

Wastewater Treatment Technologies

Ø ZDHC

The Roadmap To Zero Programme

Signatory Brands:



Value Chain Affiliates:



Associates:



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Foreword

The apparel industry uses vast quantities of fresh water and discharges significant volumes of wastewater. These discharges contribute to pollution of waterways in China, Southeast Asia and other production countries around the world. The ZDHC Roadmap to Zero Programme released the first ZDHC Wastewater Guidelines for the apparel, textile and footwear industry at the end of 2016. These Guidelines are an attempt to document a unified set of global wastewater quality expectations.

Wastewater treatment of apparel and footwear industry discharges is a complex process and we hope that this technical overview of the wastewater treatment process, together with regional training programmes and other relevant references, will help to close the knowledge gap on wastewater treatment technologies and thereby motivate fabric mills and other relevant facilities of the global apparel and footwear industry to implement the professional treatment systems necessary to meet the ZDHC Wastewater Guidelines.

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1.0.0 Global perspective on textile effluents

One of the main sources with severe pollution problems worldwide is textile industry effluent containing synthetic dyes and other auxiliary chemicals. The textile dyeing and finishing industry is the largest user of the US\$14.5 billion commercial dyes and pigments industry which is predicted to reach US\$42 billion by 2021 according to some market research^{1, 2, 3}. The textile industry in turn depends on population growth and private consumer spending. The global ready-made garments (RMG) industry is a US\$445 billion industry⁴. The biggest exporters of RMG are in Asia, with China and Bangladesh being the leading exporters.

Since the discovery of synthetic dyes in 1856, today there are over 10,000 textile dyes being manufactured with an annual production in excess of 700,000 tonnes⁵. Thirty percent of these dyes are used in excess of 1,000 tonnes per annum. Since only 50 – 95% of the dyes used are fixated on the fabric, approximately 280,000 tonnes are discharged annually – either to wastewater treatment plants or directly to the environment^{6, 7}. Whilst some of these dyes and auxiliary chemicals are biodegradable and get absorbed into the biomass, many are not, including chemicals belonging to one of the most frequently used dye classes known as azo dyes. Azo dyes account for 70% by weight of all dyes used worldwide⁸. Figure 1 shows the percentage of dyes used by the major users which are also textile exporters.

¹ Freedonia, "World Dyes and Organic Pigments", Freedonia Group 2017.

² Dyes Chemical Economics Handbook, IHS, 2014.

³ ReportsnReports, "Dyes and Pigments Market Growing at a CAGR of 5% during 2016- 2021", www.prnewswire.com.

⁴ Faruque Hassan, "Global Trends in the Garment Sector and Opportunities for Bangladesh", BGMEA, 2016.

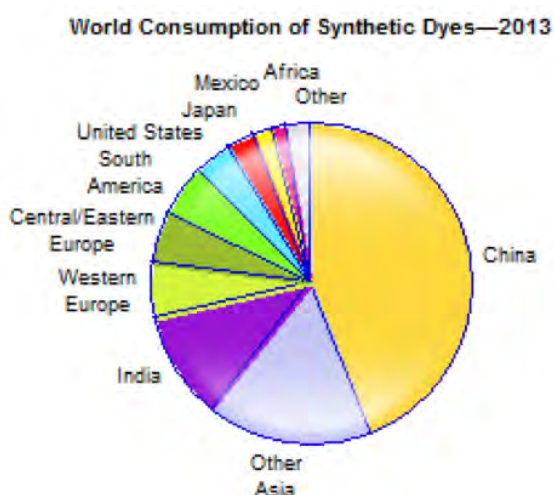
⁵ Zaharia Carmen Suteu Daniela, "Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination procedures from Industrial Effluents – A Critical Overview", Gheorge Asachi Technical University of Iasi, Romania.

⁶ Radin Maya, Saphira Radin Mohamed et al, "Colour Removal of Reactive Dye from Textile Industrial Wastewater using Different Type of Coagulants", Asian Journal of Applied Sciences, Vol. 02, Issue 05, October 2014.

⁷ R.G. Saratale et al, "Bacterial decolourization and degradation of azo dyes – A Review", Journal of Taiwan Institute of Chemical Engineers, Vol. 42, 2011.

⁸ Farah Chequer, et al., "Azo Dyes and their metabolites : Does the discharge of Azo Dyes into water bodies represent human and ecological risks?", Chapter 2, Advances in Treating Textile Effluent, Intechopen, 2011.

Figure 1: World Consumption of Synthetic Dyes (2013)



Source: Chemical Economics Handbook, 2014

The textile dyeing and finishing industry is a water intensive industry using large quantities of fresh water as process water. Specific water use can range from 25 to 180 L/kg of fabric. Much of the water use is in cotton dyeing rather than synthetic fabrics, as seen in Table 1⁹.

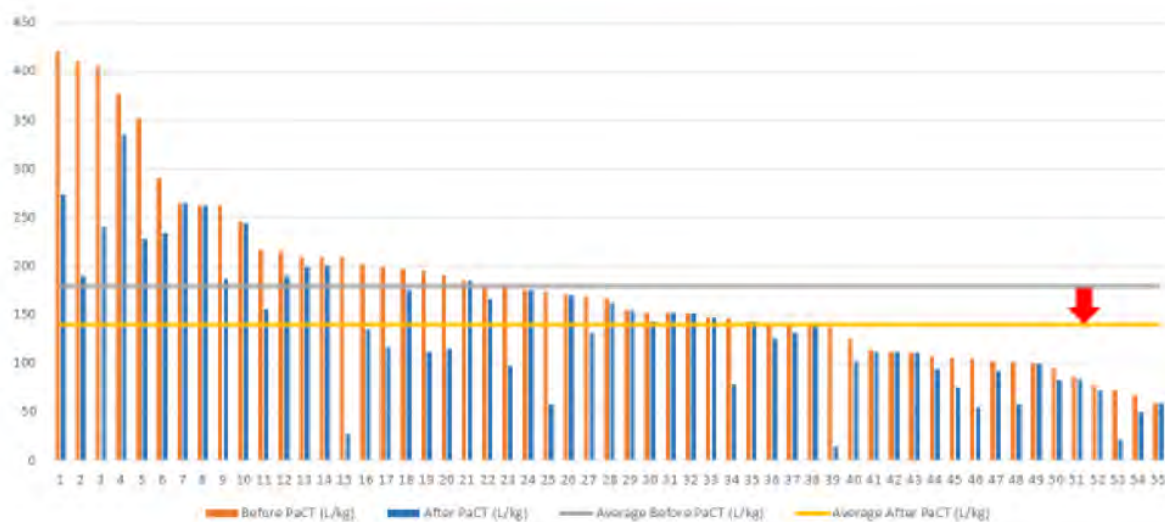
Table 1: Specific water consumption of fabric dyeing

| Fabric | Specific consumption (L/kg) |
|--------------------------------|-----------------------------|
| Cellulosic fabric | 100 – 120 |
| Synthetic fibre, yarn & fabric | 25 – 70 |
| Grey polyester fibre | 30 – 40 |
| Acrylic fibre | 25 – 30 |
| Grey viscose fibre | 70 – 80 |
| Grey cotton fibre | 100 – 140 |
| Raw wool | 40 – 50 |
| Scoured wool fibre | 80 – 100 |
| Grey cotton yarn | 70 – 80 |
| Grey cotton fabric | 150 – 180 |
| Grey polyester cotton fabric | 100 -120 |

However as seen from Bangladesh PaCT (Partnership for Cleaner Textile) experience, typical water use can be as high as 400 L/kg, as shown in Figure 2.

Figure 2: Specific water consumption in RMG (ready-made garment) sector in Bangladesh

On average, **55** factories undergoing **in-depth CP** reduced from **179 L/kg** to **140 L/kg**, a **22% reduction**



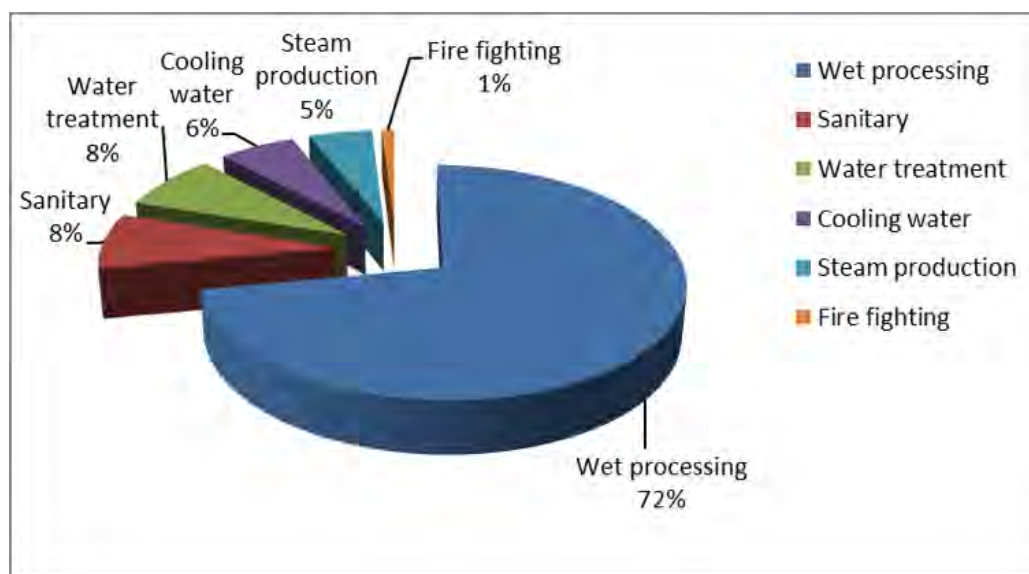
Source: Bangladesh PaCT



Of the total water used in wet dyeing and finishing facilities, nearly 72% of the water used is process water which then ends up as wastewater. Figure 3 shows a typical breakdown of water use in a textile wet dyeing facility⁹.

⁹Ministry of Environment and Forest, "Guide for Assessment of Effluent Treatment Plant", June 2008.

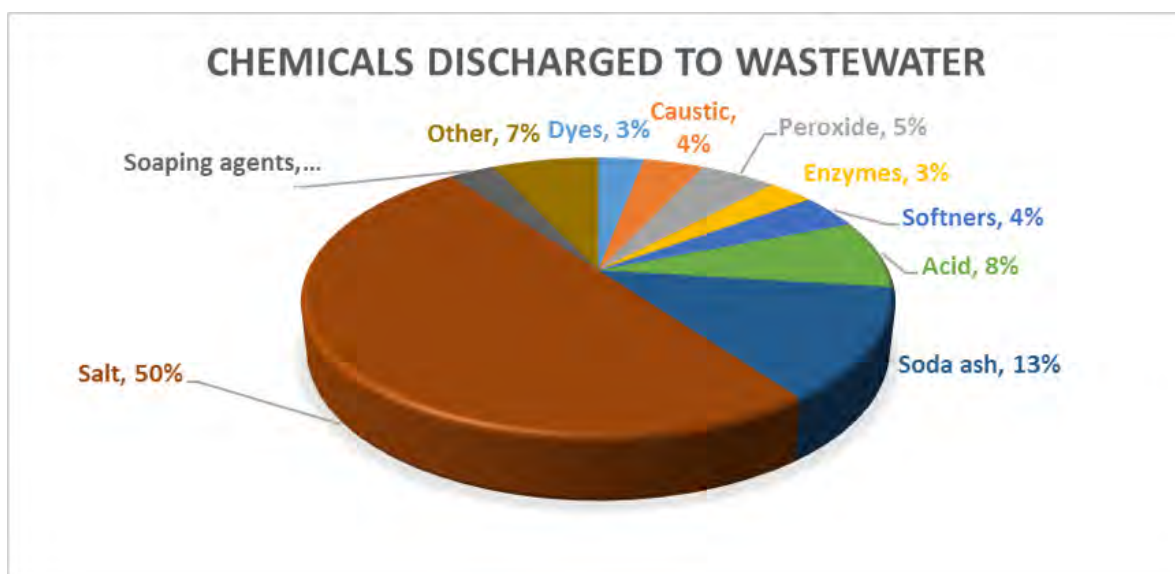
Figure 3: Breakdown of water consumption in a typical wet dyeing facility



The World Bank estimates that 17 – 20% of industrial water pollution comes from dyeing and finishing treatment given to fabrics¹⁰. Textile wastewater is a mixture of many different compounds consisting of fiber and lint, rich in colour from dyes and chemicals, salts like sodium chloride and sulfate, alkalis contributing to high pH, biodegradable organic compounds, recalcitrant compounds (persistent organic compounds) from aromatic and heterocyclic compounds, oil and grease, hydrocarbons, hazardous heavy metals, surfactants, anionic compounds and volatile compounds. Figure 4 shows the breakdown of typical wastewater effluent breakdown. Whilst salts account for close to 50% of the effluent, and contribute to the high total of dissolved solids, others contribute to biological oxygen demand (BOD) and chemical oxygen demand (COD). Some compounds without adequate treatment can remain in the environment for a long time. For example, the half-life hydrolysed Reactive Blue 19 dye has a half-life of around 47 years at a pH of 7 and at a temperature of 25°C. Breakdown products of recalcitrant organic chemicals themselves are toxic, carcinogenic or mutagenic to life forms, mainly due to them containing carcinogenic compounds such as benzidine, naphthalene and other aromatic compounds. The need for pollution control through well-designed wastewater treatment facilities is now recognised in ready-made garment exporting countries like China, India and Bangladesh. In India, after a well-documented court judgement, Tiruppur installed one of the first zero liquid discharge treatment plants. Ethiopia, which is emerging as a new sourcing location, has incorporated zero liquid discharge in their industrial parks.

Given the complexity of textile effluent, a proper understanding of textile effluent and its treatment is necessary to make the industry sustainable and pollution free.

Figure 4: Percentage breakdown of chemical contaminants in textile wastewater



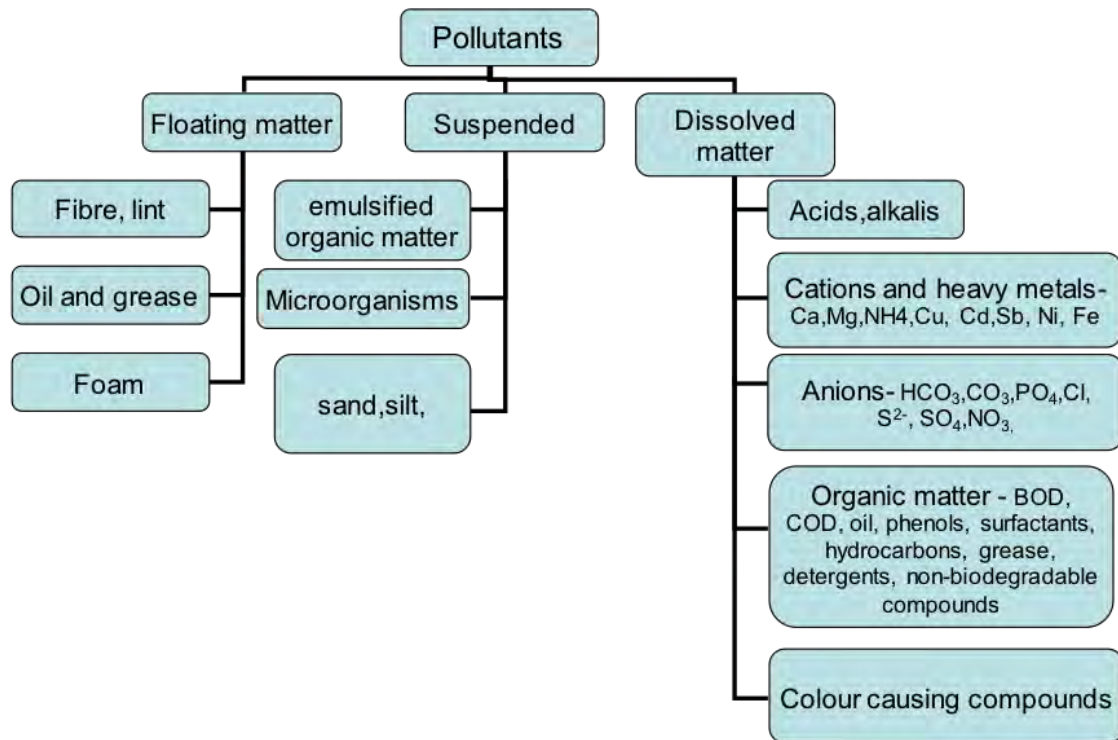
Source: Bangladesh PaCT (Partnership for Cleaner Textiles), "Feasibility Study for Setting Up CETP in the Konabari Cluster", TWIC Report, 2016

¹⁰Rita Kant, "Textile Dyeing Industry – An Environmental Hazard", Journal of Natural Science, Volume 4, No.1, 22 – 26, 2012.

2.0.0 Wastewater characteristics

The main pollutants in textile effluent can be classified into three main categories as floating matter, suspended and dissolved matter, as shown in Figure 5.

Figure 5: Classification of pollutants



Source: Mohan Seneviratne

Many sources of wastewater can be found in a textile processing plant, as shown in Table 2.

The effluent can be segregated depending on the degree of pollution into low, medium and high. Non-contact once-through cooling water and steam condensate generally requires no further treatment and can be reused.

Medium concentration contaminants like boiler blowdown, storm water, cooling tower blowdown can be reused after some initial pretreatment to remove TDS, suspended solids and oil and grease removal, etc., or after cooling of boiler blowdown to reduce the temperature. Boiler blowdown and excess steam condensate are frequently used as cooling tower makeup. High concentrations of contaminants mainly come from process wastewater. These contain

a large range of chemicals depending on the process that requires a careful evaluation of the type of contaminant, their concentration, flow and ease of biodegradability. As little as 1 mg/L concentration in the water discharged can give rise to coloured water which affects the aesthetic quality and transparency of water bodies which impacts on photosynthesis. High BOD and COD also contributes to low oxygen concentrations in water bodies and together adversely impacts the aquatic life of water bodies. Acids and alkalis create low or high pH situations. Dyes have low fixation to the fabric and some are hard to degrade through conventional treatment processes. Some azo dyes have long half-lives, bioaccumulate in the food chain and a minority of them are considered carcinogens^{11, 12, 13, 14}. Similarly, a group of chemicals – collectively known as "*Detox Chemicals*", first identified by Greenpeace in a landmark report known as *Dirty Laundry* – are banned from use by leading apparel and footwear brands, given their potential risks to human health and the environment¹⁵. These may still be found as impurities in formulations and their removal or finding suitable substitutes is a major focus for the industry. Examples are chlorinated aromatic hydrocarbons; alkyl phenol ethoxylates (APEOs); short chain chlorinated paraffins (SCCP); halogenated flame retardants; chlorinated solvents; heavy metals namely cadmium, hexavalent chromium, mercury and lead; organotin compounds, etc.

ZDHC benchmarked the prevalence of 11 chemical classes in the final effluent discharges from suppliers in Bangladesh, China, India, Vietnam and Taiwan¹⁶. These results are shown in Figure 6. Their concentrations are found in parts per billion (ppb) and may not be readily detected in effluent samples. In some locations, some of these chemicals are already present in the incoming fresh water and not necessarily added by the supplier. These 11 chemical groups are the focus of ZDHC.

¹¹ Farah Maria Drummond Chequer, et al., "*Textile Dyes – Dyeing Process and Environmental Impact*", Eco-Friendly Textile Dyeing and Finishing, Intechopen.com/books.

¹² A. Puntener and C. Page, "*European Ban on Certain Azo Dyes*", www.tfl.com.

¹³ Farah Maria Drummond Chequer, "*Azo Dyes and Their Metabolites: Does the Discharge of the Azo Dye into Water Bodies Represent Human and Ecological Risks?*", *Advances in Treating Textile Effluent*, Prof. Peter Hauser (Ed.), ISBN: 978-953-307-704-8, InTech, 2011.

¹⁴ Parliamentary Office of Science and Technology, "*Environmental Health and Economic Impact of Azo Dyes*", www.parliament.uk/post.

¹⁵ Greenpeace, "*Dirty Laundry – Unravelling the Corporate Connections to Toxic Water Pollution in China*", 2011.

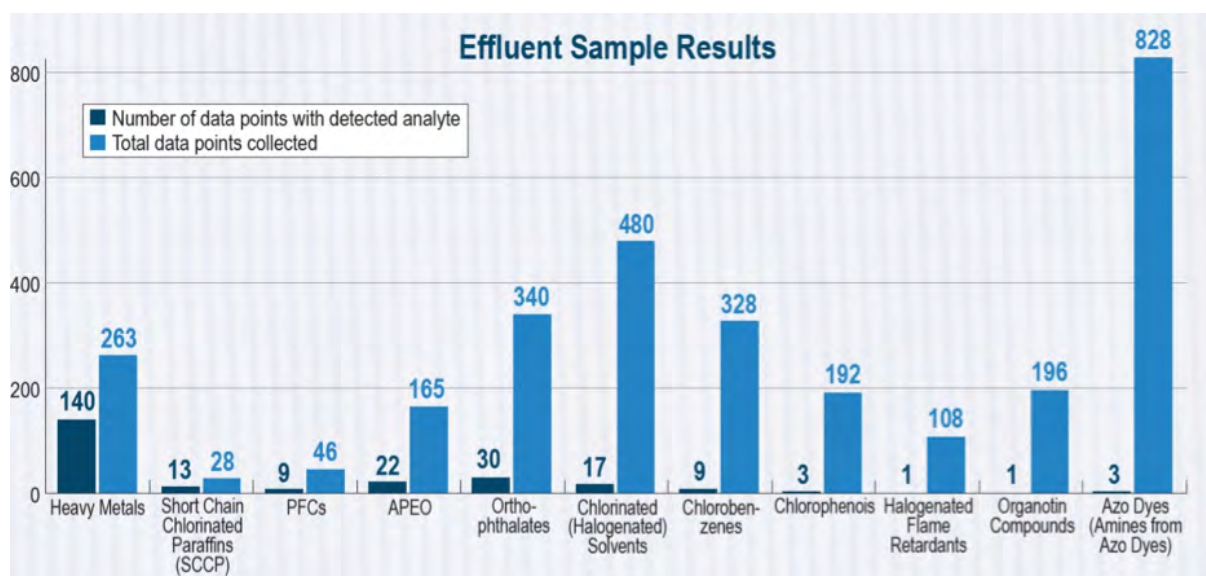
¹⁶ ZDHC, "*Zero Discharge of Hazardous Chemicals Benchmarking Report*", July 2013.

Table 2: Sources of wastewater in a textile dyeing and finishing processing plant

| Degree of pollutants | Category of wastewater | Source | Typical concentrations |
|----------------------|---|--|---|
| Low | Non-contact cooling water | Heat exchangers, generators and power boiler cooling towers steam trap leaks | Can be low in Total Dissolved Solids (TDS). Ideally needs to be segregated before treatment. Steam condensate - low TDS, sometimes high pH. |
| Medium | Storm water | Parking lots and roof drains | Oil and grease (O&G). Stormwater needs to be properly handled with a first flush system. |
| | Clean-up | Machine maintenance, filter backwash | Sodium chloride (NaCl), O&G. |
| | Boiler blowdown, cooling tower blowdown | Boiler blowdown | High temperature, Boiler blowdown - high TDS and high pH. Cooling tower blowdown - high TDS, high SS |
| High | Process Waste | Sizing | Starch, waxes, Carboxyl methyl cellulose, (CMC), Polyvinyl alcohol (PVA) and Wetting agents. High in COD and BOD. Typical water requirements are 0.5 to 8.5 L/kg with an average of 4.35 L/kg. |
| | | Desizing | Starch, CMC, PVA, Fats, Waxes, Antistatic compounds, surfactants, Enzymes, mono and dipersulfates for oxidative desizing, surfactants and complexing agents High in BOD, Suspended solids (SS), TDS. Small volume. Typical water requirements are 2.5 to 21 L/kg with an average of 11.75 L/kg. |
| | | Scouring | Strong alkali (sodium hydroxide -NaOH), alkaline resistant and electrolyte resistant surfactants (fatty alcohols ethoxylates, alkane sulfonates) and complexing agents. Typical water requirements are 20 – 45 L/kg with an average of 32.5 L/kg. |

| | | | |
|------|---------------|-------------|--|
| High | Process Waste | Bleaching | Hydrogen peroxide, sodium hypochlorite, chlorine, acids, NaOH, surfactants, sodium silicate (Na ₂ SiO ₃), sodium sulfite, sodium phosphate(Na ₃ PO ₄), enzymes to remove surplus peroxide, short cotton fibre. High in alkalinity, TDS, SS and fiber. Low BOD. Bleaching typically requires 24 – 48 L/kg |
| | | Mercerising | NaOH, ammonia, cotton wax, wetting agents stable in high pH (low molecular alkyl sulfates and alkane sulfonates), antifoaming agents, complexing agents. Low BOD (less than 1% of total), TDS and O&G. Typical water requirements are 17 – 32 L/kg with an average of 24.5 L/kg. |
| | | Dyeing | Dyes, urea, reducing agents, oxidising agents, acetic acid, wetting agents, solvents, fatty alcohol and alkyl phenol ethoxylates, aromatic hydrocarbons, chlorinated aromatic compounds, s, naphthalene sulfonic acid, polyamides, formaldehyde, nitrobenzene and other restricted substances. Strongly coloured, heavy metals, High BOD, TDS, and low in SS, sulfide (S ²⁻). |
| | | Padding | Polyacrylates, polyacryl amides, foaming surfactants, co-polymers, ethylene oxide, aryle ether sulfates. |
| | | Printing | Pastes, urea, starches, gums, binders, acids, thickeners, alkalis, reducing agents, film forming substances (styrene butadiene co-polymers), polyacrylates, mineral oils, alkylarylethoxylates (APEO), isopropanol, melamine derivatives etc. Highly coloured, high BOD, Oily appearance, heavy metals, high SS and slightly alkaline. Very small volume. |
| | | Finishing | High in BOD, COD, Toxic compounds and solvents. Very small volume |
| | | Repellents | Fluorocarbon resins, polysiloxanes, aluminium, zirconium and chromium compounds. |

Figure 6: Detox Chemicals prevalence in selected sites



Source: ZDHC Benchmarking Report July 2013

The characteristics of effluent from the various process streams are shown in Table 3¹⁷. In general, the BOD/COD ratio provides an indicator on the ease of biological treatment. Biological treatment processes generally start quickly and proceed rapidly with a BOD: COD ratio of 0.5 or greater. Ratios between 0.2 and 0.5 are amenable to biological treatment, but decomposition may proceed more slowly because degrading microorganisms need to become acclimated to the wastewater. A ratio of less than 0.2 indicates serious limitations for biological treatment. The BOD: COD ratio of industrial wastewater is typically less than 0.5, except for wastewaters from the food and beverage industries, which are often significantly higher than 0.5.

¹⁷ A.E. Gahly, R. Ananthashankar, M. Alhattab and V.V. Ramakrishnan, "Production, Characterization and Treatment of Textile Effluents – A Critical Review", Journal of Chemical Engineering & Process Technology, 2014.

Table 3: Dye processing pH, BOD and COD in unit processes

| Source of effluent | pH | BOD (mg/L) | COD mg/L | BOD/COD |
|-----------------------------------|------------|---------------|-----------------|-------------|
| Process effluent | 5.8 – 6.5 | 1,700 – 5,200 | 10,000 – 15,000 | 0.17 – 0.34 |
| Scouring | 10 – 13 | 260 – 400 | 1,200 – 3,300 | 0.22 – 0.12 |
| Bleaching | 8.5 – 9.6 | 50 – 100 | 150 – 500 | 0.3 – 0.2 |
| Mercerising | 8.0 – 10.0 | 20 – 50 | 100 – 200 | 0.20 – 0.25 |
| Dyeing | 7 – 10 | 400 – 1,200 | 1,000 – 3,000 | 0.4 |
| Wash Effluent | | | | |
| After bleaching | 8.0 – 9.0 | 10 – 20 | 50 – 100 | 0.2 |
| After acid rinsing | 6.5 – 7.6 | 25 – 50 | 120 – 250 | 0.2 |
| After dyeing (hot wash) | 7.5 – 8.5 | 100 – 200 | 300 – 500 | 0.3 – 0.4 |
| After dyeing (acid and soap wash) | 7.5 – 8.64 | 25 – 50 | 50 – 100 | 0.5 |
| After dyeing (final wash) | 7.0 – 7.8 | | 25 – 50 | |
| Printing washing | 8.0 – 9.0 | 115 – 150 | 250 – 450 | 0.46 – 0.33 |
| Blanket washing of rotary printer | 7.0 – 8.0 | 25 – 50 | 100 – 150 | 0.25 – 0.3 |

From Tables 2 and 3 it is evident that characterising and segregating the wastewater streams according to their pollution load will result in the optimal treatment of wastewater. Segregating the low concentration streams from the high concentration streams enables reducing the minimal amount of treatment to be applied without treating all of the wastewater that would otherwise get diluted from the low concentration steam condensate, storm water or cooling tower blowdown. Some factories go to the extent of segregating the sizing effluent from the dye effluent since it impacts on zero liquid discharge operations. Others segregate high pH streams from low pH streams to reduce the amount of acid required to bring the effluent to neutral pH. Water conservation practices will also help to reduce the capacity of the effluent treatment plant (ETP). Table 4 shows characteristics of typical untreated textile wastewater.

Table 4: Typical characteristics of untreated effluent¹⁸

| Parameter | Range |
|-------------------------------------|---|
| pH | 6 – 10 |
| Temperature °C | 35 – 45 |
| Total dissolved solids mg/L | 1,000 – 12,000 |
| Biological Oxygen Demand (BOD) mg/L | 80 – 6,000 |
| Chemical Oxygen Demand (COD) mg/L | 150 – 12,000 |
| Total suspended solids (TSS), mg/L | 15 – 8,000 |
| Chloride, mg/L | 1,000 – 6,000 |
| Free chlorine, mg/L | <10 |
| Oil & Grease, mg/L | 10 – 30 |
| Total Kjeldahl Nitrogen (TKN) mg/L | 70 – 80 |
| Nitrate (NO ₃) mg/L | <15 |
| Free ammonia, mg/L | <10 |
| Colour (Pt-Co) | 50 – 2,500 |
| Sulphate, (SO ₄) mg/L | 600 – 1,000 |
| Heavy metals, mg/L | <10 |
| ZDHC MRSL chemicals* | Not typically regulated or measured in influent water |

*ZDHC MRSL – ZDHC Manufacturing Restricted Substances List. For more information, refer to the ZDHC Wastewater Guidelines.

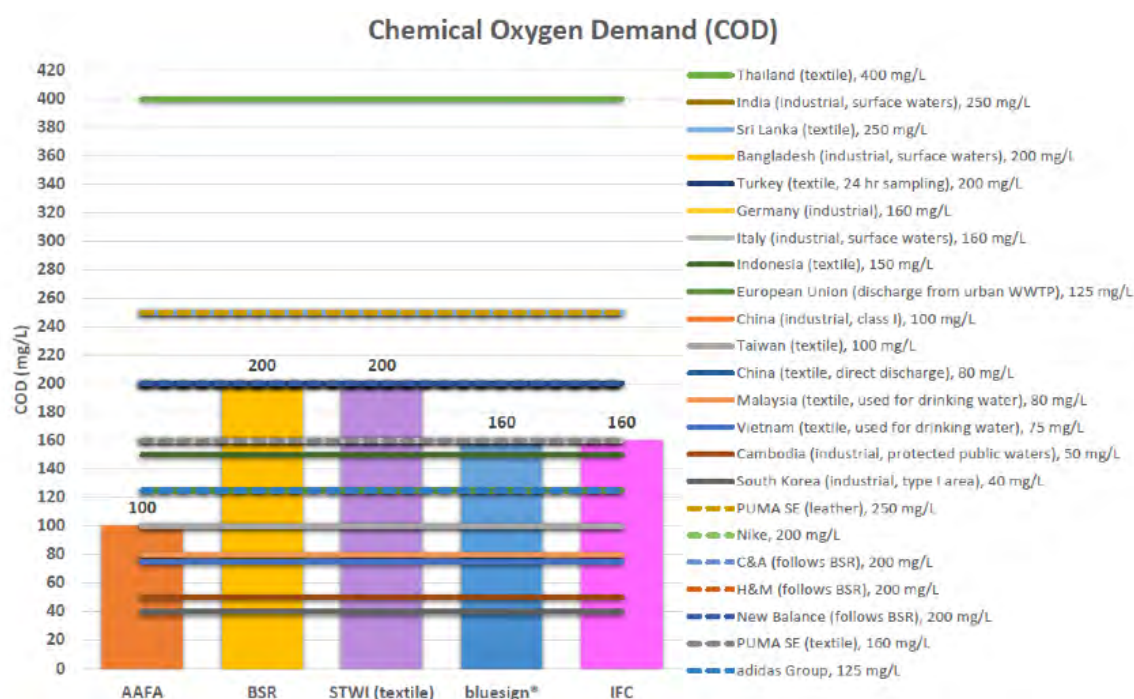
¹⁸ A.E. Gahly, et al., "Production, Characterization and Treatment of Textile Effluents: A Critical Review", Chemical Engineering Process Technology, 2014.

