 lb - BOD/day. From 1973 to 1974, the company reported a total waste flow of 3.5–4.3 MGD containing a BOD of 1710–1960 lb/day, COD of 3700–4000 lb/day, and TSS of 1040–1250 lb/day. The treatment system included the following units:

- concentration of waste streams to minimum volume;
- oversized strippers for solvent recovery;
- stripper system for waste preconditioning;
- Carver–Greenfield multistage, oil dehydration, steam evaporator system (fermentation waste);
- two John Zink thermal oxidation incineration systems (chemical wastes);
- Bartlett–Snow rotary kiln incinerator (plant trash and mycelium);
- small biological treatment plant (sanitary wastes);
- cooling water towers;
- scrubbing of air effluents from incinicators and waste heat boiler on Carver–Greenfield.

Both concentrated and dilute waste were sent to a pair of John Zink thermal oxidizers equipped with adjustable venturi scrubbers for removal of particulates prior to stack discharge. Water process waste originating primarily from fermentation sectors was sent to the Carver–Greenfield evaporation system. The evaporator utilized a multistep oil dehydration process and was equipped with a centrifuge, waste heat boiler, and a venturi scrubber. The Clinton Laboratory reported an overall BOD and COD reduction of 90 and 99%, respectively, depending upon the configuration used.

**Treatment of Fermentation, Organic Synthesis Processing, and Chemical Finishing and Packaging Type Bulk Pharmaceutical Waste**

Abbott Labs (Chicago, IL) has extensive fermentation, organic synthesis processing, and chemical finishing and packaging facilities and is engaged mainly in production of antibiotics, that is, erythromycin and penicillin, and hundreds of medicinal and fine chemicals. Characteristics of various types of wastes generated from this plant are depicted in Table 20. The typical units involved in the Abbott treatment works are as follows:

- waste screening and neutralization;
- two equalization basins (1.5 day detention);
- six activated sludge basins (100,000 gallon);
- degasification chambers for mixed liquors;

**Table 20** Characteristics of the Abbott Laboratory Wastewater [3]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Fermentation waste</th>
<th>Chemical waste</th>
<th>Combined waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (MGD)</td>
<td>0.312</td>
<td>0.262</td>
<td>0.575</td>
</tr>
<tr>
<td>pH</td>
<td>6.7</td>
<td>5.4</td>
<td>6.1</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>3620</td>
<td>2520</td>
<td>3120</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>1660</td>
<td>510</td>
<td>1140</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>3590</td>
<td>5690</td>
<td>4620</td>
</tr>
</tbody>
</table>

MGD, million gallons per day; BOD, biochemical oxygen demand; TSS, total suspended solids; TDS, total dissolved solids.
Process waste averaging 0.6–0.7 MGD was sent to the activated sludge treatment system. Cooling water flows of 14–15 MGD were sent for chlorination before final discharge. This plant also employed a spent fermentation beer recovery system integrated with an expansive incinerator ducting system. Exhaust air from the drying of spent beer was collected into a specially designed duct system. This also collected the odorous stream from the fermentors, exhaust from degassing chambers, and exhaust from the enclosed activated sludge tank and sludge holding tanks. The combined air stream was then carried to the main plant boilers and incinerated therein. Treated effluent characteristics are given in Table 21. In 1972, overall BOD and TOC reductions were reported to be 94.6 and 86%, respectively. In 1973, the average BOD and TOC reductions were reported as 96.7 and 98%, respectively. The annual costs of the Abbott treatment works were U.S. $1.2 million, which was equivalent to U.S. $4.50–5.5 per 1000 gallons of process waste. In view of the state effluent limits of 4 mg/L BOD and 5 mg/L TSS for discharges into Lake Michigan by 1975, the treated effluent is scheduled for connection to the regional municipal AWT plant [29,30,33,64].

A treatment plant including the following units was recommended for handling the wastewater from drug formulation and packaging type bulk pharmaceutical waste [3]:

- possible separate handling of process and sanitary wastes;
- screening;
- equalization (2 days detention or more) with auxiliary aeration;
- activated sludge, multichamber (approximately 24 hour detention);
- secondary settling;

<table>
<thead>
<tr>
<th>Table 21</th>
<th>Characteristics of Treated Effluent from Abbott Laboratory Works and 1972 Effluent Standards [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>Treated effluent plus cooling water flow</td>
</tr>
<tr>
<td>Flow (MGD)</td>
<td>15</td>
</tr>
<tr>
<td>pH</td>
<td>7.5</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>16</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>20</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>400</td>
</tr>
<tr>
<td>Phenolics (mg/L)</td>
<td>0.02</td>
</tr>
<tr>
<td>Mercury (mg/L)</td>
<td>0.0003</td>
</tr>
<tr>
<td>Coliforms/100 mL</td>
<td>11</td>
</tr>
</tbody>
</table>

MGD, million gallons per day; BOD, biochemical oxygen demand; TSS, total suspended solids; TDS, total dissolved solids.
- sludge thickening;
- aerobic digestion of excess sludges with residues to landfill;
- chlorination of final effluent.

A similar system with minor modifications should be fairly adaptable to biological production type pharmaceutical plants.

5.7 OPERATIONAL PROBLEMS AND REMEDIAL MEASURES

Much research has focused on bulking of the sludge in the aerobic treatment of pharmaceutical wastewater [46,65–67]. The filamentous organism *Sphaerotilus natans* has been reported to be responsible for sludge bulking. The growth of these filamentous organisms was coupled with a deficiency of nitrogen in the wastewater and shock organic and hydraulic loading applied in the system. Another researcher identified the Type 021N microorganism as being responsible for sludge bulking [46]. Three microorganisms, Type 0092, *Microtrix parvicella*, and Type 0041, were also identified to be responsible for sludge bulking. It has been further noted that another factor responsible for the bulking of sludge is influent wastewater variability. Subsequently it has been concluded that all three organisms are correlated with filamentous bulking at low organic loading [66]. To deal with the problem of sludge bulking, the addition of nitrogen was recommended, but even after doing so, operational problems continued and the decision was made to expand the treatment facility to avoid shock organic and hydraulic loading in the reactor. It was further observed that the addition of PAC in the activated sludge process resulted in some improvement in sludge settleability; however, the MLSS settling rate remained at a very low level (0.01–0.05 cm/min). The study demonstrated that due to nitrification, the pH decreased, causing a viscous floating layer of MLSS formed on the surface of the aeration basin and clarifier that resulted in significant reductions in the MLSS and PAC concentration in the system.

Chlorination of mixed liquor has been recommended to address the problem of sludge bulking. It was expected that chlorination of the mixed liquor at dosages ranging from 3 to 7.5 lb Cl₂/1000 lb MLSS could control the problem of sludge bulking; however, chlorination had in fact severely affected the treatment process and stopped nitrification. To resolve this problem, it was suggested that the plant should always operate at an F/M ratio above 0.15 to avoid filamentous growth, and that any increase in filaments should be treated before intense chlorination [46]. Another study recommended that sludge bulking be controlled by operating the system at a dissolved oxygen (DO) concentration of MLSS greater than 3 mg/L. An optimal dissolved oxygen control strategy for an activated sludge system in treatment of pharmaceutical wastewater is described by Brandel [68].

Temperature has been shown to affect the performance of the activated sludge process [46]. Pilot plant results indicated that system efficiency was excellent as long as the aeration basin temperature was less than 38°C, whereas at temperatures exceeding 38°C, BOD₅ removal efficiency decreased considerably, accompanied with the cessation of nitrification. High temperatures resulted in killing of the nitrifiers and inhibited carbonaceous removal. Hence, a heat exchanger in the influent line has been suggested to bring down the wastewater temperature.

5.8 ENVIRONMENTAL PROTECTION AGENCY EFFLUENT LIMITATIONS FOR THE PHARMACEUTICAL INDUSTRY

The EPA has developed effluent limitations in terms of percentage reductions of raw waste loads or effluent concentration as shown in Table 22 [3]. Additional parameters that should receive
attention at many bulk manufacturing plants include copper, cyanides, tin, cadmium, nickel, arsenic, chlorinated hydrocarbons, and pesticides.

In India, domestic and industrial wastewaters are required to meet the standards set out in the Environment (Protection) Third Amendment Rules (1993) and Water (Prevention and Control of Pollution) Act (1974). The tolerance limits for the disposal of industrial effluents into inland surface water are given in Table 23 [69].

5.9 SUMMARY AND CONCLUSIONS

The information included in this chapter on pharmaceutical wastewater encompasses only a fragment of the research in this area. Owing to extreme variability of pharmaceutical wastewater characteristics, treatability studies should be conducted on a case-by-case basis to identify and confirm the required design parameters. As discussed earlier, physico-chemical treatment such as air stripping and coagulation was not found effective and beneficial for this wastewater, but in many cases, sedimentation has been found effective. The treatability study of almost all kinds of waste streams has indicated that waste is biologically treatable. Hence, a combination of physical, chemical, and biological processes seem to be feasible for the treatment of pharmaceutical wastewater. A two-stage biological system or a combination of aerobic and anaerobic processes proved effective for some pharmaceutical wastewater. Keeping in mind the varying characteristics of pharmaceutical wastewater, the shock loading capacity of the treatment units must also be given much attention in identifying and evaluating the technical feasibility of the processes. After identifying the technical feasibility of the processes, the final selection should be made based on economic analysis.

