



CHAPTER 1

Introduction

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1.1 Introduction

Water, an elixir of life, a fundamental natural resource that sustains life on Earth, is liable for the sustenance of human beings. It is vital for agriculture, aquatic habitats, industry, maintaining global climate regulation, and economic growth. In essence, mitigating pollution, preserving water resources, and promoting sustainable water usage are requisite endeavors for securing freshwater resources. Unprecedented industrialization has impeded an adverse impact on freshwater availability due to the release of various toxic substances such as pesticides, heavy metals, dyes, etc. into aquatic ecosystems (Geed et al., 2018). Major industries comprising petroleum, mining, leather, paper and pulp, pharmaceutical, food processing, and textile industry are the leading contributor to global water pollution (Sonwani et al., 2021). The textile industry plays a vital role in global manufacturing, hence consumes enormous amounts of freshwater during various manufacturing processes comprising dyeing, printing, finishing, and washing. Generally, various synthetic dyes, heavy metals, suspended solids, pH-altering substances, detergents, non-biodegradable matter, additives, and organic compounds are present in a typical textile effluent (Ihsanullah et al., 2020). Wastewater emanating from it leads to detrimental effects on human health and ecosystems due to its complex composition. The direct emission of these pollutants not only leads to surface and groundwater contamination but also persists in the environment, further aggravating the overall environmental burden. Moreover, water quality decreases, and light penetration in water bodies reduces, which directly hinders photosynthesis in aquatic plants, and disrupts the food chain by affecting organisms at different trophic levels.

1.2 Synthetic Dyes: Sources and Major Consequences

Dye, a colored substance, binds chemically to the substrate upon which it has been applied. Dyes have been extensively used in paper, leather, paints, pigment manufacturing, color cosmetics, and textile materials to impart color. Natural dyes are organic compounds, made from the colored compounds of natural sources including plants and animals. The major plant sources comprise of leaves, wood, lichens, bark, fungi, berries, flowers, vegetables, and roots. Generally, these dyestuffs are used for fabrics (cellulosic and protein) and fibers dyeing, organic and mineral materials staining, beverages, food coloring, organic pigment production, cosmetics, feathers, and pharmaceutical compounds (Nowik, 2000). Natural dyes, which had been widely used in traditional societies since at least the stone age, has quickly supplanted by synthetic dyes starting in the second part of the nineteenth century. Natural colors are becoming more and more important in our life today because they almost all have considerable benefits over many synthetic colors, including being almost universally hypoallergenic and nontoxic to people.

The first ever synthetic dye, “Mauveine” was invented by William Henry Perkin (1856) (Chavan, 2011; Travis, 1990). Synthetic dyes originated from petrochemicals or coal tar and are broadly employed to impart vibrant colors to textile products, paints, soaps, mouthwashes, and shampoos. Textile industry is one of the leading consumers of synthetic dyes, accounting for a significant proportion of dye usage and production primarily for fabric dyeing and printing. Additionally, they are utilized in cosmetics, printing inks, plastics, paints, and even food and beverages. They are mainly the derived compounds of benzene, which absorb the ultraviolet spectrum of light. A substance added, also known as “Chromophores”, shifts the absorption band of light to the visible region and various colors can be produced, whereas the color deepens has imparted by an “auxochrome” (Bafana et al., 2011). Some examples of

chromophores are quinoid, nitro, azo, carbonyls, esters, nitrile, ethylene, acetylene, acids, keto, nitroso, thio groups, etc. (Chakraborty, 2014) and that of auxochromes are hydroxyl, aldehyde, amino, and methyl mercaptan groups. Modern electronic structure theory contends that dyes' color results from the stimulation of valence π -electrons by visible light, which has supplanted this hypothesis (Bafana et al., 2011).

1.2.1 Classification of Synthetic Dyes

Synthetic dyes are abundantly used for the printing, dyeing, and coloring processes (Singh et al., 2021). The American Association of Textile Chemists and Colorists (USA) and the Society of Dyers and Colorists (UK) together publish the Colour Index (C.I.), the largest collection of dyes and pigments, which includes 12,000 goods categorized under 2000 C.I. generic names based on their chemical structure (Chavan, 2011). The major classification of synthetic dyes can be carried out based on water solubility (**Figure 1.1**) (Berradi et al., 2019).

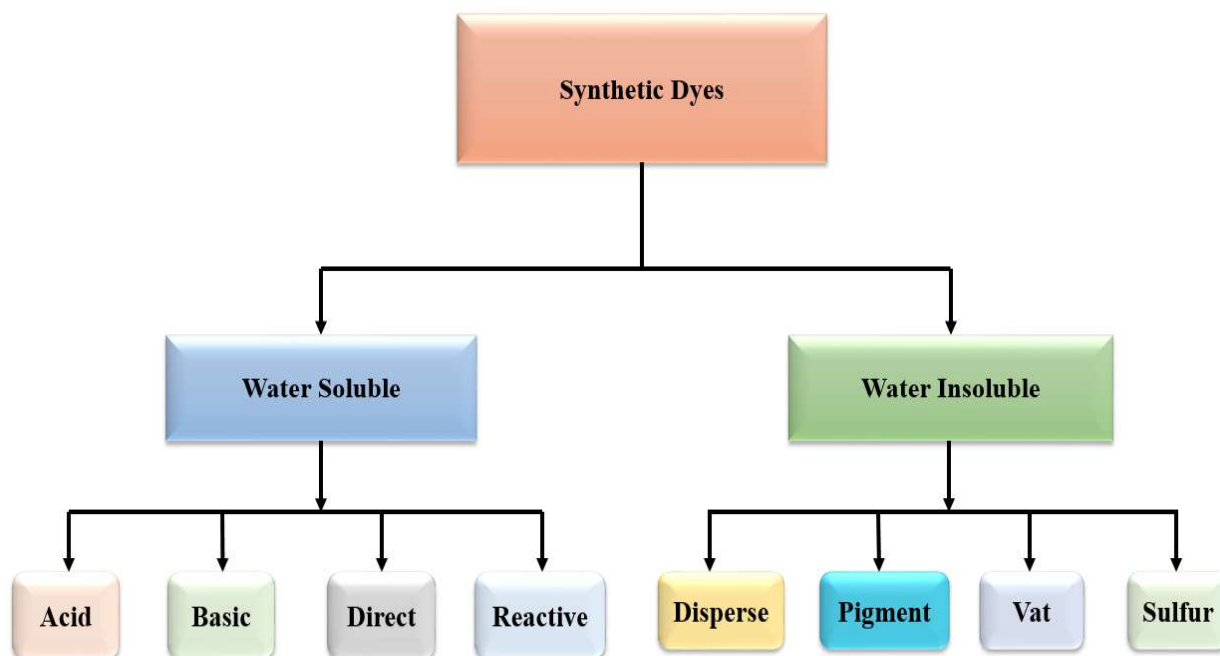


Figure 1.1. Classification of synthetic dyes based on water solubility

Some common examples of various synthetic dyes are illustrated in **Figure 1.2**.