2.1.0 Wastewater Discharge Quality Guidelines

The ZDHC Roadmap to Zero Programme took the leadership in collecting data from 7 multi-brand consortia, 18 brands and 20 countries in benchmarking the current state of effluent guidelines and published a report *"Textile Industry Wastewater Discharge Quality Standards Literature Review"*, 2015¹⁹. The study showed that there was no single guideline that covers all discharge criteria. There is a wide range of wastewater discharge quality regulations from country to country and between guidelines published by different brands and amongst multi-brand consortia as shown in Figure 7 for COD as an example.

Moreover, national standards and industry guidelines also vary in their analytical methods and techniques for measuring wastewater constituents. ZDHC took it upon themselves to develop a single unified guideline and the development of standardised analytical methods for monitoring wastewater quality. These can be found in *"ZDHC Wastewater Guidelines"*, 2016²⁰. These guidelines go beyond regulatory compliance, to help ensure that wastewater discharges do not adversely affect the environment.

Figure 7: COD Discharge Guidelines and Standards¹⁵



¹⁹ ZDHC, *"Textile Industry Wastewater Discharge Quality Standards – Literature Review"*, 2015.

²⁰ ZDHC, *"Wastewater Guidelines"*, 2016.

The Guidelines propose a three level approach, namely Foundational, Progressive and Aspirational, which are shown in Figure 8. Moreover, the wastewater parameters are classified into two categories:

- i) Conventional parameters
- ii) ZDHC MRSL parameters for wastewater and sludge

Figure 8: Three Levels of ZDHC Guidelines

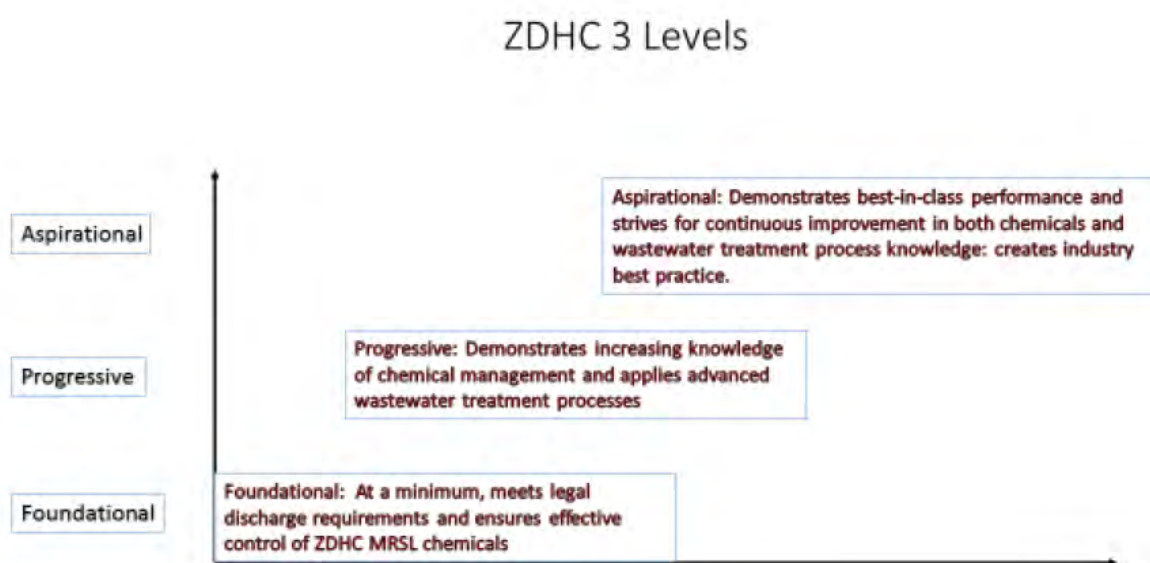


Table 5 shows the ZDHC Wastewater Guidelines in comparison to China and Bangladesh standards.

Table 5: Comparison of ZDHC reporting limits with Chinese and Bangladesh effluent standards

| Parameter | Foundational | Progressive | Aspirational | China direct discharge/ indirect discharge GB 4287-2012 with 2015 amendment | Bangladesh |
|--|--------------|-------------|--------------|--|--------------------|
| Temperature (°C) | Max 35 | 30 | 25 | | 45 max |
| Colour (m-1) (λ -436nm;525;620 nm) | 7;5;3 | 5;3;2 | 2;1;1 | 50/80 ^(a) | NA |
| pH | 6.0 - 9.0 | | | 6.0 - 9.0 | 6.5 - 9.0 |
| TSS mg/L | 50 | 15 | 5 | 50/100 | 100 |
| TDS mg/L | | | | | 2,100 |
| BOD ₅ mg/L | 30 | 15 | 5 | 20/50 | 150 |
| COD mg/L | 150 | 80 | 40 | 80/200 | 200 ^(b) |
| Total Nitrogen mg/L | 20 | 10 | 5 | 15/30 | NA |
| Ammonium-N mg/L | 10 | 1 | 0.5 | 10/20 | 50 ^(b) |
| Total Phosphorous (P) mg/L | 3 | 0.5 | 0.1 | 0.5/1.5 | 8 ^(b) |
| Oil and grease mg/L | 10 | 2 | 0.5 | 10/15/100 ^(d) | 10 |
| Phenol mg/L | 0.5 | 0.01 | 0.001 | 0.5/0.5/2.0 ^(d) | 5 |
| Adsorbable Organic Halogen (AOX) mg/L | 5 | 1 | 0.1 | 12/12 | NA |
| Coliform bacteria (bacteria/100 mL) | 400 | 100 | 25 | | |
| Persistent foam | Not visible | | | | |
| Anions | | | | | |
| Cyanide (CN) mg/L | 0.2 | 0.1 | 0.05 | 0.5/0.5/0.1 ^(d) | 0.1 ^(b) |
| Sulphide (S ²⁻) mg/L | 0.5 | 0.05 | 0.01 | 0.5/0.5 | 2.0 |
| Sulphite (SO ₃ ²⁻) mg/L | 2 | 0.5 | 0.2 | | |

| | | | | | |
|---|---------------------------|-------|-------|----------------------------|--------------------|
| Metals | | | | | |
| Antimony (Sb) mg/L | 0.1 | 0.05 | 0.01 | 0.1/0.1 | |
| Arsenic (As) mg/L | 0.05 | 0.01 | 0.005 | 0.5 ^(d) | 0.2 ^(b) |
| Cadmium (Cd) mg/L | 0.1 | 0.05 | 0.01 | 0.1 ^(d) | 0.5 ^(b) |
| Chromium Total, mg/L | 0.2 | 0.1 | 0.05 | 1.5 ^(d) | 2.0 |
| Chromium (VI) (mg/L | 0.05 | 0.005 | 0.001 | Not detectable | 0.1 ^(b) |
| Cobalt (Co) mg/L | 0.05 | 0.02 | 0.01 | | |
| Copper (Cu) mg/L | 1.0 | 0.5 | 0.25 | 0.5/1.0/2.0 ^(d) | 0.5 ^(b) |
| Lead (Pb) mg/L | 0.1 | 0.05 | 0.01 | 1.0 ^(d) | 0.1 ^(b) |
| Mercury (Hg) mg/L | 0.01 | 0.005 | 0.001 | 0.05 ^(d) | 0.1 ^(b) |
| Nickel (Ni) mg/L | 0.1 | 0.02 | 0.05 | 1.0 ^(d) | 1.0 ^(b) |
| Silver (Ag) mg/L | 0.1 | 0.05 | 0.005 | 0.5 ^(d) | |
| Zinc (Zn) mg/L | 5.0 | 1.0 | 0.5 | 2.0/5/5 ^(d) | 5 ^(b) |
| Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including all isomers (e) | Reporting limit 5 µg/L | | | | |
| Chlorophenols | Reporting limit 0.5 µg/L | | | | |
| Dyes (carcinogenic or equivalent concern (e) | Reporting limit 500 µg/L | | | | |
| Flame retardants (e) | Reporting limit 5.0 µg/L | | | | |
| Glycols (e) | Reporting limit 50.0 µg/L | | | | |
| Ortho-Phthalates – Including all ortho esters of phthalic acid (e) | Reporting limit 10.0 µg/L | | | | |

(a) – Colour method is multiple dilution.

(b) – Not specific to textile industry but applies to industrial units discharging water to inland water.

(d) – Not specific to textile industry. Values are for integrated wastewater standard GB 8978 – 1996 for Tier I/II/III.

(e) – For a full description of the relevant compounds please refer to the ZDHC Wastewater Guidelines.

3.0.0 Wastewater discharge to surface water

In most cases, most dyeing and finishing plants discharge wastewater after treatment to an inland water body such as a river. This section examines the treatment required to comply with many national wastewater standards. Where textile plants discharge to a municipal utility sewer or to a Common Effluent Treatment Plant (CETP), the wastewater effluent discharged to the common sewer does not have to achieve the same rigorous standards and only pre-treatment is required at the point of discharge to the common sewer.

The objectives of wastewater treatment are:

- i. Ensure discharge of good water quality to the natural environment
- ii. Remove pollutants most efficiently and at the lowest cost
- iii. Avoid and/or minimise other environmental impacts – odour creation, gas emission, noise production and solid disposal
- iv. Produce treated water for reuse and recycling
- v. Recover salts if economically viable

When planning for an effluent treatment plant, the following needs to be considered:

- ✓ Desired outgoing effluent quality or permit requirements to comply with national, state, local and/or brand guidelines
- ✓ Effluent volume requiring treatment
- ✓ Capacity of the textile manufacturing plant
- ✓ Complexity of the technology, ease of operation, adaptability, reliability and robustness, and energy requirements
- ✓ Capital and construction costs
- ✓ Operation and maintenance costs
- ✓ Available land area
- ✓ Mass of sludge generated and disposal requirements

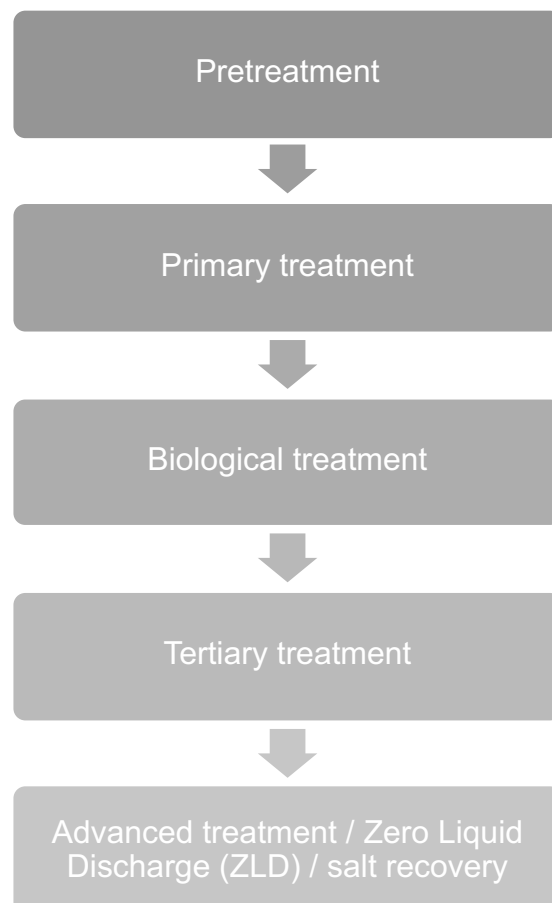
3.1.0 **Sizing design capacity of the wastewater treatment plant**

The capacity of the wastewater treatment plant is affected by the size of the textile processing plant. If the textile processing plant is large then the peaking factor can be taken as $1.1X - 1.5X$, where X is the maximum daily flow. For medium sized plants the peaking factor is typically $1.6X - 2.0X$ and for smaller plants it is $2 - 3X$ given the large flow variations that can occur. If the peaking factor is too low, the effluent treatment plant will be chronically undersized and unable to treat the full flow of effluent.

The peaking factor is defined as the ratio of maximum flow to the average flow, such as maximum hourly flow or maximum daily flow to the average daily flow.

Wastewater treatment processes can be divided into pre-treatment, primary, secondary and tertiary and advanced treatment which includes zero liquid discharge and salt recovery as shown in Figure 9.

Figure 9: Sequence of wastewater treatment



Pre-treatment includes screening to remove rags, gravel and sand which could otherwise block downstream equipment. Flow equalisation is required to balance the flows especially in batch operations. Segregation of flows can also take place where the high pH or streams containing PVA is segregated.

Primary treatment includes primary sedimentation with or without chemical coagulation to settle suspended particles.

Secondary treatment refers to biological treatment processes which use bacteria for decomposition of biologically degradable organics in the presence or absence of oxygen. The most common processes are aerobic which requires oxygen. Anaerobic takes place in the absence of oxygen.

Tertiary treatment includes filtration, disinfection, and removal of microbes or salts using membranes.

Advanced treatment includes colour removal, thermal or membrane based evaporation, and salt recovery.

Table 6 shows the types of treatment systems that come under pre-treatment, primary, secondary, tertiary treatment and advanced treatment systems and Table 7 provides details on the specific technologies and their advantages and disadvantages.

Table 6: Classification of wastewater treatment technologies

| Pretreatment | Primary | Secondary | Tertiary | Water reuse/ Zero Liquid Discharge (ZLD) and salt recovery |
|-------------------------------------|--|--------------------------------|--|---|
| Screening | Chemical/ electrochemical coagulation and flocculation | Activated sludge process (ASP) | Sand filtration/ disk filtration High rate Filtration | Membrane technologies – MF/ UF/NF/ RO |
| Grit removal | Lamella settling | Oxidation ditch | Activated carbon adsorption | Thermal / membrane evaporation |
| Flow equalisation/ flow segregation | Oil and grease removal - Dissolved air flotation | Sequencing batch reactor (SBR) | Chemical/UV / Ozone disinfection | Crystallisation |
| pH correction | Primary Sedimentation | Rotating biological disks | | Colour removal - Electrochemical oxidation/ Fenton's reaction |
| | | Moving bed bio reactor (MBBR) | | Ion exchange |
| | | Membrane bioreactor (MBR) | | Photocatalytic degradation |
| | | | | Salt recovery |
| | | Anaerobic digestion | | |
| | | UASB reactor | | |
| | | Aerated ponds | | |

Table 7: Advantages and disadvantages of wastewater treatment processes

| Process | Advantages | Disadvantages |
|----------------------------------|--|---|
| Biodegradation | Eliminates oxidisable organics by 90%. A2O process removes Nitrogen and Phosphorous. | Low biodegradability of recalcitrant chemicals. Land area required is greater than other processes. Produces high levels of sludge. |
| Coagulation – flocculation | Elimination of insoluble dyes and heavy metals | Production of voluminous sludge |
| Adsorption on activated carbon | Suspended solids and organic compounds are adsorbed on the surface | Costs for polymers and chemicals |
| Ozone treatment | Good decolourisation and COD reduction | Cost of treatment |
| Electrochemical processes | Capacity to adapt to different pollution loads and volumes. Low ferrous oxide sludge, COD reduction, colour removal | High Energy consumption of 1 – 2 kWh/ m3. Ferrous oxide sludge |
| MBR | Combines the advantages of biodegradation with membrane treatment. Good quality water for reuse. | Higher CAPEX and OPEX costs compared to conventional biological systems. |
| Ultrafiltration/ microfiltration | Low pressure membranes improves turbidity of effluent. | Produces water of lower quality than RO/NF. Cannot be used alone without biological treatment. Prone to fouling of membranes |
| Nanofiltration | Separation of low molecular organics and divalent ions. | Energy intensive due to high pressure requirements but requires less power than for RO membranes. |
| Reverse Osmosis | Removal of all mineral salts. Water of high purity is produced. | Prone to poisoning of membranes by cationic surfactants if used without biological processes. Energy intensive due to high pressure requirements |

3.2.0 Pre-treatment

Objective of pre-treatment – is the removal of materials that can cause blockages, clogging of downstream equipment and equipment abrasion. These can be removed by screening, grit removal and skimming. Examples are sand, rags, lint and other extraneous materials.

3.2.1 Screening

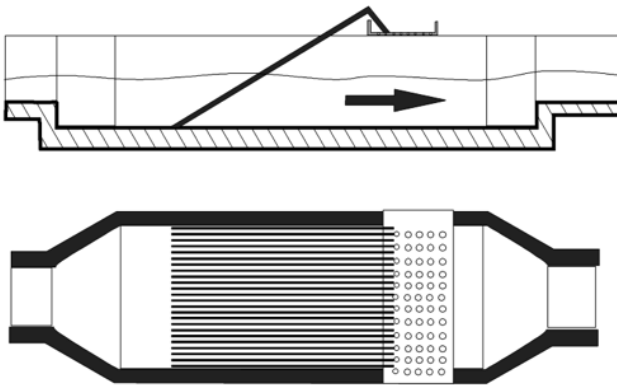
The first unit operation in many wastewater treatment plants. Screening is required to remove lint, fibre and other extraneous solids that could block pumps, MBR equipment, and damage internal machinery. It will improve plant throughput by reducing BOD and total suspended solids, reduce particle sizes for treatment and reduce contamination to water courses. Typically, any suspended solid greater than 2 – 6 mm in size must be removed by screening. Screens can be categorised according to the aperture size as shown in Table 8. Figures 10 – 14 show some examples²¹.

Table 8: Categorisation of screens

| Type | Aperture | Application |
|----------------|-------------|---|
| Trash racks | 25 – 150 mm | Designed to remove large debris |
| Coarse screens | 6 – 25 mm | Pre-treatment for municipal sewage treatment. Cleaning is either manual or mechanically driven. Mainly used in municipal treatment plants |
| Fine screens | 0.5 – 6 mm | Removes small rags, lint, fibre, plastic materials. Examples are static wedge wire, tangential and rotary drum screens. They reduce BOD and SS by 25 – 50%. |
| Micro-screens | <1mm | Mainly used to remove fine solids from treated effluent. Common application is as pre-treatment for MBR plants. Reduces SS by 20 – 80% with an average of 55%. Flow fluctuations causes incomplete solids removal. |

²¹ Suárez, J. et al. "TFSETP: Screening/sieving", 2014.

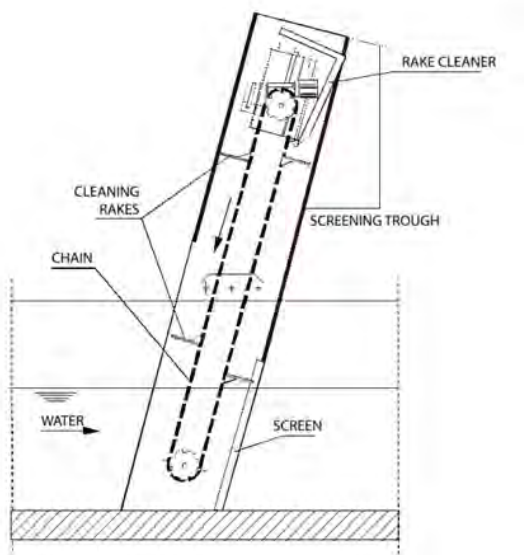
Figure 10: Hand cleaned coarse screens



Bar screens are placed in transversal or opposite direction to the water flow, so that water passes through them and solids bigger than bar separation are retained.

In general, bars can be made with a curved or straight (flat) shape. When straight, bars positioning with respect to the horizontal may be vertical or inclined.

Figure 11: Mechanically cleaned bar screens



Mechanically cleaning bars minimise clogging problems and reduce the maintenance time. The cleaning mechanism is usually a mobile rake which periodically sweeps the bars, extracting the retained waste. In curved bars, the cleaning rake has a circular mechanic motion.

The figure shows a continuous belt mechanically cleaned screen. Other types are catenary, chain-driven or reciprocating rake mechanically cleaned screens.

Fine screens – Basic types includes horizontal reciprocating screens, tangential flow screens or drum screens. These are made of stainless steel.

Rotary sieves or drum screens are in widespread use (large and small wastewater treatment facilities including textile effluent treatment plants) due to their easy maintenance and mechanical robustness. The screens have a hollow wedge wire mesh drum which rotates about its horizontal axis. The wastewater enters the drum axially and leaves radially trapping the screenings inside the drum. Flow velocity is typically 0.5 – 0.9 m/s – not too slow to allow grit to settle inside the drum, and not too fast to allow the screenings to be forced through the screens. Figure 12 shows a row of drum screens in a textile effluent treatment plant.

Figure 12: A row of drum screens in a textile effluent treatment plant



Source: Sudhi Mukherjee, International Finance Corporation

Figure 13 shows a row of tangential screens in a sewage treatment plant in China. The wastewater flows through the open front into the screen basket and through the very fine apertures of the mesh. A sealing plate between the channel and the front-end screen basket opening prevents unscreened wastewater from bypassing the screen basket. The solids can therefore not pass into the effluent but are reliably retained in the screen basket. The screen basket surface consists of a square mesh that ensures high separation efficiency and provides a large free screen surface so that the headloss remains low even with high flow rates. The solids retained on the screen basket surface lead to gradual blinding of the basket surface which has an impact on the level difference in the channel. The screen basket cleaning cycle starts at a defined water level in the channel upstream of the screen. The blinded screen basket surface is cleaned as the screen basket rotates lifting the retained solids to the spray water cleaning system where they are washed into the trough in the centre of the screen basket. The screenings are removed from the trough by a screw conveyor and dewatered and compacted as they are transported upwards through a rising pipe. The trough is decoupled from the inlet water level by an additional trough to ensure durable function even with increased water levels (backwater) on the outlet side. Spray water in the trough is removed by separate suction to ensure the reliable transport of the sludge-containing fine screenings. Periodic high-pressure washing at 120 bar (standard setting: twice a day) eliminates sedimentation on the screen basket and ensures that grease and oil is removed which might clog the screen basket surface.

Figure 13: Fine screens in a sewage treatment plant

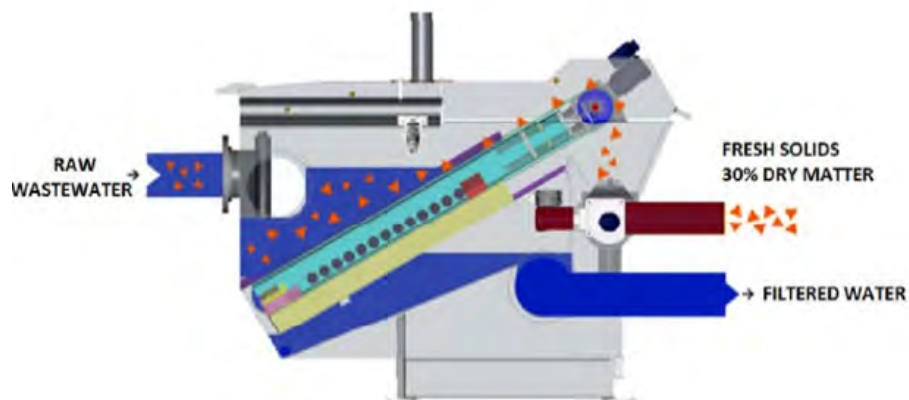


Source: Mohan Seneviratne

Microscreens commonly have the appearance of a drum screen, with a fabric cloth (opening 10-35 μm) fitted on the drum periphery. The wastewater enters the open end of the drum and flows outward through the rotating-drum screening cloth. Typical suspended solids removal of fine screens go from 5 to 45 percent, while M2R has developed microscreens with TSS removal ranges between 10 - 80%, with an average of 55% in urban wastewater treatment²². They also have the advantage of replacing a clarifier, saving a large amount of space. Figure 14 shows M2R microscreen.

²² Metcalf & Eddy, "Wastewater Engineering. Treatment and Reuse", 2003.

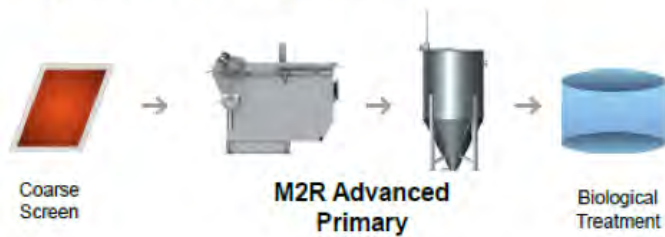
Figure 14: M2R Renewables Microscreen



**Conventional Treatment Solution: 2 to 8 Hours
Gravity Settling Process**



**M2R Solution: ONLY 20 Minutes
Physical Filtration Separation Process**

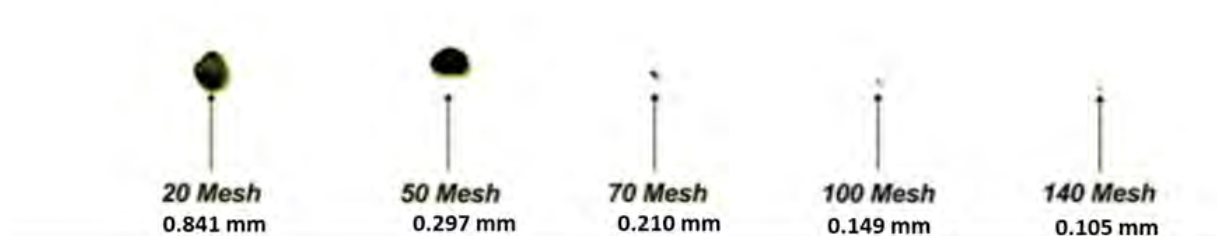


Source: M2 Renewables

3.2.2 Grit removal

Immediately downstream of screening is grit removal. Grit removal systems are commonly found where large amounts of storm water enter a wastewater treatment plant and are optional. Grit includes heavy sand, gravel and other particulate matter. In wastewater treatment plants, common grit sizes range from 50 to 100 mesh corresponding to 0.3 mm to 0.15 mm with a specific gravity of 2.65 and a settling velocity of 20 mm/s. Typical grit sizes are shown in Figure 15. At 0.1 mm or below grit takes on silt-like buoyant properties meaning they rarely settle with any measure of velocity.

Figure 15: Grit sizes



Grit removal is an important pre-treatment step for several reasons listed below:

- To protect mechanical equipment and pumps from abrasive wear
- To prevent pipe clogging from deposition of grit
- To reduce accumulation of grit in settling tanks and digesters.

Grit is removed by making use of the specific gravity to settle in grit channels. The main types of grit channels are constant velocity, aerated grit channels, vortex grit chambers and detritors. For space limited plants like textile mills, hydrocyclones are an alternative choice. A hydrocyclone is a static device that applies centrifugal force to a liquid mixture so as to promote the separation of heavy and light components. In hydrocyclones, the principle employed is centrifugal sedimentation, i.e. the particles in the suspension are subject to centrifugal forces, which cause their separation from the fluid. The main advantages of hydrocyclones are that they do not have moving parts, require a low installation and maintenance investment, and are simple to operate.

The amount of grit removed varies widely. For a combined sewer network 0.05 – 0.1 m³ grit per 1000 m³ of wastewater may be typical or for separate sewer networks 0.005 – 0.05 m³ grit per 1000 m³ of wastewater. Grit chambers are not common in textile wastewater treatment plants.

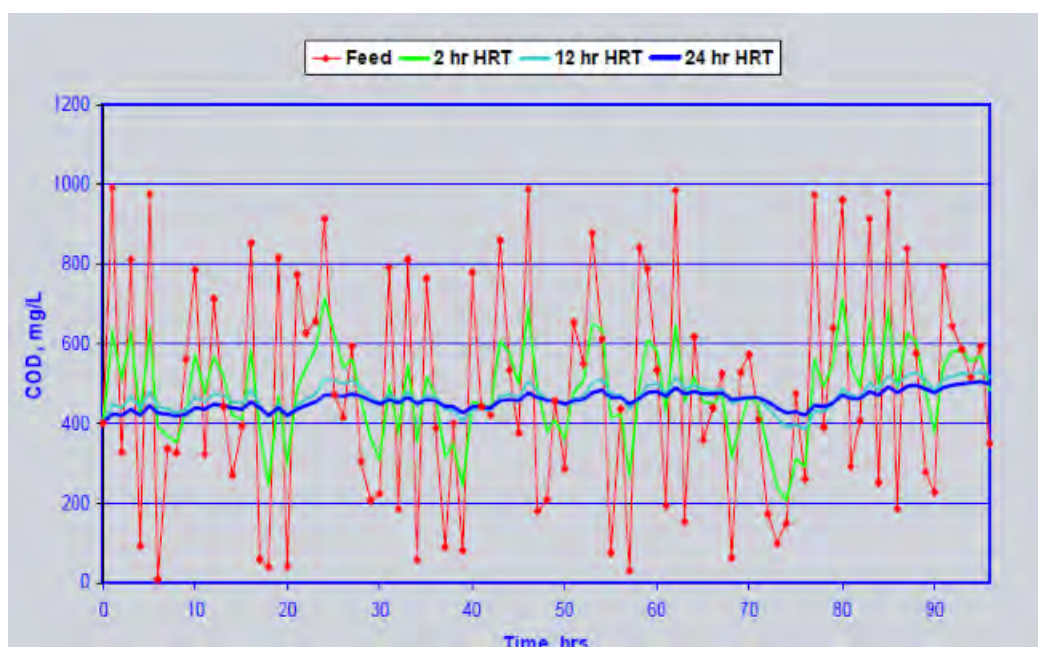
3.2.3 Flow equalisation

Textile processing in most cases is a batch process, and therefore the wastewater concentrations and flows change constantly depending on the production schedule. Homogenisation is thus required for the purposes of mixing effluent to achieve a stable composition and to avoid peak flow conditions. The main objectives of flow equalisation are:

- To minimise flow surges into the treatment plant and avoid peak flow conditions
- To neutralise high pH with low pH streams and balance the flows
- To maintain operation of the biological treatment plant when the production plants are not operating
- To minimise the impact of toxic chemicals entering the biological treatment plant.

To prevent lint, cotton seed and other slurry from settling to the bottom of the tank, air or mechanical mixing of the wastewater is required. The usual hydraulic retention time (HRT) for garment washing is 4 – 6 hours and fabric dyeing is 7 – 12 hours²³. Figure 16 shows the impact on COD concentrations with varying hydraulic residence times.

Figure 16: Variation in COD levels with varying hydraulic residence times



²³ Department of Environment, "Guide for Assessment of Effluent Treatment Plants", Ministry of Environment and Forrestr, Bangladesh, 2008.

3.3.0 Primary Treatment

Primary treatment follows preliminary treatment and involves physical and chemical treatment to correct the pH from alkaline conditions to a pH near neutral through acid addition, and physical settling of suspended solids in primary clarifiers to reduce the BOD and SS load on downstream processes.

Overall, the adoption of primary clarification units represents fewer problems on the downstream biological process operation. For example, there will be a lower quantity of oil and grease and biomass accumulation in the biological reactor, minimising possible settlements in the tank and reducing the tendency to "*non filamentous*" bulking of activated sludge biomass, etc²⁴.

Objective of primary treatment – removal of settleable organic and inorganic solids by sedimentation and removal of floating materials by skimming. Approximately 25 - 50% of the incoming BOD, 50 – 75% of total suspended solids and 65% of oil and grease are removed during primary treatment, in addition to which some organic nitrogen, organic phosphates and heavy metals are also removed in the process.

In most cases inside textile industry effluents processing, primary treatment applies coagulation-flocculation processes to improve solids separation.

Stokes' Law states that the settling velocity (V_s) is a function of the particle size (diameter²), density difference between the particle and the water and kinematic viscosity of the water.

$$v_s = \frac{2(\rho_p - \rho_f)}{9\mu} g R^2$$

Where:

v_s is the particle's settling velocity (m/s)

g is the gravitational acceleration (m/s²)

ρ_p is the density of the particles (kg/m³)

ρ_f is the mass density of the fluid (kg/m³)

μ is the dynamic viscosity (kg /m*s)

R is the radius of the settling particles (m)

²⁴ Suárez J., et al. "TFSETP: Primary clarifier", 2014.