**Table 22**  EPA Effluent Limitations for Pharmaceutical Plants [3]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average daily based on max. monthly raw waste load</td>
<td>92–95%</td>
</tr>
<tr>
<td>BOD₅</td>
<td>92–95%</td>
</tr>
<tr>
<td>COD</td>
<td>80–82%</td>
</tr>
<tr>
<td>TSS</td>
<td>82.5%</td>
</tr>
<tr>
<td>Ammonia N</td>
<td>70–75%</td>
</tr>
<tr>
<td>pH</td>
<td>6–9</td>
</tr>
<tr>
<td>Fecal coliforms</td>
<td>Average, 200/100 mL</td>
</tr>
<tr>
<td></td>
<td>Max. daily, 400/100 mL</td>
</tr>
</tbody>
</table>

For daily limitations = 2 to 3 × average daily levels given above, suggested limits for metals, trace ions

- Iron, Zinc 1.0–1.5 mg/L
- Mn, Cu 0.5–1 mg/L
- Phenolics, total Cr 0.25–0.5 mg/L
- Aluminum 1.0–2.0 mg/L
- Sulfide (approx.) 0.5 mg/L
- Lead 0.1–0.25 mg/L
- Mercury (total plant) 45.36 g/day

BOD, biochemical oxygen demand; COD, chemical oxygen demand; TSS, total suspended solids.
### Table 23  Schedule VI of Environment (Protection) Third Amendment Rules (1993) [69]

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Parameters</th>
<th>Standards&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inland surface water</td>
</tr>
<tr>
<td>1</td>
<td>Color and odor</td>
<td>b</td>
</tr>
<tr>
<td>2</td>
<td>Suspended solids (mg/L), max</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Particle size of suspended solids</td>
<td>Shall pass 850 micron IS sieve</td>
</tr>
<tr>
<td>4</td>
<td>pH value</td>
<td>5.5–9.0</td>
</tr>
<tr>
<td>5</td>
<td>Temperature</td>
<td>Should not exceed 5°C above the receiving water temperature</td>
</tr>
<tr>
<td>6</td>
<td>Oil and grease (mg/L), max</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>Total residual chlorine (mg/L), max</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>Ammonical nitrogen (as N) (mg/L), max</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>Total Kjeldahl nitrogen (as N) (mg/L), max</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>Free ammonia (as NH₃) (mg/L), max</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>Nitrate nitrogen</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>BOD₅ (mg/L), max</td>
<td>30</td>
</tr>
<tr>
<td>13</td>
<td>COD (mg/L), max</td>
<td>250</td>
</tr>
<tr>
<td>14</td>
<td>Arsenic (as As) (mg/L)</td>
<td>0.2</td>
</tr>
<tr>
<td>15</td>
<td>Mercury (as Hg) (mg/L), max</td>
<td>0.01</td>
</tr>
<tr>
<td>16</td>
<td>Lead (as Pb) (mg/L), max</td>
<td>0.1</td>
</tr>
<tr>
<td>17</td>
<td>Cadmium (as Cd) (mg/L), max</td>
<td>2</td>
</tr>
<tr>
<td>18</td>
<td>Hexavalent chromium (as Cr⁶⁺) (mg/L), max</td>
<td>0.1</td>
</tr>
<tr>
<td>19</td>
<td>Total chromium (as Cr) (mg/L), max</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>Copper (as Cu) (mg/L), max</td>
<td>3</td>
</tr>
</tbody>
</table>

(continues)
Based on extensive study and experience in treatment of pharmaceutical wastewater, the following specific conclusions may be drawn:

- Pretreatment of pharmaceutical industry wastewater such as air stripping and coagulation is not beneficial; however, sedimentation of treated effluent was found effective in further reduction of SS and COD of the effluent. Hence, the pretreatment of pharmaceutical wastewater is not advisable.

- In many cases, anaerobic filter treatment was found to successfully treat pharmaceutical industry wastewater. This can be an excellent alternative for conventional aerobic treatment, which is energy intensive and requires the disposal of sludge. The anaerobic filter, on the other hand, can produce energy in the form of biogas and does not require...
sludge disposal. Moreover, the anaerobic filter is more resistant and capable of handling shock loading as compared to the aerobic system.

- All waste streams, with the exception of acid waste streams of a synthetic drug factory, must be treated collectively rather than treated separately, as the performance efficiency of combined waste has been proved to be better than that of waste treated separately. Moreover, the segregation of acid waste streams could result in the following benefits:
  - recovery of useful acids from the waste;
  - the volume of the waste needing neutralization has been reduced to 50\% and has eliminated the necessity of adjusting the pH of the combined waste for biological treatment;
  - the burden on the biological treatment has been reduced.
- The problem of sludge bulking in the case of the activated sludge process can be controlled in the following ways:
  - chlorination of the mixed liquor;
  - operating the system at min\textsuperscript{m} DO concentration of 3 mg/L;
  - operating the system at higher organic loading.
- Treatment processes such as ASP, PAC-ASP, GAC, and resin columns can successfully remove priority pollutants from pharmaceutical wastewater.
- In general, the trickling filter and activated sludge were found to satisfactorily cope with the needs of wastewater treatment for the pharmaceutical industry.
- Addition of PAC in the activated sludge process was found beneficial in improving the effluent quality, but it cannot be recommended until the problem of viscous layer formation is solved.

5.10 DESIGN EXAMPLES

Example 1

A synthetic organic chemicals plant discharges mainly two types of waste streams, namely strong process waste and dilute process waste. The flow and BOD\textsubscript{5} of the waste streams are given in the following table.

<table>
<thead>
<tr>
<th>Type of wastes</th>
<th>Flow (GPD)</th>
<th>BOD\textsubscript{5} (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong process waste</td>
<td>11,800</td>
<td>480,000</td>
</tr>
<tr>
<td>Dilute process waste</td>
<td>33,800</td>
<td>640</td>
</tr>
</tbody>
</table>

GPD, gallons per day; BOD, biochemical oxygen demand.

In addition, the plant discharges 35,300 GPD service wastewater. If the total BOD load of the composite waste is 47,500 lb/day, estimate (i) the BOD\textsubscript{5} of the composite waste and domestic waste; and (ii) the BOD load of the each stream and their contribution to the total BOD load of the plant.

Solution

Determine the BOD\textsubscript{5} of the wastes. The first step is to find out the total flow of the composite waste by summing the flow of the various waste streams of the plant.
Total flow of the composite waste = \(11,800 + 33,800 + 35,300 = 80,900\) GPD

\[
BOD_5 \text{ of the composite waste} = \frac{\text{Total BOD load (lb/day)} \times 453.6 \text{ (g/lb)} \times 1000 \text{ (mg/g)}}{\text{Flow (GPD)} \times 3.785 \text{ (L/gal)}} \\
= \frac{47,500 \times 453.6 \times 1000}{80,900 \times 3.785} \\
= 70,364.28 \text{ mg/L}
\]

\[
\text{BOD load of the strong process waste} = \frac{\text{Flow (GPD)} \times 3.785 \text{ (L/gal)} \times BOD_5 \text{ (mg/L)}}{10^3 \text{ (mg/g)} \times 453.6 \text{ (g/lb)}} \\
= \frac{11,800 \times 3.785 \times 480,000}{1000 \times 453.6} \\
= 47,262.43 \text{ lb/day}
\]

\[
\text{BOD load of the dilute process waste} = \frac{\text{Flow (GPD)} \times 3.785 \text{ (L/gal)} \times BOD_5 \text{ (mg/L)}}{10^3 \text{ (mg/g)} \times 453.6 \text{ (g/lb)}} \\
= \frac{33,800 \times 3.785 \times 640}{1000 \times 453.6} \\
= 180.50 \text{ lb/day}
\]

\[
\text{BOD load due to domestic waste} = 47,500 - (47,262.43 + 180.5) \\
= 57.05 \text{ lb/day}
\]

\[
\text{BOD}_5 \text{ of the domestic waste, mg/L} = \frac{\text{BOD load (lb/day)} \times 453.6 \text{ (g/lb)} \times 1000 \text{ (mg/g)}}{\text{Flow (GPD)} \times 3.785 \text{ (L/gal)}} \\
= \frac{57.07 \times 453.6 \times 1000}{35,300 \times 3.785} \\
= 193.75 \text{ mg/L}
\]

Comment
The total BOD load of the plant is mainly due to strong process waste. Segregation of strong process waste can result in significant reduction in total BOD load of the plant.

Example 2
The five-days’ BOD at 20°C and flow of the various types of waste streams generated from a synthetic drug plant are given in the following table.

<table>
<thead>
<tr>
<th>Type of wastes</th>
<th>Flow (m³/day)</th>
<th>BOD₅ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline waste stream</td>
<td>1710</td>
<td>3500</td>
</tr>
<tr>
<td>Condensate waste stream</td>
<td>1990</td>
<td>1275</td>
</tr>
<tr>
<td>Acid waste stream</td>
<td>435</td>
<td>3090</td>
</tr>
</tbody>
</table>

BOD, biochemical oxygen demand.
Estimate the BOD$_5$ and subsequent BOD load of the composite waste. If the acid waste stream has to be segregated for the recovery of acids then (i) find out the BOD$_5$ of the combined waste excluding acid waste; and (ii) comment on the effect of segregation in BOD loading of the plant.

**Solution**

BOD load of the alkaline waste  
\[ \text{BOD load} = \frac{\text{Flow} \times \text{BOD}_5}{10^3} \]  
\[ = 1710 \times \frac{3500 \times 10^{-3}}{10^3} = 5985 \text{ kg BOD/day} \]

Similarly, BOD load of the condensate waste  
\[ = 1990 \times \frac{1275 \times 10^{-3}}{10^3} = 3834.61 \text{ kg BOD/day} \]

BOD load of the acid waste  
\[ = 435 \times \frac{3090 \times 10^{-3}}{10^3} = 1344.15 \text{ kg BOD/day} \]

Total BOD load of the composite waste  
\[ = 5985 + 3834.61 + 1344.15 = 11,163.76 \text{ kg BOD/day} \]

Total flow of the composite waste  
\[ = 1710 + 1990 + 435 = 4135 \text{ m}^3 \]

BOD$_5$ of the composite waste  
\[ = \frac{\text{BOD load}}{\text{Flow} \times 10^3} \]  
\[ = \frac{11,163.76 \times 10^6}{4135 \times 10^3} \]  
\[ = 2699.82 \text{ mg/L} \]

BOD load of alkaline and condensate waste  
\[ = 5985 + 3834.61 = 9819.61 \text{ kg BOD/day} \]

Total flow of the alkaline and condensate waste  
\[ = 1710 + 1990 = 3700 \text{ m}^3 \]

BOD$_5$ of combined (alkaline and condensate)waste  
\[ = \frac{9819.61 \times 10^6}{3700 \times 10^3} \]  
\[ = 2653.95 \text{ mg/L} \]

**Comment**

Segregation of the acid waste stream has resulted in significant reduction in total BOD load of the plant, but the BOD$_5$ of the composite waste remains almost the same. Hence the acid waste stream can be segregated from the main stream without affecting the treatability of the waste.