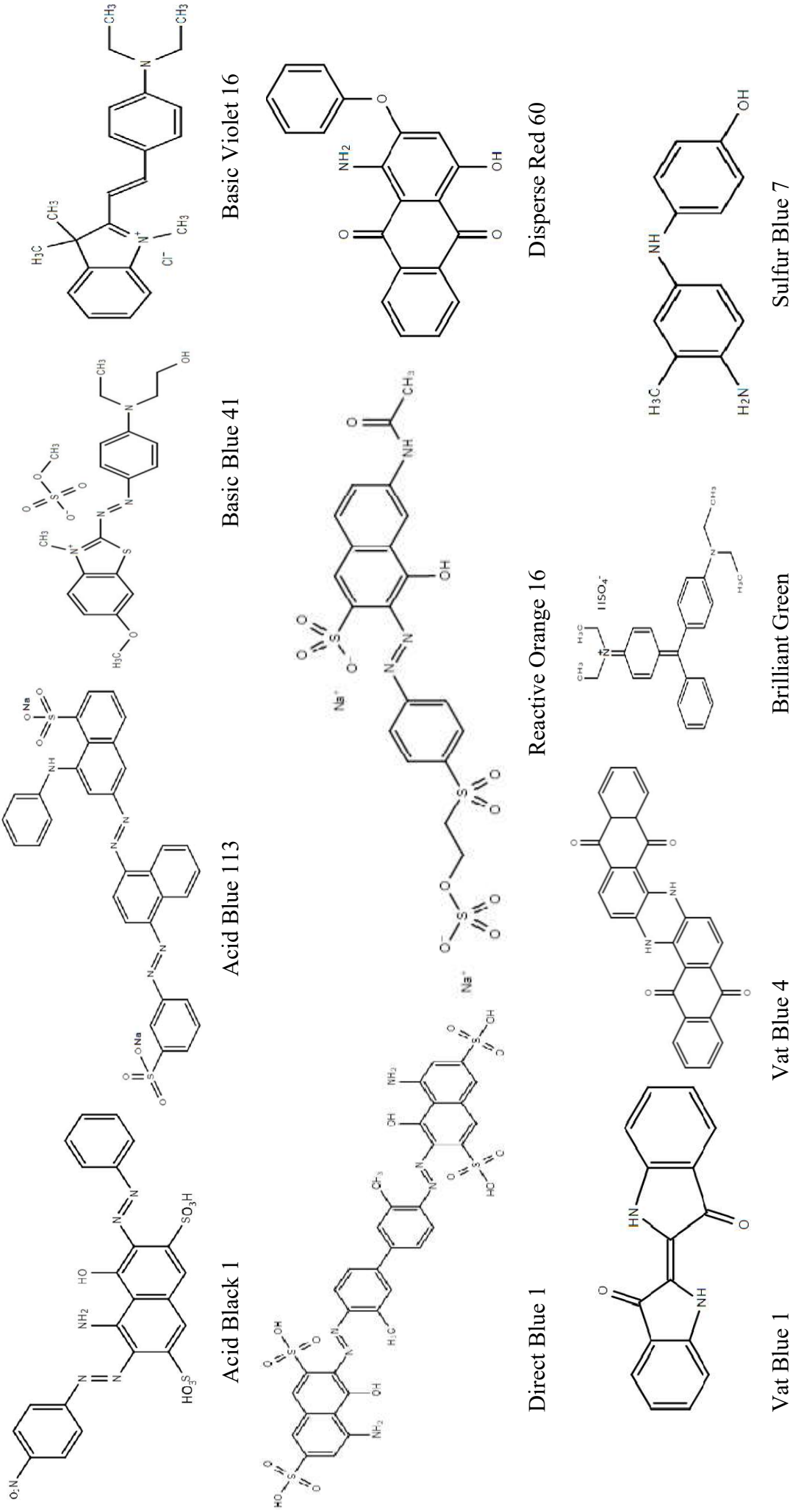


Figure 1.2. Various commonly used Synthetic Dyes in the textile industry

1.2.2 Harmful impact of textile dyes

The indiscriminate emission of textile effluents with high concentrations of toxic dyes leads to several health issues (Zubair et al., 2022). Contact dermatitis, occupational asthma, allergic conjunctivitis, allergic rhinitis, and other allergic responses are possible among employees who manufacture or handle reactive dyes (Lellis et al., 2019). Textile dyes can lead to dermatitis and central nervous system issues, among other illnesses (Al-Tohamy et al., 2022). These issues may be brought on by the inactivation of enzymes due to the substitution of their cofactors. Major health issues caused by various dyes have been summarized in **Table 1.1**.

Table 1.1 Major health-related issues caused by Textile dyes.

S.N.	Dye	Health Issue	References
1.	Methylene Blue	Cyanosis, tissue necrosis, vomiting, Heinz body formation, jaundice, enhanced heartbeat rate, shock.	(Oladoye et al., 2022)
2.	Direct black 38	Urinary bladder cancer, a liver carcinogen.	(Islam et al., 2022)
3.	Malachite green	Damages in the kidney, heart, spleen, and liver. Inflicts lesions on the eyes, lungs, skin, and bones.	(Kishor et al., 2021)
4.	Tartrazine	Allergy, skin eczema, asthma, immunosuppression, hypersensitivity.	(Kumar et al., 2020)
5.	Erythrosine and xanthene	Neurotoxic, xenoestrogenic, allergic, carcinogenic, and DNA damage.	(Kumar et al., 2020)
6.	Disperse Red 1	Cytotoxic effect with apoptosis, DNA damage, DNA adducts formation.	(Lellis et al., 2019)
7.	Crystal Violet	Mitotic poisoning, chromosomal damage, abnormal metaphase accumulation, skin and digestive system irritation, chemical cystitis, respiratory and renal failure.	(Mani and Bharagava, 2016)

8.	Basic Red 9	Allergic dermatitis, skin irritation, cancer, and mutations.	(Sivarajasekar and Baskar, 2014)
9.	Disperse Orange 1	DNA damage, apoptosis.	(Ferraz et al., 2011)
10.	Acid Violet 7	Chromosome aberration, genotoxic.	(Mansour et al., 2010)

The abundance presence of textile waste within an aquatic environment not only depletes its dissolved oxygen (DO) level but also enhances the chemical oxygen demand (COD), and biochemical oxygen demand (BOD). Textile effluent waste studies conducted over the past decade have shown that the average range of BOD₅ and COD are (80-6000) mg/L and (150-30,000) mg/L, respectively (Yaseen and Scholz, 2019). A wide range of reported dye concentrations in textile wastewater is summarized in **Table 1.2**.

Table 1.2 Dye concentration range in real textile effluent.

S.N.	Effluent Source	Dye Concentration Range	References
1.	Real textile wastewater from primary effluent	Color = 14.2 Pt/Co COD = 21 g/L	(Raza et al., 2022)
2.	Final clarifier of the textile industry, Acid Orange 10	45 mg/L	(Sivakumar, 2014)
3.	Dye houses	10-250 mg/L	(Ananthashankar, 2013)
4.	Real Textile wastewater	Color = 107 ± 6 ADMI	(Mehmood et al., 2022)
5.	Textile industry	20-50 mg/L	(Abid et al., 2012)
6.	Dye effluent	600-800 mg/L	(Vandevivere et al., 1998)
7.	Textile effluent	10-50 mg/L	(Laing, 1991)

The permissible wastewater discharge limits as governed by Central Pollution Control Board (CPCB), New Delhi, India for inland surface water have been summarized in **Table 1.3** (Choudhary and Saxena, 2017).

Table 1.3 The wastewater discharge permissible limits are governed by CPCB, New Delhi, India.

S.N.	Wastewater Parameter	Discharge Permissible limits (mg/L)
1.	COD	250
2.	BOD	30
3.	TSS	100
4.	pH	7.5
5.	Oil and Grease	10
6.	Total Hardness	180
7.	Kjeldahl Nitrogen	20

1.3 Treatment Techniques for Textile Wastewater

Textile industries pose significant environmental challenges due to the complex composition of their wastewater, which contains various pollutants such as dyes, heavy metals, and organic compounds. Effective treatment methods are essential to mitigate the adverse impacts of textile wastewater on the environment and public health. These treatment techniques can be broadly categorized into physical, chemical, and biological methods.

1.3.1 Physical Treatment Techniques for Textile Wastewater

Physical treatment techniques focus on the removal of contaminants from textile wastewater through physical processes without involving chemical or biological reactions. These methods are effective for removing suspended solids, colloidal particles, and larger contaminants. Physical treatment techniques are often employed as preliminary or primary treatment steps in wastewater treatment processes. They are particularly effective for removing large particles and suspended solids, which can interfere with subsequent chemical or biological treatment

processes. However, physical treatment alone may not be sufficient to meet discharge standards, and it is often combined with chemical or biological treatment methods for comprehensive wastewater treatment. Here are some key physical treatment techniques used in textile wastewater treatment:

1.3.1.1 Filtration

Filtration processes involve passing wastewater through physical barriers such as sand beds, multimedia filters, or membrane filters. These barriers effectively trap suspended solids, colloidal particles, and other contaminants, allowing only clean water to pass through.

1.3.1.2 Sedimentation

Sedimentation is a process where suspended particles in wastewater settle under the influence of gravity. As wastewater flows slowly through a settling tank or clarifier, heavier particles settle to the bottom as sludge, while clearer water is collected from the top.

1.3.1.3 Adsorption

Adsorption techniques utilize adsorbent materials such as activated carbon, zeolites, or silica gel to remove pollutants from wastewater. Pollutants adhere to the surface of the adsorbent material through physical forces such as Van der Waals forces or electrostatic interactions, effectively removing them from the wastewater stream.

1.3.2 Chemical Treatment Techniques for Textile Wastewater

Chemical treatment techniques involve the use of chemical agents to alter the composition of pollutants in textile wastewater, facilitating their removal or degradation. These methods are effective for treating various pollutants such as dyes, heavy metals, and organic compounds. Here are some key chemical treatment techniques used in textile wastewater treatment:

1.3.2.1 Coagulation and Flocculation

Coagulation involves the addition of coagulants such as alum (aluminum sulfate) or ferric chloride to destabilize colloidal particles in wastewater. Flocculation follows coagulation and involves the addition of flocculants such as polymers to promote the aggregation of destabilized particles into larger flocs. The formed flocs settle more rapidly, allowing for easier removal of suspended solids and colloidal particles from the wastewater.