Efficiency of solids removal or settling velocity, is a function of:

- i. **Characteristics of the solids** – the larger the solids, the faster the settling velocity. Colloidal substances take longer to settle due to the negative charge surrounding it. Table 9 shows the length of time it takes solids to settle depending on their size and type.
- ii. **Characteristics of the water** – the warmer the temperature, the lower the viscosity and the lower the density of the water and the better the settling. Cold water is denser, more viscous and has a slower settling rate.
- iii. **Characteristics of the clarifier**

Table 9: Size of particles and time to settle

| Particle size mm | Order of size | Time to settle |
|-------------------|---------------|----------------|
| 1 | Coarse sand | 3 seconds |
| 0.1 | Fine sand | 38 seconds |
| 0.01 | Silt | 33 minutes |
| 0.001 (1 mμ) | Bacteria | 55 hours |
| 0.0001 (0.1 mμ) | Colloidal | 230 days |
| 0.00001 (0.01 mμ) | Colloidal | 6.3 years |

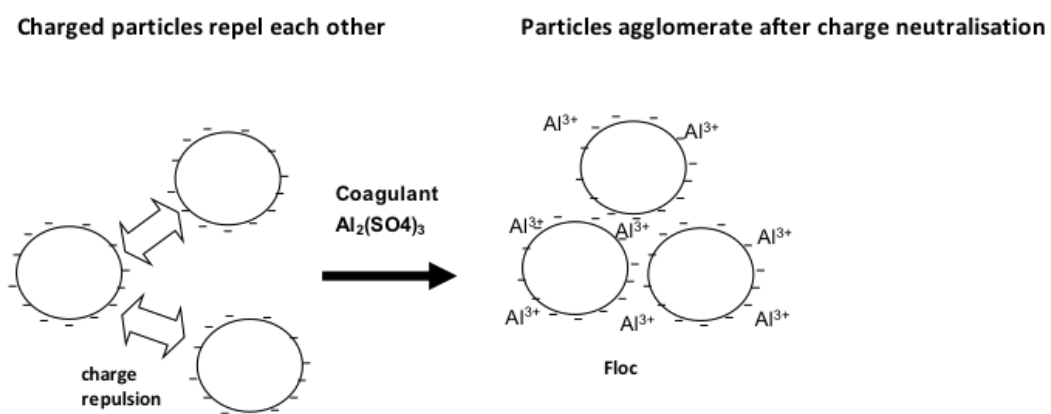
3.3.1 Chemical coagulation and flocculation

Chemical coagulation increases the size of the particles to aid in settling and is known as chemically enhanced settling.

Colloidal substances like colour typically have a diameter of 10^{-3} to $1 \text{ m}\mu$ (4×10^{-8} to 4×10^{-5} in.) with a negative electrical charge which repels other negatively charged colloids from attaching to each other and consequently do not settle naturally. Therefore, it is required to remove this negative charge by adding positively charged chemicals like aluminium sulfate, ferrous sulfate, poly aluminium chloride (PAC) or synthetic coagulants with molecular weights of 50,000 to 150,000. These chemicals as a group have a high charge to mass ratio. This is known as coagulation as shown in Figure 17. In addition to colloidal matter, heavy metals are also removed by chemical precipitation.

Once the charge is removed the colloids are free to attach to each other forming 'flocs' that ultimately become visible to the naked eye. Coagulants are added into a rapid mix tank and then pass into a flocculation tank. Sometimes to aid in faster settling, flocculants are added. These are high molecular weight anionic or non-ionic acrylamides with molecular weights over 5,000,000. They attach themselves to the pin floc making them larger and settle quickly. The dosage is determined by jar testing but can reach 200 mg/L in some cases, which increases the cost of treatment.

Figure 17: Coagulation schematic



Source: Mohan Seneviratne, *A Practical Approach to Water Conservation for Commercial and Industrial Facilities*, Elsevier, 2007.

It must be remembered that the amount of chemical sludge produced due to chemical coagulation can be high and the additional costs of sludge disposal need to be taken into account. In a medium sized wastewater treatment plant the sludge produced can be as high as 4,000 – 5,000 kg/day. Inorganic coagulants like aluminium or ferric chloride produce more voluminous sludge than organic coagulants. In Italy, sludge disposal accounts for US\$0.10/kg equating to US\$400 – 500/d or US\$180,000 per year²⁵. Thus, these aspects need to be considered when deciding on a treatment regime.

pH is a critical factor in the process of coagulation-flocculation, as there is always a specific interval where the behavior of the chemical is optimum²⁶. This is the reason why this process is normally preceded by pH-regulation.

²⁵ Euromec, "Comparison of chemical and biological treatment plants", 2013.

²⁶ Rigola Lapeña, M. "Tratamiento de aguas industriales: aguas de proceso y residuales", 1989.

Jar testing needs to be done prior to adding coagulants to work out the dosages of coagulant and flocculants.

Inorganic coagulants are also difficult to handle, requiring elaborate specialised dosing systems unlike organic coagulants. Instead of chemical coagulants, electrocoagulation is sometimes used. Electrocoagulation uses a direct current (DC) with aluminium or iron anodes. The principle is the same as chemical coagulation and also suffers from producing voluminous sludge.

A market segmentation study of ETP plants in Bangladesh conducted by PaCT (Partnership for Cleaner Textiles) showed that of the 46 factories sampled, 28% used only chemical treatment²⁷.

Not all dyes are suitable for chemical coagulation. Sulphur and disperse dyes coagulate and settle well due to the formation of good quality flocs. Acid, direct, mordant, vat and reactive dyes coagulate but the resultant floc is of poor quality and does not settle well even after the introduction of a flocculants. Cationic dyes are not suitable for coagulation/flocculation. In addition, low color removal efficiency and the large amount of sludge produced limits the effectiveness of treatment of dye-containing wastewater using only chemical coagulation²⁸.

It must be noted that chemical coagulation and primary clarifiers are not required in all instances. In some low load applications, no chemical coagulation is required. The effluent after equalisation goes directly to a biological treatment system. This reduces CAPEX (capital expenditure) and OPEX (operational expenditure) costs.

²⁷ Partnership for Cleaner Textiles, "Market Segmentation Study on the Wet Dyeing and Finishing Units in the Bangladesh Textile Sector", Dhaka, International Finance Corporation, 2016.

²⁸ Philippe Vandivivere, Roberto Bianchi and Willy Verstraete, "Treatment and Reuse of Wastewater from the Textile Wet Processing Industry: A Review of Emerging Technologies", J. Chem. Technol. Biotechnol. 1998, 72, 289-302.

3.3.2 Primary sedimentation tanks (primary clarifier)

As mentioned, the efficiency of solids removal depends on the characteristics of the clarifier. A sedimentation device that includes inlet baffling for the dissipation of energy, a quiescent zone for particulate settling, mechanical means for the removal of settled solids, and low flow velocity to the outlet is commonly called a "*clarifier*". This section discusses the common clarifier types. The below description is not intended as a comprehensive design manual but as a brief description on clarifiers. For more details on clarifiers two good reference books are: Metcalf and Eddy, "*Wastewater Engineering – Treatment and Resource Recovery*" and Water and Environment Federation, "*Clarifier Design*"^{29, 30}.

Flocculation and sedimentation tanks can be rectangular, circular or inclined plate (Lamella), the selection of which is based on local site conditions, area available, and experience of the design team. Ideally, two more tanks need to be available. Rectangular and Lamella tanks use less land area than circular tanks and are useful where land is at a premium.

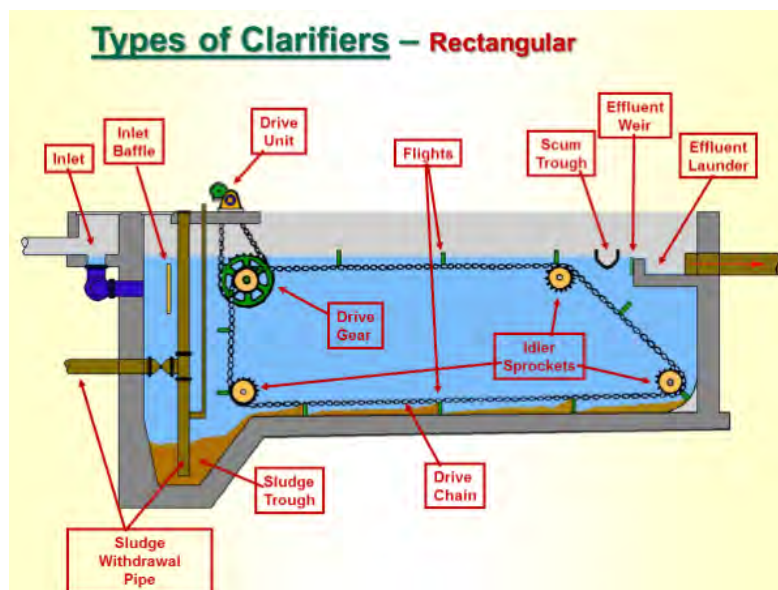
3.3.2.1 Rectangular tanks

Rectangular tanks have straight flow patterns to increase flocculation (in chemically aided sedimentation) and reduce retention time. The water enters at one end, passes through an inlet baffle arrangement and traverses the length of the tank to the effluent weirs and trough. They are designed to have a length: width ratio of 3:1 to 5:1 providing a large effective settling zone closely resembling ideal conditions, and a bottom slope of 1%. A mechanical scraper at the bottom moves collecting the settled sludge into a collection zone which is then pumped out subsequently. Important issues for rectangular tanks are: sludge removal, flow distribution and scum removal. Sludge removal is carried out using a conveyor chains known as chain-and-flight solids collectors or traveling-bridge type collectors. Flow distribution is critical in rectangular tanks to minimise short circuiting. To improve flow distribution, inlet weirs/baffles are installed to distribute the flow over the widest possible cross sectional area. Figure 18 shows a schematic of a rectangular tank. Figure 19 shows a rectangular sedimentation tank in a textile effluent treatment plant in China.

²⁹ PMetcalf and Eddy, "*Wastewater Engineering – Treatment and Resource Recovery*", Fifth Edition, McGraw Hill 2014.

³⁰ Water Environment Federation, "*Clarifier Design*", Manual of Practice FD-8, 2008.

Figure 18: Schematic of a rectangular clarifier



Source: Michigan Department of Environmental Quality

Figure 19: Rectangular sedimentation tank in a textile effluent treatment plant, China



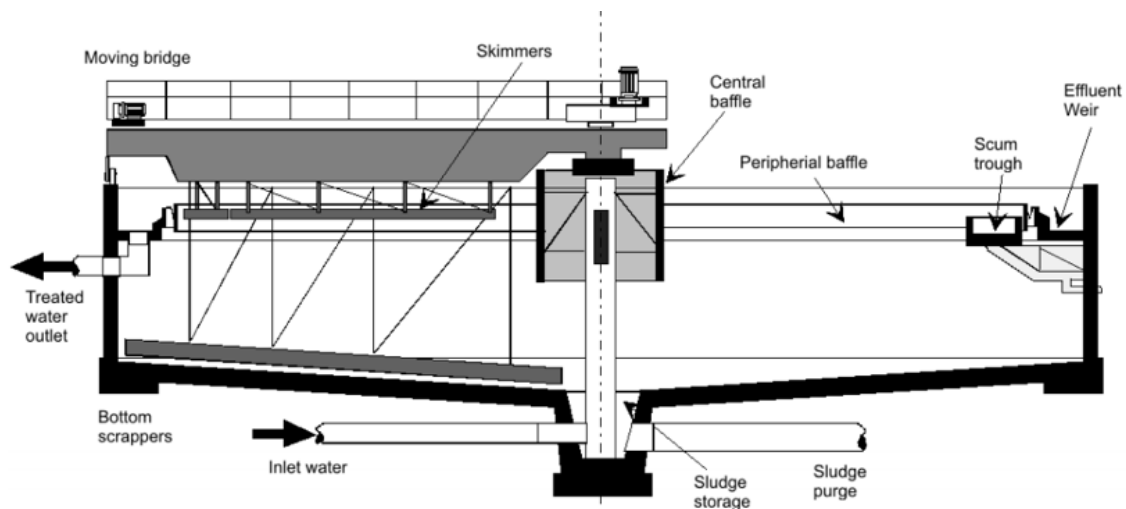
Source: Mohan Seneviratne

3.3.2.2 Circular Clarifiers

In circular clarifiers, the flow pattern is radial. To achieve the radial flow pattern, wastewater is introduced in the majority of designs in the center or sometimes around the periphery of the tank. In the center design, the wastewater is transported through a pipe and central baffle known as the "center well" and flows radially towards a weir which runs around the circumference of the tank. The center well has a diameter typically between 15 – 25% of the total tank diameter and height of 1 – 2.5m. The quiescent settling zone must be large enough to meet the overflow rate and depth requirements for discrete and flocculant settling. Treated water is discharged over v-notched weir plates. The floor is sloped to aid in sludge concentration and removal. Sludge is removed using mechanical rakes.

Typical detention time in a sedimentation tank is 2 – 3 hours. Suspended solids removal is 45 – 55%. Figure 20 shows a schematic of a circular sedimentation tank.

Figure 20: Schematic of a circular sedimentation tank³¹



Problems in sedimentation tanks occur due to short-circuiting. In a rectangular tank, it is easy to observe this. In circular tanks it is much harder to detect short-circuiting. Pin flocs in certain places, at the periphery or uneven buildup of sludge at the bottom of the tank are some of the signs of short-circuiting. High inlet velocity results in short-circuiting, due to improper baffling, or lack of and uneven weirs. Temperature stratification due to differences in influent and clarifier temperatures, trash in weirs, and wind sweep are other factors contributing to this.

³¹ Suárez, J. et al. "TFSETP in textile industry: Primary clarifier", 2014.

A number of operational parameters to be considered are shown below:

Hydraulic loading rate (HLR) = Flow/Area = Wastewater flow rate/Area, m³/d/m².

For industrial and municipal wastewater treatment, the primary clarifier is usually designed based on 33 – 41 m³/d/m² based on the 24 hour average flow for typical suspended solids removal of 40 – 60%. Typical BOD removal under these conditions ranges from 20 - 30%.

Hydraulic retention time: Related to water depth. A deeper water depth increases the probability of particles collision (flocculation), increasing the falling rate:

Where:

HRT= hydraulic retention time (hours)

h = water depth (m)

V = settling effective volume (m³)

$$HRT = \frac{V}{A} = \frac{A h}{Q}$$

Hydraulic load over weir: Corresponds to the effluent flow per linear meter of the outlet weir.

The outlet velocity is limited in order to prevent sludge entrainment.

Where:

HLW = hydraulic load over weir (m³/h/m)

L_w = weir length (m)

$$HLW = \frac{Q}{L_w}$$

Table 10 shows design values for primary settling tanks

Table 10: Design values for primary settling tanks

| Parameter | Descriptor | Value |
|--|-------------------|--------------------------------|
| Suspended solids removal efficiency ⁽¹⁾ | SS | > 60% |
| BOD removal efficiency | BOD ₅ | > 30% |
| Surface Loading rate (SLR) | F _{AV} | < 1.0 m/h |
| Hydraulic retention time (HRT) | F _{AV} | > 2 hours |
| Weir overflow rate (WOR) ⁽²⁾ | F _{PEAK} | < 10.0 m ³ /h/m |
| Side water depth ⁽²⁾ | | > 2.50 m (maximum 5 hours) |
| Overhead space | | > 0.5 m |
| Primary sludge concentration (for calculation) | | 1% |
| Primary sludge extraction period | | 10 h/day |
| Bottom scraper velocity | Circular | <120 m/h |
| | Rectangular | <60 m/h |
| Bottom slope with scrapers | Circular | 8 % |
| | Rectangular | 2% |
| Central baffle | Diameter | 10 – 20% of clarifier diameter |
| Sizing ⁽³⁾ | Maximum length | 40 m |
| | Maximum width | 12 m |
| | Maximum diameter | 40 m |
| Sump sludge storage time ⁽⁴⁾ | | <5h |

(1) In case of wastewaters with a high sedimentable solids fraction, maximum removal efficiency could be higher.

(2) With the aim of minimising the sludge drag-out with the effluent

(3) Maximum limitation taking into account constructive effects, climatology, etc.

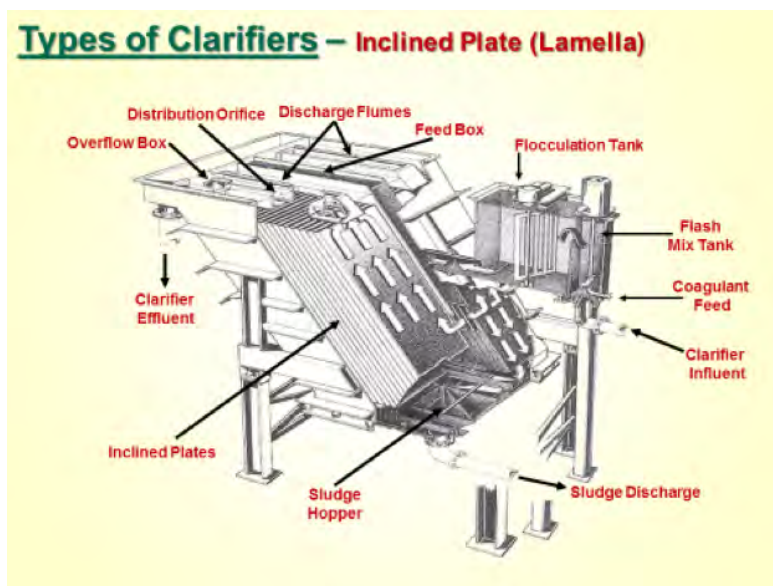
(4) In order to avoid sludge rot and hydrolysing

3.3.2.3 Lamella Plate Clarifier and tube settlers

When space is limited or when a tank is overloaded, one way to overcome the problem is to install a Lamella plate clarifier to reduce the hydraulic loading rate by increasing the surface area whilst keeping the flow constant. In Lamella plate clarifiers, the increase in surface area is accomplished by installing a series of inclined plates (at an angle of $40^\circ - 60^\circ$) up to a vertical depth of 2m and spaced at intervals of 40 – 120 mm. The surface area is the number of plates multiplied by the surface area of the plate. The settled sludge falls to the base of the tank. Lamella clarifiers increase the effective surface area by a factor of 6 – 12 times compared to a conventional tank. Reducing the angle also increases the surface area but impacts on sludge sliding down the plates. Counter current design is best where the inlet is at the bottom of the plate and rises to the top. A variation of the Lamella clarifier is the tube settler. Both of these designs can be retrofitted into an existing tank. Figure 21 shows a schematic of a Lamella clarifier.

Efficiencies are no better than the conventional clarifiers. Fouling of plates and their cleaning can be an issue.

Figure 21: Schematic of Lamella Clarifier



Source: Mohan Seneviratne

3.3.2.4 Dissolved Air Flotation

For removal of oil and grease dissolved air flotation (DAF) is well suited especially where the specific gravity of suspended solids is close to 1.0. Wool scouring effluent, for instance, contains as much as 12,500 mg/L of oil. Oil exists in the form of dissolved ($<20\ \mu$), emulsified (between $20 - 150\mu$) and free oil ($>150\mu$) as shown in Figure 22.

DAF process uses pressurised air to release micro air bubbles ($10 - 50$ micrometers in diameter) which attach to the particles, making it easy for the free oil particles to rise to the surface and then be skimmed off. DAF is very effective in the removal of oil and grease since oil doesn't naturally settle, having a specific gravity less than that of water. When the oil is present in the emulsified form, it requires chemicals to destabilise the oil emulsion layer.

The pressurised water flow can be the entire inflow of wastewater, part of the inlet flow, or water already treated by the process (effluent). This results in DAF three types of usable process, called full flow, partial flow or recirculated flow (R-DAF), respectively. Figure 23 shows a schematic of the DAF process. The most common DAF application for wastewater treatment is a recirculated flow system, as it requires less equipment for pressurisation (lower energy consumption), it avoids pump abrasion problems, and prevents the formation of colloids and emulsions within the pumping system.

DAF units can reduce oil concentrations to $10 - 25$ mg/L as long as the influent concentration is not greater than 500 mg/L. DAF systems operate at higher hydraulic loading rates than gravity sedimentation systems at $5 - 15$ m/h and consequently detention times are shorter by $15 - 30$ minutes. This allows the DAF system to be more compact and has a smaller footprint. DAF systems are available in circular or rectangular configurations.

Figure 22: Three types of oil

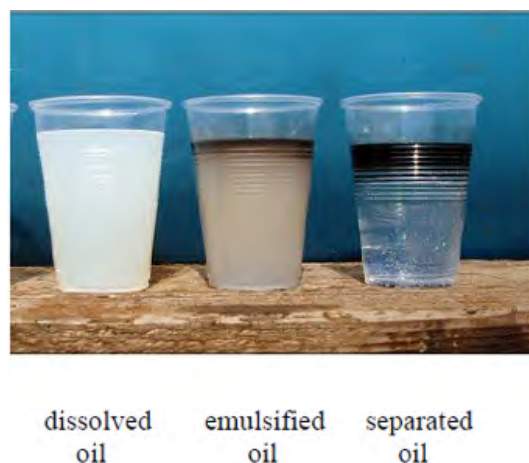
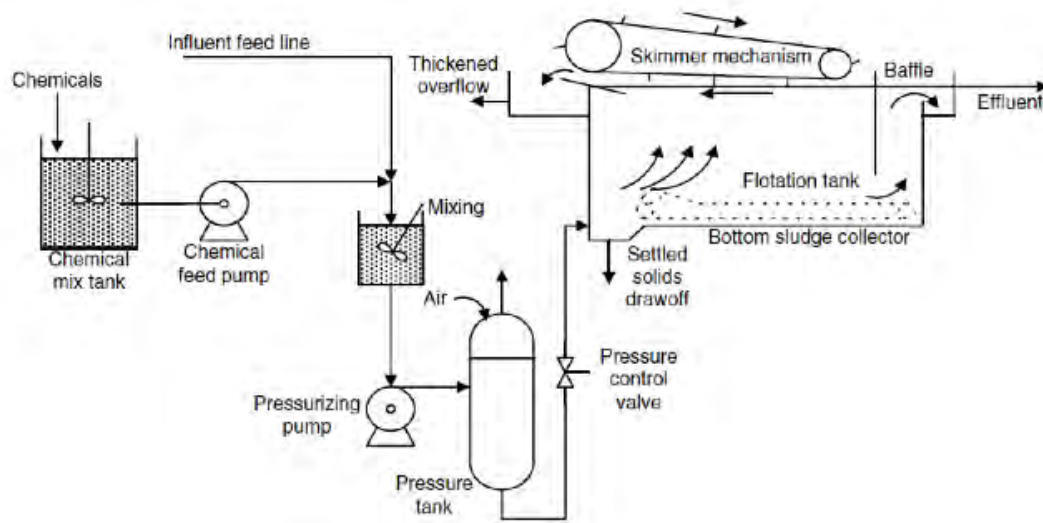


Figure 23: Schematic of full flow dissolved air flotation system³²



The operating parameters important to DAF control are: hydraulic loading rate (HLR), solids loading rate (SLR) and air to solids ratio (A/S).

HLR is effluent flow divided by the area of the tank and expressed as m/h.

SLR is determined by dividing the solids loading by the surface area of the tank and is expressed as kg/h/m. It is a parameter used to evaluate whether a DAF unit is overloaded or underloaded with respect to solids loading².

A/S expressed in mL/mg – is the volume of air available / mass of solids to be removed.

Typical design values and performance values are given in Table 11.

³² Mohan Seneviratne, "A Practical Approach to Water Conservation in Commercial and Industrial Facilities", Elsevier, 2007.

Table 11: Key operating parameters for DAF

| Design parameter | Value | Performance parameter (with coagulation) ³³ | % reduction |
|--|--------------|---|-------------|
| Typical operating pressure, bar | 4 - 10 | BOD ₅ | 45 - 50 |
| Typical tank height, m | 2 - 4 | SS | 65 - 80 |
| Air to solids ratio, mL/mg | 0.005 - 0.09 | Oil and Grease | 70 - 90 |
| Solids loading rate, kg/h.m ² | 4.5 - 5.0 | | |
| Hydraulic loading rate, m/h | 5 - 12 | | |
| Hydraulic Retention time, min | 15 - 40 | | |

Table 12 shows the percentage of COD and colour removal in the physicochemical processes.

Table 12: Removal characteristics of chemical coagulation³⁴

| Type of mill | Dyes and additives | Main process | Coagulant dosage (mg/L) | Influent Water quality | | Removal Efficiency | |
|----------------------------|-------------------------------------|--|--|------------------------|-------------|--------------------|---------|
| | | | | Colour (times) | COD (mg/L) | Colour (%) | COD (%) |
| Knitting | Napthol, Direct, Acidic, Reactive | Coagulant PAC, Sedimentation | 60 - 80 | 70 - 120 | 267 | >90% | 60 |
| Printing and dyeing | Vat dye, napthol | Coagulant, Floatation | 400 | 400 | 600 - 800 | 80 - 90 | 60 |
| Printing and dyeing | Acidic, Disperse, Reactive | Coagulation, Sedimentation, Floatation, filtration | ND | 174 - 347 | 228 - 352 | 97 | 75 |
| Silk and dyeing | Disperse, Reactive, Direct, Sulfide | FeSO ₄ , Lime Coagulation, tube sedimentation | FeSO ₄ 0.7 kg/tonne Lime 0.38 kg/tonne | 720 - 830 | 1114 - 1153 | 92 | 55 - 59 |

³³ Inditex, "Supporting Guide for Sustainable Manufacturing for Green to Wear Products", August 2015.

³⁴ Zongping Wang, et al., "Textile Dyeing Wastewater Treatment", Huazhong University of Science and Technology, China.

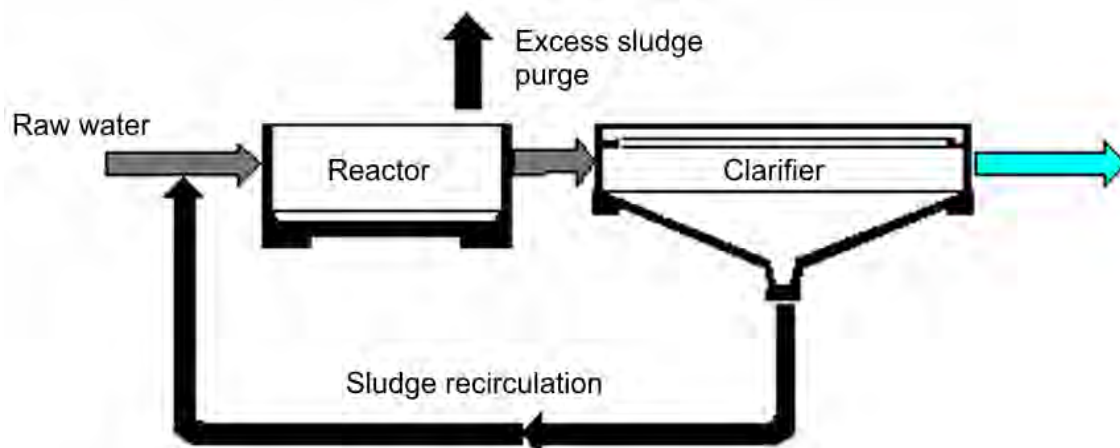
3.4.0 Secondary treatment

For removal of organic pollutants, the most efficient process is biological treatment known as *Secondary treatment*. It primarily employs microbes naturally present in wastewater to break down organic contaminants. Some inorganic compounds like ammonia, cyanide, sulphide, sulphate and thiocyanate are also biologically degradable. Biological processes can be broadly classified as:

- i) Aerobic – microbes that require oxygen to grow
- ii) Anaerobic – microbes that grow in the absence of oxygen but uses other compounds such as sulphate, phosphate or other organics present in the wastewater other than oxygen
- iii) Facultative – microbes that can grow in the presence or absence of oxygen.

Aerobic processes consist of a biological reactor with a controlled amount of biomass and a clarifier for separation of the biomass from the final effluent as shown in Figure 24.

Figure 24: Basic principle of an aerobic secondary system



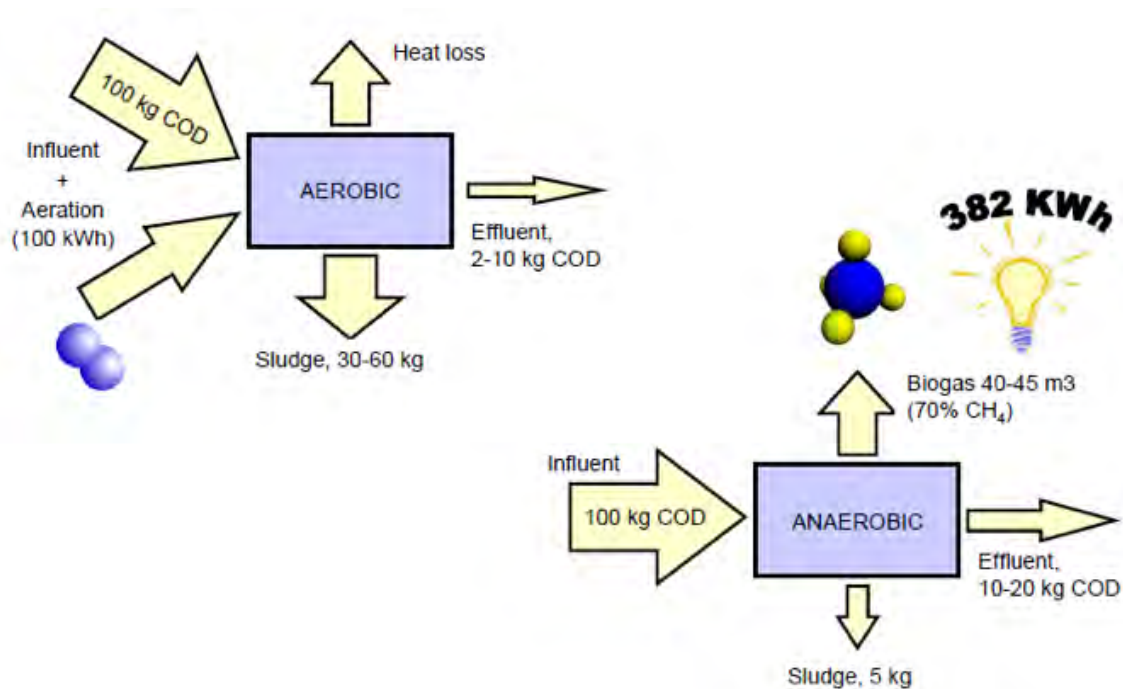
Aerobic processes require higher energy inputs and produce greater amounts of sludge compared to anaerobic systems. Figure 25 shows that for the same 100kg COD load entering the aerobic treatment plant, the energy required is 100kWh for aeration and produces 30 – 60kg of sludge with the outlet effluent COD load of 2 – 10kg. In the anaerobic treatment plant for the same 100kg load COD, the sludge production is only 5kg, or six – twelve times

³⁵ Jácóme A., et al. "TFSETP in textile industry: Activated sludge", 2013.

less, and produces 40 – 45m³ of biogas which can be converted to produce 382kWh of electricity. However, the outlet water COD is twice that of the aerobic plant, and therefore of a lower quality.

In textile wastewater treatment, dyes react differently to aerobic biological treatment depending on the class of dyes. Dyes are generally resistant to oxidative biodegradation since one of the most important properties built into commercial dyes is to resist fading caused by chemical and light induced oxidation. Another challenge in the biological treatment of textile effluent is that the constant changing product mix poses problems for microorganisms to acclimatise to the substrate. Disperse and acid dyes are removed in aerobic systems through adsorption in the biomass and settle in the secondary clarifier. On the other hand, reactive azo dyes are not degraded by aerobic treatment, whilst anaerobic treatment is able to degrade reactive azo dyes to aromatic amines which are still toxic, and aerobic systems located downstream of an anaerobic plant are able to degrade them further. Therefore the two together, where an anaerobic system is used followed by an aerobic system, produces the best results. In anaerobic systems if there is sufficient COD, then sufficient biogas can be produced to power a generator. Table 13 shows the essential differences between aerobic and anaerobic systems.