**Example 3**

A primary sedimentation tank has been designed for the pretreatment of 0.312 MGD of fermentation waste generated from the pharmaceutical industry. The raw waste SS concentration is 1660 mg/L. At a detention time of 2 hours the effluent SS concentration is reduced to 260 mg/L. Determine (i) the SS removal efficiency of the sedimentation tank; and (ii) the quantity of sludge generated per day. Assume the specific gravity of sludge ($S_d$) is 1.03, which contains 6% solids.
Solution

(A) SS removal efficiency of the tank can be obtained as follows:

$$SS\ removal\ efficiency = \frac{(1660 - 260) \times 100}{1660}$$

$$= 84.34\%$$

(B) Determine the mass of dry solids removed per day.

$$W_s = 0.312 \text{ (MGD)} \times 10^6 \text{ (gal/M)} \times 3.785 \text{ (L/gal)} \times (1660 - 260) \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} = 1653.29 \text{ kg/day}$$

(C) Determine the volume of sludge produced per day.

$$V_{sl} = \frac{W_s}{\rho_w \times S_{sl} \times P_s}$$

where $$W_s$$ is the mass of dry solids removed per day, $$\rho_w$$ is the density of the water, and $$P_s$$ is the percentage of sludge solids.

$$V_{sl} = \frac{1653.29 \text{ (kg/day)}}{1000 \times 1.03 \times 0.06}$$

$$= 26.752 \text{ m}^3 (7067.96 \text{ GPD})$$

Example 4

Physicochemical treatment of a typical pharmaceutical plant generating 33,800 GPD wastewater has indicated that at optimum doses of FeSO$_4$ (500 mg/L), FeCl$_3$ (500 mg/L), and alum (250 mg/L), COD and SS removal of the effluent of 25 and 70%, respectively, can be achieved. Determine the quantities of various chemicals required per day. If 49% strength alum is to be used and 30 days supply is to be stored at the treatment facility, estimate the storage capacity required for the alum.

Solution

(A) The quantities of the various chemicals required per day can be obtained as follows:

Quantity of FeSO$_4$ required per day = 500 (mg/L) $\times 10^{-6}$ (mg/kg) $\times$ 33,800 (GPD) $\times$ 3.785 (L/gal)

$$= 63.97 \text{ kg/day}$$

Quantity of FeCl$_3$ required per day = 500 (mg/L) $\times 10^{-6}$ (mg/kg) $\times$ 33,800 (GPD) $\times$ 3.785 (L/gal)

$$= 63.97 \text{ kg/day}$$

Quantity of alum required per day = 250 (mg/L) $\times 10^{-6}$ (mg/kg) $\times$ 33,800 (GPD) $\times$ 3.785 (L/gal)

$$= 31.98 \text{ kg/day}$$

(B) Determine the weight of alum per m$^3$ of 49% liquid alum.

$$\text{Weight per m}^3 = 0.49 \times 80 \text{ (lb/ft}^3) \times 16.0185 \text{ (kg/m}^3 \cdot \text{ lb/ft}^3)$$

$$= 627.925 \text{ kg/m}^3$$

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(C) Determine the storage capacity required for 30 days.

\[
\text{Storage capacity} = 31.98 \text{ (kg/day) } \times 30 \text{ (days)} / 627.925 \text{ (kg/m}^3\text{)}
\]

\[
= 1.527 \text{ m}^3 \text{ (1527 L)}
\]

**Example 5**

Estimate the quantity of sludge produced in a chemical precipitation of 1710 m\(^3\)/day of pharmaceutical wastewater with SS concentration 560 mg/L. The addition of the FeSO\(_4\) (500 mg/L), FeCl\(_3\) (500 mg/L), and lime (600 mg/L) increases the SS removal efficiency of the primary sedimentation tank from 60 to 70%. Comment on the chemical precipitation process on the basis of sludge production. Assume CaCO\(_3\) solubility = 15 mg/L, specific gravity of sludge = 1.03, and moisture content of the sludge = 95%.

**Solution**

(A) Determine the mass of SS removed per day without chemical addition.

\[
M_{ss1} = 1710 \text{ (m}^3\text{/day)} \times 10^3 \text{ (L/m}^3\text{)} \times 0.6 \times 560 \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)}
\]

\[
= 574.56 \text{ kg/day}
\]

(B) Determine the mass of SS removed per day after chemical addition.

\[
M_{ss1} = 1710 \text{ (m}^3\text{/day)} \times 10^3 \text{ (L/m}^3\text{)} \times 0.7 \times 560 \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)}
\]

\[
= 670.320 \text{ kg/day}
\]

(C) Determine the volume of the sludge without chemical addition.

\[
V_{sl} = \frac{W_s}{\rho_w \times S_{sl} \times P_s}
\]

\[
= \frac{574.56 \text{ (kg/day)}}{1000 \times 1.03 \times (1 - 0.95)}
\]

\[
= 11.16 \text{ m}^3\text{/day (2948.48 GPD)}
\]

(D) Determine the quantity of sludge produced due to addition of chemicals. This can be calculated from the stoichiometry of the chemical reactions taking place with the addition of these chemicals. The chemical reactions taking place are described below.

When FeSO\(_4\) and lime are added:

\[
\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca(HCO}_3\text{)}_2 \rightleftharpoons \text{Fe(HCO}_3\text{)}_2 + \text{CaSO}_4 + 7\text{H}_2\text{O}
\]

\[(278) \quad (100) \quad (178) \quad (136) \quad (7 \times 18)\]

\[
\text{Fe(HCO}_3\text{)}_2 + 2\text{Ca(OH)}_2 \rightleftharpoons 2\text{CaCO}_3 + \text{Fe(OH)}_2 + 2\text{H}_2\text{O}
\]

\[(178) \quad (2 \times 56) \quad (2 \times 100) \quad (89.9) \quad (2 \times 18)\]

\[
4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{Fe(OH)}_3
\]

\[(4 \times 89.9) \quad (32) \quad (2 \times 18) \quad (4 \times 106.9)\]

\[
\text{Ca(OH)}_2 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + 2\text{H}_2\text{O}
\]

\[(56) \quad (44) \quad (100) \quad (2 \times 18)\]

\[
\text{Ca(OH)}_2 + \text{Ca(HCO}_3\text{)}_2 \rightleftharpoons 2\text{CaCO}_3 + 2\text{H}_2\text{O}
\]

\[(56) \quad (100) \quad (2 \times 100) \quad (2 \times 18)\]
When FeCl₃ is also added:

\[
2\text{FeCl}_3 + 3\text{Ca(OH)}_2 \leftrightarrow 2\text{Fe(OH)}_3 + 3\text{CaCl}_2
\]

\((2 \times 162) \quad (3 \times 56) \quad (2 \times 106.9) \quad (3 \times 111)\)

The addition of FeSO₄ mainly produces precipitable flocs of CaCO₃ and Fe(OH)₃. The quantity of CaCO₃ precipitated by addition of 500 mg/L of FeSO₄ can be estimated as:

Quantity of CaCO₃ = 500 (mg/L) \times (200/278)

= 359.71 mg/L

Similarly, the quantity of Fe(OH)₃ precipitated by addition of 500 mg/L of FeSO₄

= 500 (mg/L) \times (106.9/278)

= 192.27 mg/L

Amount of lime consumed in formation of Fe(OH)₃ flocs

= 192.27 (mg/L) \times (56/106.9)

= 100.72 mg/L

Similarly, the quantity of Fe(OH)₃ precipitated by addition of 500 mg/L of FeCl₃

= 500 (mg/L) \times (106.9/162)

= 329.94 mg/L

Amount of lime consumed in formation of Fe(OH)₃ flocs by addition of FeCl₃

= 329.94 (mg/L) \times (3 \times 56/2 \times 106.9)

= 259.26 mg/L

Total amount of lime remaining

= 600 - (100.72 + 259.26)

= 240.02 mg/L

Amount of CaCO₃ precipitated by addition of lime

= 240.02 \times (3 \times 100/2 \times 56)

= 642.91 mg/L

Determine the total amount of CaCO₃ precipitated per day

= 1710 (m³/day) \times 10^5 \text{ (L/day)}

\times (359.71 + 642.91 - 15) \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)}

= 1688.83 kg/day
Similarly, the total amount of Fe(OH)₃ precipitated per day

\[ = 1710 \text{ (m}^3/\text{day}) \times 10^3 \text{ (L/day)} \]

\[ \times (192.27 + 329.94) \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} \]

\[ = 892.98 \text{ kg/day} \]

Total volume of sludge on dry basis per day

\[ = 670.32 + 1688.83 + 892.98 \]

\[ = 3252.13 \text{ mg/L} \]

Hence the volume of the sludge produced per day with chemical addition:

\[ V_{sl} = \frac{W_s}{\rho_w \times S_{sl} \times P_s} \]

\[ = \frac{3252.13 \text{ (kg/day)}}{1000 \times 1.03 \times (1 - 0.95)} \]

\[ = 63.15 \text{ m}^3/\text{day} (16,684.28 \text{ GPD}) \]

Comment

The problem of sludge disposal increased to a greater extent in the case of chemical precipitation than in the sedimentation without the chemical.

Example 6

Estimate the food–microorganism ratio (F/M) and sludge age (solid retention time) of an activated sludge process designed to reduce the BOD₅ of the spent stream generated from a biological production plant from 1500 mg/L to 50 mg/L. The wastewater flow is \( Q = 15,000 \text{ GPD} \), aeration tank volume = 45 m³, MLVSS = 3000 mg/L, and net biomass yield coefficient \( (Y_n) \) = 0.28 kg/kg. Also compute the performance efficiency of the plant.