1.3.2.2 Precipitation

Precipitation methods involve the addition of chemicals to textile wastewater to induce the formation of insoluble precipitates. Common precipitating agents include lime (calcium hydroxide) or sodium hydroxide, which raise the pH of wastewater, causing the precipitation of metal hydroxides or sulfides. The precipitated solids can then be separated from the wastewater through settling or filtration.

1.3.2.3 Oxidation-Reduction Reactions

Chemical oxidation methods involve the use of oxidizing agents such as chlorine, hydrogen peroxide, or ozone to degrade organic pollutants in textile wastewater. Oxidizing agents react with organic compounds, breaking them down into simpler, less harmful substances through oxidation-reduction reactions. Advanced oxidation processes (AOPs), such as ozonation or photocatalysis, generate highly reactive hydroxyl radicals to effectively degrade persistent organic pollutants.

1.3.3 Biological Treatment Techniques for Textile Wastewater

Biological treatment techniques harness the metabolic activities of microorganisms to degrade organic pollutants present in textile wastewater. These methods are environmentally friendly and can effectively treat a wide range of organic contaminants. Here are some key biological treatment techniques used in textile wastewater treatment:

1.3.3.1 Activated Sludge Process

The activated sludge process is a widely used biological treatment method for wastewater. In this process, wastewater is aerated and mixed with a culture of aerobic microorganisms (activated sludge) in aeration tanks. The microorganisms metabolize organic pollutants present in the wastewater as a food source, converting them into carbon dioxide, water, and biomass. The treated wastewater is then separated from the biomass in a secondary clarifier, and excess biomass (activated sludge) is recycled back to the aeration tank to maintain the microbial population.

1.3.3.2 Biological Aerated Filters (BAFs)

Biological aerated filters (BAFs) are fixed-film biological treatment systems that utilize attached growth microorganisms to degrade organic pollutants. Wastewater flows through a filter media bed containing biomass, where organic pollutants are metabolized by aerobic microorganisms attached to the media surface. BAFs provide a large surface area for microbial growth and are particularly effective for treating high-strength wastewaters with variable flow rates.

1.3.3.3 Anaerobic Digestion

Anaerobic digestion is a biological treatment process that operates in the absence of oxygen and utilizes anaerobic microorganisms to degrade organic pollutants. Organic pollutants in textile wastewater are converted into methane, carbon dioxide, and other byproducts through a series of microbial metabolic pathways. Anaerobic digestion not only reduces the organic content of wastewater but also produces biogas, a renewable energy source that can be utilized for heat and power generation.

1.4 Bioreactor

A bioreactor, the core of biological processes, is a vessel in which biochemical transformation takes place. The medium comprises microorganisms, enzymes, animal cells, and plant cells in which environmental conditions, viz. temperature, dissolved oxygen, pH, etc., have to be tuned to meet the stringent optimum parameter so that yield is enhanced. The biological transformation and integration of physical and chemical aspects of the process make it complicated. The design of the bioreactor system considers the cell growth, metabolic activity, genetic transformations, and enzyme activity, accordingly adjusts the physical and chemical environment, and favors the hostile conditions for microorganisms or enzymes. The general design of a bioreactor system has illustrated in **Figure 1.3**. The bioreactor system is a cylindrical vessel having a central shaft controlled by an electrical motor that supports impellers. Baffles are installed for attaining a maximum mixing with suppression of swirling of fluid streams. The cooling jacket is attached to the outer periphery of the bioreactor assembly for controlling the temperature. To regulate environmental factors like temperature, oxygen concentration, pH, cell mass, levels of vital nutrients, and product concentration, a variety of devices are used. Sampling, feeding, cleaning, emptying, and sterilization ports are attached to the bioreactor assembly. Aeration is necessary for a continuous bioprocess and is achieved with the introduction of air through attached spargers. Materials of construction should be corrosive resistant and tolerate high pressure, steam sterilization, and pH change. It is crucial to keep the amount of foam in the bioreactor to a minimum level to prevent contamination. The bioreactor has a foam-controlling mechanism attached to the top with an entrance into the bioreactor.

Various types of bioreactors are designed according to the process. The hydrodynamic parameters such as flow rate, liquid level, agitation/mixing, mass transfer parameter (e.g., dissolved oxygen concentration), and the supplement of nutrient concentrations have to be optimized (S. J. Wang and Zhong, 2007a). The bioreactor system has a batch and fed-batch

(continuous) mode based on the operation. A Bioreactor should possess the characteristic features including perfect aeration and agitation for attaining maximum mass transfer, energy consumption should be the minimum, ability to monitor and control pH and temperature fluctuations. Process control and monitoring are one of the most important operation requirements that should be achieved by every bioreactor.

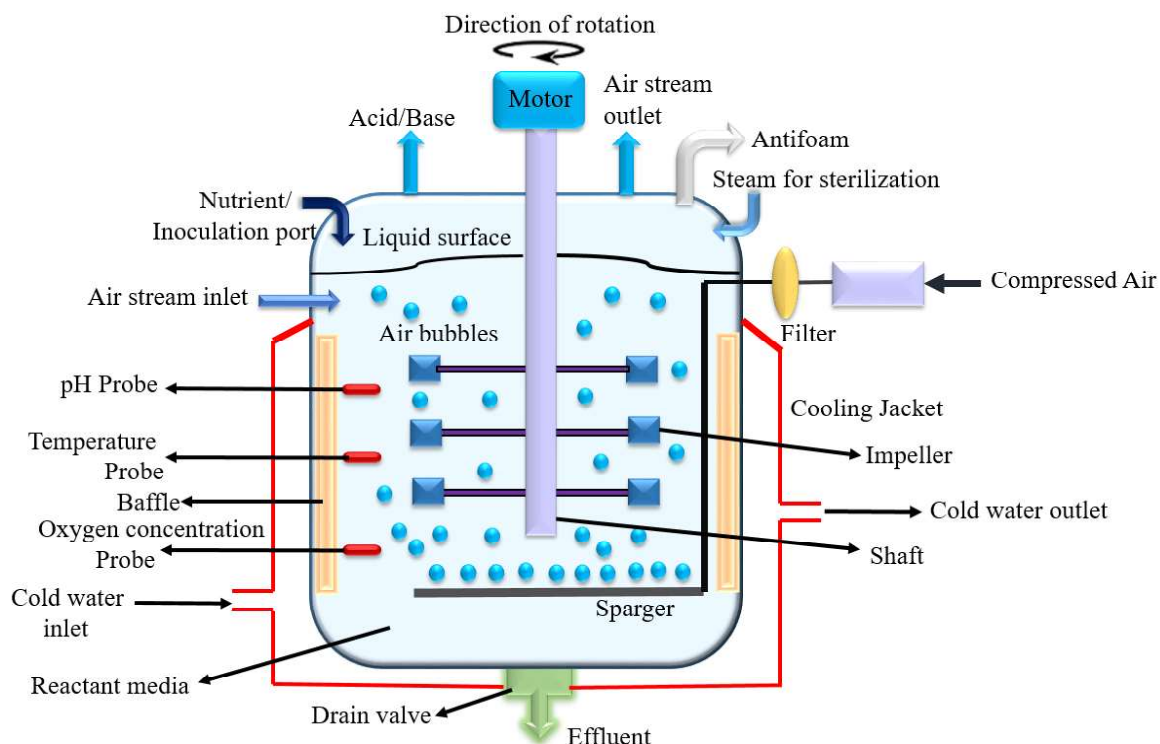


Figure 1.3. General layout of a typical bioreactor setup

1.5 Types of Bioreactors

The bioreactor is an essential apparatus for the smooth conducting of biochemical transformations. Based on the requirement of the process, various types of bioreactors are employed. Membrane Bioreactor, Fluidized Bed Bioreactor, Moving Bed Bioreactor, Packed Bed Bioreactor, Airlift Bioreactor, Stirred Tank Bioreactor, Fixed Bed Bioreactor, and Rotating Biological Contactor are usually used for textile wastewater treatment. Among them Packed bed bioreactor is abundantly useful for laboratory-scale textile wastewater treatment. It can be

considered the best in terms of removal, energy consumption, and dye degradation (Tiwari et al., 2023).

1.5.1 Membrane Bioreactor (MBR)

A membrane bioreactor (MBR) is a wastewater treatment process that combines biological treatment with membrane filtration. In traditional wastewater treatment plants, microorganisms break down organic matter, and then the treated water is separated from the biomass through settling. In MBR systems, however, membranes with fine pores are used to separate the treated water from the biomass, allowing for a higher level of purification. The membranes used in MBRs can be made of various materials such as polymeric or ceramic, and they act as barriers to bacteria, suspended solids, and pathogens, producing high-quality effluent. MBRs offer several advantages over conventional wastewater treatment methods, including smaller footprint, better treated water quality, and the ability to operate at higher biomass concentrations. Membrane bioreactors can operate either in an aerobic or anaerobic mode for the treatment of textile industry wastewater.