Figure 25: Difference between aerobic and anaerobic biological treatment systems



Source: Lettinga Associates Foundation

Table 13: Detailed differences between aerobic and anaerobic treatment systems

| Feature | Aerobic | Anaerobic |
|-----------------------------------|---|------------------------------------|
| Organic removal efficiency | High | High |
| Effluent quality | Excellent | Moderate to poor |
| Organic loading rate | Moderate | High |
| Sludge production | High | Low |
| Nutrient requirement | High | Low |
| Alkalinity requirement | Low | High for certain industrial waters |
| Energy requirement | High | Low to moderate |
| Temperature sensitivity | Low | High |
| Start-up time | 2 - 4 weeks | 2 - 4 months |
| Odours | Less opportunity for odours | Potential odour problems |
| Bioenergy and nutrient recovery | No | Yes |
| Mode of treatment | Total depending on (feedwater characteristics) | Essentially pretreatment |
| Removal of reactive azo dyes | Not degraded | Degraded to aromatic amines |
| Phenolics (aromatic -OH) | 90 - 1,000 | 100 - 200 |
| Polynuclear aromatic hydrocarbons | 1 | N/A |
| Oil and grease | 100 | 100 |
| | | |
| Ammonia (-N), mg/L | 480 | 1,500 - 3,000 |
| Cyanide, mg/L | 0.1 - 5 | 0.1 - 4 |
| Arsenic, mg/L | 0.04 - 0.4 | 0.1 - 1.0 |
| Cadmium, mg/L | 0.5 - 10 | 0.02 - 1.0 |
| Copper, mg/L | 0.1 - 1.0 | 0.5 - 100 |
| Chromium Total, mg/L | 0.1 - 20 | 1.5 - 50 |
| Nickel, mg/L | 1 - 5 | 2 - 200 |
| Benzene, mg/L | 100 - 500 | 100 - 870 |
| Toluene, mg/L | 200 | |
| Surfactants, mg/L | 100 - 500 | N/A |

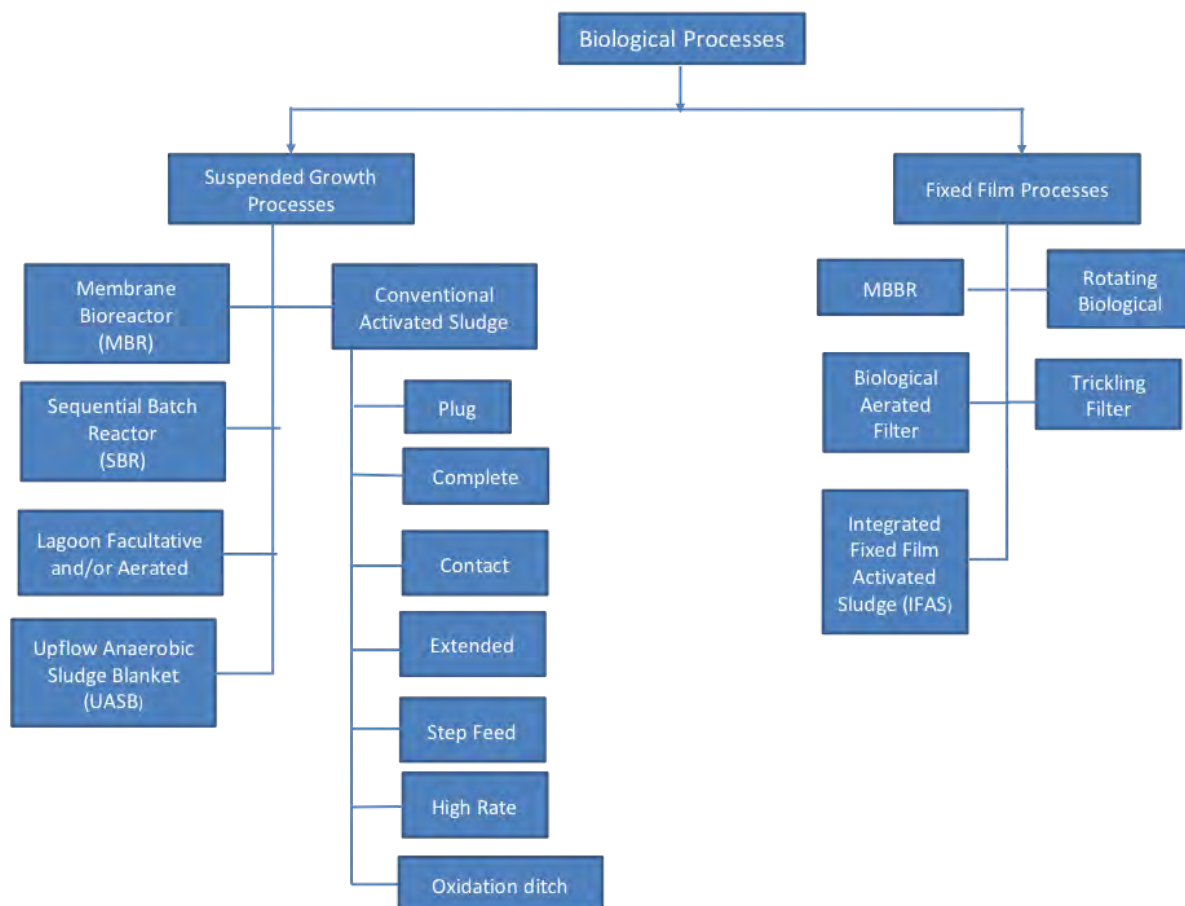
Adapted from: Mark Sustarsic, "Understanding the Activated Sludge Process", CEP November 2009 and US EPA, "Guidance Manual for Preventing Interference at POTWs", September 1987.

Factors that are important in the selection of biological treatment includes:

1. The type of fibres being dyed and dye types
2. Desired effluent quality – MBR produces a quality suitable for reuse
3. Wastewater characteristics – BOD, COD treatability – aerobic and/or anaerobic systems
4. Ultimate sludge disposal options
5. Available land area – lagoons require large land mass
6. Operator skills required
7. Capital and operating costs – vary across the spectrum
8. Power consumption – MBR consumes more power than other systems

Biological processes can also be segregated to suspended and fixed film as shown in Figure 26³⁶.

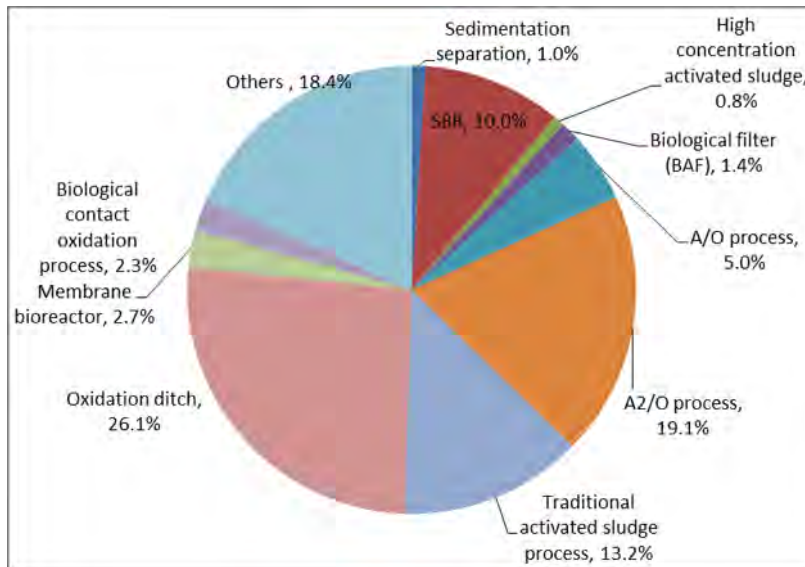
Figure 26: Characterisation of biological processes



³⁶ Mohan Seneviratne.

Figure 27 shows the types of biological treatment processes prevalent in China's municipal wastewater utilities³⁷.

Figure 27: Biological treatment processes used in the municipal sector in China



Basic parameters to operate a biological reactor are given below.

Basic parameters of the biological reactor

- i) **Hydraulic retention time (HRT):** is the average time in the aeration basin equivalent to the volume (V) of the basin divided by the average flow (F_{av}) and expressed as hours. The HRT needs to be sufficiently long to remove the prerequisite BOD and is dependent on the type of the biological treatment system. It can range from 0.5 to 120 hours but typically, in conventional activated sludge processes for textiles, wastewater treatment is around 20 – 25 hours and extended aeration is around 36 – 48 hours for textile wastewater treatment plants. The lower the HRT, the quicker it will reach the outlet and lower HRT.

Where:

HRT = hydraulic retention time (hours)

$$HRT = \frac{V}{F_{av}} \times 24$$

³⁷ Keqiang Zhang, "Wastewater Treatment and production and use in China", March 2013.

ii) **Mixed Liquor Suspended Solids (MLSS)** – Suspended solids level is one of the most important control parameters in biological wastewater treatment processes. It is not only directly related to sludge settling properties and effluent quality, but also related to food/microorganism ratio that is in turn related with all aspects of sludge properties. MLSS represents the total suspended solids including bacteria, dead biomass and higher life forms, irrespective of biological activity. The organic portion of MLSS is represented by Mixed Liquor Volatile Suspended Solids (MLVSS) which represents the biomass. MLSS is controlled by the sludge wasting rate. Typical MLSS are dependent on the process type as shown in Table 15. The more concentrated the MLSS, the smaller the equipment footprint and hence the popularity of membrane bioreactors in space constrained locations. To obtain MLVSS, multiply MLSS by 0.75.

Table 14: MLSS of biological treatment systems

| Process | MLSS (mg/L) |
|---|---------------|
| Activated sludge conventional w/o nitrification | 1,000 – 3,000 |
| Activated sludge conventional w/o nitrification | 3,000 – 5,000 |
| Extended aeration | 3,000 – 5,000 |
| Moving bed bioreactor | 6,000 |
| Membrane bioreactor | >10,000 |

iii) **Food to microorganism (F/M) ratio:** A term for expressing the organic loading of an activated sludge process F/M is a critical factor in process design and operation, especially in determining the aeration basin volume. F/M range is about 0.5 – 1.5. For conventional plants, F/M of 0.2 – 0.5 is aimed for. In biological treatment plants operating at high F/M loads (0.8 – 1.5), the rate of treatment increases but at the cost of poor settlability of the sludge. Processes operating at low F/M loads (0.05 – 0.2) are associated with slow BOD removal rates but with good sludge settling. However, the system can be easily upset by a spike load of organics. It is usually defined as:

Where:

F_{av} = average daily inflow (m^3/d)

L_0 = average daily concentration BOD₅ influent to reactor (kg/m^3) = Inlet BOD₅ – outlet BOD₅

X = concentration of suspended solids in the mixed liquor (kg MLSS/ m^3)

F/M = food to microorganism ratio (kg BOD₅/ kg MLSS/ d) or (d^{-1})

V = Volume of aeration basin, m^3

$$F/M = \frac{F_{av} \cdot L_0}{V \cdot X}$$

v) **Sludge age** is also known as **Mean Cell Residence Time (MCRT)** and **Solids Retention Time (SRT)**: is calculated as the total quantity of sludge in the aeration tank and clarifier divided by the daily sludge losses through waste activated sludge and effluent. Sludge age can vary from 0.5 to 75 days in low-growth rate systems. However, in conventional systems it is 3 – 15 days and in textile wastewater treatment plants 20 – 30 days. Sludge Age is an indication of F/M ratios. Shorter times are indicative of high F/M ratios and longer times are indicative of low F/M ratios. Sludge age is expressed as:

Sludge age = Sludge mass in (Aeration tank + Clarifier) / daily sludge losses

Where:

MCRT = cellular retention time (days)

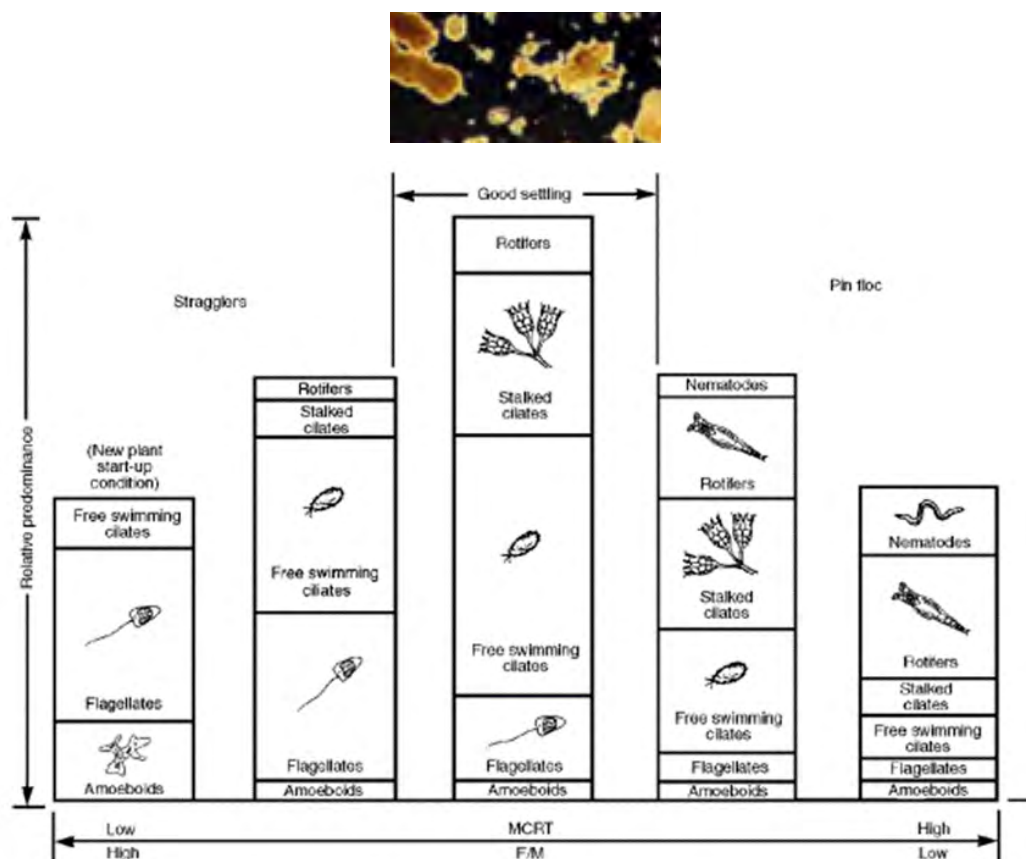
P_{sl} = excess sludge production (kg/d)

$$Sludge\ Age = SRT = MCRT = \frac{V \cdot X}{P_{sl}}$$

The quality of sludge age can be determined using a microscope at 100X magnification. Daily microscopic analysis can prevent problems. Microorganisms considered important in biological treatment are bacteria, fungi, algae, protozoa, rotifers and worms. The presence of higher life form indicator organisms usually correlates to plant performance. They can indicate if the sludge is young, medium or old. Good settling sludge is characterised by the presence of protozoa such as stalked ciliates and suctorians and usually is golden brown in colour (sewage treatment plants). Low sludge age is characterised by the absence of stalked ciliates and predominance of free swimming ciliates such as *Paramecium* (these expend a lot of energy in swimming) and high BOD slugs by the absence of higher life forms. Old sludge is characterised by the presence of many worms (nematodes) or rotifers. Figure 28 shows graphically the organisms and sludge quality.

Another useful indicator is the Sludge Volume Index (SVI). Sludge is poured to a 1L graduated cylinder and the percentage of settled sludge in 5 minute intervals is noted for 30 minutes. SVI is expressed in mL/g. It is a reliable troubleshooting test. SVI values can vary from 30 to 400 mL/g. Values below 150 indicate good sludge settling and above this indicate sludge bulking.

Figure 28: Sludge age and indicator organisms



Source: USEPA "Activated Sludge Process," Section 4, Laboratory Control

Other key variables that affect the operation of the biological reactor:

- **Oxygen requirements:** oxygen is required for the decomposition of organic matter. The concentration depends on organic matter consumption, endogenous respiration demand and total nitrification of TKN oxidation. Typical oxygen concentration in an aeration tank is 2 – 4 mg/L. The higher values are maintained for nitrogen removal. Above this, electricity is wasted.
- **Sludge production (Sludge yield):** The decay of biomass produces sludge. For conventional systems in municipal treatment for every kg of BOD removed, sludge production is around 0.5 – 0.8 kg. However, in industrial systems, sludge production can be as low as 0.15 kg/BOD kg, such as in coke making, to 0.7 kg/BOD in food processing.
- **Sludge recirculation rate:** A portion of the sludge produced is recirculated to promote the production of more sludge in the aeration tank. It is the ratio between the sludge recirculation volumetric flow, Q_R , and treatment volumetric inflow:

$$\frac{F_R}{F} = R = \frac{X}{X_R - X}$$

In any case, the capacity of the sludge recirculation system will not be less than 200% of the daily average total inflow.

Another design criterion is established: X_R concentration is 6000 mg SS / L (= 6 kg/m³).

- **Nutrient requirements - C:N:P ratio** - Besides carbon, hydrogen and oxygen biomass requires nitrogen (N), phosphorous (P) and micronutrients such as iron, calcium, magnesium, copper, zinc and so on. Unlike domestic sewage which has a C:N:P = 100:17:5 – 100:19:6, most industrial wastewaters lack N and P which should be added (in the form of urea, superphosphate or ammonium phosphate) to maintain optimal microbial growth conditions. The minimum C:N:P ratio required for optimal microbial growth in the in aerobic and anaerobic processes are:

Aerobic processes: C:N:P = 100: 5: 1

Anaerobic processes: C:N:P = 330: 5: 1

The most common biological processes are described briefly below.

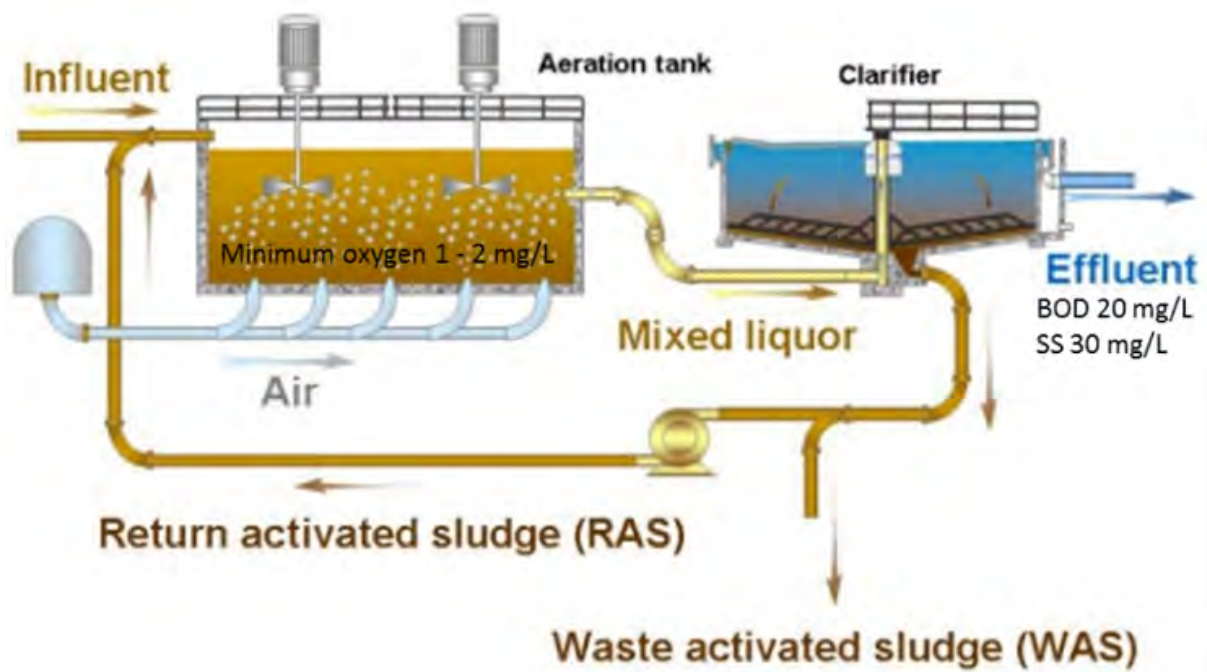
3.4.1 Aerobic processes – Activated sludge process (ASP)

Biological processes, employing aerobic biomass in suspension, have traditionally been known as activated sludge processes. The Activated Sludge Process (ASP) was developed in the United Kingdom in the early 1900s for the treatment of the domestic sewage and it has since been adapted for removing biodegradable organics in industrial wastewater. Today it is widely employed in industries such as oil refining, textile, pulp and paper chemical manufacturing and food processing. The ASP process and its variants are capable of treating biodegradable wastewater of moderate strength (10 – 1000 mg/L BOD) to high strength (>1000 BOD mg/L). The ASP process does not remove heavy metals or TDS. Some contaminants such as cyanide, and heavy metals such as chromium and mercury, present in industrial wastewater act as inhibitors for the proper functioning of the ASP process as well as other biological processes.

ASP processes have been categorised, according to the mass loading design, in three groups: low load activated sludge (extended aeration, oxidation ditches, etc.), medium load (or conventional) and high loading.

The ASP process involves blending settled primary wastewater or equalised influent with a culture of microorganisms into a fluid called "*mixed liquor*". This mixed liquor is passed through an aeration tank which provides an adequate oxygen rich environment for the microbes to eat and stabilise the organic matter in water. Mixing brings oxygen and food to microorganisms allowing the microorganisms to clump together whilst preventing floc settling in the aeration tank. The process produces Waste Activated Sludge (WAS) consisting of microbes and excess microbial matter. The solids and treated wastewater are separated in a secondary clarifier or other solids separation step such as an MBR. Here the majority of the WAS is returned to the aeration tank as Returned Activated Sludge (RAS) to maintain the microbial population in the aeration tank, as well as ensuring that the activated sludge is old enough to degrade COD and aromatic hydrocarbons. The remainder is removed and undergoes thickening. The secondary clarifier has the dual purpose of clarifying the wastewater as well as concentrating the sludge. The process is sensitive to pH fluctuations, where a high or low pH can upset the system and cause overloading of the clarifier. Figure 29 shows a schematic of the activated sludge process. Figure 30 shows a photo of a rectangular aeration tank in a textile effluent treatment plant in China.

Figure 29: Schematic of activated sludge process



Source: Water Institute of Southern Africa (2002): "Handbook for the operation of waste water treatment plants".

Figure 30: Aeration tank in a textile effluent treatment plant in China



Source: Mohan Seneviratne

Nitrogen containing compounds are toxic to aquatic life, deplete oxygen in the receiving waters, adversely affect public health and reduce the potential for water reuse. Therefore, nitrogen containing compounds are removed, if deemed excessive, by nitrification and then denitrification processes. Organic nitrogen is converted to ammonia, then converted to nitrite, which is further oxidised to nitrate and finally to gaseous nitrogen. Denitrification consumes alkalinity and needs to be sufficient so as not to depress the pH. It requires 7.14mg/L of bicarbonate alkalinity for each 1mg/L of ammonia nitrogen removed. Oxygen also needs to be maintained at concentrations closer to 4mg/L for denitrification. General guidelines for process control for are shown in Table 16. These are customised for each effluent treatment system depending on wastewater characteristics and for optimal operation.

Table 15: Process control parameters for activated sludge treatment

| Parameter | Level to be maintained in aeration tank | Comments |
|--|---|---|
| Mixed liquor suspended solids (MLSS), mg/L | 2,000 - 4,000 | Mixed liquor volatile solids to be 80% of MLSS |
| Oxygen concentration | 1 - 2 mg/L | Closer to 4 mg/L for denitrification |
| Sludge age, days | 10 - 15 | High sludge age of 10 – 15 days is required for denitrification |
| Food /Mass (F/M) | 0.2 - 0.5 | Without nitrification. With nitrification 0.05 – 0.25 |
| Hydraulic Retention Time | 12 - 24 hours | |
| Dissolved oxygen, mg/L | 2 - 4 | Higher values in presence of ammonia. Requires 4.5 mg/L of Oxygen for 1 mg/L of ammonia |
| pH | 6.5 - 9.5 | pH provides the alkalinity in the water. Below pH < 7, nitrification is depressed. For denitrification pH is controlled between 7 – 8.5 |
| Alkalinity as HCO ₃ , mg/L | 100 | Influent alkalinity needs to be higher than 100. |
| Temperature, °C | | Below 5°C nitrification doesn't occur. Under such conditions, sludge age and MLVSS needs to be increased. |

| | | |
|-----------------------|--------|--|
| BOD: Total Kjeldahl N | | The fraction of nitrifying organisms decrease as this ratio increases. |
| Chloride, mg/L | | Higher values possible as long as the concentration is stable in the influent. |
| Heavy metals, mg/L | <5 | Total of all heavy metals |
| Phenol, mg/L | <20 | |
| Cyanides, mg/L | <20 | |
| Benzene, mg/L | <13 | Nitrosomonas bacteria is inhibited |
| Sulfide mg/L | 5 - 30 | |

3.4.2 Aerobic processes – Oxidation ditch

The oxidation ditch process, developed in the 1950's in the Netherlands, is a variant of the Activated Sludge Process and is a special form of extended aeration. A schematic and photo is shown in Figures 31 and 32. The shape of the oxidation ditch is like a ring. Wastewater, microorganisms and activated sludge is mixed in a continuous loop ditch in order to complete nitrification and denitrification reactions. The oxidation equipment consists of ditch body, aeration mixers and inlet and outlets. Given its long hydraulic retention time (HRT) of 20 – 36 hours, low organic loading and long sludge age compared to conventional ASP, equalisation, primary sedimentation and sludge digestion tanks are omitted.

Oxidation ditch has many advantages in that it provides:

- ✓ Low energy consumption
- ✓ Low maintenance
- ✓ Ease of operation
- ✓ Low CAPEX (capital expenditure)
- ✓ Less sludge due to long extended solids retention time
- ✓ Resistance to shock loads and hydraulic surges due to long hydraulic retention time

The disadvantages are that the effluent SS quality is inferior to the ASP process and requires a large land area.

Figure 31: Schematic of oxidation ditch

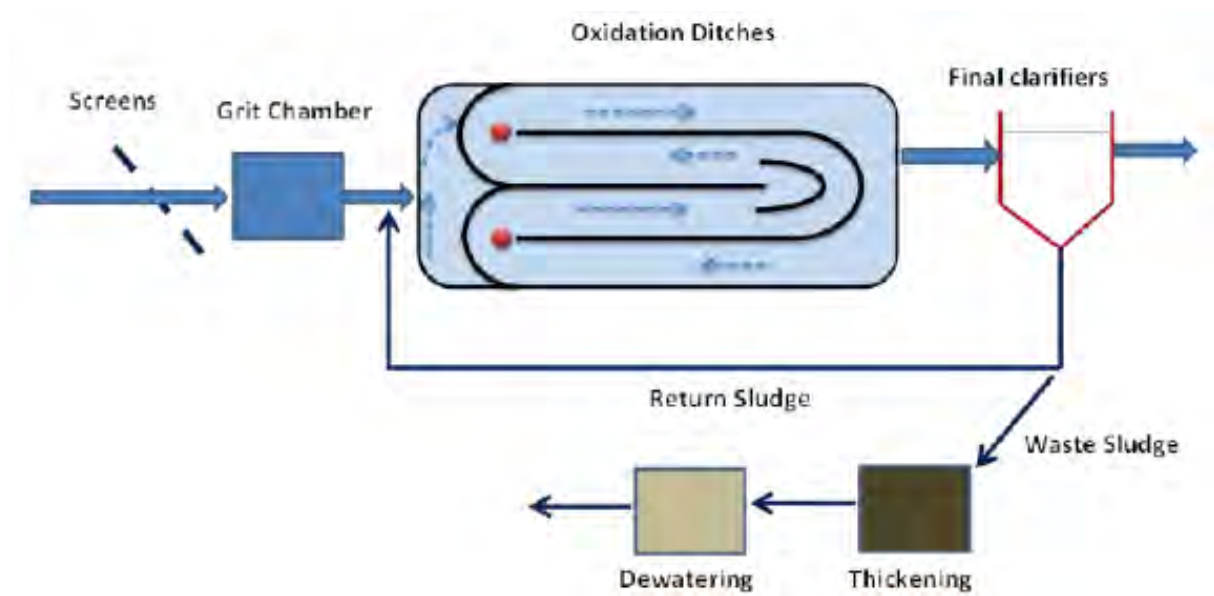


Figure 32: Photo of an oxidation ditch, China

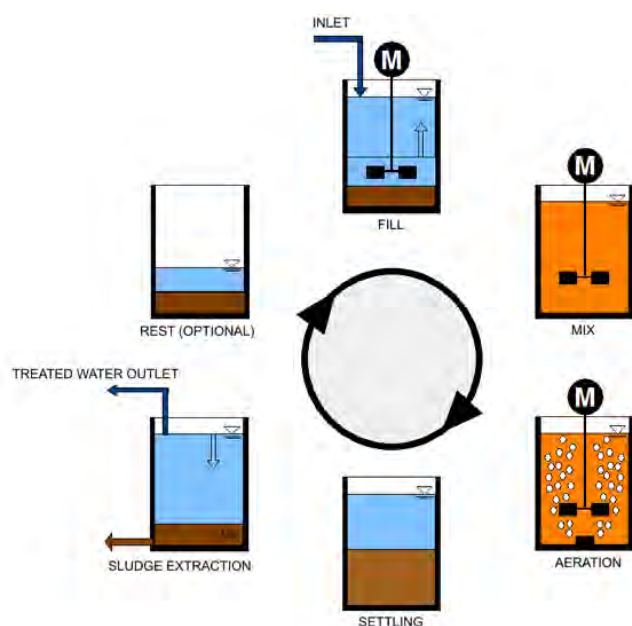


Source: Sudhi Mukherjee, IFC

3.4.3 Aerobic processes – Sequencing batch reactor (SBR)

The SBR process differs from the other ASP processes described in that it is a batch process rather than a continuous process. The principle is that all of the processes of ASP, i.e. primary settling, biological oxidation and secondary settling takes place in a single tank. The process steps as shown in Figure 33 are fill, react, settle, draw and idle. SBRs are compact and low CAPEX (capital expenditure). It is used in municipal wastewater treatment plants extensively especially when land area is scarce given it only requires one tank to fulfill the aeration and clarification steps. In India, it is also used to treat nitrogen and phosphorous. Standard cycles are commonly 4 – 6 hours long, resulting in 4 – 6 reaction cycles per day. For exceptional cases, systems dedicated exclusively to nitrification-denitrification process or high polluted flows, the duration of the cycles can be extended to 12 or even 24 hours.

Figure 33: Phase sequence during one SBR cycle³⁸



SBR systems removal rate for BOD5 range between 85 – 95%. Technology suppliers usually refer to effluent quality levels of 10 mg/L of BOD and SS, total nitrogen and phosphorus range between 5 – 8 and 1 – 2mg/L, respectively. In the textile industry, use of SBRs is not very common, though research papers refer to achieving colour removal of 71% and COD reduction of 79%³⁹.

³⁸ Suárez J., et al., "TFSETP in textile industry: SBR", 2015.

³⁹ S.Sathian, et al., "Performance of SBR for the Treatment of Textile Wastewater: Optimization and kinetic studies", Alexandria Engineering Journal, 3 April 2014.

Compared to the conventional ASP, it is resistant to shock loading, flexible operation due to adjustment of run time and low sludge production. SBR systems prevent arising of filamentous bulking, which is one of the most frequent troubles in low load biological treatments applied to textile effluents . Typical design values are shown in Table 17.

Table 16: Design Values for SBR reactor

| Parameter | SBR ^{41,42} | SBR ⁴³ | SBR (sequential intermitent flow) | Industrial SBR ⁴⁴ |
|----------------------------------|----------------------------------|-------------------|---|---------------------------------|
| Sludge age (MCRT) (d) | *4 - 6 **8 - 10 ***20 - 25 | 20 - 40 | 10 - 30 | |
| F/M ratio (kg BOD5/kg MLSS/d) | 0.050 - 0.30 | 0.04 - 0.2 | 0.04 - 0.10 | 0.15 - 0.4 |
| Volumetric load (kg.m3.d) | 0.08 - 0.24 | 0.08 - 0.24 | 0.08 - 0.24 | |
| MLSS (X) (mg/L) | 1,500 - 5,000 | 2,000 - 6,500 | 2,000 - 8,000 | 2,000 - 2,500 |
| Cycle length (h) | | 4 - 12 | | 4 |
| HRT (h) | 12 - 50 | 9 - 30 | 12 - 50 | 6 - 14 |

*without nutrient removal

**with nutrient removal and

***extended aeration process with nutrient removal

⁴⁰ Nicolau M. and Hadjivassilis I. "Treatment of wastewater from the textile industry", 1992.

⁴¹ Metcalf & Eddy, "Wastewater Engineering: Treatment and Reuse", 2003.

⁴² Sperling M., "Biological Wastewater Treatment Series. Volume 5. Activated Sludge and Aerobic Biofilm Reactors", 2007.

⁴³ U.S. EPA, "On-site Wastewater Treatment Systems – Sequencing Batch Reactors Systems", 2000.

⁴⁴ U.S. EPA, "Wastewater Technology Fact Sheet: Sequencing Batch Reactors", 1999.

3.4.5 Trickling filters

Developed in the 1890s, trickling filters are an example of a fixed film biological process compared to the ASP process which is a suspended process.