Solution

Total substrate removed (kg BOD/day)

\[ = Q(\text{GPD}) \times 3.785 \text{ (L/gal)} \]

\[ \times (S_i - S_e) \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} \]

\[ = 15,000 \times 3.785 \times (1500 - 50) \times 10^{-6} \]

\[ = 82.32 \text{ kg BOD/day} \]

Total MLVSS (kg MLVSS) = MLVSS (mg/L) \times 10^{-6} \text{ (kg/mg)} \times V \text{ (m}^3) \times 10^3 \text{ (L/m}^3) \]

\[ = 3000 \times 10^{-6} \times 45 \times 10^3 = 135 \text{ kg MLVSS} \]

Total substrate applied per day

\[ = 15,000 \times 3.785 \times 1500 \times 10^{-6} \]

\[ = 85.16 \text{ kg BOD/day} \]

\[ \text{F/M ratio (day}^{-1}) = \frac{\text{Total substrate applied (kg BOD/day)}}{\text{Total MLVSS (kg MLVSS)}} \]

\[ = (85.16/135) = 0.63 \text{ day}^{-1} \]

Net MLVSS produced (kg VSS/day) = \( Y_n \) (kg/kg) \times total substrate removed (kg/day)

\[ = 0.28 \times 82.32 \]

\[ = 23.05 \text{ kg VSS/day} \]
Sludge age (solid retention time) \( (\theta_c) \) = \( \frac{\text{Total MLVSS}}{\text{Net VSS produced per day}} \)
\[ = \frac{135}{23.05} = 5.86 \text{ day} \]

BOD removal efficiency \( = \frac{(S_i - S_o) \times 100}{S_i} \)
\[ = \frac{(1500 - 50) \times 100}{1500} \]
\[ = 96.67\% \]

**Example 7**

Design a complete-mix activated sludge process for the treatment of 1710 m\(^3\)/day of settled condensate wastewater with BOD\(_s\), 1500 mg/L generated from a synthetic organic chemical type of pharmaceutical industry. Assume the following conditions are applicable:

1. Effluent contains 25 mg/L biological solids, of which 65\% is biodegradable;
2. MLSS concentration in the reactor = 5000 mg/L;
3. MLVSS \( (X) \) = 0.8 \times MLSS;
4. Solid retention time, \( \theta_c \) = 5 days;
5. BOD\(_s\) = 0.68 BOD\(_L\) (ultimate biological oxygen demand);
6. Return sludge concentration = 1\%;
7. Effluent BOD\(_s\) = 50 mg/L;
8. Maximum yield coefficient, \( Y \) = 0.6 mg/mg;
9. Decay constant, \( K_d \) = 0.07 day\(^{-1}\).

**Solution**

(A) Determine the influent soluble BOD\(_s\) escaping the treatment:

(i) BOD\(_L\) of the biodegradable effluent solid
\[ = 25 \text{ (mg/L)} \times 0.65 \times 1.42 \text{ (mg O}_2\text{ consumed/mg cell oxidized)} \]
\[ = 23.075 \text{ mg/L} \]

(ii) BOD\(_s\) of the effluent SS = 23.075 (mg/L) \times 0.68
\[ = 15.69 \text{ mg/L (say 15.7 mg/L)} \]

(iii) Influent soluble BOD\(_s\) escaping the treatment
\[ = 50 - 15.7 \]
\[ = 34.3 \text{ mg/L} \]

(B) Efficiency of the process:

(i) Process efficiency based on soluble BOD\(_s\)
\[ E_s = \frac{(1500 - 34.3) \times 100}{1500} \]
\[ = 97.71\% \]
Similarly, overall plant efficiency of the system

\[ E_s = \frac{(1500 - 50) \times 100}{1500} = 96.67\% \]

(C) Determine the capacity of the aeration basin:

\[ V = \frac{Y \theta_c Q (S_i - S)}{X(1 + K_d \theta_c)} \]

where \( Y \) = maximum yield coefficient (mg/mg), \( \theta_c \) = mean cell residence time (day), \( Q \) = flow (m\(^3\)/day), \( S_i \) = substrate concentration in the influent (mg/L), \( S \) = substrate concentration in effluent (mg/L), \( X \) = mass concentration of microorganism in reactor (mg/L), and \( K_d \) = endogenous decay coefficient (day\(^{-1}\)). On substituting the values, the above equation results in:

\[ V = \frac{0.6 \text{ (mg/mg)} \times 5 \text{ (day)} \times 1710 \text{ (m}^3\text{/day)} (1500 - 50) \text{ (mg/L)}}{0.8 \times 5000 \text{ (mg/L)} \times [1 + 0.07 \text{ (day}^{-1}\text{)}] \times 5 \text{ (day)}] \]

\[ = 1377.5 \text{ m}^3 \]

Check for the F/M ratio and OLR:

\[ \text{HRT (}\theta\text{)} = \frac{V}{\theta} \]

\[ \theta = 1377.5 \text{ (m}^3\text{)/1710 (m}^3\text{/day)} \]

\[ = 0.805 \text{ day (19.33 hours)} \]

\[ \text{F/M ratio} = \frac{S_i}{\theta X} \]

\[ = \frac{1500 \text{ mg/L}}{0.805 \text{ (day)} \times 0.8 \times 5000 \text{ (mg/L)}} \]

\[ = 0.466 \text{ day}^{-1} \]

Amount of BOD\(_5\) consumed = \((1500 - 34.3) \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} \times 1710 \text{ (m}^3\text{/day)} \times 10^3 \text{ (L/m}^3\text{)} \]

\[ = 2506.35 \text{ kg BOD/day} \]

\[ \text{OLR} = \frac{(1500-34.3) \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} \times 1710 \text{ (m}^3\text{/day)} \times 10^3 \text{ (L/m}^3\text{)}}{1377.5 \text{ (m}^3\text{)}} \]

\[ = (2506.35/1377.5) \]

\[ = 1.82 \text{ kg BOD/m}^3\text{day} \]

(D) Sludge recycling

The recycling ratio \((r)\) can be computed as follows:

\[ r = \frac{X}{(X_r-X)} \]
where \( X_r = \text{MLVSS in the recycled effluent} \)

\[
\frac{0.8 \times 5000 \text{ (mg/L)}}{0.8 \times (10,000 - 5000) \text{ (mg/L)}} = 0.5
\]

Hence the recycling flow \( Q = 0.5 \times 1710 \text{ (m}^3/\text{day)} = 855 \text{ m}^3/\text{day}. \)

(E) Sludge production

(i) Net VSS production \( = \frac{X V}{\theta_c} \)

\[
= \frac{0.8 \times 5000 \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} \times 1377.5 \text{ (m}^3/\text{day}) \times 10^3 \text{ (L/m}^3) \times 5 \text{ (days)}}{1377.5 \text{ (kg/day)}} = 1102 \text{ kg/day}
\]

(ii) Net SS production \( = 1102 \text{ (kg/day)}/0.8 = 1377.5 \text{ kg/day} \)

(iii) Volume of the sludge produced

\[
= \frac{1377.5 \text{ (kg/day)}}{1000 \text{ (kg/m}^3) \times 1.03 \times 0.01} = 133.73 \text{ m}^3/\text{day}
\]

(iv) VSS production per kg BOD\(_r\) (biological oxygen demand removed)

\[
= \frac{1102 \text{ (kg/day)} \times 10^6 \text{ (mg/kg)}}{(1500 - 34.3) \text{ (mg/L)} \times 1710 \text{ (m}^3/\text{day}) \times 10^3 \text{ (L/m}^3) \times 10 \text{ (kg/mg)}} = 0.44 \text{ mg/mg}
\]

(F) Oxygen requirement

(i) Theoretical \( \text{O}_2 \) required \( = (\text{BOD}_L \text{ removed}) - (\text{BOD}_L \text{ of solids leaving}) \)

\[
= 1.47 (1500 - 34.3) \text{ (mg/L)} \times 1710 \text{ (m}^3/\text{day}) \times 10^3 \text{ (L/m}^3) \\
\times 10^{-6} \text{ (kg/mg)} - 1.42 \times 1102 \text{ (kg/day)} = 2119.49 \text{ kg/day}
\]

(ii) Theoretical air requirement assuming that air contains 23.2% oxygen by weight and density of air \( = 1.201 \text{ kg/m}^3 \)

\[
= \frac{2119.49 \text{ (kg/day)}}{0.232 \times 1.201 \text{ (kg/m}^3)} = 7606.47 \text{ m}^3/\text{day}
\]

(iii) Actual air requirement at an 8% transfer efficiency

\[
= 7606.47 \text{ (m}^3/\text{day})/0.08 = 95,084.65 \text{ m}^3/\text{day}
\]
(iv) Check for the air requirement per unit volume
\[
= 95,084.65 \text{ (m}^3/\text{day})/1710 \text{ (m}^3/\text{day})
\]
\[
= 55.60 \text{ m}^3/\text{m}^3
\]

(v) Air requirement per kg of BOD\textsubscript{5} removed
\[
= 95,084.65 \text{ (m}^3/\text{day})/2506.35 \text{ (kg/day)}
\]
\[
= 37.94 \text{ m}^3/\text{kg BOD}\textsubscript{5} removed
\]

(G) Power requirement assuming the aerators are designed to give 2 kgO\textsubscript{2}/kWh and the field efficiency is 70%.
\[
\text{Power required} = \frac{2119.49 \text{ (kg/day)}}{2 \text{ (kg/kWh)} \times 0.7 \times 24 \text{ (h/day)}}
\]
\[
= 63.08 \text{ (kW)} \times 1.3410 \text{ (hp/kW)}
\]
\[
= 84.59 \text{ hp (say 85 hp)}
\]

Example 8
1710 m\textsuperscript{3}/day of alkaline waste stream with BOD\textsubscript{5} = 3500 mg/L is treated in an extended aeration system. The BOD removal efficiency of the system is 96%. If the volume of the aeration basin is 1780 m\textsuperscript{3}, estimate (i) detention time (hydraulic retention time, HRT) and organic loading rate (OLR). Also compute the BOD\textsubscript{5} of the treated effluent.