MBR generally has two configurations reported by Galinha et al. (2018). These are the external loop recycle reactor and submerged membrane reactor, as shown in **Figure 1.4**. In the first configuration, membrane assembly is attached externally to a reactor system; retentate is allowed to recycle within the reactor system while the permeate free from biocatalyst allows to effluent stream. The operating conditions independently change either in the reactor unit or in the membrane assembly. The submerged membrane reactor unit incorporates the direct submergence of the membrane modules into the reactor system, flat sheet, and hollow fiber configurations use. This reactor assembly operated in an aerobic environment, aeration allows the improved mass transfer, solid contents to be in suspension, maintains necessary oxygen content for microbial growth, and reduction in membrane fouling.

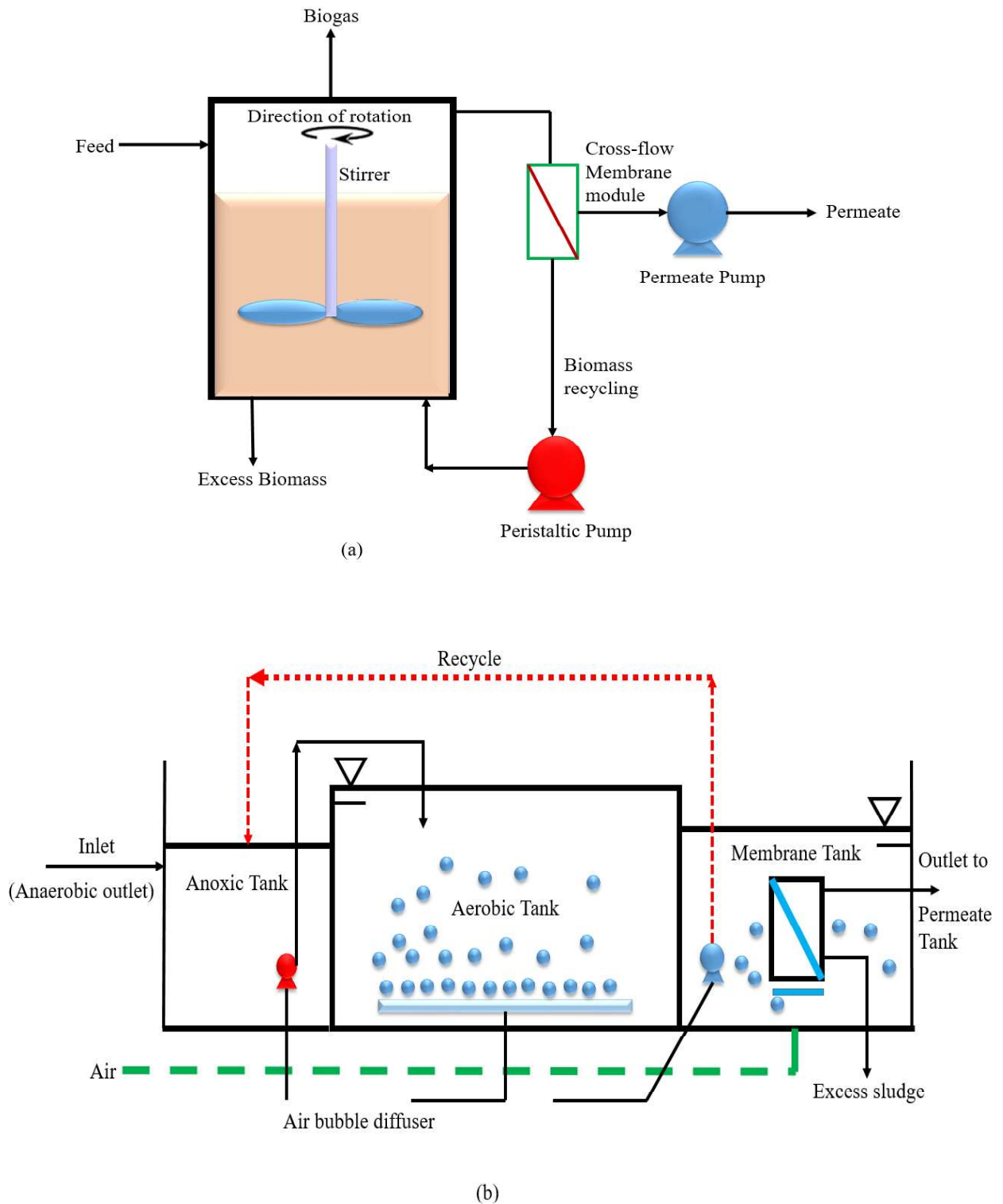


Figure 1.4. (a) External loop recycle reactor, (b) Submerged membrane reactor

1.5.2 Fluidized Bed Bioreactor (FBBR)

A fluidized bed bioreactor (FBBR) is a type of bioreactor used for various biological processes, including wastewater treatment, fermentation, and bioconversion of organic materials. In an

FBBR, solid particles (often granular media like sand or activated carbon) are suspended and fluidized by the upward flow of a liquid or gas, creating a bed of particles that behaves like a fluid (**Figure 1.5**). In wastewater treatment applications, FBBRs utilize microbial activity within the fluidized bed to degrade organic pollutants present in the wastewater. The fluidized bed provides an ideal environment for microbial growth and activity, as the constant mixing ensures efficient contact between the microorganisms and the wastewater. The biofilm formed on the surface of the fluidized particles serves as the active site for pollutant degradation. It offers several key features, such as low operating cost, simplicity in design and construction, high tolerance to system upsets, perfect mixing between interphases decreases mass transfer resistance, and elimination of bed clogging and high-pressure drop (Burghate and Ingole, 2013; Jaafari et al., 2014; Sivakumar V et al., 2010).

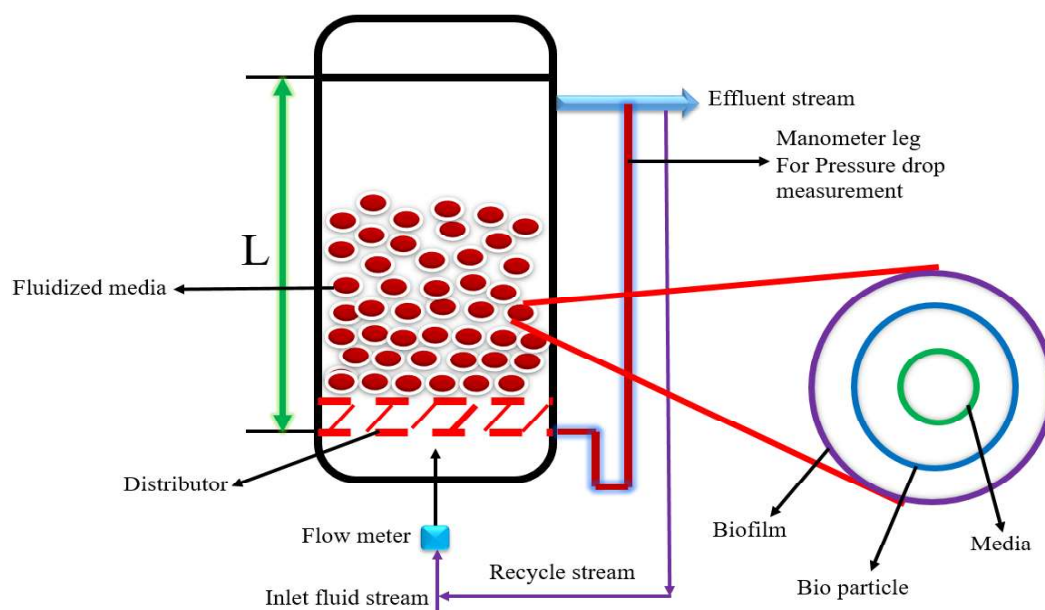


Figure 1.5. Fluidized bed bioreactor

1.5.3 Moving Bed Bioreactor (MBBR)

MBBR, also popularly known as biofilm-based reclamation technology, allows to grow of biofilm into/onto the surface of the carrier elements, and is floated freely by the moving fluid

stream, leading the significant contribution in the field of wastewater treatment (Tang et al., 2021; Vyrides et al., 2018; S. Wang et al., 2020). Different types of biofilm carrier elements, examples including polyethylene (density is 0.95 g/cm^3), high-density polyethylene (HDPE), and polypropylene (PP) (Barwal and Chaudhary, 2014), containing high specific surface area for biofilm development, easily flow in the presence of either aerobic or anaerobic conditions in the bioreactor, successfully used (Kora et al., 2020; S. Wang et al., 2020).