A trickling filter consists of bed of coarse material, such as rounded rocks (25 – 102mm in diameter), crushed stone, wooden or plastic slats and plastic rings over which wastewater is discharged from moving spray distributors or fixed nozzles. The filter media provides a large amount of surface area for the microorganisms to cling and grow a jelly like biofilm of around 10mm thickness. In the outer portions of the biofilm (0.1 – 0.2mm) the aerobic bacteria break down the organic matter. When the biofilm becomes very thick it falls off and a new biofilm layer forms. Modern trickling filters use plastic media over rocks given they weigh less and filter media can be up to 6.1m in depth compared to 3m in depth for rock filters, allowing taller filters using less land area. The filter effluent is recycled to minimise drying of the filter media, improve filter efficiency and reduce odour potential. Sometimes, two filters are assembled in series to handle strong wastewater. The sprays rotate at 2 – 5 revolutions per minute (rpm) and a typical wetting rate is 0.6 – 2.44 m³/m/h⁴⁵. When the wetting rate is too low, the water may not penetrate the depth of the filter bed uniformly causing channeling and acts as an incubator for flies, as well as creating odour problems. Low rate filters operate on natural ventilation, whereas high rate filters require forced draft fans to provide adequate ventilation. The trickling filter is followed by a secondary clarifier.

Trickling filters are classified according to the organic and hydraulic loads to low rate, intermediate, high rate, roughing filter and super high rate. The design loadings for sewage treatment is given in Table 18.

⁴⁵ Alireza Bahadori, "Waste Management in the Chemical and Process Industries", John Wiley & Sons Ltd, 2014.

Table 17: Trickling filter process applications and representative design parameters

| Parameter | Units | Low rate | Intermediate | High rate | Super high rate | Roughing filter (partial) |
|--------------------------|------------------------------|----------------------|-----------------------|--------------------------------|--------------------------------|---------------------------|
| Media | | Stone | Stone | Stone/plastic | Plastic | Stone/plastic |
| Organis loading | Kk BOD/ m ³ /d | 0.08 – 0.4 | 0.24 – 0.4 | 0.4 – 4.8 | Up to 4.8 | 1.6 – 3.2 |
| Hydraulic loading | m ³ /m/h | 0.04 – 0.15 | 0.15 – 0.4 | 0.4 – 1.5 | 0.6 – 3.6 | 2.5 – 7.0 |
| Depth | m | 1.8 – 2.4 | 1.8 – 2.4 | 0.9 – 2.4 | Up to 12 | 0.9 – 6.0 |
| BOD removal | % | 80 – 85 | 50 – 70 | 65 – 85 | 65 – 85 | 40 – 65 |
| Ventilation | Type | Natural | Forced air | Forced air | Forced air | Forced air |
| Effluent quality | BOD mg/L | <30 | <30 | <30 | <20 | <30 |
| | NH ₄ -N mg/L | <5 Well nitrified | Some nitrification | Limited nitrification >5 | Limited nitrification >5 | No nitrification |

Adapted from: Metcalf & Eddy, "Wastewater Engineering" 2014 and Inditex "Technology Fact Sheet For Industry FS BIO 003- Trickling Filters".

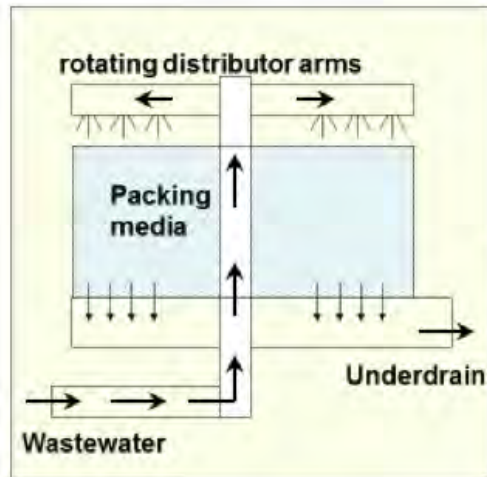
The advantages of a trickling filter are:

- ✓ Lower energy requirements than ASPs
- ✓ Simple operation with no issues of MLSS inventory control and sludge wasting
- ✓ Better recovery from shock toxic loads
- ✓ No problems of bulking sludge in secondary clarifiers
- ✓ Compact and suitable where land is scarce
- ✓ Less equipment maintenance needs
- ✓ Effective in treating high concentration of organics dependent on type of media used
- ✓ Better sludge thickening properties

The disadvantages are organic loading levels, that the effluent water quality (in terms of BOD and TSS) is lower than ASP and may require further treatment, odour problems, flies, prone to plugging of filter media and at low temperatures natural ventilation systems don't operate that well. Figure 34 shows a schematic of a trickling filter.

Figure 34: Schematic of a circular trickling filter with natural ventilation and plastic modules

Trickling Filter (TF)- side view



- TF consists of:
 - A rotating arm that sprays wastewater over a filter medium.
 - Filter medium: rocks, plastic, or other material.
- The water is collected at the bottom of the filter for further treatment.

3.4.6 Moving Bed Bioreactor (MBBR)

Developed in the 1980s by Kaldnes in Scandinavia, the MBBR process is a more modern fixed film process in which the microorganisms grow on plastic media as shown in Figure 35. The media are made from high density polyethylene or polypropylene with a diameter of 13 – 25mm, and therefore have a large surface area which helps the biomass to grow inside the surface and are in constant motion due to the compressed air that is blown from under the tank. The typical MLSS is higher than conventional ASPs at 6,000mg/L. The process been applied in a variety of industrial wastewater treatment applications in aerobic and anaerobic modes with or without denitrification depending on the mode of mixing.

Benefits of MBBR are that it is good for high organic loading applications, improved settling characteristics, no need for sludge recirculation from secondary clarifier thereby making it a 'once through' process, compact and low footprint compared to the ASP process and modular construction. Figure 36 shows the lower footprint of MBBR compared to a trickling filter and Figure 37 shows a media carrier. It can also retrofit existing ASP systems, requires fewer operational controls than ASPs, and contains fewer mechanical and instrumentation controls compared to a MBR system. A typical HRT for MBBR is 2 – 3 hours, compared to 12 – 24 HRT for ASPs.

Disadvantages of MBBRs compared to the ASP are that it requires a higher oxygen concentration, the need for improved influent wastewater screening, and additional hydraulic profile head losses due to flow through the media screening devices. Typical performance characteristics are – BOD in effluent <3 mg/L; energy consumption 0.17 – 0.27 kWh/m³ (for domestic sewage).

Figure 35: MBBR system

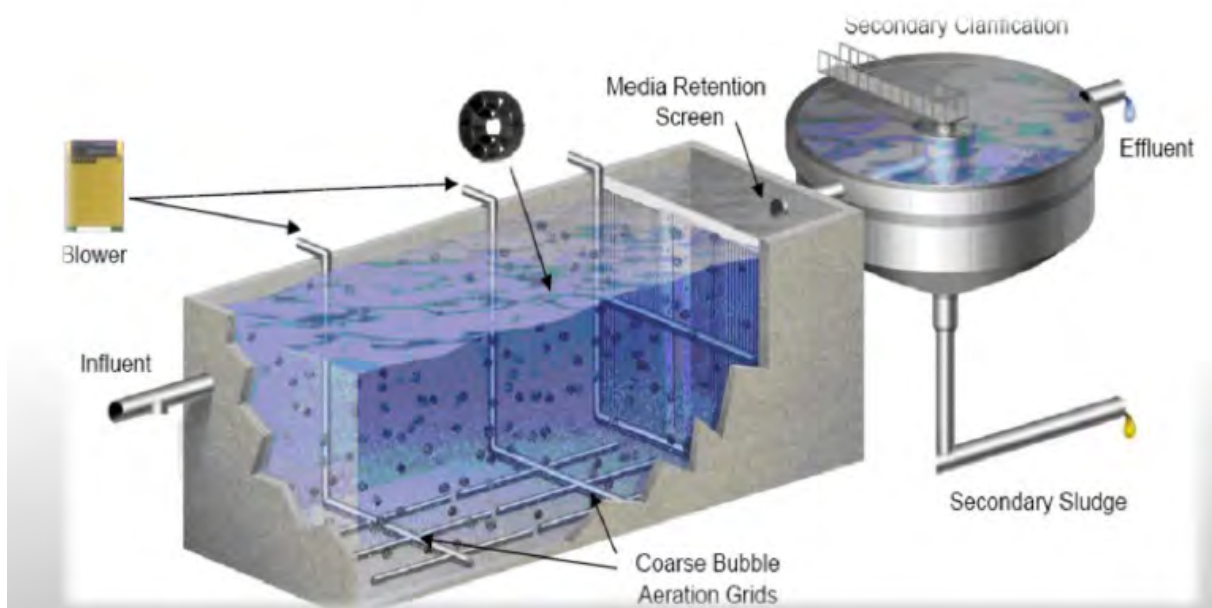
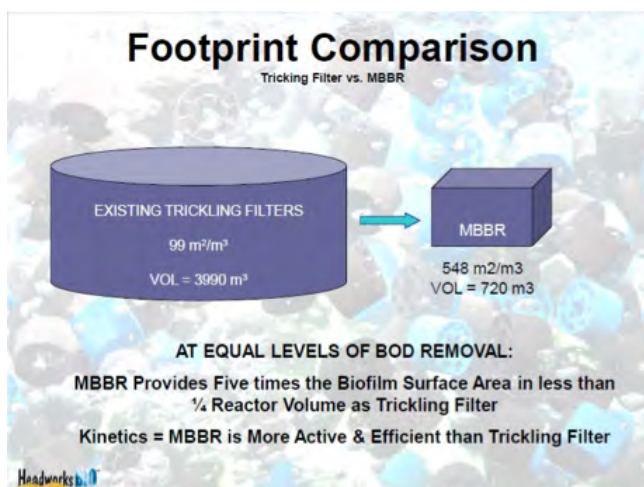


Figure 36: Footprint of MBBR vs trickling filter



Source: Headworks Bio

Figure 37: MBBR Media carriers in an Italian steel plant



Source: Mohan Seneviratne

3.4.7 Membrane bioreactor (MBR)

Though external membrane bioreactors were originally developed in the 1960s, they became popular only after the development of the immersed (*submerged*) MBRs in the late 1980s. The lower operating cost of the submerged MBR configuration and the decreasing cost of the membranes have made MBRs a popular choice for domestic and industrial wastewater treatment. MBRs are used for industrial wastes with BOD of 5,000 to 40,000 mg/L and domestic waste with BOD ranges of 200 – 600 mg/L⁴⁶. There are currently over 1,200 installations and half of them are in industrial applications. In China, 29% of MBRs are in industrial applications. The third most popular application of MBRs, after food and beverage and pulp and paper, is the textiles industry⁴⁷. The global market for MBRs has had a compound annual growth of 12.8% since 2014 and is expected to reach US\$778 million in 2019⁴⁸.

The quality of the final effluent from a conventional ASP unit is highly dependent on the hydrodynamic conditions in the clarifier and settling characteristics of the sludge. This leads to variable performance. Consequently, large clarifiers are required with long residence times. The MBR process was developed to remove these disadvantages of conventional ASPs. MBRs are a hybrid with two interdependent treatment processes: biological treatment and membrane treatment. It is similar to a conventional ASP in that both have mixed liquor solids in suspension in an aeration tank. The difference in the two processes lies in the method of separation of bio-solids. In the MBR process, the membranes create a solid barrier to bio-solids based on microfiltration (MF) with a pore size of 0.6µm, or ultrafiltration (UF) with a pore size of 0.04µm, and therefore are not subject to gravity settling solids characteristics. Consequently, a MBR unit brings aeration, clarification and filtration in a single step with MLSS concentrations reaching 20,000mg/L or higher resulting in a smaller footprint than conventional ASP processes.

⁴⁶ Thomas C. Schawatz, "Membrane Bioreactor Performance Compared to Conventional Wastewater Treatment", GE Technical Paper TP1036EN 0601, 2005.

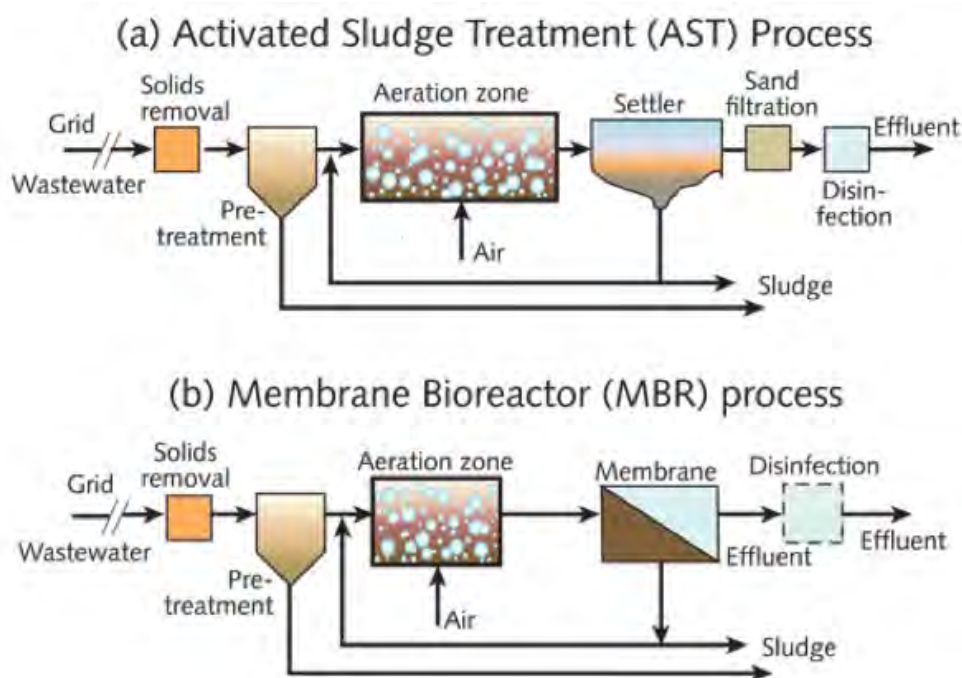
⁴⁷ Hongjun Lin, et al., "Membrane Bioreactors for Industrial Wastewater – A Critical Review", Critical Reviews in Environmental Science and Technology, Taylor and Francis, 2012.

⁴⁸ BCC Research, "Global MBR Market Flowing at 12.8% CAGR as New Applications, Environmental Regs Push Growth", 2 July 2015.

MBRs provide a final effluent quality independent of sludge conditions with higher removal of organics and persistent pollutants, and nutrients with COD removal of 98% and SS removal efficiency of 100%⁴⁹. The high quality effluent produced is ideal for reuse applications. Another feature of MBRs is the long sludge age. However, this also contributes to fouling of membranes. Moreover, MBRs units can be installed directly to a reverse osmosis (RO) plant, bypassing the need for an ion exchange or other equipment to protect a membrane plant provided the hardness or scaling compounds are not excessive.

Figure 38 shows the difference between the ASP and MBR processes. Note the absence of a clarifier in MBR units.

Figure 38: Difference between MBR and conventional systems



Source: Waterworld.com

⁴⁹ Saima Fazal, et al., "Industrial Wastewater Treatment by using MBR Review Study", Huazhong University of Science and Technology, Wuhan China, 2015.

As already noted, there are two types of MBR configurations – immersed and side-stream. Immersed systems are more common in municipal and large industrial units, whereas side-stream is limited to smaller units. The schematics in Figures 39 and 40 explain the differences in layout. There are also differences in the membrane employed from hollow fibre, flat plate and tubular. Immersed MBRs use hollow fiber or flat plate whereas tubular membranes are used in side-stream MBRs as shown in Figure 41. Rotating MBRs are also used in textile wastewater treatment plants.

Figure 39: Schematic of submerged MBR⁵⁰

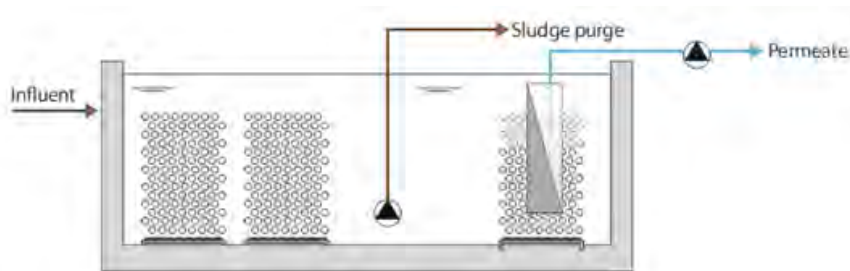


Figure 40: Side-stream MBR

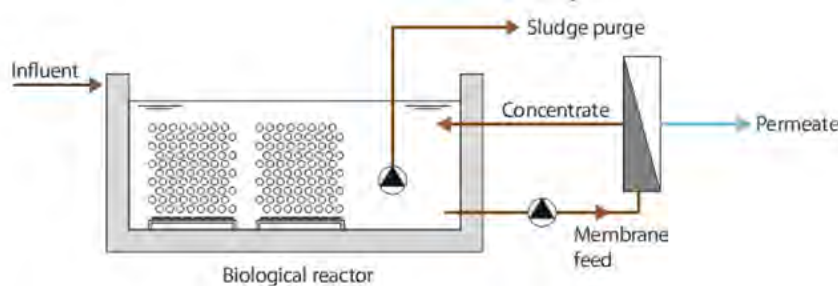
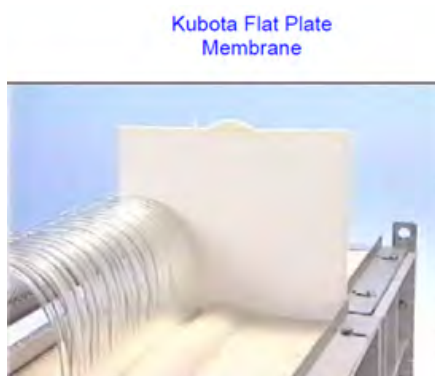


Figure 41: Flat plate and hollow fiber immersed membranes



Source: Kubota



Source: GE Water and Power

⁵⁰ Ures P., et al. "TFSETP in textile industry: MBR", 2015.

MBR produces an equivalent treatment level to an activated sludge process followed by microfiltration (MF) or Ultrafiltration (UF). A review of aerobic MBR applications in textile wastewater treatment shows that MBRs are capable of treating wastewater with COD from 500 to 6000 mg/L, BOD from 90 to 1375 mg/L and colour from 70 to 2700 Pt-Co unit. The MBR systems used in those studies removed (i) 50 – 98% of COD (most of the time the COD removal was more than 80%) and (ii) 20 – 100% of colour (most of the time the colour removal was more than 70%). The MLSS in the MBR varied between 4 – 15 g/L⁵¹. To reduce the high energy demand of MBRs, anaerobic MBRs are being trialled.

It must be noted that the main mechanism of colour removal in MBRs similar to other aerobic systems is adsorption of dye molecules onto the biomass, since biodegradation played a minor role due to the persistent nature of dye compounds. For optimal results, it has been observed that an anoxic (with low oxygen concentrations) or anaerobic tank prior to the aerobic stage provides optimal conditions for the biodegradation of reactive dye compounds⁵².

Figure 42 shows the removal efficiencies of MBR in textile wastewater. The photo on the right shows the influent and effluent.

⁵¹ TVeeriah Jegatheesan, et al., "*Treatment of textile wastewater with membrane bioreactor: A Critical Review*" Bioresource Technology, 204, 2016.

⁵² S. Fazal, et al., "*Industrial Wastewater Treatment by Using MBR Review Study*", Journal of Environmental Protection, June 2015.

Figure 42: Physicochemical characteristics of influent and treated effluent of textile mill by MBR⁵³

| Parameter | Influent (average \pm SD) | Treated Effluent (average \pm SD) |
|---|--------------------------------|--|
| pH | 8.05 \pm 0.9 | 8.27 \pm 0.06 |
| Conductivity (mS/cm) | 3.03 \pm 0.5 | 3.43 \pm 0.38 |
| TSS (mg/L) | 196.1 \pm 108.8 | 3.3 \pm 0.5 |
| VSS (mg/L) | 146.3 \pm 101.8 | - |
| COD (mg/L) | 2966 \pm 438 | 209 \pm 47 |
| Soluble COD (mg O ₂ /L) | 1218 \pm 351 | - |
| BOD ₅ (mg O ₂ /L) | 655 \pm 247 | 14.1 \pm 5.6 |
| TP (mg/L) | 2.9 \pm 1.3 | 1.96 \pm 1.38 |
| PO ₄ -P (mg/L) | 1.73 \pm 1.3 | 0.23 \pm 0.42 |
| NH ₄ -N (mg/L) | 2.24 \pm 1.00 | 3.23 \pm 2.16 |
| NO ₃ -N (mg N/L) | 2.08 \pm 1.47 | 7.48 \pm 0.38 |
| TN (mg N/L) | 32.1 \pm 18.5 | 16.8 \pm 5.1 |
| Cu (μ g/L) | 54 \pm 25 | - |
| Mn (μ g/L) | 15 \pm 11 | - |
| Zn (μ g/L) | 292 \pm 110 | 39 \pm 12 |
| Pb (μ g/L) | <5 | - |



MBR inlet and outlet textile effluent

Despite the advantages of MBRs there are still challenges in using MBRs in industrial applications, which are tabulated in Table 18.

Table 18: Advantages and disadvantages of MBRs

| Advantages | Disadvantages |
|--|--|
| 25% lower footprint – replaces the clarifier and gravity filter of conventional systems – ideal for land constrained sites and lower HRT of 4 – 8 hours compared to 8 – 24 hours for conventional ASP. | Higher CAPEX and installation costs for smaller units. |

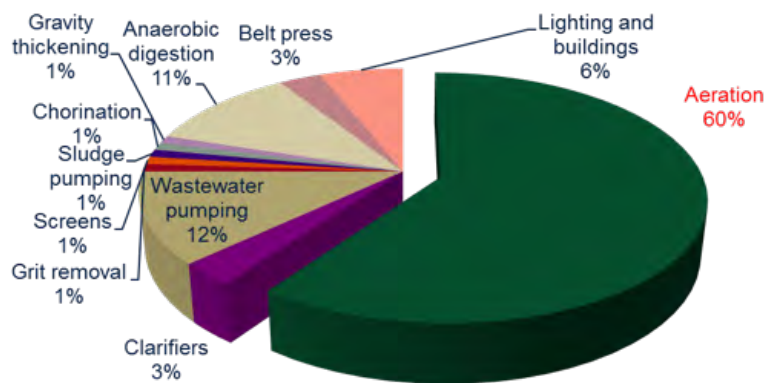
⁵³ Source: P. Damala, et al., "Application of MBR for the treatment of textile wastewater", Athens, 2015.

| | |
|---|--|
| Provides impermeable barrier for solids producing highest quality effluent with BOD < 5 mg/L and turbidity <0.1 NTU. | Higher power requirement than conventional ASP systems especially for side-stream units. |
| Ideal for water reuse with sufficient treatment for direct feed to reverse osmosis units | Membrane fouling is one of the major challenges which results in reduced performance and frequent cleaning or membrane replacement leading to increased maintenance and operating costs. All MBRs require a minimum of fine screens of 3 mm. |
| High biomass concentrations (MLSS) reaching 20,000 mg/L good for recalcitrant wastewater found in textile effluent | Sludge produced can be difficult to dewater. |
| Compact process | Designs are supplier specific and can be difficult to standardise |
| Sludge retention time (SRT) is independent of HRT. High sludge age of 15 – 140 days can be obtained reducing sludge production and lower sludge production of 20 – 40% of conventional. | |
| Modular expandability | |
| Less odour | |
| Flexible operation - Less susceptible to upsets | |
| Can be automated | |

3.4.8 Energy consumption of aerobic processes

The energy consumption of aerobic processes is critical for the overall operating cost and accounts for at least 60% of energy consumption in conventional activated sludge systems, as shown in Figure 43. Therefore, aeration above a maximum of 2mg/L of oxygen wastes energy and money unless denitrification is required. High aeration also disrupts floc and also leads to gasification of sludge.

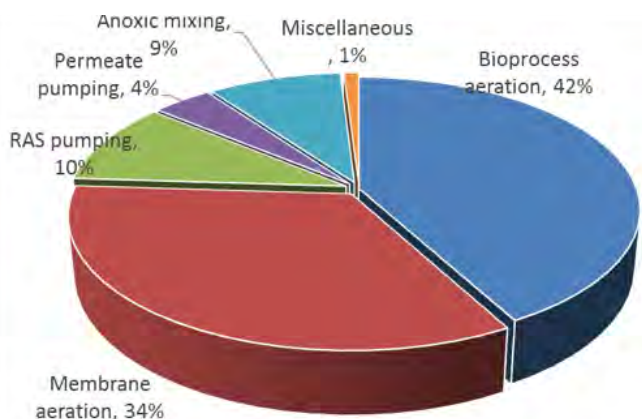
Figure 43: Breakdown of energy consumption in ASP



In MBR's, aeration (bioprocess and membrane aeration) accounts for 76% of total energy use as shown in Figure 44. MBRs energy consumption is higher, since the efficacy of air usage is relatively low. MBRs use more air and hence have a higher energy usage than conventional treatment, due to air being required for both the biological process and membrane cleaning. The type, volume and location of air required for the two processes are not matched. Bio-treatment utilises fine air bubbles since oxygen needs to be absorbed for the biological reaction step. In contrast, membrane fouling control is best achieved by larger bubbles which are best suited for scouring of the membrane surface.

Submerged systems consume from 1.0 kWh/m³ for larger systems to 1.5 kWh/m³ for smaller systems^{54, 55}. Side-stream systems consume more power (4 – 12 kWh/m³) compared to submerged units in order to maintain high cross flow velocities. Whilst the CAPEX costs for submerged units are higher, they have lower operating costs compared to side-stream units.

Figure 44: Energy use in MBR plants



⁵⁴ Asun Larrea, et al., "10 years of Industrial and Municipal MBR Systems – Lessons from the field", Praxair.

⁵⁵ F.I. Hai, K. Yamamoto, "Membrane Biological Reactors", University of Wollongong, 2011.

Table 20 compares the energy consumption of the aerobic processes described earlier. The range of differences in energy consumption is related to country specific issues and nitrification requirements. When denitrification is required, the energy consumption is higher due to the increased oxygen levels that need to be maintained. Whilst the data relate to large utility systems, it is possible to get a comparative understanding of the relative energy intensity of the processes.

Table 19: Power consumption of aerobic processes

| | ASP | ASP+ MF/UF | Trickling Filter | ASP + Biological Filter | Oxidation ditch | MBBR | MBR |
|-------------------------------------|---|-----------------------------|--------------------------------|-------------------------------|------------------------------|----------------|--------------------------------------|
| Power consumption kWh/m3 | 0.15 ⁴⁴ - 0.64 ^{45*} | 0.35 - 0.5 ⁴⁵ | 0.186 - 0.426 ⁴⁴ | 0.25 ⁵⁶ | 0.48 - 1.04 ⁵⁷ | 0.17 - 0.27 | 0.75 - 12.0 ^{44, 54, 55} |

*Higher values where denitrification is used

3.4.9 Anaerobic/aerobic processes

Given the difficulties of removing colour and dyes purely using an aerobic process, an effective approach is to include an anaerobic process prior to the aerobic process, as shown in Figure 45.

The anaerobic process makes use of anaerobic bacteria to decompose organic matter in the absence of oxygen. Textile effluent organic concentrations and recalcitrant compounds like azo dyes, phthalocyanine dyes, anthroquinoid and vat and sulfur dyes are difficult to be treated by aerobic processes alone and can reach a concentration as high as 1000 mg/L. These contain rather persistent chromophores. In the aerobic process the main process for the removal of dyes is the adsorption on the biomass.

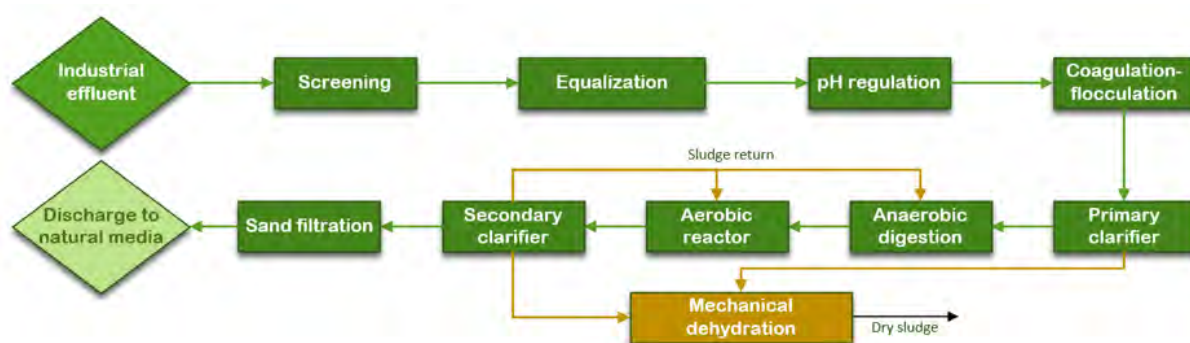
Hydrolysis acidification is the main anaerobic process adopted in the textile industry. This process enables the degradation of recalcitrant organic molecules and heterocyclic molecules, which are responsible for colour to be broken down, into smaller organic molecules

⁵⁶ F. Hai and K. Yamamoto, "Membrane Biological Reactors", Treatise on Water Science (pp. 571-613). UK: Elsevier, 2011.

⁵⁷ Valentina Lazarova, et al., "Water – Energy Interactions of Water Reuse", IWA Publishing, 2012.

by the action of anaerobic and facultative bacteria resulting in a reduction in colour of the wastewater. Aerobic treatment which follows the anaerobic step completes the decolouration process.

Figure 45: Combination of chemical coagulation, anaerobic and aerobic treatment within a textile ETP China



During the anaerobic process the pH of the wastewater reduces by 1.5 units, helping to neutralise the alkaline wastewater to around pH 8, which is ideal for bacterial decomposition of organic compounds under aerobic conditions. The effluent is then clarified and disinfected. This process is particularly effective in the removal of sizing chemicals like PVA and starch. The energy requirements for removal of BOD for an aerobic process is around 1kWh/kg of BOD, whereas for the anaerobic process it can be 0.5 – 1.5kWh/kg of BOD⁵⁸. Overall, due to the anaerobic process, less sludge is produced than the standalone aerobic process. Another advantage of the combined process is the removal of nitrogen compounds (nitrates that are added for dye fixation) due to the denitrification and nitrification processes. Sometimes the reaction products of dye compounds after undergoing anaerobic treatment can be more toxic to the environment than the original compound. This has an impact on colour removal since these compounds can become toxic to the biomass⁵⁹. Table 20 shows the percent reduction of colour, BOD, TOC and COD effluent containing Navy 106 dye under laboratory conditions under the aerobic process and under a combination of anaerobic and aerobic treatment processes⁶⁰.

⁵⁸ Thomas Bechtold, et al., "Treatment of Textile Wastes", Leopold Franzens University, Austria.

⁵⁹ Ali Assadi, et al., "Anaerobic – aerobic sequencing batch reactor treating azo dye containing wastewater: effect of high nitrate ions and salt", Journal of Water Reuse and Desalination, 2017.

⁶⁰ M. Joshi, R. Bansal and R. Purwar, "Colour Removal from Textile Effluents", Indian Journal of Fiber and Textile Research, Vol. 29, June 2004, pp 239 – 259.

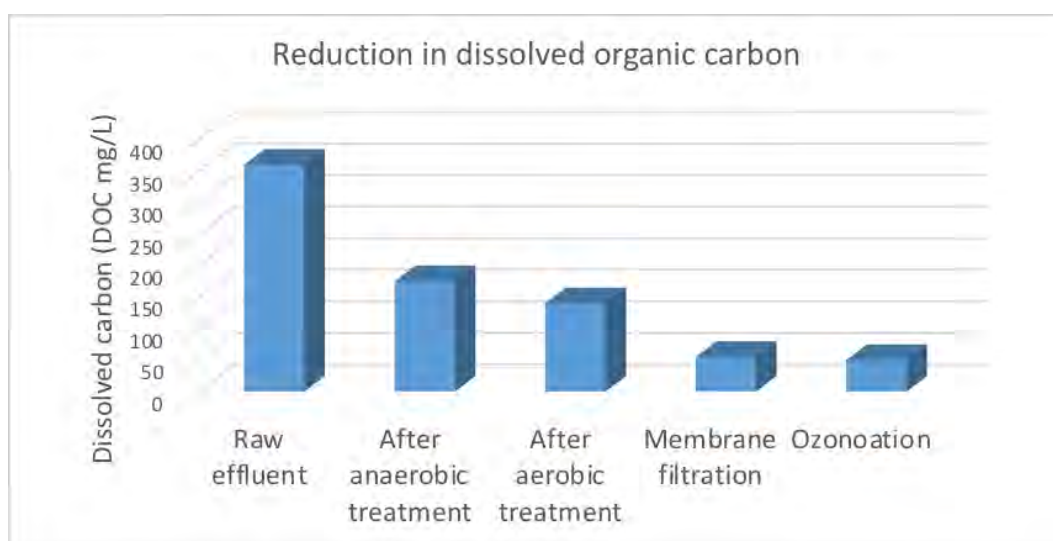
HRT can vary depending on the process selected, but generally 10 – 30 hours in the anaerobic phase is typical.