Solution
\[
\text{HRT} = \frac{\text{Volume of the tank}, V}{\text{Flow}, Q} \text{ (m}^3/\text{day)}
\]
\[
= 1780/1710 = 1.04 \text{ day = 24.98 hours}
\]

\[
\text{OLR} = \frac{Q \times 10^3 \text{ (L/m}^3) \times E \times S_i \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} }{V \text{ (m}^3)}
\]
\[
= (1710 \times 10^3 \times 0.96 \times 3500 \times 10^{-6})/1780
\]
\[
= 3.23 \text{ kg BOD/m}^3 \text{ day}
\]

\[
\% \text{ BOD removal efficiency} = \frac{(S_i - S_e) \times 100}{S_i}
\]
\[
96 = \frac{(3500 - S_e) \times 100}{3500}
\]
\[
S_e = 140 \text{ mg/L}
\]

Example 9
An extended aeration activated sludge process is designed to treat 2000 m\textsuperscript{3}/day of condensate waste generated from a synthetic organic chemical plant. The system is operating at an organic
loading rate of 1.2 kg COD/m³ day. If the BOD₅ of influent raw waste and treated effluent is 1275 mg/L and 76.5 mg/L, respectively, determine the HRT and performance efficiency of the system.

Solution

\[
\text{OLR (kg BOD/m³ day)} = \frac{Q (m³/day) \times 10^3 (L/m³) \times (S_i - S_e) (mg/L) \times 10^{-6} (kg/mg)}{V (m³)}
\]

\[
1.2 = \frac{[2000 \times 10^3 \times (1275 - 76.5) \times 10^{-6}]}{V}
\]

\[
V = 1997.5 \text{ m}³
\]

\[
\text{HRT, } \theta \text{ (day)} = \frac{V (m³)}{Q (m³/day)}
\]

\[
= 1997.5/2000 = 0.99 \text{ day, say } 1 \text{ day (24 hours)}
\]

\[
\text{% BOD removal efficiency} = \frac{(S_i - S_e) \times 100}{S_i}
\]

\[
= \frac{(1275 - 76.5) \times 100}{1275}
\]

\[
= 94\%
\]

Example 10

Design an extended aeration process for the treatment of 1275 m³/day of pharmaceutical wastewater with a BOD₅ of 3500 mg/L. Assume the following conditions are applicable:

- Effluent contains 20 mg/L biological solids of which 70% is biodegradable;
- MLSS concentration in the reactor = 6000 mg/L;
- MLVSS = 0.75 × MLVSS;
- Solid retention time, \( \theta_e \) = 12 days;
- BOD₅ = 0.68 BOD₅;
- Return sludge concentration = 2%;
- Effluent BOD₅ = 30 mg/L;
- \( Y \) = 0.65 mg/mg;
- Decay constant, \( K_d \) = 0.075 day⁻¹.

Solution

(A) Determine the influent soluble BOD₅ escaping the treatment:

(i) BOD₅ of the biodegradable effluent solid

\[
= 20 \text{ (mg/L) } \times 0.70 \times 1.42 \text{ (mg } O_2 \text{ consumed/mg cell oxidized)}
\]

\[
= 19.88 \text{ mg/L}
\]
(ii) BOD$_5$ of the effluent SS
\[= 19.88 \text{ (mg/L)} \times 0.68 \]
\[= 13.52 \text{ mg/L (say 13.5 mg/L)} \]

(iii) Influent soluble BOD$_5$ escaping the treatment
\[= 30 - 13.5 \]
\[= 16.5 \text{ mg/L} \]

(B) Efficiency of the process:

(i) Process efficiency based on soluble BOD$_5$
\[E_s = \frac{(3500 - 16.5) \times 100}{3500} \]
\[= 99.5\% \]

(ii) Similarly, overall plant efficiency of the system
\[E_s = \frac{(3500 - 30) \times 100}{3500} \]
\[= 99.1\% \]

(C) Determine the capacity of the aeration basin:
\[V = \frac{Y \theta Q(S - S_i)}{X(1 + K_d \theta)} \]
\[= \frac{0.65 \text{ (mg/mg)} \times 12 \text{ (day)} \times 1275 \text{ (m}^3/\text{day)} \times (3500 - 30) \text{ (mg/L)}}{0.75 \times 6000 \text{ (mg/L)} \times [1 + 0.075 \text{ (day}^{-1}) \times 12 \text{ (day)}]} \]
\[= 4036.15 \text{ m}^3 \text{ (say 4050 m}^3) \]

Check for the F/M ratio and OLR and HRT:

\[\text{HRT(}\theta) = \frac{V}{Q} \]
\[\theta = 4050 \text{ (m}^3)/1275 \text{ (m}^3/\text{day)} \]
\[= 3.18 \text{ day} \]

\[\text{F/M ratio} = \frac{(S_i/\theta X)}{3500 \text{ (mg/L)}} \]
\[= \frac{3.18 \text{ (day)} \times 0.75 \times 6000 \text{ (mg/L)}}{0.24 \text{ day}^{-1}} \]
\[= 4441.46 \text{ kg/day} \]

Amount of BOD$_5$ removed
\[= (3500 - 16.5) \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} \]
\[= 1275 \text{ (m}^3/\text{day)} \times 10^3 \text{ (L/m}^3) \]
\[= 4441.46 \text{ kg/day} \]

\[\text{OLR} = \frac{(3500 - 16.5) \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)} \times 1275 \text{ (m}^3/\text{day)} \times 10^3 \text{ (L/m}^3)}{4050 \text{ (m}^3)} \]
\[= (4441.46/4050) \]
\[= 1.10 \text{ kg BOD/m}^3 \text{day} \]
(D) Sludge recycling

The recycling ratio \( r \) can be computed as follows:

\[
    r = \frac{X}{X_r - X} = \frac{0.75 \times 6000 \text{ (mg/L)}}{0.75 \times (20,000 - 6000) \text{ (mg/L)}} = 0.43
\]

Hence the recycling flow = \( 0.43 \times 1275 \text{ (m}^3/\text{day)} = 548.25 \text{ m}^3/\text{day} \)

(E) Sludge production

(i) Net VSS production = \( \frac{XV}{\theta_c} \)

\[
    0.75 \times 6000 \text{ (mg/L)} \times 10^{-6} \text{ (kg/mg)}
    \times 4050 \text{ (m}^3) \times 10^3 \text{ (L/m}^3) \\
    = \frac{1}{12 \text{ (day)}}
    = 1518.75 \text{ kg/day}
\]

(ii) Net SS production = \( \frac{1518.75 \text{ (kg/day)}}{0.75} \)

= 2025 kg/day

(iii) Volume of the sludge produced = \( \frac{2025 \text{ (kg/day)}}{1000 \text{ (kg/m}^3) \times 1.03 \times 0.02} \)

\[
    = 98.3 \text{ m}^3/\text{day}
\]

(iv) VSS production per kg BOD\(_r\),

\[
    = \frac{1518.75 \text{ (kg/day)} \times 10^6 \text{ (mg/kg)}}{(3500 - 16.5) \text{ (mg/L)} \times 1275 \text{ (m}^3/\text{day)} \times 10^3 \text{ (L/m}^3)}
    = 0.34 \text{ mg/mg}
\]

(F) Oxygen requirement

(i) Theoretical \( O_2 \) required = \( (\text{BOD}_L \text{ removed}) - (\text{BOD}_L \text{ of solids leaving}) \)

\[
    = 1.47 \times (3500 - 16.5) \text{ (mg/L)} \\
    \times 1275 \text{ (m}^3) \times 10^3 \text{ (L/m}^3) \\
    \times 10^{-6} \text{ (kg/mg)} - 1.42 \times 1518.75 \text{ (kg/day)}
    = 4372.32 \text{ kg/day}
\]

(ii) Theoretical air requirement assuming that air contains 23.2% oxygen by weight and density of air = 1.201 kg/m\(^3\),

\[
    = \frac{4372.32 \text{ (kg/day)}}{0.232 \times 1.201 \text{ (kg/m}^3)}
    = 15,692.11 \text{ m}^3/\text{day}
\]
(iii) Actual air requirement at an 8% transfer efficiency
\[ 15,692.11 \text{ (m}^3/\text{day})/0.08 = 196,151.41 \text{ m}^3/\text{day} \]

(iv) Check for the air requirement per unit volume
\[ 196,151.41 \text{ (m}^3/\text{day})/1275 \text{ (m}^3/\text{day}) = 153.84 \text{ m}^3/\text{m}^3 \]

(v) Air requirement per kg of BOD\(_5\) removed
\[ 196,151.41 \text{ (m}^3/\text{day})/4441.46 \text{ (kg/day)} = 44.16 \text{ m}^3/\text{kg BOD}_5 \text{ removed} \]

(G) Power requirement assuming the aerators are designed to give 2 kgO\(_2\)/kWh and the field efficiency is 70%.
\[
\text{Power required} = \frac{4372.32 \text{ (kg/day)}}{2 \text{ (kg/kWh)} \times 0.7 \times 24 \text{ (h/day)}} = 130.13 \text{ (kW)} \times 1.3410 \text{ (hp/kW)} = 174.5 \text{ hp (say 175 hp)}
\]

**Example 11**

A powdered activated carbon fed activated sludge process is designed to treat 15,000 GPD of pharmaceutical wastewater. The SCOD (soluble chemical oxygen demand) of the treated effluent is 590 mg/L. Determine the dose of PAC (powdered activated carbon) required for further reduction of effluent SCOD from 590 mg/L to 200 mg/L. Use the Freundlich equation [48]: \( X/M = (3.7 \times 10^{-6})C_e^{2.1} \) to determine the dose of powdered activated carbon.

**Solution**

(A) SCOD concentration at equilibrium \( C_e = 200 \text{ mg/L} \).

(B) Amount of SCOD removal attributed to the PAC, \( X \text{ (mg/L)} = 590 - 200 = 390 \text{ mg/L} \).

(C) The dose of activated carbon (\( M \)) can be determined by the Freundlich equation:
\[
\frac{X}{M} = (3.7 \times 10^{-6})C_e^{2.1} \\
M = X/3.7 \times 10^{-6} \times C_e^{2.1} \\
M = 390/3.7 \times 10^{-6} \times 200^{2.1} \\
M = 1551 \text{ mg/L (1.55 g/L)}
\]

(D) The dose of PAC per unit SCOD removed:
\[
\frac{X}{M} = \frac{1551 \text{ (mg/L)}}{390 \text{ (mg/L)}} = 3.98 \text{ mg PAC/mg SCOD}_e
\]
Example 12

The result of a pilot plant study of PAC-fed activated sludge process is given in the following table.