Microorganisms tend to agglomerate and proliferate their colonies by forming a biofilm. Biofilm is either an attached growth system or a suspended growth system (Asri et al., 2019). The existence of biofilm on the carrier is dynamic, where simultaneous attachment and detachment of biofilm happens at a steady-state (Eldyasti et al., 2013; Q. Gu et al., 2014; Walter et al., 2013). The presence of biofilm on packing material adheres to a large number of substrates from wastewater. The biofilm comprises different microbial species, and the mineralization of substrates containing carbon, and nitrogen constituents take place and enhances the removal efficiency (Wang et al., 2019). MBBR can be operated in either aerobic or anaerobic processes, as illustrated in **Figure 1.6**. The movement phenomenon of carrier elements containing biofilm is different in aerobic and anaerobic MBBRs. Air current agitation is responsible for the upward movement of the carrier in the oxic/aerobic system, while in the case of an anaerobic/anoxic system, either a horizontal or vertical mechanical mixer is impelling the resulting motion of the carrier element (Rusten et al., 2006).

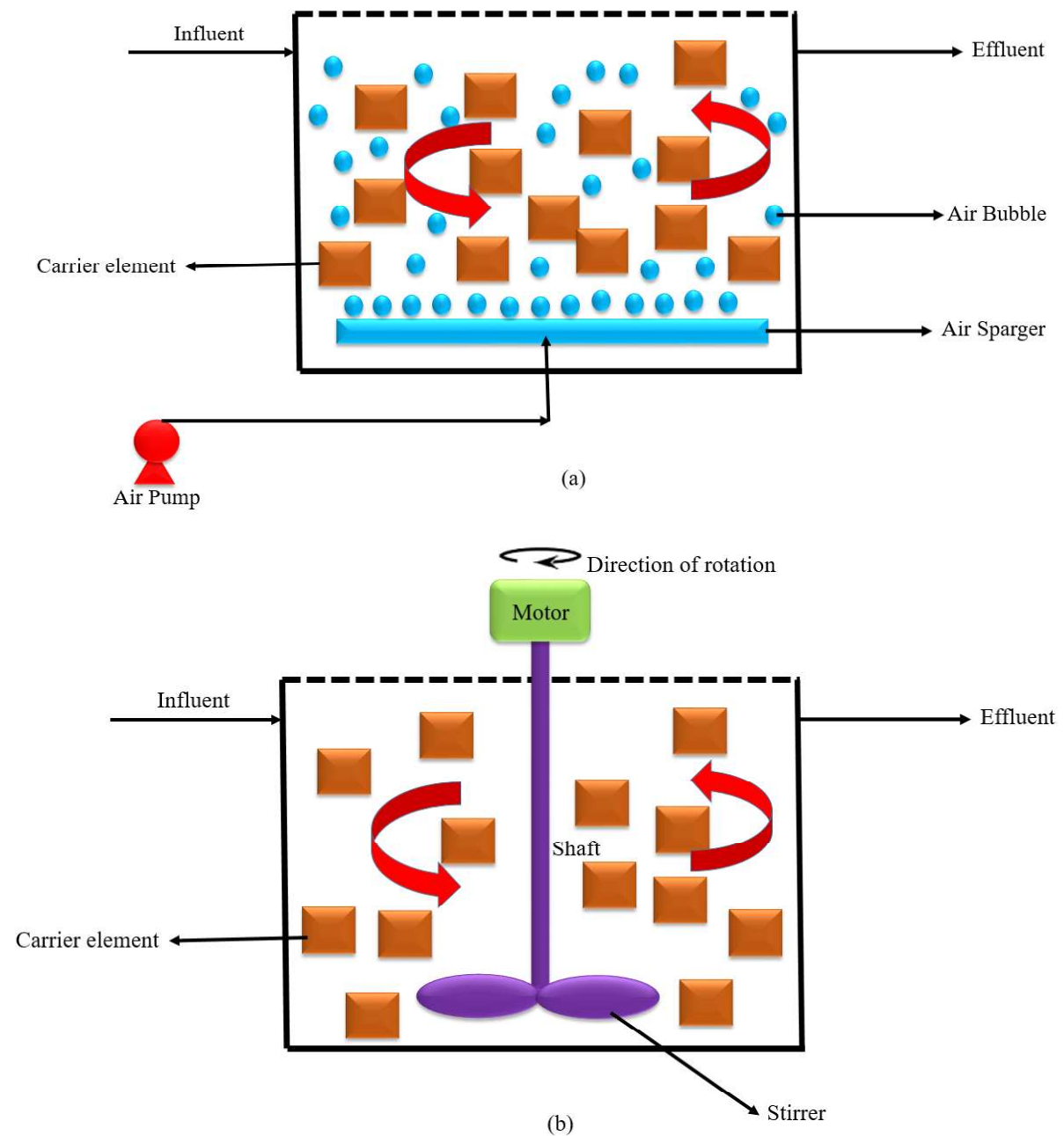


Figure 1.6. (a) Oxidic/Aerobic MBBR, (b) Anaerobic/Anoxic MBBR

1.5.4 Packed Bed Bioreactor (PBBR)

A packed bed reactor (PBR) is considered the most common device for carrying out a two-phase catalytic (heterogeneous) reaction in a typical chemical plant. Moreover, it prevails the continuous contact of the reaction mixture within the vertical stationary tubular bed filled with

catalyst particles. The same operating principle has been applied to the design and operation of the packed bed bioreactor (Sen et al., 2017).

A packed bed bioreactor (PBBR) consists of a cylindrical column, equipped with an air inlet, the feed liquid inlet, and distributing space at the bottom, air and treated liquid outlets at the top, and supported with a mass of inert solids, called column packing, is abundantly used for wastewater bioremediation (Swathi et al., 2021). Porous or non-porous solid particles are placed over the packing support, imparted to give it strength, and randomly packed in the reactor. A typical PBBR schematic has been illustrated in **Figure 1.7**.

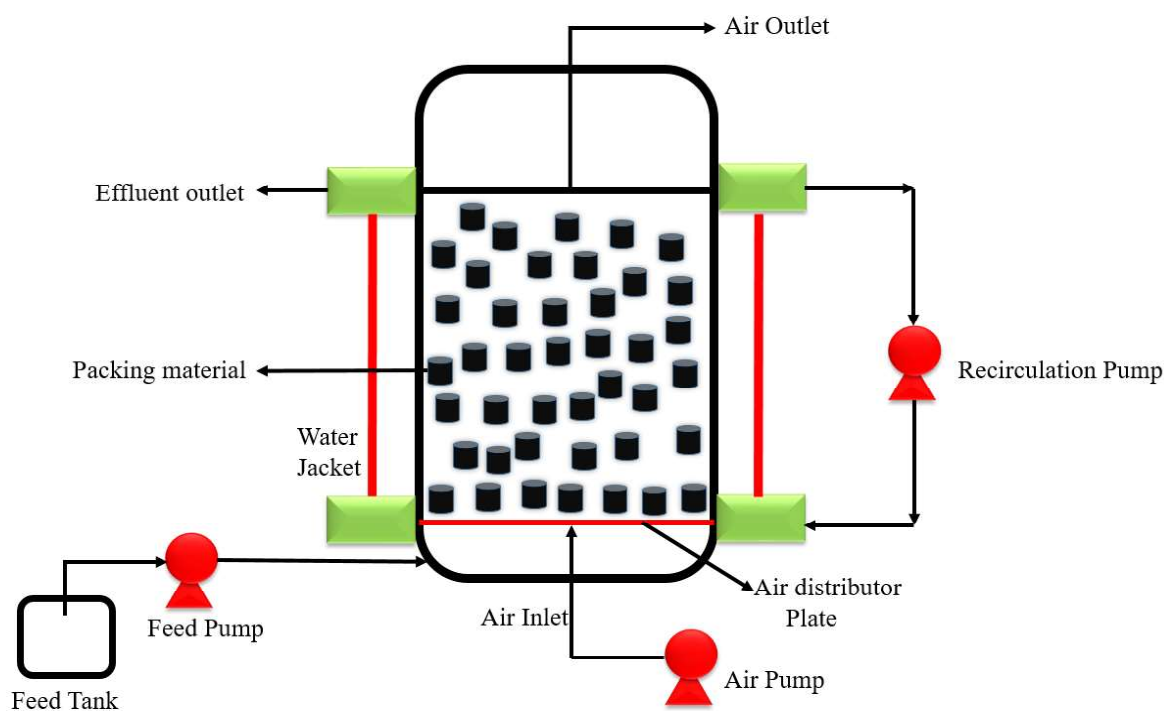


Figure 1.7. Schematic layout of a general Packed Bed Bioreactor

Common dumped packing is made of polymers such as polyurethane foam (PUF) (Swain et al., 2021), polyethylene terephthalate (PET) (Hermann et al., 2020), low-density polyethylene (LDPE) (Sonwani et al., 2019) and macroporous polymeric support (MPPS) (Arikan et al., 2019) are proposed. Biochar is considered an alternate cheap packing material, synthesized from raw biomass, and abundantly available in nature (Abu Talha et al., 2018; Bharti et al.,