Table 20: Percent reduction in laboratory scale treatment processes involving Navy 106 under Anaerobic/Aerobic conditions

| Treatment process | Treatment step | Colour | TOC | BOD | COD |
|-------------------|-----------------|--------|-----|-----|-----|
| Anerobic-aerobic | Dilution | 40 | 41 | 13 | 38 |
| | Anaerobic | 50 | 3 | -2 | 1 |
| | Aerobic | -2 | 38 | 80 | 38 |
| | Total reduction | 88 | 82 | 91 | 77 |
| Aerobic | Dilution | 28 | 38 | 15 | 39 |
| | Aerobic | 1 | 36 | 75 | 30 |
| | Total reduction | 29 | 74 | 90 | 69 |

Figure 46 shows the reduction in dissolved organics as it passes through anaerobic, aerobic and other treatment processes.

Figure 46: Reduction in organics after anaerobic, aerobic, MBR and ozonation treatment processes⁶¹



⁶¹ Carsten Owerdieck, "UF/MBR Textile Wastewater Treatment Experience", GE, 2008.

3.4.10 Secondary Clarifiers

The purpose of the clarifier is twofold. One is to thicken the solids after biological treatment and then settle them out. The second is to produce a clear effluent of the settled solids. Clarifiers in activated sludge systems must be designed not only for hydraulic overflow rates, but also for solids loading rates. This is because both clarification and thickening are needed in activated sludge clarifiers. Of the process variables the most important is Sludge Age or MCRT (Mean Cell Residence Time). Another important control parameter is the Solids Loading Rate. It is expressed as:

Solids Loading Rate: defines required surface for suitable sludge thickening in the bottom of the unit (compression zone).

Where:

SLR = solids loading rate (kg SS/m²/h)

F = outflow (m³/h)

Fr = sludge recirculation flow rate (m³/h)

X = MLSS concentration in the bioreactor (kg/m³)

A_{SLR} = horizontal surface for compressing sludge (m²)

$$SLR = \frac{(F + Fr) X}{A_{SLR}}$$

The most common clarifiers are either circular or rectangular shaped. The differences between the two designs are shown in Table 21.

Table 21: Difference between circular and rectangular clarifiers

| Circular design | Rectangular design |
|--|---|
| Advantages | Advantages |
| Short detention time for settled sludge | Less land and construction cost |
| Simple and reliable sludge collection system | Less chance for short circuiting |
| Low maintenance requirements | More even distribution of sludge load on collectors |
| | Can be easily covered for odour control |
| | Is not affected by wind |

| Disadvantages | Disadvantages |
|--|---|
| Center feed have higher potential for short circuiting | Longer detention time for sludge settling |
| More susceptible to wind effects | Increased maintenance of collectors |
| Lower limits for effluent weir loading | Possibly less effective for high solids loading |

Figure 47 shows a large clarifier in a municipal treatment plant in China.

Figure 47: A photo of a circular clarifier



Source: Sudhi Mukherjee, IFC

3.5.0 Tertiary Treatment

Conventional secondary treatment frequently is not sufficient to meet the required effluent quality standards to discharge water to surface water bodies. Textile effluents may require tertiary processes so as to complete solids and organic matter removal, for color reduction or recalcitrant compounds degradation, nutrient (ammonia and phosphorous more common in domestic sewage) reduction and disinfection. These processes are classified as "*tertiary treatments*", as they are installed after secondary treatment, but some of them, like oxidation processes, can be also placed before biological treatment to improve the biodegradability of recalcitrant compounds. The most common tertiary treatment applications are filtration and disinfection and where applicable ammonia and phosphorous removal. Ammonia is toxic to fish and phosphorous causes algal blooms.

3.5.1 Filtration

Filtration is a separation process that consists in passing a solid-liquid mixture through a porous material (filter media) which retains the solids and allows the liquid filtrate to pass through. Granular media polishing filters are used for the removal of suspended solids for the removal of suspended solids in the 5 – 50 mg/L range. The most common filters are the multimedia filters. The quality of the filtrate depends on the size, surface charge, and geometry of both suspended solids and filter media, as well as on the water analysis and operational parameters. Based on media filters can be categorised as:

- Single media – sand or anthracite
- Dual media – sand and anthracite
- Multimedia – garnet, sand and anthracite.

The most common filter media in water treatment are sand and anthracite. The effective grain size for fine sand filter is in the range of 0.35 – 0.5mm, and 0.7 – 0.8mm for anthracite filter. In comparison to single sand filter media, dual filter media with anthracite over sand permit more penetration of the suspended matter into the filter bed, thus resulting in more efficient filtration and longer runs between cleaning. The design depth of the filter media is a minimum of 0.8m. In the dual filter media, the filters are usually filled with 0.5m of sand covered with 0.3m of anthracite.

In industrial applications, filters are housed in steel pressure vessels where the interior is epoxy coated, with interior manifolds for distribution of water and an underdrain system for collection of filtrate and backwashing.

As the filter vessel for pressure filtration is designed for pressurisation, a higher-pressure drop can be applied for higher filter beds and/or smaller filter grains and/or higher filtration velocities. The design filtration flow rates are usually 10 – 20m/h and the backwash rates are in the range of 40 – 50m/h. The available pressure is usually about 2 bar to more than 4 bar. For feed waters with a high fouling potential, flow rates of less than 10m/h and/or second pass media filtration are preferred. If the flow rate has to be increased to compensate for one filter that goes out of service, the flow rate increase must be gradual and slow to prevent the release of previously deposited particles.

During operation, influent water to be filtered enters at the top of the filter, percolates through the filter bed, and is drawn off through the collector system at the bottom. Periodically, when the differential pressure increase between the inlet and outlet of the pressure filter is 0.3 – 0.6 bar, the filter is backwashed and rinsed to carry away the deposited matter. Backwash time is normally about 10 minutes. Before a backwashed filter is placed back into service, it must be rinsed to drain until the filtrate meets the specification. Backwash rates when excessive leads to loss of filter media. Variations of the deep rate filtration are high rate filtration which operates at much faster inlet flow rates.

Aside from media filters, other types of filters are disc filters and cartridge filters. These are also used to protect membrane filtration systems. Disc filters made from pleated cloth media have very high flow rates and a small footprint, producing very high quality water suitable for reuse applications and do not require extensive backwashing. Figure 48 shows the inside of a disc filter.

Figure 48: Schematic of a disc filter



Source: Mohan Seneviratne

4.0.0 Colour removal

Textile colourants include both soluble dyes and insoluble pigments and exceed 10,000 compounds. Colour in textile effluent is due to the presence of soluble and insoluble dyes and pigments. These contain compounds called chromophore groups (an example: N=N double bonds known as Azo). They absorb a fraction of the visible light producing colour. Even at concentrations as low as 0.005mg/L, colour is visible. Colour intensity is a function of the number of chromophore groups present. Dyes can be grouped as acid, basic, direct, disperse, mordant, pigment, reactive, solvent, sulphur and vat dyes. Acid, direct, and reactive dyes are water soluble anionic dyes; basic dyes are cationic and disperse, solvent and pigment dyes are nonionic and sparingly soluble in water. Most mordant dyes are anionic but some are cationic; especially dyes used for dyeing cotton, which include reactive and sulphur dyes, have very low exhaustion and fixation rates which means that significant amounts end up in the effluent. Table 22 shows the fixation rates⁶². Many have low biodegradability and are known as "*recalcitrant compounds*" as indicated by the ratio of BOD/COD as shown in Table 23. Of all the dyes, reactive dyes are the most difficult to treat using only aerobic biological process given their low BOD/COD ratio, stability and high solubility. Therefore, for complete colour removal more advanced treatment processes (including physical adsorption processes and/or chemical oxidation) are used in conjunction with biological processes. Whilst many adsorbents for physical adsorption of colour and auxiliary chemicals are cited in literature, the most practical remains activated carbon since the performance of the waste materials whilst abundant and inexpensive are prone to variations in adsorption performance. Ion exchange is also used in certain instances for colour removal. However, due to the cost of ion exchange resins, they are only used at the tertiary treatment stage. The common chemical processes are chlorination using sodium hypochlorite, calcium hypochlorite, sodium hydrosulfite, ozonation, hydrogen peroxide (H₂O₂) and advanced oxidation processes. Membranes, in particular ultrafiltration (UF) and nanofiltration (NF), are also used for colour removal.

⁶² M. Joshi, R. Bansal and R. Purwar, "*Colour removal from Textile effluents*", Indian Journal of Fibre and Textile Research, Vol. 29, June 2004.

Table 22: Exhaustion range of various dye classes

| Dye class | Fibre | Degree of fixation, % | Loss to effluent, % |
|-----------------|-----------|-----------------------|---------------------|
| Acid | Polyamide | 80 - 95 | 15 - 20 |
| Basic | Acrylic | 95 - 100 | 0 - 5 |
| Direct | Cellulose | 70 - 95 | 5 - 30 |
| Disperse | Polyester | 90 - 100 | 0 - 10 |
| Metal - complex | Wool | 90 - 98 | 2 - 10 |
| Reactive | Cellulose | 50 - 90 | 10 - 50 |
| Sulphur | Cellulose | 60 - 90 | 10 - 40 |
| Vat | Cellulose | 80 - 95 | 5 - 15 |

Table 23: BOD/COD ratio of selected dyes⁶³

| Dye | BOD/COD ratio |
|--------------------------|---------------|
| Reactive Blue 59 | 0.016 |
| Direct Blue 80 | 0.056 |
| Vat Violet 21 | 0.093 |
| Disperse Red 68 | 0.143 |
| Typical textile effluent | 0.33 - 0.25 |

4.1.0 Adsorption - Activated carbon

Activated carbon (AC) is the most commonly used adsorption material used in commercial applications. It has high surface area to volume ratio, mechanical strength to withstand attrition, stability in acidic conditions, and versatility. Activated carbon is made either from coconut shell charcoal or coal. For textile dye effluent coconut shell charcoal is widely used. AC is manufactured as granular (GAC) or powder (PAC) forms. GAC are irregular shaped particles formed by milling and sieving. These products range in size from 0.2 – 5mm. They have the advantages of being harder and longer lasting than PAC, clean to handle, purify large volumes of gas or liquids of a consistent quality, and can be reactivated and reused many times. Figure 49 shows a photo of GAC.

⁶³ O. Marmagne, D. Coste, "Colour Removal from Textile Effluent Plants", Degremont S.A., Cedex France, 1996.

PACs generally have a particle size distribution ranging from 5 to 150Å, although coarser and finer grades are available. Advantages of PAC are their lower processing costs and their flexibility in operation. The dosage of PAC can be easily increased or decreased as process conditions vary. They are added to the liquid to be treated, mixed with the liquid and, after adsorption, are removed by sedimentation and filtration.

Generally, the higher the internal surface area, the higher the effectiveness of the carbon. The surface area of AC is impressive, ranging from 500 – 1500m²/g⁶⁴. Charcoal is activated using steam to create the vast surface area. The high surface area permits the accumulation of a large number of contaminant molecules. The specific capacity of a GAC to adsorb organic molecules is related to molecular surface attraction, total surface area available per unit weight of carbon and the concentration of contaminants in the wastewater stream. It is commonly added to adsorb small quantities of dyes as a polishing step for textile wastewater treatment following physicochemical or secondary biological treatment. The process is easy to operate, has a low footprint and uses proven technology.

The wastewater pH, surface area of AC, contact time, temperature, dye concentration and type of dye play a part in activated carbon colour removal performance. Activated carbon surfaces are amphoteric in nature and therefore, the solution pH plays a role in dye adsorption. High pH is better for cationic dyes adsorption and conversely, low pH is preferred for anionic dyes. GAC in particular can operate in a wide pH range to adsorb dyes, sulfides, heavy metals and nitrogen compounds.

Contact time is known as "*Empty Bed Contact Time*" (EBCT). EBCT is defined as the total volume of AC bed divided by the liquid flow rate. EBCT of 10 – 15 minutes and temperature between 30 – 40°C is generally recommended for optimal performance. High removal rates of over 90% are achieved using activated carbon for cationic, mordant and acid dyes. For direct, dispersed, reactive and sulphur dyes removal efficiency is moderate at 40%⁶⁵. Insoluble dyes such as vat, dispersed dyes and pigments are not easily adsorbed by activated carbon due to their low solubility and colloidal properties. A partial list of organic compounds amenable to adsorption by GAC and PAC is shown in Table 24. Typical consumption of activated carbon is around 0.5 – 1.0kg/m³ wastewater for dye removal rates of 60 – 90%⁶⁶.

⁶⁴ <http://www.haycarb.com/activated-carbon>

⁶⁵ Marmagne C. Coste, "*Colour removal from textile plant effluents*", Degremont SA.

⁶⁶ Z. Carmen and S. Daniela, "*Textile Organic Dyes – Characteristics, Pollution Effects, Separation/Elimination Procedures from Industrial Effluents - A Critical Review*", Chapter 3, www.intechopen.com.

The biggest disadvantage of activated carbon is its high cost. It is not specific to a compound, thus dye adsorption competes with other organic chemicals. Without pretreatment the suspended solids will plug activation sites and large quantities of activated carbon are required, making the process expensive. Therefore, suspended solids should be less than 20mg/L. Usually two units are used in series and rotated when one becomes exhausted. Regeneration of the activated carbon is required. Even then about 10 – 15% of it is lost.

Figure 49: Granular coconut activated carbon

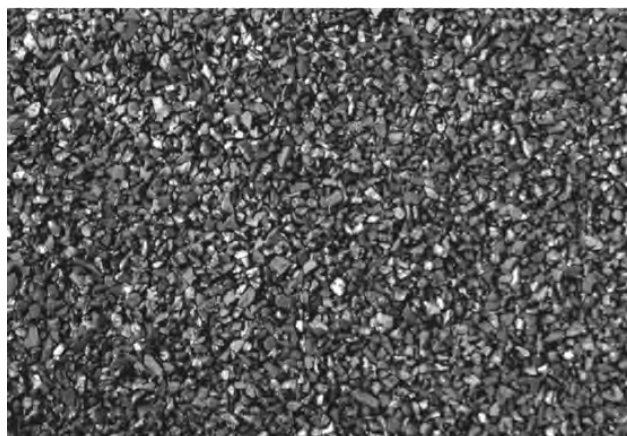


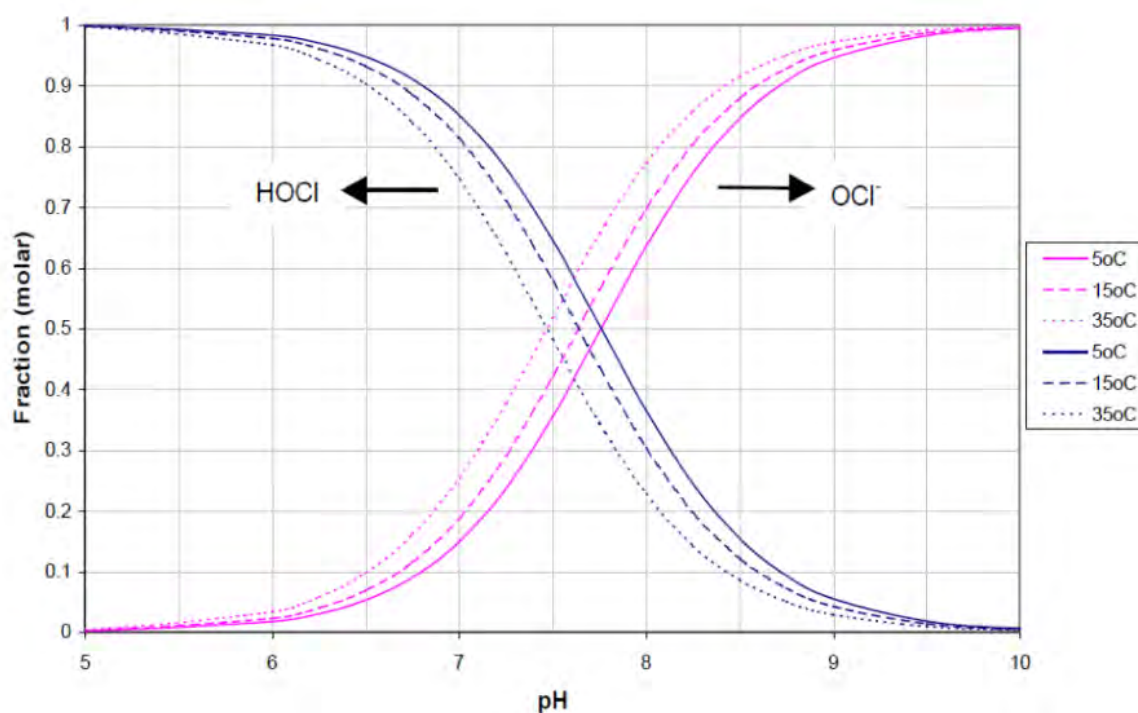
Table 24 : Compounds amenable to GAC

| Class | Comments |
|---|--------------------------------|
| Aromatic solvents | Benzene, toluene, xylene |
| Chlorinated aromatics | Chlorobenzene |
| Phenolics | Phenol |
| Cationic, mordant and acid dyes | 90% removal rate |
| Reactive, dispersed, basic and sulphur dyes | 40% removal efficiency |
| Vat dyes | Dye removal is very low at 20% |
| Surfactants | Alkyl benzene sulfonates |

4.2.0 Sodium hypochlorite for colour removal

The most common form of chlorine today is liquid sodium hypochlorite (NaOCl) which has a strength of 10 – 15% NaOCl by weight. The active constituent is hypochlorous acid (HOCl). The effectiveness of decolourisation is a function of chlorine concentration, pH and type of dye. The higher the concentration reaching 150mg/L, the better the effect. Decolourisation is better at a low acidic pH of 4 – 6.8, since here the HOCl is the more predominant species than at a basic pH of 8 – 10 where the weaker hypochlorite ion (OCl^-) ion is more prevalent⁶⁷. Figure 50 shows the HOCl – OCl equilibrium with pH at various temperatures. Whilst reactive and acid dyes were decolourised, disperse and direct dyes were resistant to chlorination⁶⁸.

Figure 50: pH and temperature dependency of HOCl - OCl equilibrium



⁶⁷ M. Joshi, R. Bansal and R. Purwar, "Colour removal from textile effluents", Indian Journal of Fiber and Textile Research Volume 29, June 2004.

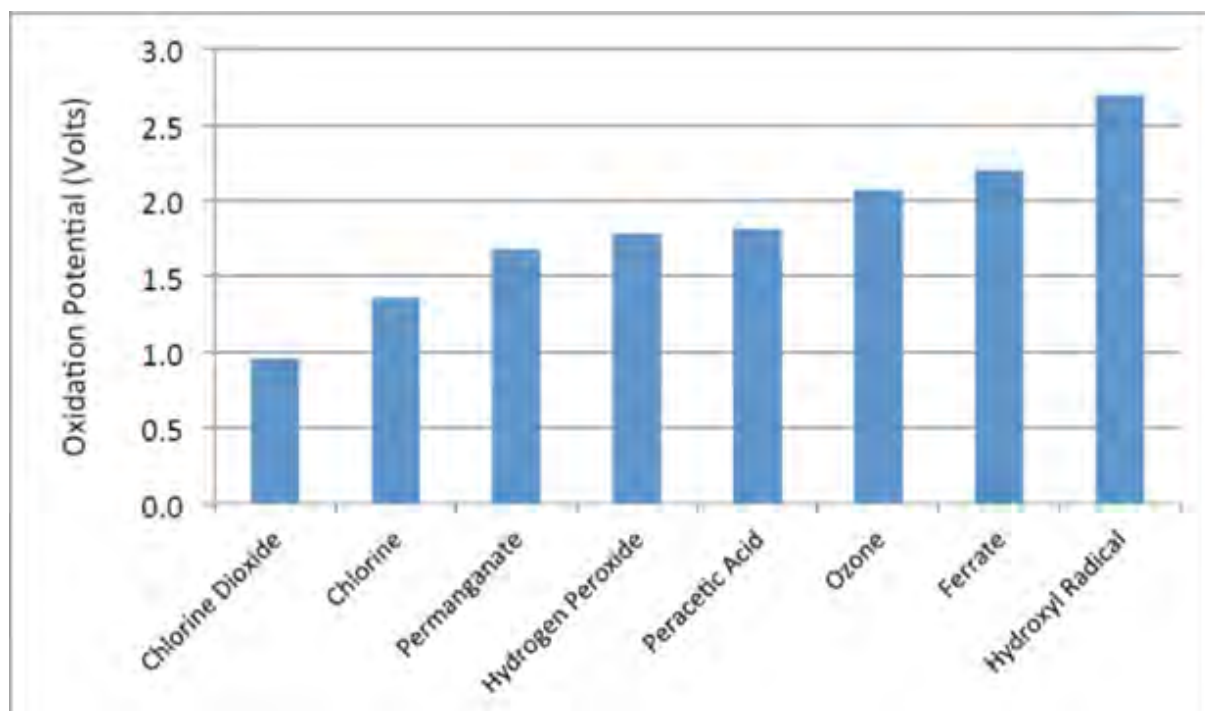
⁶⁸ Tomasz Puzyun and Alexandra Mostrag-Szlichtyng, "Organic Pollutants Ten Years After the Stockholm Convention – Environmental And Analytical Update", www.intechweb.org, 2012.

Whilst NaOCl has a low installation cost, the life cycle cost can become expensive given the large dosages required. The reaction products can lead to the release of aromatic amines and the formation of toxic absorbable organic halides (AOX) which are carcinogens. Aromatic amines are released when the hypochlorite attacks the amino group of the dye molecule initiating and accelerating azo bond cleavage. NaOCl degrades with time. For an example a 12.5% solution will degrade to 10% over a 30-day period.

4.3.0 Advanced oxidation processes

Advanced oxidation processes (AOPs) are defined as processes which involve generation and use of powerful but relatively non-selective *hydroxyl radicals* in sufficient quantities to be able to oxidise the majority of the complex chemicals present in the effluent water. The AOPs show specific advantages over conventional treatment alternatives because they can eliminate non-biodegradable organic components and avoid the need to dispose of residual sludge. After fluorine ($V = -3.06$), hydroxyl free radicals (OH^\bullet) have the highest oxidation potential ($V = -2.86$). Figure 51 shows the oxidation potential of selected oxidants.

Figure 51: Oxidation potential of oxidants



Source: Katherine Y. Bell and Allegro De Silva, "Innovations in Wastewater Disinfection Technology", CDM Smith.

In the AOP process, OH^- radicals are generated which in turn react with organic molecules to generate CO_2 and water. AOPs can be classified into two groups, non-photochemical AOPs and photochemical AOPs. Photochemical means a light source is required. Most commonly ultra violet (UV) light is used as the photochemical source. Low pressure UV lamps have a wavelength of 254nm. Maximum ozone absorption takes place at a wavelength of 253.7nm. Of the non-photochemical technologies, those most prevalent in the treatment of textile effluent are Ozonation, Ozone/ (H_2O_2) and Fenton's reaction. Table 25 shows these processes.

Table 25: Advanced Oxidation Processes

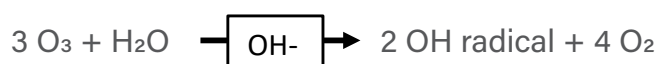
| Non-photochemical - Advanced Oxidation Processes | Photochemical-Advanced Oxidation Processes |
|--|---|
| Cavitation – the process of formation and collapse of a large number of microbubbles imparting great amount of energy in milliseconds. | $\text{H}_2\text{O}_2/\text{UV}$ |
| Ozonation at high pH | $\text{H}_2\text{O}_2/\text{UV}/\text{Fe}^{2+}$ – photo assisted Fenton reaction. |
| Ozone/Hydrogen peroxide (H_2O_2) | Ozone/UV |
| Fenton's reaction and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ | Ozone/UV/ H_2O_2 |
| Electrochemical oxidation | |
| Super critical wet air oxidation | |
| Gamma-ray | |
| X-ray | |
| Electron beam irradiation – with TiO_2 | |

4.3.1 Ozonation

Discovered in 1785, Ozone (O_3) is a widely applied strong oxidising agent (-2.07V) for disinfection of potable water and wastewater, decolourisation, odour removal, organics degradation and cyanide destruction, etc. O_3 at room temperature is a bluish pungent gas, sparingly soluble in water, highly corrosive, toxic and explosive when the concentrations in air exceed 20% (commercial O_3 generators produce 1 – 6% concentration of O_3). As a germicide, it is 3,125 faster than chlorine⁶⁹.

Ozonation efficacy is increased with high pH, increasing dye concentration, and temperature. When O_3 dissolves in water or wastewater it can remain as the O_3 molecule (at pH <7 and slower reaction) or decompose (pH > 8) producing the hydroxyl free radical (OH^\bullet) which is a 35% stronger oxidising agent than O_3 . Both reactions occur simultaneously and hence reaction kinetics strongly depend on the characteristics of the treated wastewater (e.g. pH, organic concentrations, type of dyes, presence of foaming agents and surfactants, ozone concentration and temperature, etc.). A pH of 8 – 10 is most suitable for oxidation of organic compounds. Ozone is sparingly soluble in water and rapidly decreases with increasing temperature. At a temperature of 20°C 100% ozone solubility in water is 570mg/L⁷⁰. The preferred temperature ranges from 25 to 50°C.

A simplified reaction mechanism of ozone at a high pH is given below:



Molecular O_3 is a very selective oxidant. It only reacts with certain compounds and for this reason it can be applied in low dosages for industrial wastewater applications. It has a preference for dyes containing double bonds like azo dyes (which contain nitrogen double bond) and is not suitable for non-soluble dispersed and vat dyes which react slowly and take longer time⁷¹. It can also inhibit or destroy the foaming properties of residual surfactants as well as oxidising a good portion of the COD⁷². Thus, O_3 improves the overall

⁶⁹ Shashank Singh Kaldra, et al., "Advanced Oxidation Processes for Treatment of Textile Dye Wastewater: A Review", 2nd International Conference on Environmental Science and Development, Singapore, 2011.

⁷⁰ U.S. Environmental and Protection Agency, "Alternative Disinfectants and Guidance Manual", EPA- 815-R- 99-014, 1999.

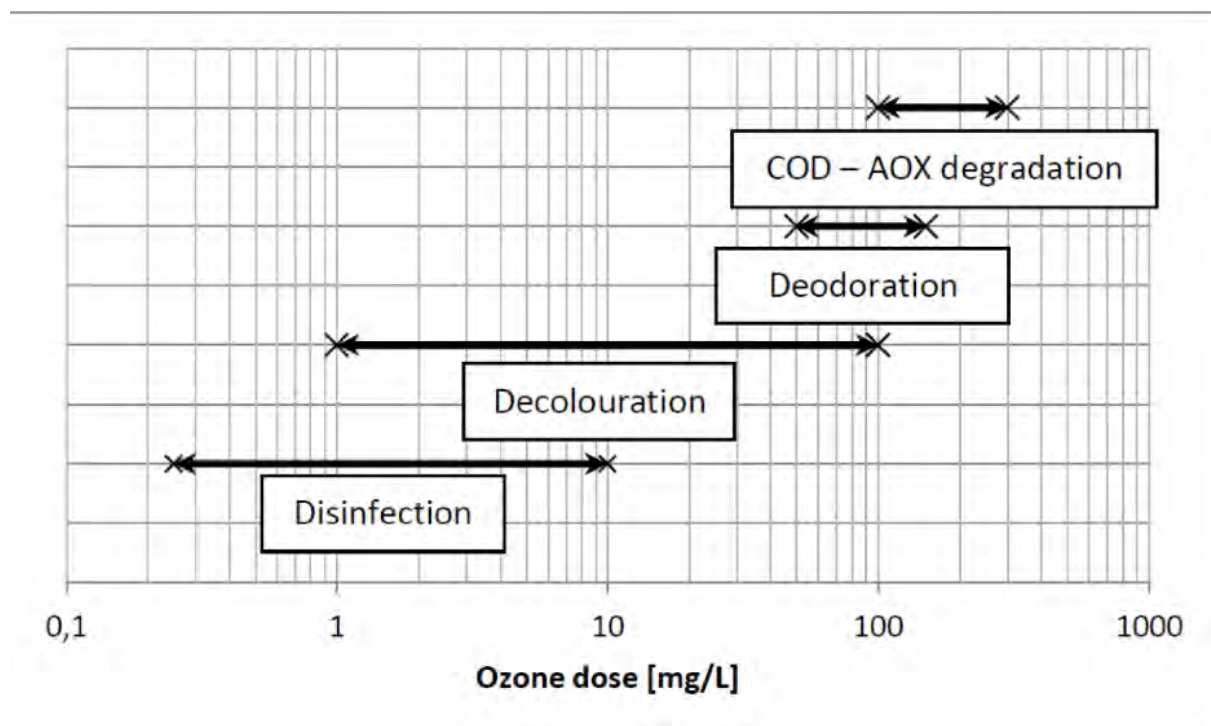
⁷¹ Adel Al Kdasi, et al., "Treatment of Textile Wastewater by Advanced Oxidation Processes – A Review", Global Nest: the International Journal, Vol. 6, No. 3, 2004.

⁷² Zongping Wang, et al., "Textile Dyeing Wastewater Treatment", Huazhong University of Science and Technology, China.

biodegradability of the effluent by converting recalcitrant compounds to easily digestible compounds and can be applied upstream or downstream of a biological treatment plant. The residual oxygen in the vent gas can be recycled back to the secondary biological treatment plant, reducing aeration requirements. Another advantage is that it doesn't increase sludge mass. Typical dosage for decolourisation can range from 1 -100mg/L⁷³. Figure 52 shows the typical dosages of O₃ for disinfection, decolourisation, deodouration and COD – AOX degradation. O₃ can be applied in the gaseous form and given its unstable nature, it needs to be generated on-site from air or pure oxygen using UV radiation, electrochemistry or corona discharge generators. O₃ leak detectors should be installed to give audible and visible warnings and shut down the generators in the event of a leak. O₃ is deactivated in the presence of high concentration of salts.

A variation of this process is the O₃/H₂O₂ process. Developed to reduce the O₃ concentrations, the H₂O₂ acts as a catalyst enhancing the capability of O₃ to produce more OH radicals. At a low pH, H₂O₂ reacts very slowly with O₃ and at a high pH (alkaline conditions) reacts rapidly.

Figure 52: Ozone dosages



Source: Actis Grande Guiseppe, "Treatment of wastewater from textile dyeing by ozonation", 2015.

4.3.2 Hydrogen Peroxide (H₂O₂)

Hydrogen peroxide (H₂O₂) decolourises by attacking the aromatic ring of dye compounds. Whilst environmentally friendly, its decolourisation effectiveness is limited in acidic or alkaline mediums given its oxidation potential is only 1.78V compared to OH[•] free radical oxidation potential of 2.78V. Therefore, in the presence of UV light H₂O₂ releases two OH[•] radicals. The UV-H₂O₂ combination is able to totally destroy the chromophore structures with varying reaction rates for different dyes⁶⁹.

4.3.3 Fenton's reaction

Fenton's reaction is mainly used as a pre-treatment for wastewater resistant to biological treatment or/and toxic to biomass. The reaction is exothermic and should take place at a temperature higher than ambient. Ferrous ions in an acidic medium, in the presence of H₂O₂, generates free OH radicals as shown below.



The efficiency of oxidation with Fenton's reagent is best at a pH ranging from 2 – 5 and for a molar ratio of H₂O₂: Fe = 1:1. The optimal value for pH is 3.5. pH values above or below tend to decrease COD reduction by 8 – 12% . Some researchers have found Fenton's reagent to be very effective on surfactants. The main disadvantages of the process are the large amount of acid required to drop the pH from alkaline conditions and the voluminous sludge production due to the presence of FeOH₃.

⁷⁴ Lech Kos, et al., "Textile Wastewater Treatment by the Fenton Method", Fibres and Textiles in Eastern Europe, 2010, Vol. 18, No.4.

4.3.4 Electrochemical oxidation

Electrochemical oxidation is a powerful and yet a low-cost option offering high removal efficiencies, especially for those containing acid dyes, metal complexes and disperse dyes. It is a low temperature process and requires no additional chemicals.