<table>
<thead>
<tr>
<th>PAC dose (mg/L)</th>
<th>Effluent SCOD in control reactor (mg/L)</th>
<th>Effluent SCOD in PAC-fed reactor (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>825</td>
<td>459</td>
</tr>
<tr>
<td>827</td>
<td>825</td>
<td>265</td>
</tr>
<tr>
<td>496</td>
<td>670</td>
<td>314</td>
</tr>
<tr>
<td>1520</td>
<td>583</td>
<td>194</td>
</tr>
</tbody>
</table>

PAC, powdered activated carbon; SCOD, soluble chemical oxygen demand.

Using the Freundlich equation \((X/M) = kC_e^{1/n}\), find the values of constants \(k\) and \(n\).

Solution

(A) The first step is to estimate the values of \(X/M\) against the equilibrium SCOD concentration. The SCOD removal attributed to PAC can be calculated by subtracting the effluent SCOD in the PAC-fed reactor from the effluent SCOD of the control reactor. The estimated values of \(X\) and \(X/M\) are given in the following table.

<table>
<thead>
<tr>
<th>PAC dose (mg/L) ((M))</th>
<th>Effluent SCOD ((mg/L)) (C_e)</th>
<th>SCOD removal by PAC ((mg/L)) (X)</th>
<th>Ratio ((X/M))</th>
<th>log (C_e)</th>
<th>log((X/M))</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>459</td>
<td>366</td>
<td>1.76</td>
<td>2.66</td>
<td>0.25</td>
</tr>
<tr>
<td>827</td>
<td>265</td>
<td>560</td>
<td>0.68</td>
<td>2.42</td>
<td>−0.17</td>
</tr>
<tr>
<td>496</td>
<td>314</td>
<td>356</td>
<td>0.72</td>
<td>2.50</td>
<td>−0.14</td>
</tr>
<tr>
<td>1520</td>
<td>194</td>
<td>389</td>
<td>0.20</td>
<td>2.29</td>
<td>−0.70</td>
</tr>
</tbody>
</table>

(B) The second step is to plot the log\((X/M)\) values against the various values of the log \(C_e\) as shown in Figure 7. By taking the log of both sides of the Freundlich equation we get a straight line whose intercept gives the value \(K\) and slope gives the value of \(1/n\). The log of the Freundlich equation results in the following equation:

\[
\log\left(\frac{X}{M}\right) = \log K + \left(\frac{1}{n}\right) \log C_e
\]

The values of log\((X/M)\) and log \(C_e\) have been calculated and given in the table above and plotted as shown in Figure 7. From the graph, the slope of the line gives a value of \(1/n = 2.4218\), hence \(n = 0.41\) and the intercept gives the value of log \(K = −6.1665\), hence \(K = 6.81 \times 10^{-7}\).

Example 13

An aerated lagoon is to be designed to treat 15,000 GPD of spent stream generated from a biological production plant. The depth of the lagoon is restricted to 3.3 m and the HRT of the...
Figure 7  Determination of $K$ and $n$. 

$y = 2.4218x - 6.1665$

$R^2 = 0.9467$
lagoon is 4 days. Determine the surface area of the lagoon. If the wastewater enters the lagoon at a temperature of 65°C and the mean ambient temperature is 30°C, estimate the lagoon temperature assuming complete mixing condition and exchange coefficient \( f = 0.5 \text{ m/day} \). Also comment on the effect of temperature on process efficiency.

**Solution**

Volume of the aerated lagoon (m\(^3\)) = \( \text{flow, } V \text{(GPD)} \times 3.785 \text{ (L/gal)} \times 10^{-3} \text{ (m}^3/\text{L)} \times \text{HRT, } t \text{(day)} \)

\[
= 15,000 \times 3.785 \times 10^{-3} \times 4 \\
= 227.1 \text{ m}^3
\]

Surface area of the lagoon (m\(^2\)) = \( \frac{\text{Volume, } V \text{ (m}^3\)}{\text{Depth, } D \text{(m)}} \)

\[
= (227.1/3.3) = 68.82 \text{ m}^2
\]

The lagoon temperature can be obtained by the law of conservation of energy:

Total heat gain = Total heat loss

\[
Q \text{ (GPD)} \times 3.785 \text{ (L/gal)} \times 10^3 \text{ (m}^3/\text{L)} \times (T_i - T_e) \text{ (°C)} = f \text{ (m/day)} \times A \text{ (m}^2\) \times (T_w - T_a) \text{ (°C)}
\]

For complete mixing condition:

\[
T_w = T_e = \frac{15,000 \times 3.785 \times 10^3 \times (65 - T_w)}{0.5 \times 68.82 \times (T_w - 30)}
\]

\[
T_w = 65^\circ \text{C}
\]

**Comment**

The temperature of the aerated lagoon of more than 38°C has been reported to decrease the system efficiency. At this high temperature nitrifiers cannot survive. Hence, a heat exchanger on the influent line must be provided to reduce the high temperature of the raw wastewater.

**Example 14**

Design a flow-through aerated lagoon to treat 0.575 MGD of composite wastewater generated from a pharmaceutical plant. Assume that the following conditions and requirements apply.

1. Mean cell residence time, \( t_c = 10 \text{ days} \);
2. Depth of the lagoon = 3.3 m;
3. Kinetic coefficients: \( Y = 0.6 \text{ mg/mg, } K_s = 210 \text{ mg/L, } k = 4.6 \text{ day}^{-1}, K_d = 0.1 \text{ day}^{-1} \);
4. Influent BOD\(_5\) after settling = 3100 mg/L;
5. Influent SS concentration = 1140 mg/L;
6. O\(_2\) transfer capacity of the aerator in field = 1.22 kg O\(_2\)/kWh;
7. Power requirement for mixing = 0.6 hp/1000 m\(^3\).

**Solution**

(A) Determine the size of the aerated lagoon based on \( t_c \) (solid retention time):
(i) Volume of wastewater generated per day
\[ = 0.575 \text{ (MGD)} \times (3.785 \times 10^3) \text{ (m}^3\text{/Mgal)} \]
\[ = 2176.37 \text{ m}^3/\text{day} \]

(ii) Volume of the aerated lagoon required
\[ = 2176.37 \text{ (m}^3/\text{day)} \times 10 \text{ (day)} \]
\[ = 21,763.75 \text{ m}^3 \]

(iii) Surface area of the lagoon
\[ = 21,763.75 \text{ (m}^3) \div 3.3 \text{ (m)} \]
\[ = 6595.07 \text{ m}^2 \]

(B) Determine the soluble effluent BOD$_5$ using the kinetic data:
\[ S = \frac{K_s(1 + \theta K_d)}{\theta (Y_k - K_d) - 1} \]
\[ = \frac{210 \text{ (mg/L)}[1 + 10 \text{ (day)} \times 0.1 \text{ (day}^{-1}])]}{10 \text{ (day)}[0.60 \text{ (mg/mg)} \times 4.6 \text{ (day}^{-1}) - 0.1 \text{ (day}^{-1})] - 1} \]
\[ = 16.41 \text{ mg/L} \]

(C) Determine the O$_2$ requirement:
(i) Estimate the concentration of biological solids produced
\[ = \frac{Y(S_i - S)}{1 + K_d \theta \xi} \]
\[ = \frac{0.6 \text{ (mg/mg)} (3100 - 16.41) \text{ (mg/L)}}{1 + 0.1 \text{ (day}^{-1}) \times 10 \text{ (day)}} \]
\[ = 925.08 \text{ mg/L} \]

(ii) Estimate the SS concentration in the lagoon before settling
\[ = 925.08 + 1140 \]
\[ = 2065.08 \text{ mg/L} \text{ (2065.08 g/m}^3\text{)} \]

(iii) Estimate the amount of solids wasted per day
\[ = 925.08 \text{ (g/m}^3\text{)} \times 10^{-3} \text{(kg/g)} \times 2176.37 \text{ (m}^3/\text{day)} \]
\[ = 2013.32 \text{ kg/day} \]

(iv) Estimate the amount of O$_2$ required
\[ = 1.47 \times 2176.37 \text{ (m}^3/\text{day)} \times (3100 - 16.41) \text{ (mg/L)} \]
\[ \times 10^{-3} \text{ (kg/mg} \cdot \text{L/m}^3\text{)} - 1.42 \times 2013.32 \text{ (kg/day)} \]
\[ = 7006.33 \text{ kg/day} \]
(D) Determine the power required to meet the O₂ requirement:

\[
\text{Power} = \frac{7006.33 \text{ (kg/day)}}{(1.22 \text{ kgO₂/kWh}) \times 24 \text{ (h/day)}}
\]

\[
= 239.29 \text{ kW}
\]

\[
\text{Power} = 239.29 \text{ (kW)} \times 1.3410 \text{ (hp/kW)}
\]

\[
= 320.89 \text{ hp}
\]

(E) Determine the power required for mixing:

(i) Lagoon volume = 21,763.75 \text{ (m³)} \times 35.3147 \text{ (ft³/m³)}

\[
= 768,580.3 \text{ ft}^3
\]

(ii) Power required for mixing

\[
= 768,580.3 \text{ (ft}^3) \times 0.6 \left(\frac{\text{hp}}{1000 \text{ ft}^3}\right)
\]

\[
= 461.15 \text{ hp}
\]

(F) Determine the horse-power rating of the aerator:

Horse power rating = 461.15 hp to fulfill the requirement of both mixing and O₂ supply

Example 15

Design a trickling filter to treat 33,800 GPD of pharmaceutical wastewater using the empirical method of Ten States for the data given below:

1. Influent BOD₅ of the raw wastewater, \( S_i = 6000 \text{ mg/L} \);
2. Efficiency of the filter, \( E = 90\% \);
3. Depth of filter is restricted to 1.8 m.