2019). Microbial cell cultures and enzymes as biocatalysts have immobilized on or within the stationary inert solid particles (Arikan et al., 2019; Sondhi et al., 2018; Zolfaghari et al., 2019). The construction and operation of PBBR are simple and facilitate efficient contact between the two phases (Jaibiba et al., 2020). The substrate is introduced in a packed section with three possible flow patterns, namely downward flow, upward flow, and recycling (Sen et al., 2017). The behavior of flowing fluid in the vertical tubular column is resembled somewhat "Plug flow or rod-like flow" in the case of an ideal PBBR. Exothermic biochemical reaction reasonably transfers the released heat to the surrounding environment by introducing fluid circulation through an attached jacketed section. Packed bed bioreactors provide several benefits: comprising process simplicity, ease in product quality control, and fastening the reaction rate, and so the mass transfer rate (Sen et al., 2017).

1.5.5 Airlift Bioreactor (ALR)

Airlift bioreactor also resembles a pneumatically driven agitated reactor (Pereira et al., 2021; S. J. Wang and Zhong, 2007), which is used for mixing, and circulation of liquid phase induced by the rising stream of injected air (Kadic and Heindel, 2014). A given nutrient culture-rich liquid medium can transfer the gaseous components, i.e., oxygen, with no difficulty. Since it contains no mechanical moving parts, therefore, comes under the motionless bioreactor. The reactor system has a draft tube that partitions the entire reactor into two interconnected regions: riser (inner gassed region) and downcomer (outer ungassed zone), respectively, the gas-liquid separator is supported for efficient disengagement of two phases at the top, and the base connects the riser and downcomer specifically (Aragão et al., 2020; Cozma and Gavrilescu, 2012; Guieysse et al., 2011), as illustrated in **Figure 1.8**.

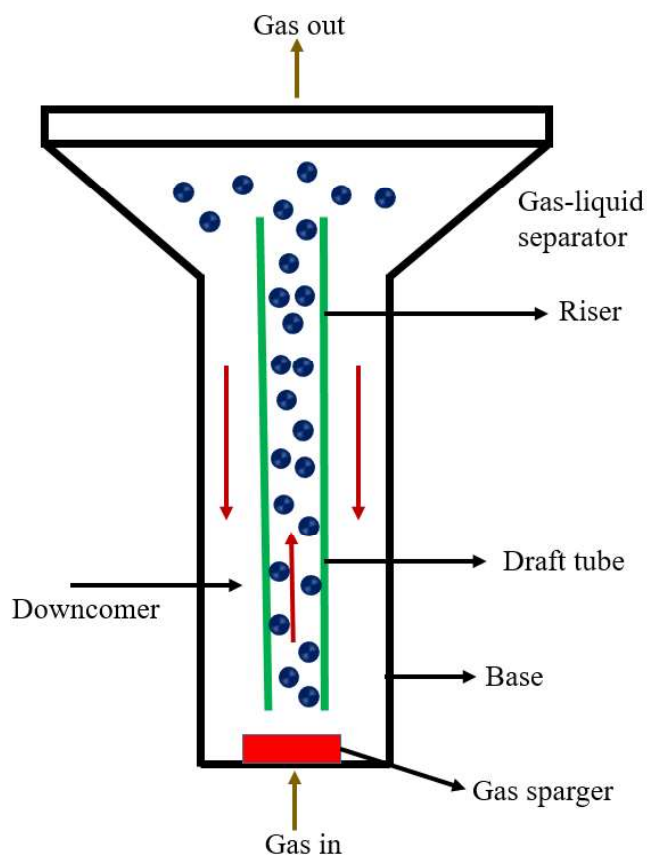


Figure 1.8. The general layout of an airlift bioreactor

These four zones have a distinct characteristic flow pattern; upward flow in the riser, recirculation flow in the downcomer, mixing at the base, and separation of phase at the gas-liquid separator (Cozma and Cozma, 2010; Mendoza Martnez and Escamilla Silv, 2013; Zhang et al., 2008). Circulation of liquid between the riser and downcomer attain at the top of the reactor, which distinguishes this reactor system from fluidized bed reactors, stirred tank reactors, and bubble column contactors (Cozma and Gavrilesco, 2012; Das and Mahalingam, 2020; Guieysse et al., 2011). Compressed air is injected through an airlift pump below the riser from the gas sparger at the bottom and withdrawn by the gas-liquid separator at the top (Rawat et al., 2019). Moreover, the mixing of compressed air with liquid reduces its density (apparent density) with the remaining liquid, induces a mean density gradient (acts as the driving force for continuous circulation) between riser and downcomer sections, and prevails the liquid circulation concomitantly (Aragao et al., 2020; Prado Barragán et al., 2016). Indeed, the fluid

dynamics of an airlift reactor has governed by circulation currents of liquid streams between a riser and the downcomer zones (Guieysse et al., 2011). Since the entire circulatory liquid motion has driven by the density gradient, so there is no specific section/point that dissipates energy, the homogeneous shear forces everywhere in each section exert low shear stress distribution even thoroughly into the reactor (Mendoza Martnez and Escamilla Silv, 2013; S. J. Wang and Zhong, 2007).

1.5.6 Stirred Tank Bioreactor (STBR)

Stirred tank bioreactor, a cylindrical well-mixed fermenter, is abundantly used for culturing suspension cells, enzymatic reactions, and yeast fermentation, therefore, is known as the “workhorse of the fermentation industry” (Garcia-Ochoa et al., 2011; Liu et al., 2021). A standardized STBR design as that illustrated in **Figure 1.9** is extensively applicable in industrial bioprocesses (Zhong, 2011).

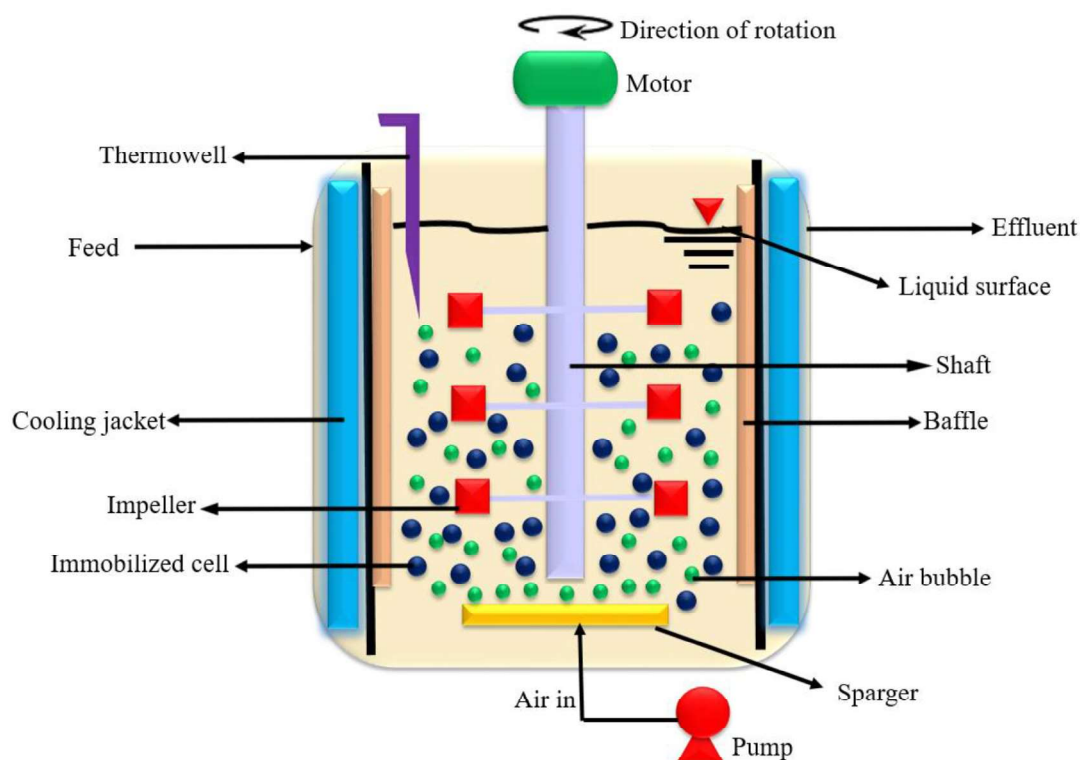


Figure 1.9. Typical stirred tank bioreactor

The rounded bottom tank, not flat, is applied to eliminate sharp corners and allows fluid currents penetration to an entire region. An impeller agitator has mounted on the supported

shaft, driven by the motor electrically (Sadhasivam et al., 2010). Axial-flow and radial-flow impellers, the two classes of agitated impellers, are often used in the fermentation industry (S. Wang and Zhong, 2007). As the impeller revolves, liquid circulation occurs through the bioreactor and is finally returned to the impeller. Two or more initial separate phases are randomly distributed through and into one another until they attain the degree of homogeneity, are called perfectly mixed, moreover, facilitate oxygen transfer (Liu and Wilkins, 2020), heat, and mass transfer (S. Wang and Zhong, 2007). STBR has certain practical advantages; such as easy scale-up, a higher degree of fluid mixing and an excellent transportation ability of oxygen, and the availability of various impellers to handle liquids of moderate-to-high viscosity (Schneider et al., 2018; Zhong, 2011).