Electrochemical oxidation consists of an electrolytic cell which uses electrical energy to affect a chemical change. It contains an anode (positive) where oxidation occurs and a cathode (negative) where reduction occurs immersed in an electrolyte-like salt. Dye wastewater is an ideal conducting medium, given that it contains high concentrations of salt. At the anode, several complex reactions occur producing hypochlorite ions, and OH free radicals which degrade the dye compounds. Figure 53 shows a typical electrolytic cell. The anode could be platinum, cobalt, palladium, copper, nickel, irridium or other materials. At the anode, chloride ions become oxidised to chlorine and then form hypochlorous ions (OCl^-), and at the cathode water molecules gets oxidised to OH^- .

On average, 80 – 96% reduction in COD is achieved⁷⁵. COD removal equals 100% when the salt concentration reaches 0.1M. Figure 54 shows the reduction in COD in mg/L as a function of salt concentration. The increased chloride concentration and mass transport to the anode results in the generation of hypochlorite ions available to oxidise more organic chemicals. Optimal current density is at 20 mA/cm². Energy consumption is reported as 3.25 – 6.0 kWh/kg COD⁷⁶. Optimal pH is at 4. As the pH increases to alkaline conditions COD removal decreases. This means that pH correction is required after treatment.

⁷⁵ Norazzizi Nordin, et al., "Textile Industries Wastewater Treatment by Electrochemical Oxidation Using Metal Plate", Journal of Electrochemical Science, Vol. 8, 2013.

⁷⁶ E. Kavitha, "Electrochemical Oxidation of Textile Industry Wastewater Using DSA in a Tubular Reactor", International Journal of Engineering Research and Applications, Vol. 2, Issue 6, December 2012.

Figure 53: Schematic of an electrolytic cell⁷⁷

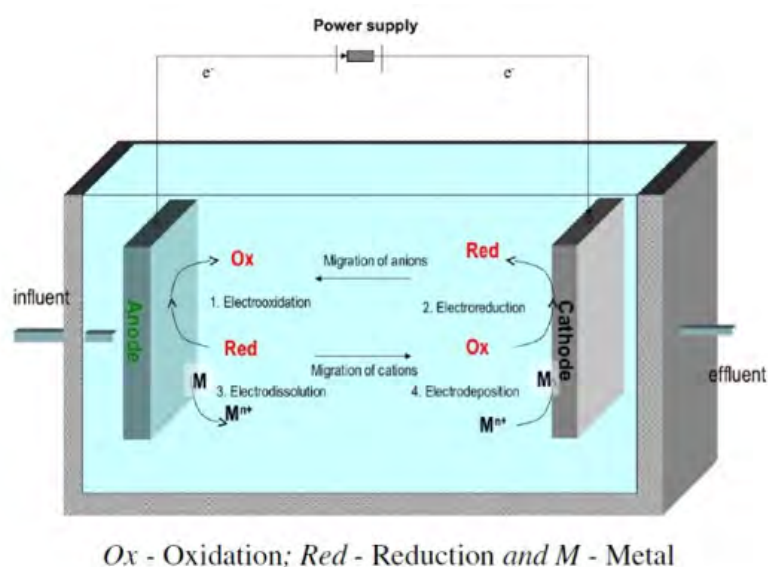
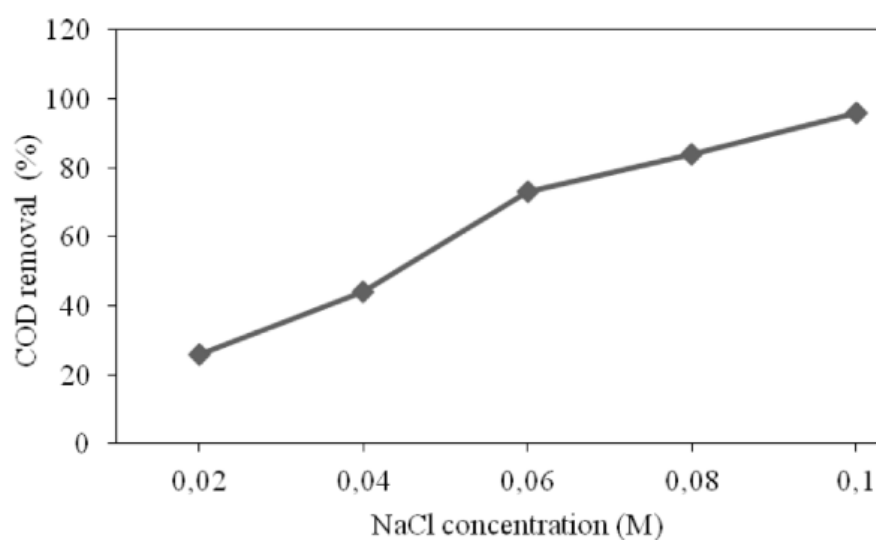


Figure 54: Reduction in COD as a function of salt concentration



The cost of colour removal varies widely from US\$ 0.07 to 0.20/m³ for coagulation; US\$4.21 – 5.35/m³ for ozonation; US\$ 0.23 – 0.59 for Fenton's process and US\$1.26 – 4.56/m³ for UV/H₂O₂.

⁷⁷ Enviros India Pvt. Ltd.

4.4.0 Membranes for colour removal

UF and NF membranes remove colour from printing, washing, and dyeing effluent. For an example, in printing washwater, BOD removal is 90% and colour removal is 100%. The water can be recycled back to the process. In dyeing operations, UF is capable of completely separating many dyes from the wastewater, including vat, acid, metal – complex, dispersed and direct dyes, from the brine. NF can be used to separate cationic and reactive dyes from the brine⁷⁸. However, membranes are prone to clogging from dye compounds which makes them expensive if used in the absence of secondary treatment.

Membranes are discussed in greater detail under water reuse.

⁷⁸ D. Woerner, *"Membrane technology in textile operations"*, Koch Membrane Systems.

5.0.0 Antimony removal

Antimony (Sb) in its oxide form is found in ground and surface water in low concentrations typically at 0.1 to 0.2 µg/L⁷⁹. It is a suspected carcinogen and toxic to the heart, lungs, liver and skin. The World Health Organization (WHO) guideline for the maximum concentration of Sb in drinking water is 6 µg/L. Given its amphoteric nature it is soluble at low and high pHs. The lowest water solubility is at a pH of 4.5 – 5.5. However, Sb concentrations in the environment are increasing due to human activity and natural processes. The demand for synthetic fibers is one cause of this. The vast majority of synthetic fibers are based on polyester and PET. Antimony oxide is used as a catalyst in the production of polyester and PET.

In fabrics, made of 100% polyester, Sb concentrations as much as 208 mg/kg were found in China⁸⁰. PET fibre contains Sb concentrations from as low as 160 mg/L to as much as 600 – 700 mg/L⁸¹. During dyeing at high temperature, Sb leaches into the wastewater. Concentrations can reach as high as 175 mg/L⁸². ZDHC recommendations for concentrations of Sb are 0.1, 0.05 to 0.01 mg/L (100, 50 and 10 µg/L) as the supplier progresses from foundational and progressive to aspirational. Due to its toxicity, Sb needs to be removed from wastewater.

Sb exists in many valent forms from the trivalent (Sb³⁺) to the pentavalent form (Sb⁵⁺) which makes its removal more challenging. The trivalent form is ten times more toxic than other forms. Methods recommended for its removal range from precipitation, ferric chloride coagulation/floculation, ozone oxidation, membrane separation and adsorption⁸³. Ferric chloride at dosages of 40 – 50 mg/L at a low pH followed by microfiltration is a low cost measure^{84, 85}.

⁷⁹ J. Ilavsky, "Removal of antimony from water by sorption materials", Slovak Journal of Civil Engineering, 2008.

⁸⁰ Kevin Brigden, et al., "Hazardous chemicals in a selection of textile products manufactured in Shishi City & Huzhou City during 2013", Greenpeace Research Laboratories Technical Report 05-2013, December 2013.

⁸¹ Victor Innovatex, "Sustainable textile development at Innovatex", 2003, www.victor-innovatex.com

⁸² Ecotextiles, "Antimony in fabrics", 6 February 2013.

⁸³ Hussani Mubarak, et al., "Antimony (Sb) – pollution and removal techniques – critical assessment of technologies", Journal of Toxicological and Environmental Chemistry, Taylor and Francis, 2015.

⁸⁴ Joe R. Tamburini, H.C. Liang and Sam J. Billin, "Single process arsenic and antimony removal using coagulation and microfiltration", Tailings and Mining Waste 2010, Tetrattech.

⁸⁵ Tomas Vengris, Rima Bienkiene and Algis Selskis, "Antimony removal from the polyethylene terephthalate manufacture wastewater", Vol. 1, Environmental Research and Engineering Management, 2010.

6.0.0 Water reuse and resource recovery

Reclaimed or recycled water is the process of converting wastewater into water that can be reused for purposes. Reuse may include irrigation of agricultural fields, gardens, toilet flushing or used within the process – with or without further treatment. Reclaimed water, on the other hand, is the water available from a sewage-treatment plant after undergoing secondary, tertiary or advanced treatment to augment or substitute fresh water supplies.

Traditionally, industrial wastewater treatment is undertaken to meet regulatory compliance. Consequently, wastewater treatment is seen more as *the cost of doing business* rather than as a valuable resource. Therefore, the minimum treatment required to comply with a regulatory requirement is typically selected by business. In recent years this view has been changing. There is the realisation that security of water supply, drought, scarcity of water, climate change impacts, social license to operate, and increased treatment costs for potable water and wastewater discharge are forcing some companies to rethink this minimalist and linear strategy. The European Union is in the vanguard of promoting a circular economy and in June 2016 guidelines were issued under the Common Implementation Strategy for the Water Framework Directive⁸⁶. Moreover, multinational brands are promoting water minimisation and reuse strategies to their suppliers. For example, Levi Strauss & Co. were one of the earliest to publish water Recycle/Reuse standards. Given the high caustic and salt usage in dyeing operations, there are cost benefits to be achieved to recover materials like caustic and sulphate, even when the price of water is low. As a result of this, some visionary companies have embraced the notion of '*circular economy*'. The objectives of a circular economy are to recycle water and nutrients or valuable chemicals.

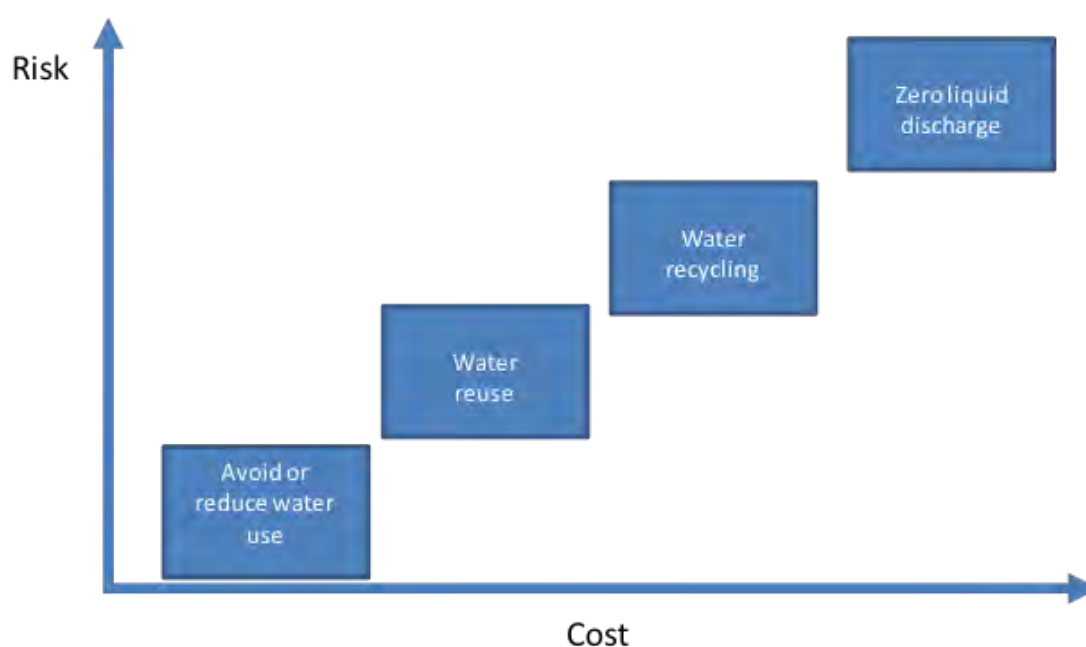
To reduce wastewater discharge, start at the source. End of pipe treatment is always costlier than water minimisation. Figure 55 shows the water minimisation hierarchy. Reducing or avoiding at the source is the first step. Rethink of the process steps is encouraged. For instance, for colour removal, substituting low fixation dyes with high fixation dyes, modified dye formulation, investing in fully automated dye equipment to improve shade repeatability and optimising dye usage will reduce the concentration of dyes in the effluent. Water reuse

⁸⁶ European Commission, "REPORT FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS - on the implementation of the Circular Economy Action Plan", Brussels, 26 January 2017.

should be looked at as part of the broader water management strategy rather than a stand-alone exercise. For a project to be feasible, the proposed treatment technologies need to be reliable, economical, meet water-quality specifications and be safe to use as determined by regulatory authorities. After reuse, water recycling opportunities could be considered to augment fresh water supplies if there are municipal treatment plants in close proximity and willing to supply reclaimed water. Then only 'Zero Liquid Discharge' (ZLD) should be considered. ZLD is when no wastewater leaves the facility. ZLD has been practiced for decades in many US and Australian power plants and in the oil and gas industry due to water scarcity. Following from the well documented, Tiruppur experience, in India, there is a draft regulation making ZLD mandatory for wastewater treatment for textile industries discharging more than 25m³/d^{87, 88}. None of the other major textile exporting countries have adopted ZLD. Ethiopia, where cheap power is available, has installed ZLD in the new industrial zones.

While the notion of ZLD is appealing, in practice, achieving it is far from simple. High upfront capital costs, land requirements, high power consumption, operator capabilities and technical requirements can make ZLD challenging.

Figure 55: Water minimisation hierarchy



⁸⁷ Industrial Pollution Prevention Group, "The Concept note for Challenges against implementation of ZLD in textile processing industries and clusters in India", Center for Environment Education, Ahmedabad, April 2016

⁸⁸ S. Joseph and M.Karthik, "Is India ZED Ready?", Indian Textile Journal, July 2016.

6.1.0 Membrane systems

Membranes are a popular choice for water reuse applications since their advent in the 1960s. Costs of membrane systems have reduced dramatically and, coupled with technological advances in membrane design, membrane options and operating limits, the range of applications in water and wastewater treatment is increasing rapidly. In pressure driven membrane filtration, membranes separate the components of a fluid under pressure. The membrane pores, being extremely small, allow the selective passage of solutes. This section will briefly discuss membrane systems. The popularity of membrane processes arises from the fact that they are effective in the removal of both dissolved and suspended solids. The advantages and disadvantages of membranes are shown in Table 26. There are four types of pressure driven membranes which are tabulated in Table 27. Microfiltration (MF) and Ultrafiltration (UF) are low pressure applications given their larger pore size. Nanofiltration (NF) requires medium pressure, and Reverse Osmosis (RO), given the smaller pore size, requires significant pressure to push the solute through the membrane.

Table 26: Advantages and disadvantages of membranes

| Advantages | Disadvantages |
|---|---|
| Ability to recover both the clean water (permeate) and concentrated streams (reject) without chemically modifying them | High upfront capital cost |
| Applicable to a wide range of processes | Finite membrane life requires periodic replacement of membrane |
| Contain relatively few moving parts | Prone to fouling by cationic surfactants found in textile effluent |
| Modular construction enables scaling up or down | Prone to membrane degradation, e.g. strong oxidising agents like chlorine, high pH and selected solvents. |
| Membranes can be custom selected to achieve the desired water quality, or recover chlorides and/or sulfates commonly found in textile effluent. | Limited applications at high temperatures |
| Compact design – means reduced foot print | Produces a concentrated brine stream that requires disposal |
| Short start up times compared to biological systems | High energy consumption for Reverse osmosis membranes |
| Minimal chemical pre-treatment | |

Table 27: Pressure driven membrane systems

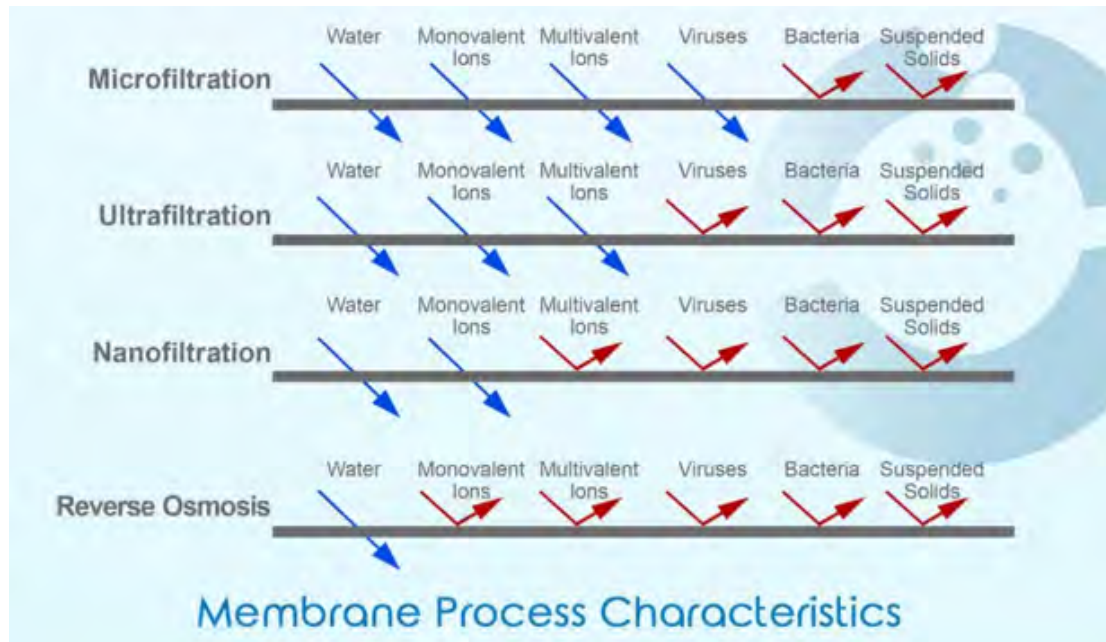
| Process | Main objective | Typical fluxes (L/m ² /h) ⁷³ |
|-----------------------------|--|--|
| Microfiltration (MF) | Suspended solids removal including microorganisms and colloids. Reduction in turbidity 90+%. | >50 |
| Ultrafiltration (UF) | Elimination of long chain dissolved substances including colloidal, oil and fatty substances. Turbidity reduction 99%. Good for removal of metal hydroxides to 1 mg/L or less. In textile applications, COD removal is 21 – 77%, colour 31 – 76% and surfactants 32 – 94%. Requires NF or RO to polish the permeate further for dyeing lighter colours ⁸⁹ . | 50 - 100 |
| Nanofiltration (NF) | Selectively removing of charged ions including calcium and polar substances. Water softening applications and decolourisation. Prone to fouling from colloidal materials and polymers. COD removal 79 – 81% ⁷³ | 1.4 - 12 |
| Reverse osmosis (RO) | Inorganic ions removal to very low concentrations used in de-salination. Very sensitive to fouling. Pretreatment required. COD removal 89 – 91% ⁷³ | 0.05 -1.4 |

Other pressure driven membrane systems include electrodialysis (ED), electrodialysis reversal (EDR), electrodeionisation (EDI) forward osmosis and membrane distillation (MD). These are not covered in this section.

⁸⁹ Priyanka Saini, "Pretreatment of Textile Industry Wastewater Using Ceramic Membranes", School of Energy and Environment, Thapar University, July 2014.

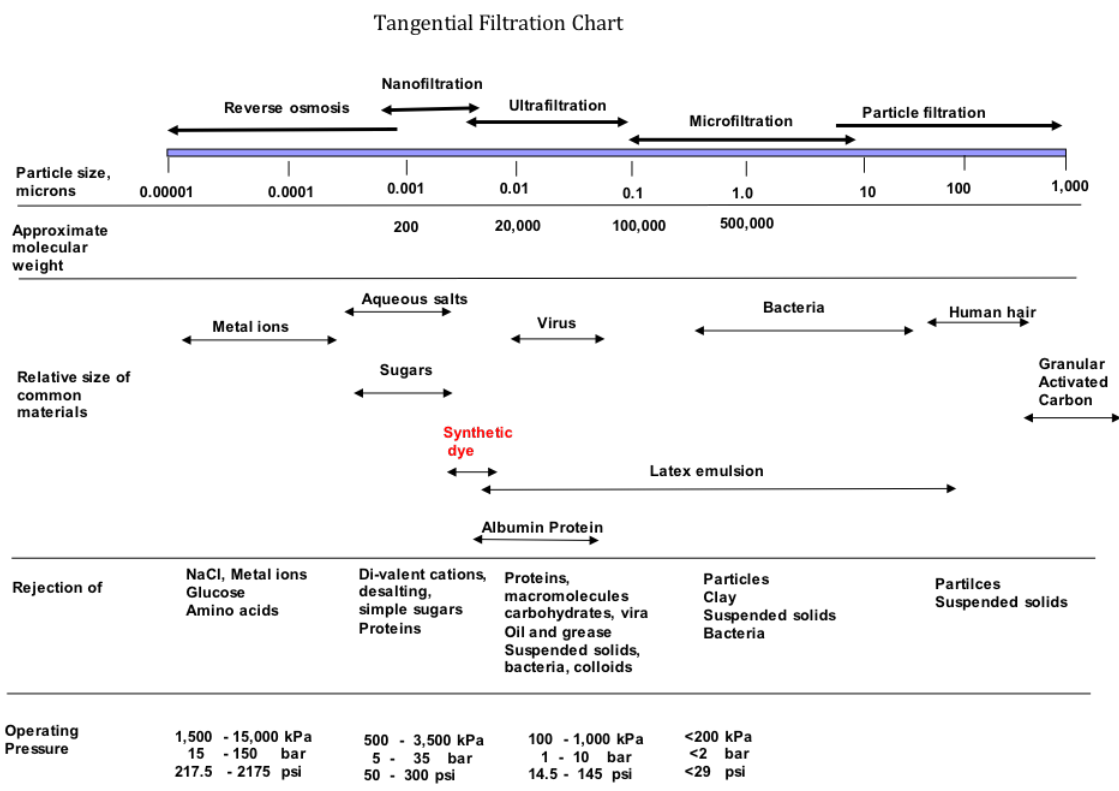
Figures 56 and 57 show the relative filtration ability of each of the four pressure driven membrane systems as well their relative pressure requirements.

Figure 56: Membrane process characteristics



Source: Koch Membrane Systems

Figure 57: Tangential Filtration Chart

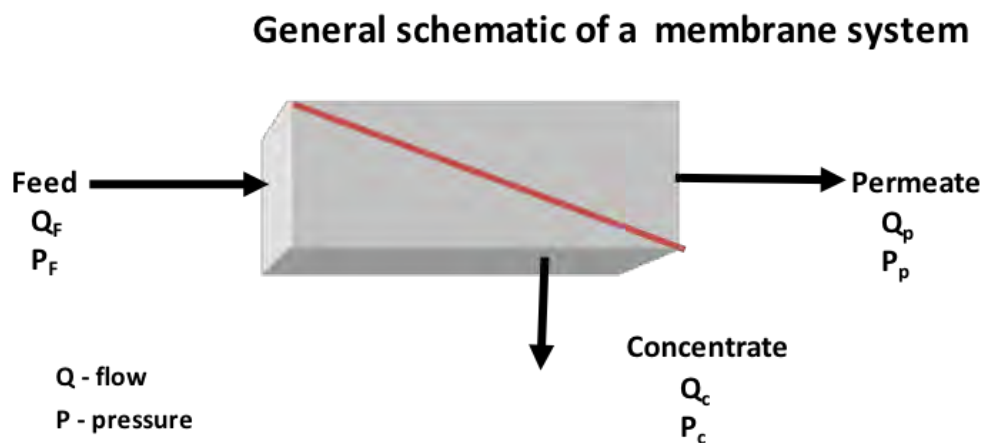


Source: Mohan Seneviratne

Filtration can happen in two different modes, namely dead end and cross-flow. In dead end filtration, the flow is perpendicular to the media surface. This is how conventional macrofiltration in sand filters, cartridge and multimedia filters takes place. There are only two streams present. The entire feed solution passes through the filter media creating only one exit stream. Macrofiltration is limited to suspended particle sizes greater than 1 micrometre.

For the removal of small particle sizes and dissolved salts cross-flow membrane filtration is used. Cross-flow membrane filtration uses a pressurised feed stream which flows parallel to the membrane surface. A portion of the stream passes through the membrane surface known as the permeate, leaving behind the rejected particles in the concentrated remainder of the stream. This stream is known as the reject stream or brine. Since there is a continuous flow across the membrane surface, the rejected particles do not accumulate as much in dead-end filtration and are continuously swept away by the reject stream. A schematic is shown in Figure 58.

Figure 58: Pressure driven membrane systems



Membranes come in a variety of module configurations from spiral wound, hollow fibre, tubular and plate and frame. Spiral wound is common in RO plants, whereas MBRs use hollow fibre membranes. Tubular membranes are used in UF applications predominantly. Four to six spiral wound membranes are housed in a single pressure vessel. The choice of the most suitable membrane module selection for a particular membrane separation must balance a number of factors. The principal module design parameters that enter into the purchasing decision are summarised in Table 28.

Table 28: Comparison between several membrane modules⁹⁰

| Parameter | Spiral wound | Tubular High price/ low price | Plate and frame | Hollow wide fiber | Hollow fine fiber | Ceramic |
|---|---------------------|-------------------------------------|-----------------------|-----------------------|-------------------------------|-----------|
| Membrane density m ² /m ³ | High | Low | Average | Average | Very high | Low |
| Plant investment | Low | High / Low | High | Very high | Medium | Very high |
| Tendency to fouling | Average | Low | Average | Low | Very high | Medium |
| Cleanability | Good | Good | Good | Low | None | Good |
| Variable costs | Low | High / Low | Average | Average | Low | High |
| Prefilter | <50µm. No fibers | Sieve | <100µm. Few fibers | <100µm. Few fibers | <5µm. extreme pretreatment | Sieve |

Membranes are prone to fouling both reversibly and irreversibly. Reversible fouling is due to suspended particles, biological, colloidal particles settling on the surface of the membrane or certain chemicals forming scale when it exceeds their solubility concentration, such as calcium carbonate. These can be removed by backwashing or regular acidic or alkaline chemical cleaning. On the other hand, once a membrane is irreversibly fouled the membrane needs to be discarded, since the fouling occurs in the interior of the membrane. Textile effluent contaminants containing cationic surfactants, quaternary ammonium based fabric softeners and biocides can irreversibly foul the negatively charged membranes. Therefore, selection of membrane systems needs to be done with due consideration to fouling potential which can lead to frequent membrane replacement. Enzymatic treatment and other processes cause fibres to be released from the cotton. These are sometimes smaller than a typical 20µm pore size used for pre-filtration before an RO system. In this case UF filters are installed before RO membranes. Where an MBR precedes an RO plant the MBR acts as the pre-filtration.

Fouling also increases energy consumption. Typical specific energy consumption of membrane systems is shown in Table 29. For comparison, brackish water RO energy consumption is much lower than sea water RO given the lower TDS. It also shows the typical energy consumption of ZLD brine concentrators and crystallisers.

⁹⁰ Jorgen Wagner, "Membrane Filtration Handbook – Practical Tips", Osmonics, 2001.

Disposal of brine is an issue for RO membrane applications. The reject stream is four to five times more concentrated than the feed. RO product recovery for brackish water is typically 65 – 85% and the brine stream constitutes around 15 – 35% of the feedwater. As the reject stream is concentrated using two or three passes the salt concentration in the reject stream increases dramatically. The higher the salt concentration, the greater the osmotic pressure that needs to be overcome by increasing the pressure on the membrane. ZLD is used as one option for disposal of brine. Another option is solar evaporation.

Table 29: Energy consumption of membrane systems

| Membrane process | Specific energy consumption kWh/m³ |
|--|--|
| MF /UF | 0.1 – 0.2 |
| Electrodeionisation (EDI) | 0.2 – 0.3 |
| RO with feed water TDS <1000 mg/L | 0.3 – 0.5 |
| Brackish water RO (BWRO) with feed water TDS > 1,500 mg/L | 0.6 – 1.0 |
| High recovery BWRO with second stage RO, with feed water TDS> 1,500 mg/L | 0.7 – 1.0 |
| Immersed MBR as pre-filtration to RO | 0.3 – 0.9 |
| External MBR as pre-filtration to RO | 2.0 – 4.0 |
| Sea water reverse osmosis membrane (SWRO) with energy recovery | 2.6 – 3.5 |
| 2 pass SWRO with energy recovery | 3.0 – 4.0 |
| ZLD – Brine concentrator | 21 – 26 |
| ZLD – Crystalliser | 66 – 79 |

Adapted from: Rajindar Singh, *"Using alternative energy sources – Decentralized Membrane Systems"*, Filtration+Separation, May/June 2009.

6.2.0 Resource recovery

Rather than end of pipe treatment there are advantages in recovering valuable resources from the concentrated streams. Some examples are shown below.

6.2.1 UF Membrane Applications

Printing - The printing operation uses large quantities of water for washing the continuous rubber belt. The wastewater is laden with fine pigments and polymeric binders, giving the stream high color and BOD. UF tubular membranes are best suited for this application to remove colour and the binder. The clean permeate has a 90% reduction in BOD and 100% reduction in color. The water is recycled back to the print machine for reuse. Given the large opening of tubular 1 inch membranes they can be easily cleaned using sponge balls. Figure 59 shows an array of tubular membranes for such applications and a single membrane element.

Scouring operations – Scouring operations generate large amount of BOD, oil and grease in the effluent. The oil and grease form stable emulsions which are hard to separate through conventional means. UF membranes retain and concentrate the emulsion to 30 – 50% which can be hauled away or used as a supplementary fuel source. The UF/RO system cost for this application is around US\$0.86 per tonne⁹¹.

Indigo dye recovery – Indigo dye is only 80% fixed to the fabric, with the remainder washed away. In the quinone form it is insoluble in water and can be concentrated using UF membranes. The recovered concentrate can be added to fresh indigo and reused.

Latex recovery – Latex is an expensive material used as a binder in carpet manufacturing. It can be recovered using UF membranes.

Other applications are PVA recovery from desizing operations.

⁹¹ Toray Wastewater Reuse Technology presentation, PaCT Wastewater Reuse Workshop, Bangladesh, Dhaka 30 June 2017.

Figure 59: Koch Tubular membranes



Source: Koch Membrane Systems

6.2.2 Salt recovery

Salt in the form of sodium chloride (NaCl) or sodium sulphate ($\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}$) is a major expense during the dyeing of cotton. Dyeing one kg of fabric with reactive dyes demands 70 – 150L of water, 600 – 800g of salt and 30 – 60g dyestuff⁹². Salts increase the affinity of dyes to cotton but create an operational expense as well as increasing the dissolved salt concentration of effluent. Dye baths water volume is 10 – 20% of the total effluent but has the highest colour, TDS, and temperature at 70 – 90°C. Salt can be recovered from dye baths.

⁹² B. Ramesh Babu, A.K. Parande, S. Raghu and T. Prem Kumar, "Cotton textile processing: Waste Generation and Effluent Treatment", Journal of Cotton Science, 11: 141 – 153, 2007.