Solution

(A) Determine the recirculation ratio required to give 90% efficiency:

\[
E = \frac{(1 + R/Q)}{1.5 + (R/Q)}
\]

\[
0.90 = \frac{(1 + R/Q)}{1.5 + (R/Q)}
\]

\[
R/Q = 3.5
\]

\[
R = 3.5 \times 33,800 \text{ (GPD)}
\]

\[
= 118,300 \text{ GPD}
\]
(B) Determine the filter volume required by providing the maximum organic loading rate 1.2 kg/m³ day:

\[
V = \frac{[33,800 \text{ (GPD)} \times 3.785 \text{ (L/gal)} \times 0.9 \times 6000 \text{ (mg/L)}}{10^{-6} \text{ (kg/mg)}]/1.2 \text{ (kg/m³ day)}} = 575.70 \text{ m}^3
\]

(C) Determine the size of filter required:

Surface area required = 575.70 (m³)/1.8 (m)

\[
\frac{(\pi/4)D^2}{40.18 \text{ m (say 20.2 m)}} = 1.80 \text{ m}^3/\text{m}^2 \text{ day}
\]

(D) Hydraulic loading including the recirculation

\[
= \frac{(33,800 + 3.5 \times 33,800) \text{ (GPD)} \times (3.785 \times 10^{-3}) \text{ (m³/gal)}}{\frac{(\pi/4) \times (20.2)^2}{\text{m²}}} = 1.80 \text{ m}^3/\text{m}^2 \text{ day}
\]

Example 16

Design a UASB (upflow anaerobic sludge blanket) reactor for treatment of 435 m³/day of wastewater generated from a typical pharmaceutical plant. The COD removal efficiency of the reactor at HRT of 2 days and organic loading of 3.52 kg/m³ is 94%. Assume the following design data are applicable:

1. Influent COD = 7000 mg/L;
2. Methane yield = 0.35 m³/kg COD removed;
3. Solubility of methane = 0.028 m³/m³ effluent;
4. Biomass yield = 0.027 mg/mg;
5. MLVSS of the sludge bed = 70 kg/m³;
6. MLVSS of the sludge blanket = 4 kg/m³;
7. Depth of the sludge bed = 1.5 m;
8. Depth of the sludge blanket = 3.5 m.

Solution

(A) Determine the size of the reactor:

(i) Volume of the reactor, \( V = Q \times \theta \)

\[
V = 435 \text{ (m}^3/\text{day}) \times 2 \text{ (day)}
\]

\[
= 870 \text{ m}^3
\]

(ii) Depth of the reactor, \( H = 1.5 + 3.5 \)

\[
H = 5 \text{ m}
\]
(iii) Surface area required, \( A = \frac{V}{H} \)
\[ A = \frac{870 \text{ (m}^3\text{)}}{5 \text{ (m)}} = 174 \text{ m}^2 \]

(iv) Diameter of reactor, \( D = (4 \times \frac{A}{\pi})^{1/2} \)
\[ D = (4 \times \frac{174}{\pi})^{1/2} = 14.88 \text{ m (say 14.9 m)} \]

(B) Determine the organic loading rate
\[ = (Q \times S_i \times E / V) \]
\[ = 435 \text{ (m}^3\text{/day}) \times 7000 \text{ (mg/L)} \times 10^{-3} \text{ (kg/mg \cdot L/m}^3\text{)} \times 0.94/870 \text{ (m}^3\text{)} \]
\[ = 3.29 \text{ kg/m}^3 \text{ day} < 3.52 \text{ kg/m}^3 \text{ day, hence OK} \]

(C) Determine the upflow velocity, \( v = \frac{H}{\theta} \)
\[ v = 5 \text{ (m)/[2 (day) \times 24 (h/day)]} \]
\[ = 0.1 \text{ m/h} \]

(D) Determine the SRT:
(i) Total COD removed per day
\[ = 435 \text{ (m}^3\text{/day}) \times 7000 \text{ (mg/L)} \times 10^{-3} \text{ (kg/mg \cdot L/m}^3\text{)} \times 0.94 \]
\[ = 2862.3 \text{ kg/day} \]

(ii) Biomass produced per day
\[ = 0.027 \text{ (mg/mg)} \times 2862.3 \text{ (kg/day)} \]
\[ = 77.28 \text{ kg/day} \]

(iii) Total biomass in the reactor
\[ = \text{Biomass in the sludge bed + biomass in the sludge blanket} \]
\[ = 70 \text{ (kg/m}^3\text{)} \times \pi/4 \times (14.9)^2 \text{ (m}^2\text{)} \times 1.5 \text{ (m)} + 4 \text{ (kg/m}^3\text{)} \]
\[ \times \pi/4 \times (14.9)^2 \text{ (m}^2\text{)} \times 3.5 \text{ (m)} \]
\[ = 20,749.58 \text{ kg} \]

(iv) SRT = Total biomass in the reactor/biomass produced per day
\[ = 20,749.58 \text{ (kg)/77.28 \text{ (kg/day)}} \]
\[ = 268.5 \text{ day} \]

(E) \( F/M \) ratio
\[ = \frac{435 \text{ (m}^3\text{/day}) \times 7000 \text{ (mg/L)} \times 10^{-3} \text{ (kg/mg \cdot L/m}^3\text{)}}{20,749.58 \text{ (kg)}} \]
\[ = 0.15 \text{ day}^{-1} \]

(F) Methane production
(i) Total quantity of methane generated
\[ = 0.35 \text{ (m}^3\text{/kg CODr)} \times 2862.3 \text{ (kg CODr/day)} \]
\[ = 1001.8 \text{ m}^3\text{/day} \]
(ii) Methane leaving as dissolved in the effluent = 0.028 (m$^3$/m$^3$) $	imes$ 435 (m$^3$/day) 
= 12.18 m$^3$/day

(iii) Usable methane = 1001.8 – 12.18
= 989.62 m$^3$/day

(G) Specific gas production
(i) Specific gas production per m$^3$ per m$^3$ of reactor per day 
= 1001.8 (m$^3$/day)/870 (m$^3$) 
= 1.15 m$^3$/m$^3$/day

(ii) Specific gas production per m$^3$ per m$^3$ of effluent 
= 1001.8 (m$^3$/day)/435 (m$^3$/day) 
= 2.3 m$^3$/m$^3$

(H) Energy equivalent of biogas 
= 989.62 m$^3$/day $\times$ 10,000 (kcal/m$^3$) 
= 989.62 $\times$ 10$^4$ kcal/day 
= 989.62 $\times$ 10$^4$ (kcal/day) $\times$ 1.1633 $\times$ 10$^{-3}$ (kWh/kcal) 
= 11,512.25 kWh/day

(I) Coal equivalent of biogas = 989.62 $\times$ 10$^4$ (kcal/day)/4000 (kcal/kg) 
= 2474.05 kg/day 
= 2.47 tonnes/day

Example 17
Determine the size of the UASB reactor for the treatment of 1275 m$^3$/day of wastewater generated from a typical pharmaceutical plant with COD of 16,000 mg/L. The COD removal efficiency at an HRT of 4.7 days is 97%. If the following data and conditions are applicable, estimate (i) OLR and upflow velocity and (ii) methane yield and energy equivalent.

1. Overall depth = 4 m;
2. Percentage of methane in biogas = 65%;
3. Specific biogas production rate = 7.64 m$^3$/m$^3$ effluent.

Solution
(A) Determine the size of the reactor:
(i) Volume of the reactor, $V = Q \times \theta$
$V = 1275$ (m$^3$/day) $\times$ 4.7 (day)
= 5992.5 m$^3$
(ii) Surface area required, \( A = \frac{V}{H} \)
\[
A = \frac{5992.5 \text{ (m}^3\text{)}/4 \text{ (m)}}{4 \text{ (m)}} = 1498.125 \text{ m}^2
\]

(iii) Diameter of reactor, \( D = (4 \times \frac{A}{\pi})^{1/2} \)
\[
D = (4 \times \frac{1498.125}{\pi})^{1/2} = 43.67 \text{ m}
\]

Because the diameter required is much more, therefore three parallel units must be designed with area of each unit as follows:
Area = 1498.125 (m\(^2\))/3
\[
= 499.375 \text{ m}^2
\]
(iv) Diameter of each unit = \((4 \times \frac{499.375}{\pi})^{1/2}\)
\[
= 25.21 \text{ m}
\]

(B) Determine the OLR:

(i) Total COD removed/day = 1275 (m\(^3\)/day) \times 16,000 (mg/L) \times 10^{-3} (kg/mg \cdot L/m^3) \times 0.97
\[
= 19,788 \text{ kg/day}
\]

(ii) COD removed per unit = 19,788 (kg/day)/3
\[
= 6596 \text{ kg/day}
\]

(iii) OLR = 6596 (kg/day)/499.375 (m\(^2\))
\[
= 13.21 \text{ kg COD/m}^3\text{ day}
\]

(C) Determine the upflow velocity = \( \frac{H}{\theta} \)
\[
= 4 \text{ (m)}/[4.7 \text{ (day) \times 24 \text{ (h/day)}]}
= 0.035 \text{ m/h}
\]

(D) Determine the methane yield:

(i) Total quantity of methane generated
\[
= 7.64 \text{ (m}^3\text{/m}^3\text{ effluent) \times 1275 (m}^3\text{/day) \times 0.65}
= 6331.65 \text{ m}^3\text{/day}
\]

(ii) Methane yield = total methane generated/total COD removed
\[
= 6331.65 \text{ (m}^3\text{/day)}/19,788 \text{ (kg/day)}
= 0.32 \text{ m}^3/\text{kg COD}_r
\]

(E) Determine the energy equivalent:

(i) Methane leaving as dissolved in the effluent
\[
= 0.028 \text{ (m}^3\text{/m}^3\text{) \times 1275 (m}^3\text{/day)}
= 35.7 \text{ m}^3\text{/day}
\]
(ii) Usable methane = \(6331.65 - 35.7\)  
= \(6295.95\) \(\text{m}^3/\text{day}\)

(iii) Energy equivalent of biogas  
= \(6295.95\) \((\text{m}^3/\text{day}) \times 10,000\) (kcal/\(\text{m}^3\))  
= \(6295.95 \times 10^4\) kcal/day  
= \(6295.95 \times 10^4\) (kcal/day) \(\times 1.1633 \times 10^{-3}\) (kWh/kcal)  
= \(73,240.79\) kWh/day

5.11 DISCUSSION TOPICS AND PROBLEMS

1. The BOD\(_5\) and flow of various types of waste streams generated from Abbott Laboratory (a typical pharmaceutical plant) are given in the following table.