1.5.7 Fixed Bed Bioreactor (FBR)

FBR is a cylindrical column or vessel, useful for shear-sensitive mammalian and tissue cells (Pörtner and Faschian, 2019). In FBR, the support material is allowed to pack in a fixed section of the bed, and culture media trickles, and circulate through it (Lazar, 1991). It consists of three phases, and the solid phase always remains fixed. Based on flow direction, it can be categorized into: (1) Packed bed reactors (PBRs), where countercurrent flow takes place, the liquid has sprayed at the top, and gas is introduced from the bottom section; (2) trickle bed reactors (TBRs), downward co-current flow of both liquid and gas phases occur from the top section (Kadic and Heindel, 2014). The culture medium can percolate between packing materials either continuously or in batches with low superficial velocity (De Oliveira Cruz et al., 2020). It facilitates the growth and subsequent immobilization of microorganisms on the macroporous support material (Beltrán-Flores et al., 2021; Pörtner and Faschian, 2019). Immobilization of microbial cells leads to an increase in the interfacial contact area and reaction rate. Fixed-bed reactor system exhibits low mass and heat transfer coefficients because of the lower liquid

superficial velocity (Zhong, 2011). Formation and accumulation of stagnant gas pockets alleviate gas flooding and seriously affect liquid distribution (S. Wang and Zhong, 2007).

Figure 1.10 depicted a general layout of FBR with two possible configurations having plug flow behavior.

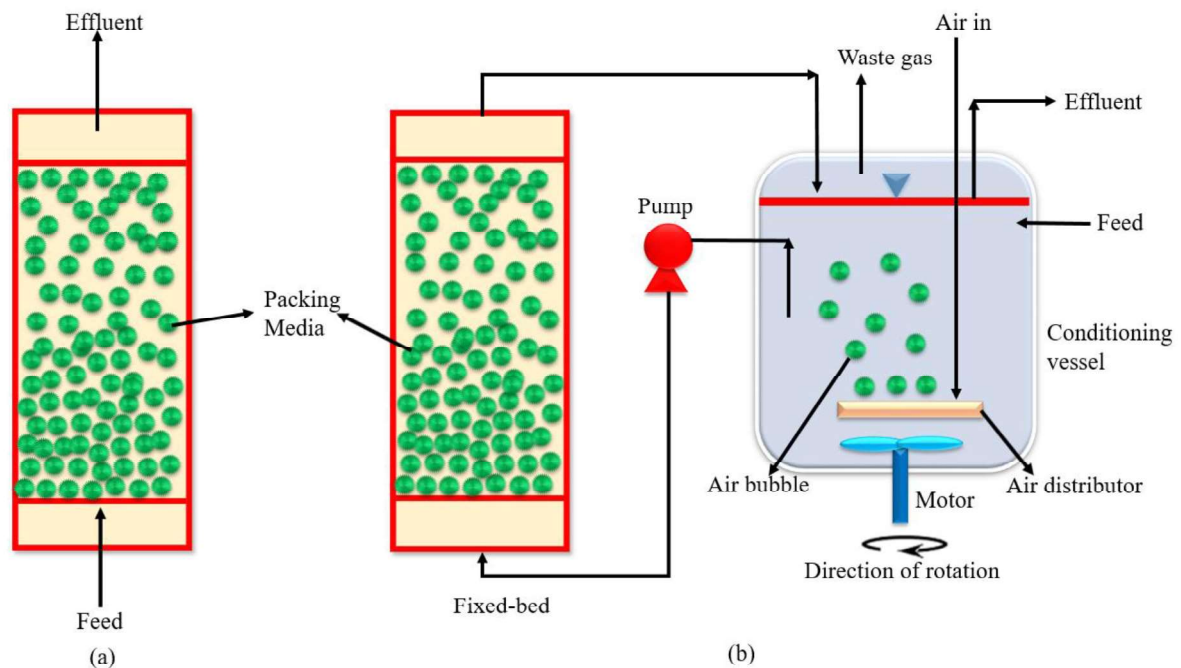


Figure 1.10. A general design of a Fixed-bed bioreactor system: (a) Axial-flow fixed bed with plug flow, (b) Axial-flow fixed bed with external conditioning vessel

1.5.8 Rotating Biological Contactor (RBC)

Rotating biological contactor (RBC) is an open biofilm-based attached growth reactor system and the best-known application is aerobic biological wastewater treatment (Courten et al., 2014; Li et al., 2019; Mized, 2021). A typical bioreactor system contains a series of equally spaced discs, either flat or corrugated, partially submerged (around 40%) in the wastewater tank, and are mounted on a central rotating shaft (Cortez et al., 2008; Datta Madamwar, Onkar Tiwari, 2019; Šíma et al., 2016) (**Figure 1.11**).

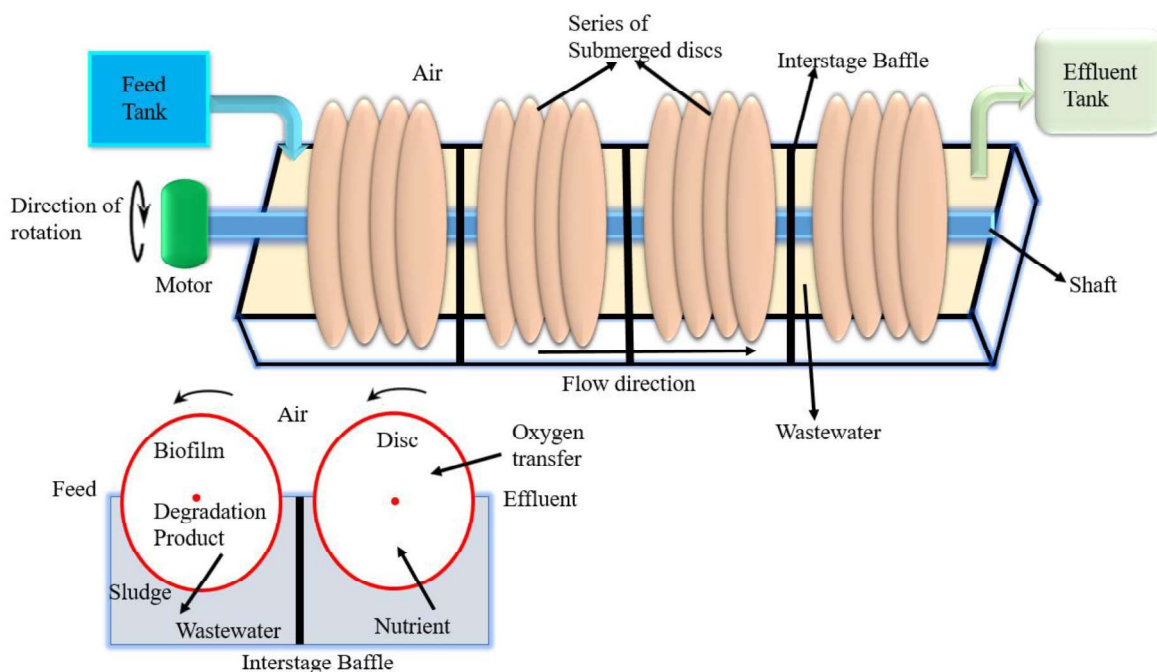


Figure 1.11. Rotary Biological Contactor (RBC)

Whenever possible, a disc made of polymers such as polyvinyl chloride (PVC), polyethylene, and polystyrene has been used. The configuration, surface area, submergence level, and texture considers the principal measure of the reactor performance (Li et al., 2019; Skybová et al., 2015). The specific surface area of discs has further improved by fixing them with softwood, polypropylene, and polyurethane sponges (Hewawasam et al., 2017; Sirianuntapiboon, 2006). Thus, the increased specific surface area of discs facilitates biomass attachment and growth (Gopi Kiran et al., 2017), moreover, improves the contact between the pollutants and microorganisms (Pakshirajan and Kheria, 2012). The rotation brings the disc surface, alternately in direct contact with wastewater and atmospheric air, which allows the microorganisms to grow on the disc surface, and ultimately biofilm formation occurs (Ravi et al., 2013). The submergence of discs into the wastewater allows the biofilm in direct contact with target pollutants, which are getting adsorbed with biofilm, the remaining fraction of rotation alleviates the diffusion of oxygen through the layer of wastewater within the biofilm, beginning the biodegradation of pollutants (Ravi et al., 2013).