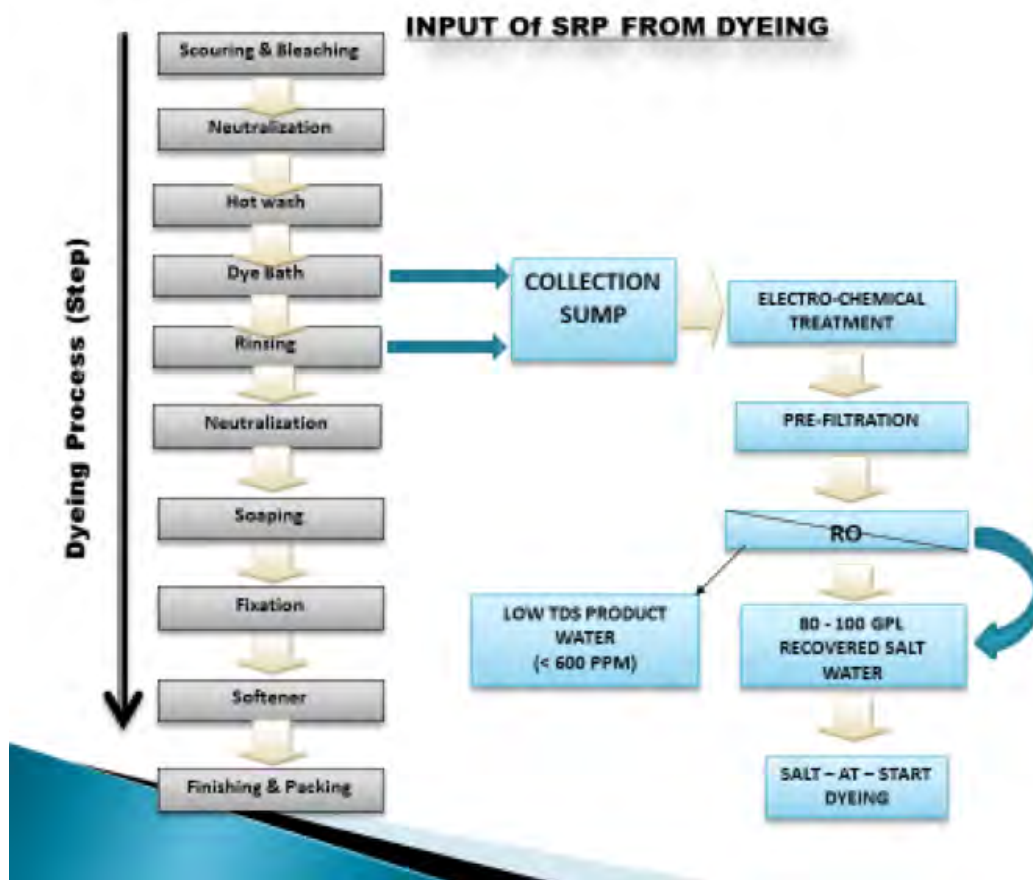
The process undergoes fine screening with suspended solids reduced to <5mg/L, chemical oxidation, and ultrafiltration using ceramic membranes, followed by NF or RO. UF units provides protection to the NF membranes or RO from blockage from large molecules and suspended solids. The NF unit separates the sodium chloride or sulphate from the rest of the water which is sent to the effluent treatment plant. The brine that is recovered has a concentration of 70 – 100g/L. This can be used as it is in the dyeing process or concentrated further in multiple effects evaporator to 250g/L. Figure 60 shows a salt recovery system.

The business case for such a system in Bangladesh is presented in Table 30.

Table 30: Salt Recovery Plant business case

| Parameters | Values |
|--|------------------------------|
| Plant capacity | 160m ³ /d |
| Average salt concentration | 40 – 80g/L |
| Per day salt consumption | 6,400kgs |
| Cost of salt @ BDT 14/kg | BDT 89,600 |
| Salt Recovery plant operating cost/day | BDT 28,800 |
| Savings in salt per day | BDT 60,800 (USD 760) |
| CAPEX cost | BDT 57,720,000 (USD 721,500) |
| Payback | 2.6 years |

Figure 60: Salt recovery system



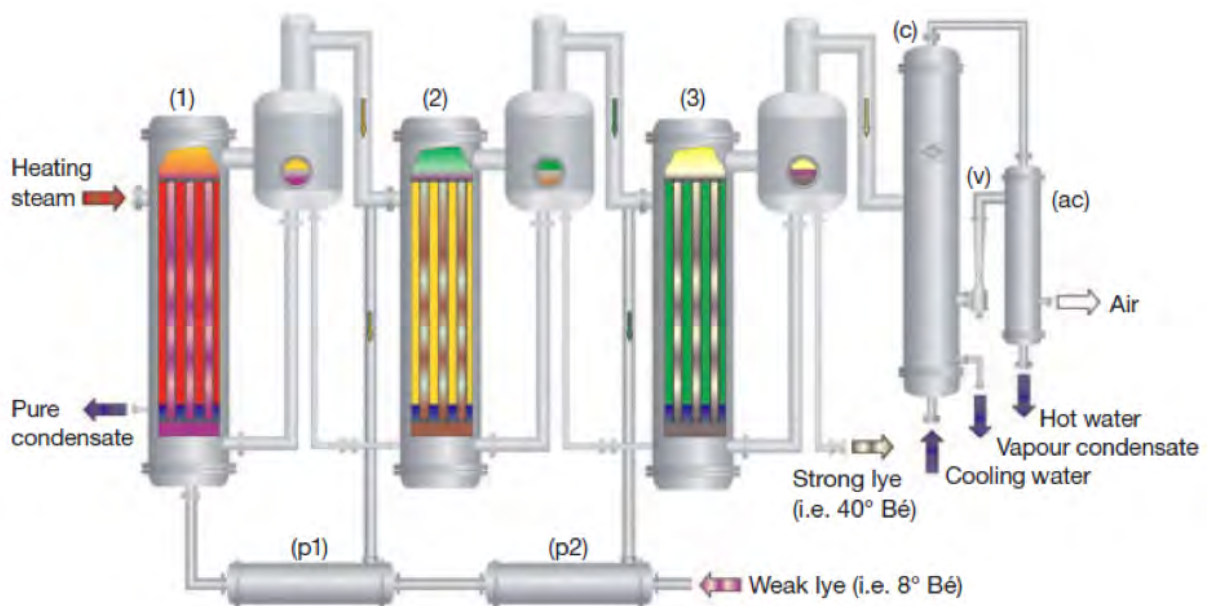
Source: Aquatech Engineers Ltd.

6.2.3 Caustic recovery

Mercerisation is used in cotton dyeing to improve the luster, absorbency and strength of cotton. The process requires large quantities of high strength caustic (NaOH) at a Baume of 28 – 30Be° (270 – 300g/L) creating a high pH effluent with caustic concentration of 5 – 8 Be0 (30 – 40 g/L), commonly known as 'weak lye'. The caustic from the process can then be recovered and thereby reduces the amount of neutralisation that is required in the effluent treatment plant and reduces the volume of water requiring treatment. Caustic recovery also produces a hot water stream that can be utilised for heating of water.

Using a multiple effects evaporation system, the weak caustic solution is concentrated in stages until it reaches a concentration of 40Be°. Figure 61 shows a schematic of the process. In the multiple effects evaporators, the water is boiled off under a vacuum producing vapour condensate which in turn is used to produce a hot water stream. The recovered caustic solution contains is bleached using H₂O₂ to decolour the recovered caustic. Figure 61 shows the caustic recovery process and Figure 62 colour of recovered caustic.

Figure 61: Caustic recovery process



Three-stage caustic recovery plant with two pre-heaters (p1) and (p2) and a steam jet vacuum ejector (v) with after-condenser (ac).

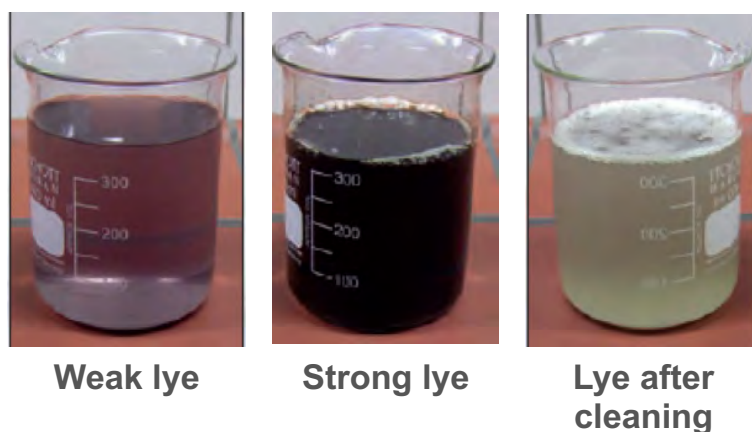
- Fresh steam heats 1st stage
- Vapour 1st stage heats 2nd stage
- Vapour 2nd stage heats 3rd stage
- Vapour 3rd stage for hot water generation

Lye concentration during recovery



Source: Korting.

Figure 62: Colour of recovered caustic



PaCT (Partnership for Cleaner Textile) partner factory Zaber and Zubair Fabrics Ltd in Bangladesh installed a caustic recovery plant on their site⁹³. The benefits are summarised in Table 31.

Table 31: Environmental and financial benefits of a caustic recovery plant

| Environmental benefit | | Financial benefit | |
|-----------------------------|--|-------------------|-----------------|
| Caustic soda saved | 6.5 million L/year | Total investment | US\$2.3 million |
| Hot water generated | 28 million L/year | Cost savings | US\$3.8 million |
| Sulphuric acid saved | 400,000kg/month | Payback period | <1 year |
| Other benefits | Reduced steam consumption in bleaching units; reduced water consumption for boiler feed water. | | |

6.3.0 Zero Liquid Discharge (ZLD)

No discussion on wastewater treatment of textile effluent is complete without discussing ZLD. ZLD is the holy grail of wastewater treatment. In a ZLD system no water is discharged except solid waste. All of the wastewater is treated using advanced wastewater treatment technologies and reused. ZLD's were introduced in the 1970s in the US power plant industry due to water scarcity and salination of rivers from cooling tower blowdown. However, ZLDs for textile wastewater is a more recent phenomenon.

⁹³ Partnership for Cleaner Textiles, "Case Study - Caustic Recovery Plant - Zaber and Zubair Fabrics Ltd", March 2017.

ZLD came to attention of the textile industry due to the landmark case in Tiruppur, India where the Madras High Court in 2005 directed the textile dyeing and finishing industries to set up common effluent treatment plants and ZLDs to address the large-scale pollution of the environment.

Tiruppur is a mid-sized industrial town located in the Cauvery river basin. The basin suffers from water scarcity due to erratic seasonal rainfall, limited reservoir capacity and a high demand on the already limited resource. The water supply to the textile industry is abstracted from the Bhaveni river over 50km away, whilst the effluent is discharged to the Noyyal river. Due to the court order, nine existing effluent treatment plants were upgraded, with combined RO and thermal evaporation system which enables 96% of the effluent to be treated and recovered as freshwater. As a result, the demand on the municipal water supply reduced by 876,000m³/year. Water demand on the Bhaveni river reduced from 1,200,000m³/y to 300,000m³/year⁹⁴. The operating cost was US\$4/m³.

ZLDs systems, in addition to recovering fresh water, also recover NaCl salt and Glauber salt (Na₂SO₄·10H₂O) with very high purity which can be reused in the process.

A process flow diagram of ZLD system is shown in Figure 63. It consists of physical and chemical treatment, and biological treatment followed by RO membrane treatment. The concentrated reject stream from the RO system is sent to a mechanical vapour recompression (MVR) unit. Here water which is initially heated using steam produces vapour which is compressed in a compressor, and the heat from this vapour is used to heat the bulk of the incoming reverse osmosis reject stream. This is then sent to the multiple effect evaporators (MEE). In a MEE, under vacuum water is evaporated and the concentrate stream gets concentrated with each effect. The ratio of steam to water evaporated is typically 1:5 (1kg of steam to 5L of water). The combination of MEE and MVR enable the recovery of an additional 16% of incoming water. The evaporated water is low in TDS (50 – 100mg/L) and is used as boiler feed water. The concentration of salts can reach upto 200,000mg/L. Adiabatic chillers or crystalliser are used to recover the Glaubers salt from this stream, or the slurry is simply evaporated in solar ponds.

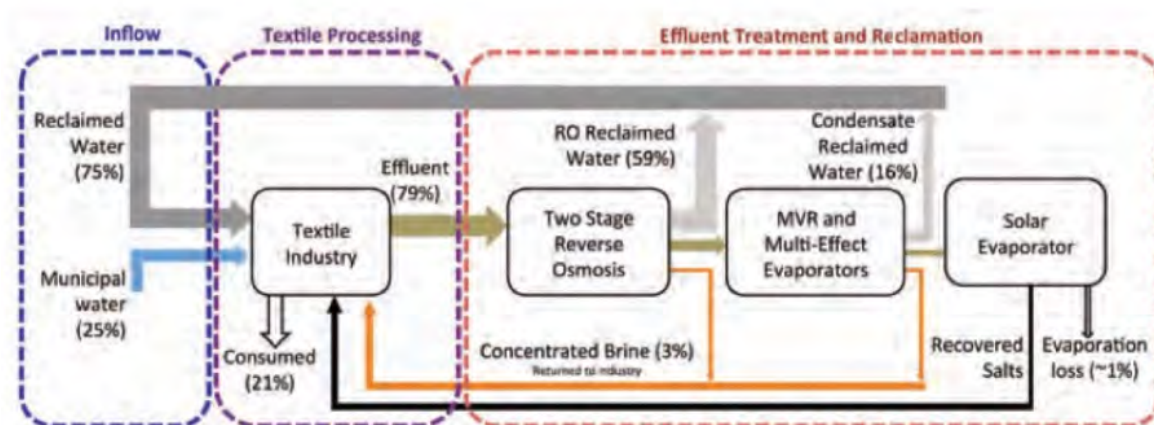
A disadvantage of ZLD, aside from high CAPEX (capital expenditure) costs and power consumption, is that it produces a hazardous waste which needs to be disposed of responsibly. Secondly, it requires significant land area which may not be suitable for

⁹⁴ Siraj Tahir, "Water Reuse in the Textile Sector India", Arup.

most dyeing units. Thirdly, operation of ZLD is technically complex and maybe beyond the capacity of an average textile dyeing facility. Therefore, central effluent treatment plants to where a number of these units can discharge are better suited for such technologies. Power consumption for ZLD evaporators and crystallisers is around 21 – 26 and 66 – 79 kWh/m³ respectively.

In order to better understand the impact of ZLD on total dyeing costs the following case study is presented in Table 32⁹⁵. In the example shown, the cost of fresh water is high at US\$1.14/m³. Whilst most developing countries have lower costs for fresh water, what is not considered is that the total cost of water, after it undergoes treatment operations like demineralisation for boiler feedwater treatment, is frequently around US\$1.00/m³. ZLD produces high quality water as condensate which requires minimal additional treatment. Secondly, the ability of ZLD to recover high purity sodium sulfate and reuse it helps to reduce the operating cost. Even then there is still a net operating cost to the site. However, if water is scarce, then an overall increase in costs of 3.7% may be justified to reduce the water risk to the site or risk future regulatory pressure to minimise water use.

Figure 63: ZLD process flow diagram⁸²



⁹⁵ I. Sajid Hussain, "Case study of a Zero Liquid Discharge Facility in Textile Dyeing Effluents in Tiruppur", TWIC, 2012.

Table 32: Cost of ZLD on Processing cost of dyeing unit

| Parameter | Description | |
|---|------------------------|---------------------|
| Design capacity | 5,500m ³ /d | |
| Type of dyeing | Knitted fabric | |
| | Rs | US\$ |
| Capital cost | Rs 70 crore | 11.6M |
| Operating cost per m ³ of water processed | Rs/m ³ | USD/m ³ |
| - Variable cost (chemicals, diesel, power, cartridge filter, maintenance) | Rs 112.4 | 1.87 |
| - Fixed costs | Rs 34.5 | 0.57 |
| - Financial costs (including financing and depreciation) | Rs 34.3 | 0.57 |
| - Total operating cost | Rs 181.2 | 3.02 |
| Recovery cost | Rs/m ³ | US\$/m ³ |
| Cost of recovering water including brine @ Rs 70/m ³ @98% recovery | 68.6 | 1.14 |
| Cost of recovered Glaubers salt @Rs 10/kg for 90% recovery of salt | Rs 63 | 1.05 |
| Revenue from Recovery of resources | Rs 131.6 | 2.19 |
| Net operating cost | Rs 49.6 | 0.83 |
| | | |
| Financial impact of ZLD on 5,500 m³/d dyeing factory | | |
| Water consumption/kg of fabric | 60 L/kg | |
| Total production capacity per day | 92 Tonnes | |
| | Rs | US\$ |
| Processing cost of dyed fabric/kg | 80 | 1.33 |
| Processing cost per day | 7.4 Million | 123,333 |
| Cost of ZLD /d (Rs 49.6 or US\$0.83 x 5,500 m ³ /d) | 273,000 | 4,565 |
| Cost of ZLD/kg of dyed fabric | 2.79 | 0.05 |
| % of ZLD cost on processing cost of dyed fabric | 3.7% | 3.7% |

7.0.0 Sludge production

Sludge disposal is a major headache for textile wastewater treatment plants, especially in countries like Bangladesh which lack a hazardous waste disposal infrastructure such as secure landfills. Therefore, effluent treatment technologies that produce the lowest sludge volumes are of equal importance in the selection of treatment technologies. Sludge production from the various technologies are shown in Table 33⁹⁶. It is not the intent of this document to discuss sludge treatment.

8.0.0 Conclusion

ZDHC has published Guidelines for Wastewater Quality. This manual was developed to showcase the Best Practices for treatment of textile effluent and also serve as a companion to the ZDHC Programme's Wastewater Treatment Guidelines. It is intended to give the reader technical and practical insights into the selection of treatment technologies for wastewater treatment and their limitations.

Wastewater treatment of textile dyeing effluent is more complex than municipal sewage treatment, given the complex chemical contaminants found in such waste streams. The manual shows the common contaminants found in wet dyeing and finishing operations, and their methods of treatment from primary, secondary and tertiary treatment. In addition to this, colour removal is discussed in detail with a particular emphasis on advanced chemical oxidation methods. Water reuse, membrane treatment and recovery of valuable resources such as caustic soda is also discussed. A short description on zero liquid discharge is also presented, given the industry-wide interest in zero liquid discharge. Sludge treatment is also discussed very briefly.

⁹⁶ F. Hai and K. Yamamoto, "*Membrane Bioreactors*", University of Wollongong, 2011.

Definitions and Terminology

Acid dyes – Acid dyes are mainly applied to polyamide (70 – 75%) and wool (25 – 30%). They are also used for silk and some modified acrylic fibres. Acid dyes exhibit little affinity for cellulose and polyester fibre. Colours are generally bright and fastness to light and washing range from poor to excellent, depending on the chemical structure of the dyestuff. Azo dyes are the largest group of acid dyes.

Activated carbon adsorption – a process which adsorbs colour causing particles and other soluble organic molecules on the surface of the adsorbent-like activated carbon. Activated carbon also removes other toxic chemicals like phenols, cyanides, etc., which cannot be treated by using conventional wastewater treatment. It is also used to sterilise water. Activated carbon is available in granular or in powdered form.

AOX compound – Adsorbable Organic Halogen. A possible result when chlorine comes into contact with organic substances in waste water. AOX compounds are toxic to aquatic life and persistent in the environment.

Azo dyes – nitrogen-based compounds commonly found in dyeing. 70% of dyes produced in the world are azo dyes. These types of dyes are used to produce yellow, orange and red colours. Some azo dyes can

break down to release harmful compounds called aromatic amines that can be carcinogenic or allergenic.

Basic (cationic) dyes – dyestuffs are almost exclusively used on acrylic fibres, modified polyamide fibres, and blends. Basic dyes contain a quaternary amino group imparting a cationic charge and are slightly soluble in water, while they show higher solubility in acetic acid, ethanol, ether and other organic solvents.

Bleaching – Bleaching removes the natural colouring materials and renders the cloth white. Bleaching is done using chlorine, hydrogen peroxide or ozone. Bleaching of yarn typically uses 24 to 32L/kg of water, whereas cloth bleaching requires 40 – 48L/kg of water.

BOD₅ – Biological Oxygen Demand. Measures oxygen uptake for biological oxidation of organics. The standard BOD is five days' incubation at 20°C when 60 – 70% of organic matter is degraded. Industrial wastewater can contain inhibitors like phenol leading to low BOD results. Ammonium ions are also oxidised which can lead to high BOD results.

Brackish water – Brackish water contains higher salinity levels than fresh water (TDS <500mg/L) but less than sea water (TDS >30,000mg/L).

Carcinogenic – A compound having the potential to cause cancer in living organisms.

Chlorobenzenes – A group of 12 chemical substances, each consisting of a benzene ring with one or more hydrogen atoms replaced by chlorine atoms. Chlorobenzenes are mainly used as intermediates in the synthesis of other chemicals and may be present as impurities in chemical formulations. Leading apparel and footwear brands have banned the use of chlorobenzenes in their products.

COD – Chemical Oxygen Demand. Oxidation of organic matter in the presence of potassium dichromate at 145°C to CO₂, water and NH₃.

Cross-flow filtration – A filtration technique where the inlet liquid stream passes along the surface of the membrane under pressure. The solute and particles smaller than the pore size of the membrane goes through the membrane.

Desizing – The sizing components which are rendered water soluble during sizing are removed from the cloth to make it suitable for dyeing and further processing. Desizing is done with sulphuric acid or enzymes. Typical water requirements are 2.5 to 21L/kg with an average of 11.75L/kg.

Direct dyes – Direct dyes are used for dyeing cotton, rayon, linen, jute, silk and polyamide fibres. Colours are bright and deep, but light-fastness can vary greatly depending on the dyestuff. Wash-fastness properties are also limited unless the textile is after-treated. Direct dyes (also called substantive dyes) can be azo compounds, stilbenes, oxazines, or phthalocyanines. They always contain solubilising groups (mainly sulphonic acid groups, but carboxylic and hydroxyl groups can also be found) that ionise in aqueous solution. To enhance the dyeing effect, salts and auxiliaries such as wetting and dispersing agents are required.

Disperse dyes – They have worldwide usage in textile industry, basically for synthetic fibers like polyester and cellulose acetate such as Di-acetate, Tri-acetate and nylon. They are applied on the dye bath at a high temperature range around 120 – 140°C. Disperse dyes are insoluble in water. Fastness to light is generally quite good, while fastness to washing is highly dependent on the fibre. In particular, in polyamides and acrylics they are used mostly for pastel shades because in dark shades they have limited build-up properties and poor wash fastness. To enhance the dyeing effect of chemicals and auxiliaries such as dispersing agents and thickeners, reducing agents are required.

Dyeing – Dyeing is the most complex step in wet processing which provides attractive colour to the product. Dyeing is carried out either at the fibre stage, as yarn or as fabrics. Hundreds of different dyes and auxiliary chemicals are used. Typical water requirements are 36 to 400L/kg with an average of 100L/kg.

Endocrine Disruptor – Chemicals that can disrupt hormone systems in mammals, potentially leading to cancers, developmental problems, problems with reproduction, or birth defects.

Flux – flux is the amount of water that passes through a given membrane area during a unit of time. Flux is expressed in liters per square metre per hour (L/m²/h). It is an important design variable, as the flux rate can have a direct impact on the degree and rate of fouling and scaling of the membrane.

Glauber's salt – also known as sodium sulphate decahydrate (Na₂SO₄·10H₂O). A white solid highly soluble in water. Cotton fibres are negatively charged and in the absence of salt repel the negatively charged dye molecules. Due to its high solubility, Glauber's salt helps certain dye molecules attach themselves to the textile. It helps in the maximum exhaustion of the dyes after the dyeing process.

Halogenated Solvents – Halogenated solvents are a large class of substances defined as aliphatic (straight chain or branched) compounds containing at least one halogen atom (typically chlorine). Aliphatic halogenated solvents potentially used in apparel and footwear production belong to dichloroethane, methylene chloride, trichloroethylene and tetrachloroethylene. These may cause serious damage to human health, aquatic environments and have long-term effects on aquatic environments above certain concentrations. Leading apparel and footwear brands have banned the use of certain halogenated solvents in their products.

Hardness – In water treatment hardness is the concentration of calcium and magnesium ions in water expressed as mg/L CaCO₃. Waters are often categorised based on hardness: soft < 75 mg/L; moderately hard 75 – 150 mg/L; hard 150 – 300 mg/L; very hard > 300 mg/L. When the Ca ion is expressed as the ion, multiply by 2.5 to get the concentration as CaCO₃.

HRT – Hydraulic residence time. A measure of the average time wastewater remains in a process unit to undergo treatment. Expressed in days or hours.

Kiering – refer to scouring

Ion exchange – A process used for the removal of inorganic salts and some specific organic anion components such as phenol. Ion exchange is used widely for water softening where the calcium salts are replaced with sodium ions. The ion exchange resin traps the calcium ions and after a time needs to be regenerated with brine solution to bring it back to its original form. The calcium rich stream is discarded. This process is known as regeneration.

Long-Chain Perfluoro Alkyl Acids (LCPFAAs) – Found in durable water repellents as impurities, some LCPFAAs may cause long-term effects to the aquatic environment and above certain concentrations may have adverse effects on human fertility or to unborn children.

MBR – Membrane bioreactor. A specific type of membrane system used in wastewater treatment plants in suspended aerobic systems for the removal of suspended solids and BOD.

MEE – Multiple effect evaporators. A process unit used in ZLD systems to evaporate wastewater using steam under vacuum. Several designs are available, the most common being falling film evaporator. High purity water produced can be reused as boiler feed water. The brine which contains the concentrated solids is sent for further processing in a crystalliser or evaporation ponds.

Mercerisation – a process used only in cotton dyeing to improve the lustre, dye affinity and strength of cotton. Mercerisation can be carried out through cold caustic solutions followed by washing with water several times. Typical water requirements are 17 to 32L/kg with an average of 24.5L/kg.

Metal-complex dyes – Metal-complex dyes (also called pre-metallised dyes) have great affinity for protein fibres. Among metal-complex dyes, 1:2 metal-complex dyes are also suitable for polyamide fibres. More than 65% of wool is dyed with chrome dyes or metal-complex dyes and about 30% of PA is dyed with 1:2 metal-complex dyes.

Mixed Liquor Suspended Solids (MLSS) – suspended solids in the mixed liquor of an aeration tank and expressed as mg/L.

Mixed Liquor Volatile Suspended Solids (MLVSS) – the organic or volatile suspended solids in the mixed liquor of an aeration tank and expressed as mg/L. The volatile portion is used as a proxy for the microorganisms present.

Molecular Weight Cut Off (MWCO) – refers to the lowest molecular weight solute (in Daltons) in which 90% of the solute is retained by the membrane or the molecular weight of the molecule (e.g. globular protein) that is 90% retained by the membrane.

Mordant dyes – Mordant dyestuffs are generally used for protein (wool and silk). They are practically no longer used for polyamide fibres or for printing. Due to their good levelling properties and very good wet fastness after chroming, chrome dyes are used principally to obtain dark shades (greens, blues and blacks) at moderate cost. There are disadvantages, however, in their use: long dyeing times, difficulties with shading, the risk of chemical damage to the fibre during chroming and the potential release of chromium in waste water.

Mutagenic - Something having the physical or chemical ability to cause mutations in the DNA of in living things.

Naphtol dyes (Azoic dyes) - Azoic dyes, also known as naphthol dyes, are used for cellulosic fibres (particularly cotton), but may also be applied to viscose, cellulose acetate, linen and sometimes polyester. Azoic dyes have excellent wet fastness properties as well as good light, chlorine and alkali fastness, while rubbing fastness is poor. From a chemical point of view naphtol dyes are very similar to azo dyes, the main difference being the absence of sulphonic solubilising groups.

Nitrification – an aerobic process in which the bacteria change the ammonia and organic nitrogen in wastewater into oxidised nitrogen (usually nitrate).

PPB – Parts per billion = $\mu\text{g/L}$ (microgram per Liter), $\mu\text{g/kg}$ (microgram per kilogram)

PPM – Parts per million = mg/L (milligrams per Liter), mg/kg (milligrams per kilogram)

PPT – Parts per trillion = ng/L (millinano grams per Liter), ng/kg (nanograms per kilogram)

Peaking factor – ratio of maximum flow to the average flow, such as maximum hourly flow or maximum daily flow to the average daily flow.

Precautionary principle – A fundamental principle within environmental and chemical policy, which means that if there is a threat of serious or irreversible damage to the environment, the absence of scientific proof may not be used as an excuse to delay cost-effective measures in order to prevent environmental impact.

Protozoa – A group of motile microscopic single celled aerobic organisms which often consume bacteria as an energy source.

Reactive dyes – Reactive dyes are mainly used for dyeing cellulose fibres such as cotton and viscose, but they are also increasingly gaining importance for wool and polyamide. They provide high wet fastness (better than the less expensive direct dyes), but their use is not always viable because of the difficulty in obtaining level dyeing. Chlorine fastness is slightly poorer than that of vat dyes, as

is light fastness under severe conditions. Reactive dyes are unique in that they contain specific chemical groups capable of forming covalent links with the textile substrate. Poor dye fixation has been a long-standing problem with reactive dyes in particular, in batch dyeing of cellulose fibres, where a significant amount of salt is normally added to improve dye exhaustion (and therefore also dye fixation). On the other hand, shade reproducibility and level dyeing were the major obstacle in "*right-first-time*" production using the most efficient dyes (high exhaustion and fixation rate). High fixation, bifunctional dyes address these disadvantages.

RSL – Restricted Substances List. This is a tool used by brands to highlight to their supply chain partners which chemicals are restricted on final products.

Scouring – The process involves the removal of natural impurities such as grease, waxes and fats, etc. The process follows desizing and uses boiling in an alkaline solution containing caustic soda, soda ash, sodium silicate and sodium peroxide. Typical water requirements are 20 – 45L/kg with an average of 32.5L/kg.

Scum – A layer or film of oil or grease that has risen to the surface of the wastewater.

Sizing – The process involves the sizing of yarn with starch, poly vinyl alcohol (PVA) or carboxyl methyl cellulose (CMC) to give necessary tensile strength and smoothness required for weaving. The water required for sizing varies from 0.5 to 8.2L/kg with an average of 4.35L/kg.

Solids, Settleable – suspended solids that will settle out of suspension within a specified period of time, expressed in mL/L.

Solids Total (TS) – Material residue left in a vessel after evaporation of a sample subsequent to drying to a constant weight in an oven at 105°C. Includes total suspended solids and total dissolved solids. Typically expressed in mg/L.

Solids, Total Dissolved (TDS) – Material that passes through a 2µm or smaller nominal pore size, evaporated to dryness in a weighed dish and subsequently dried to a constant weight at 1800C and expressed as mg/L. Given their instantaneous results, electrical conductivity measurements have become popular as a proxy for TDS and is expressed as µS/cm. 1 µS/cm = 0.67 – 7 mg/L TDS for fresh water and for sea water it is around 0.5 mg/L.

Solids, Total Suspended (TSS) – That portion of total solids that is retained on a filter of 2µm or smaller nominal pore size at constant temperature of 105°C.

Sulphur dyes – Sulphur dyes are mainly used for cotton and viscose substrates. They may also be used for dyeing blends of cellulose and synthetic fibres, including polyamides and polyesters for dyeing silk. Apart from black shades, sulphur dyes play almost no part in textile printing. Bleach and wash fastness properties are very good, while light fastness varies from moderate to good. Although they encompass a broad shade range, sulphur dyes are mostly used for dark shades because lighter shades have poor resistance to light and laundering. Sulphur dyes tend to be dull compared with other dye classes. Sodium sulphide and sodium hydrogen sulphide are generally employed as reducing agents to bring the dye into solution (unless ready-for-use sulphur dyes are applied). Binary systems made of glucose and sodium dithionite (hydrosulphite) or thiourea dioxide are also used as alternative reducing agents. They are used in alkaline solutions.

Tertiary Wastewater Treatment – Following secondary treatment the clarified water may undergo further treatment to destroy the remaining bacteria and remove solids or nutrients. Generally tertiary wastewater treatment levels are BOD < 10 mg/L and TSS < 10 mg/L.

Total Kjeldahl Nitrogen (TKN) – measures the organic nitrogen expressed as mg/L.

Total Nitrogen – Total nitrogen is the sum of Total Kjeldahl Nitrogen, nitrate and nitrite and expressed as mg/L.

Vat dyes - Vat dyes are used most often in dyeing and printing of cotton and cellulose fibres. They can also be applied for dyeing polyamide and polyester blends with cellulose fibres. Vat dyes have excellent fastness properties when properly selected and are often used for fabrics that will be subjected to severe washing and bleaching conditions (towelling, industrial and military uniforms, etc.). The range of colours is wide, but shades are generally dull. From a chemical point of view, vat dyes can be distinguished into two groups: indigoid vat dyes and anthraquinoid dyes. Indigo dyes are almost exclusively used for dyeing warp yarn in the production of blue denim. Like sulphur dyes, vat dyes are normally insoluble in water, but they become water-soluble and substantive for the fibre after reduction in alkaline conditions (vatting). They are then converted again to the original insoluble form by oxidation and in this way they remain fixed into the fibre.

ZDHC MRSL – ZDHC Manufacturing Restricted Substances List. A list of chemical substances that are banned from intentional use in facilities that process textile materials and trim parts in apparel and footwear. The ZDHC MRSL establishes acceptable concentration limits for substances in chemical formulations used within manufacturing facilities.

ZLD – Zero liquid discharge. A process where no liquid leaves the wastewater treatment. It is capital intensive and energy intensive and combines several unit processes such as RO, brine concentrators, ion exchange, MEE, MVR, adiabatic chillers and solar evaporation ponds. Best suited for water scarce regions and / or where the cost of water is high.