<table>
<thead>
<tr>
<th>Type of waste stream</th>
<th>Flow (MGD)</th>
<th>BOD(_5) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical waste</td>
<td>0.262</td>
<td>2520</td>
</tr>
<tr>
<td>Fermentation waste</td>
<td>0.312</td>
<td>3620</td>
</tr>
</tbody>
</table>

In addition, the plant generates 470 \(\text{m}^3/\text{day}\) of domestic wastewater with BOD\(_5\) = 675 mg/L. Calculate (a) BOD\(_5\) of the composite waste and (b) total BOD load of the plant.  
[Answers: (a) = 2684.09 mg/L; (b) 7091.18 kg BOD/day]

2. A synthetic organic chemical plant generates mainly two types of waste streams, i.e., strong process waste and dilute process waste. The BOD\(_5\) of the 45,000 GPD of combined waste generated from the plant is 75,000 mg/L. If the BOD\(_5\) and flow of the dilute process waste are 1200 mg/L and 33,800 GPD, respectively, estimate (a) BOD\(_5\) of the strong process waste and (b) the BOD load of each waste stream and their contribution to the total BOD load of the plant.  
[Answer: (a) = 297,717.73 mg/L; (b) BOD load of strong and dilute process waste = 12,620.85 kg/day (98.8%) and 153.52 kg/day (1.2%), respectively]

3. A primary settling tank is designed for the pretreatment of 0.575 MGD of wastewater with SS concentration of 1140 mg/L generated from a typical pharmaceutical plant. If the SS removal efficiency of the sedimentation tank is 60%, find (a) the effluent SS concentration and (b) the quantity of sludge generated. Assume the specific gravity of the sludge is 1.03 and that the sludge contains 5% solids.  
[Answer: (a) = 456 mg/L; (b) 7636.89 GPD]

4. A typical pharmaceutical industry generates 15,000 GPD of wastewater with SS concentration 800 mg/L. The addition of alum (200 mg/L) and FeCl\(_3\) (150 mg/L) reduces the SS concentration of effluent from 800 mg/L to 50 g/L. Determine the quantity of sludge generated per week. Assume the specific gravity of the sludge is 1.04 and that the sludge contains 3% solids.  
[Answer: 3014.5 GPD]

5. The BOD removal efficiency of an activated sludge process treating 2000 \(\text{m}^3/\text{day}\) of condensate waste generated from a synthetic organic chemical plant is 94%. If the organic loading rate and BOD\(_5\) of the raw waste are 3.171 kg/\(\text{m}^3\) day
and 1275 mg/L, estimate (a) \( \text{BOD}_5 \) of the treated effluent and (b) hydraulic retention time.

[Answer: (a) 76.5 mg/L; (b) 9.12 h]

6. An activated sludge process is designed to treat 1950 m\(^3\)/day of pharmaceutical wastewater with \( \text{BOD}_5 \) concentration of 3250 mg/L. If the performance efficiency of the process based on \( \text{BOD}_5 \) removal is 85%, determine (a) the organic loading rate (OLR) and \( \text{BOD}_5 \) of the treated effluent, assuming the following data and conditions are applicable:

(i) Aeration tank volume = 1500 m\(^3\);
(ii) Depth of the aeration tank = 2.5 m;
(iii) MLVSS = 6000 mg/L.

Also compute (b) the hydraulic loading rate and F/M ratio.

[Answer: (a) OLR = 3.59 kg/m\(^3\) day and \( \text{BOD}_5 = 487.5 \text{ mg/L} \); (b) HLR = 3.25 m\(^3\)/m\(^2\) day and F/M ratio = 0.7 day\(^{-1}\)]

7. Determine the F/M ratio and solid retention time of an extended aeration system designed for the treatment of 33,800 GPD of pharmaceutical wastewater. The \( \text{BOD}_5 \) of the raw wastewater and treated effluent are 5000 mg/L and 560 mg/L, respectively. Assume the following data and conditions are applicable:

(i) HRT = 5 days;
(ii) MLSS = 5600 mg/L;
(iii) MLVSS/MLSS = 0.75;
(iv) \( Y_n = 0.45 \text{ mg/mg} \).

[Answer: F/M = 0.24 day\(^{-1}\) and SRT = 10.51 days]

8. The PAC-fed activated sludge process is designed to treat the alkaline waste stream generated from a synthetic organic chemical plant. The influent \( \text{BOD}_5 \) of the alkaline waste is 1275 mg/L, which can be treated to a \( \text{BOD}_5 \) of 275 mg/L by the activated sludge process. The addition of PAC at a dose of 500 mg/L gives a further reduction of effluent \( \text{BOD}_5 \) from 275 mg/L to 150 mg/L. Determine the constant \( K \) of the Freundlich equation given below \( (X/M) = KC_x^{1/2} \). Also comment on the efficiency of the system before and after addition of PAC.

[Answer: \( K = 4.08 \times 10^{-6} \); performance efficiency of the system can be increased by approximately 10% by addition of PAC]

9. An aerated lagoon is designed to treat 435 m\(^3\)/day of acid waste stream with a \( \text{BOD}_5 \) of 3500 mg/L generated from a synthetic organic chemical plant. The depth of lagoon is restricted to 4 m and organic loading rate is 0.7 kg/m\(^3\) day. Estimate (a) the surface area and hydraulic loading rate. If the performance efficiency of the lagoon is 97%, determine (b) the \( \text{BOD}_5 \) of the treated effluent.

[Answer: (a) \( A = 527.44 \text{ m}^2 \) and HLR = 0.82 m\(^3\)/m\(^2\) day; (b) 105 mg/L]

10. An aerated lagoon is designed to treat 0.575 MGD of composite waste (including chemical and fermentation waste) with a \( \text{BOD}_5 \) of 3150 mg/L. The depth and HRT of the lagoon are restricted to 3.5 m and 5 days, respectively. Find (a) the surface area of the lagoon. If the temperature of composite waste entering into the lagoon is 60°C and mean ambient temperature is 15°C during winter, estimate (b) the lagoon temperature assuming complete mixing condition and exchange coefficient \( f = 0.54 \text{ m/day} \). Also comment (c) on the effect of wastewater temperature in the process efficiency of the lagoon.

[Answer: (a) \( A = 3109.10 \text{ m}^2 \); (b) \( T_w = 40.4°C \); (c) the temperature of waste 60°C will result in the temperature in aerated lagoon being >38°C, which is found to reduce the process efficiency]
11. A trickling filter is designed to treat 435 m$^3$/day of acid waste stream generated from a synthetic organic chemical plant. The BOD$_5$ of the acid waste before and after the primary sedimentation is 3250 mg/L and 2850 mg/L, respectively. The efficiency of the filter at a recirculation ratio of 4.5 is 92%. If the depth of filter is restricted to 1.6 m and the value of the constant in Eckenfelder’s equation is $n = 0.5$, determine the value of constant $K_f$ assuming the hydraulic loading rate $= 17.5$ m$^3$/m$^2$·day.

Answer: $K_f = 3.12$ m$^{1/2}$·day$^{1/2}$

12. A pharmaceutical wastewater with BOD$_5$ of 3000 mg/L is to be treated by a trickling filter. Design the filter for 15,000 GPD of wastewater to give the desired effluent BOD$_5$ of 50 mg/L. Use the NRC (U.S. National Research Council) equation for the design of the filter. The following data and conditions are applicable:
(i) Depth of filter $= 1.7$ m;
(ii) Recirculation ratio $= 2:1$;
(iii) Wastewater temperature $= 20^\circ$C;
(iv) Assume efficiencies of the two-stage filters are equal: $E_1 = E_2$.

Answer: (a) $E_1 = E_2 = 87%$; (b) diameter of 1st stage filter $D_1 = 23$ m and 2nd stage filter $D_2 = 63.95$ m

13. A UASB reactor is designed to treat 1275 m$^3$/day of wastewater with a BOD concentration of 2000 mg/L generated from a typical pharmaceutical industry. At an HRT of 1.5 days, the COD and BOD removal efficiencies of the reactor are 80 and 95%, respectively. Determine (a) the size of the reactor; (b) the total quantity of methane produced; and (c) the coal equivalent and energy equivalent. Assume that the following data and conditions are applicable:
(i) Depth of the reactor is restricted to 4.5 m;
(ii) Biogas yield = 0.6 m$^3$/kg COD$_r$;
(iii) Methane content of biogas = 70%;
(iv) Solubility of methane = 0.028 m$^3$/m$^3$ effluent;
(v) Calorific value of methane = 10,000 kcal/m$^3$;
(vi) Calorific value of coal = 4000 kcal/kg.

Answer: (a) Diameter = 23.26 m; (b) 1102.24 m$^3$/day; (c) 2.67 tons/day and 12,410 kWh/day

14. The COD removal efficiency of a UASB reactor treating pharmaceutical wastewater is 96% at an organic loading rate of 0.5 kg COD/m$^3$·day. If the plant generates 33,800 GPD wastewater with a COD concentration of 1000 mg/L and the depth of reactor is restricted to 3 m, estimate (a) the size of the UASB reactor; (b) the HRT; and (c) the specific gas production rate assuming a methane yield of 0.3 m$^3$/kg COD$_r$.

Answer: (a) Diameter = 10.21 m; (b) 1.92 days; (c) 0.29 m$^3$/m$^3$ effluent and 0.15 m$^3$/m$^3$·day

**NOMENCLATURE**

<table>
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<tr>
<th>Abbreviation</th>
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<tr>
<td>APCI</td>
<td>Alexandra Company for Pharmaceutical and Chemical Industry</td>
</tr>
<tr>
<td>AMFFR</td>
<td>anaerobic mesophilic fixed film reactor</td>
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<td>ASP</td>
<td>activated sludge process</td>
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<tr>
<td>ATFFR</td>
<td>anaerobic thermophilic fixed film reactor</td>
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<tr>
<td>Symbol</td>
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<td>--------</td>
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<tr>
<td>BOD</td>
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**REFERENCES**


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