RBC systems are simple in design, can be easily operated, and are resistant to high hydraulic and organic loadings. It considerably consumes a low amount of energy, compactness, and a small ecological footprint, which provided the utmost importance for wastewater treatment (Hewawasam et al., 2017). However, the agglomeration of reproduced biomass on the disc surface restricts the substrate and oxygen transmission, which causes the bioactivity and oxygen transfer rate (OTR) to diminish (Chern et al., 2001). The higher substrate degradation rate and oxygenation capacity achieve by increasing the rotational speed but at a price of large power consumption (Israni et al., 2002; Ramsay et al., 2006). Meanwhile, due to the higher rotational speed of discs, biofilm detaches from the periphery of the discs, so the degradation rate declines (Cortez et al., 2008; Courtens et al., 2014). The rotational speed of the disc ranges from 100 to 300 rounds per hour (rph), which results in the oxygen transfer coefficients (K_{La}) magnitude varying from 30 to 100 d^{-1} (Courtens et al., 2014). Hewawasam et al. (2017) have designed a novel rotating sponge (RS) reactor to study the oxygen transfer dynamics and nitrification; the volumetric oxygen transfer rate in the reactor is 245 $mg\ O_2\ L^{-1}d^{-1}$ at the disc rotational speed of 10 rounds per hour (rph).

The rotating biological contactor is particularly effective for the treatment of greywater, wastewater contaminated with heavy metal, industrial wastewater, hospital wastewater, domestic sewage, organic pollutant, oxygen-limited autotrophic nitrification/denitrification, and gas-phase biodegradation of volatile organic carbon (Abdel-Kader, 2013; Gopi Kiran et al., 2017; Li et al., 2019; Rana et al., 2018; Ravi et al., 2013; Vlaeminck et al., 2009). Furthermore, the implementation of the RBC system has proliferated for the biological treatment of textile wastewater (Axelsson et al., 2006; Karapinar Kapdan and Kargi, 2002; Novotný et al., 2012; Sima et al., 2016, 2012; Vairavel and Murty, 2020).

1.6 Hybrid Techniques

Hybrid techniques for textile wastewater treatment combine different treatment techniques to mineralize the pollutants efficaciously. It is anticipated that each dye removal process has its advantages and shortcoming too, so a synergistic combination of different techniques can comprehensively remove the dye from wastewater (Samsami et al., 2020). In hybrid processes, the integration of different treatment techniques provides the flexibility to adjust and optimize each method according to the specific requirements of the wastewater (Su et al., 2016). However, some textile dyes are recalcitrant and have a low biodegradability index (BOD/COD < 0.2), exhibiting a slow rate of biodegradation (Thorat and Sonwani, 2022). In such cases, single biodegradation is not sufficient for the complete degradation, hence some additional technique is needed which facilitate the preliminary treatment and enhance the biodegradability. One such hybrid technique that has received critical attention is the combination of photocatalysis and biodegradation (Lu et al., 2022; Yu et al., 2020). The integration of photocatalysis and biodegradation eliminate the challenges posed by recalcitrant dye compounds. Photocatalytic oxidation liable for the preliminary treatment of dye wastewater, efficiently degrade a significant portion of dye molecules, and thereby form small and more biodegradable intermediate compounds (Waghmode et al., 2019). These intermediates serve as a feedstock for the microorganisms in a sequential biodegradation step, promoting their growth and ensure the complete mineralization (Chen et al., 2014). There are two main ways to combine photocatalysis and biodegradation for wastewater treatment: a) Independent Sequence of Photocatalysis and Biodegradation (ISPB) and b) Intimate Coupling of Photocatalysis and Biodegradation (ICPB) (Lu et al., 2022).

1.6.1 Independent Sequence of Photocatalysis and Biodegradation (ISPB)

Independent sequence of Photocatalysis and Biodegradation (ISPB) refers to the textile wastewater treatment approach where photocatalysis and biodegradation are performed as separate and sequential steps (Lu et al., 2022). In this technique, wastewater is subjected to photocatalytic oxidation with a suitable photocatalyst, such as Titanium (IV) Oxide, which incorporates light energy for the cleavage of organic compounds into smaller compounds. After the photocatalytic oxidation, the treated water is subjected to biodegradation, where microorganisms subsequently degrade the photocatalytic oxidized products into harmless substances (**Figure 1.12**). ISPB facilitates the efficient removal of organic pollutants by sequentially utilizing two distinct techniques, contributing to a more efficient and comprehensive treatment process (Deveci et al., 2016).

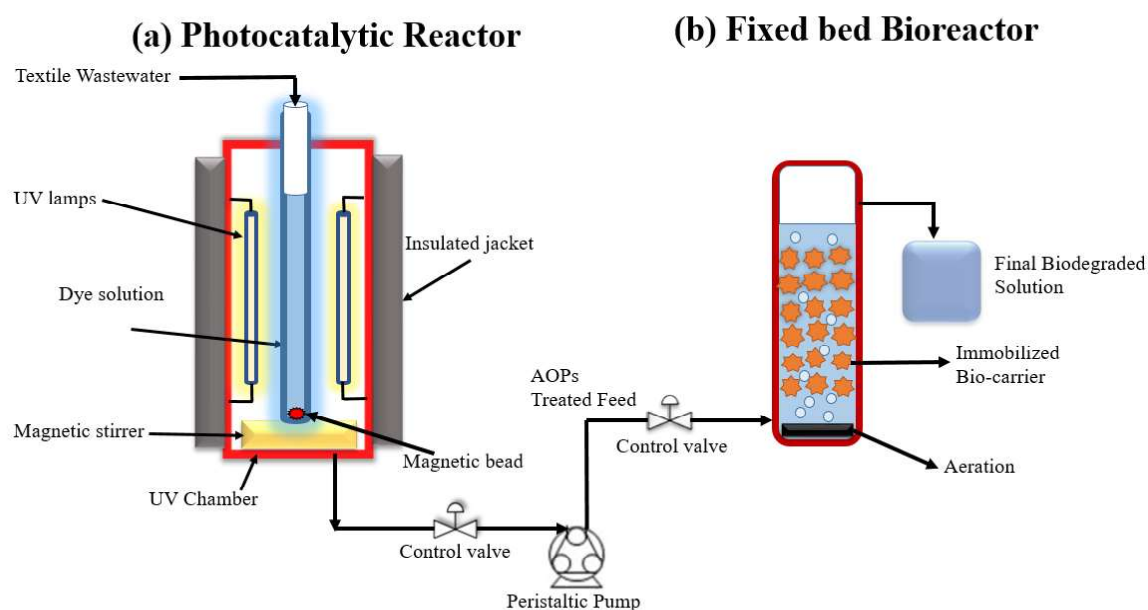


Figure 1.12. A typical sequential Photocatalytic and Fixed-Bed Bioreactor setup

1.6.2 Intimate Coupling of Photocatalysis and Biodegradation (ICPB)

Intimate coupling of Photocatalysis and Biodegradation (ICPB) is a textile wastewater treatment technique incorporating the simultaneous integration of photocatalysis and

biodegradation processes (**Figure 1.13**). In this method, photocatalysis and biodegradation processes occur in close proximity within the same reactor, viz. Photobioreactor, creating a synergistic effect that enhances the overall treatment efficiency (Zhang et al., 2021). The reactor is typically designed to provide optimal conditions for both processes. The photocatalyst is subjected to immobilization on a support material within the reactor. The photocatalyst generates reactive oxidative species (ROS) when exposed to light, and is liable for the organic pollutants breaking down and converting them into smaller and more biodegradable compounds (Yu et al., 2020). Simultaneously, the microorganisms are introduced, thrive in the environment of photocatalytically generated ROS, begin the degradation of biodegradable compounds, and convert them into simple non-toxic compounds such as water and carbon dioxide.

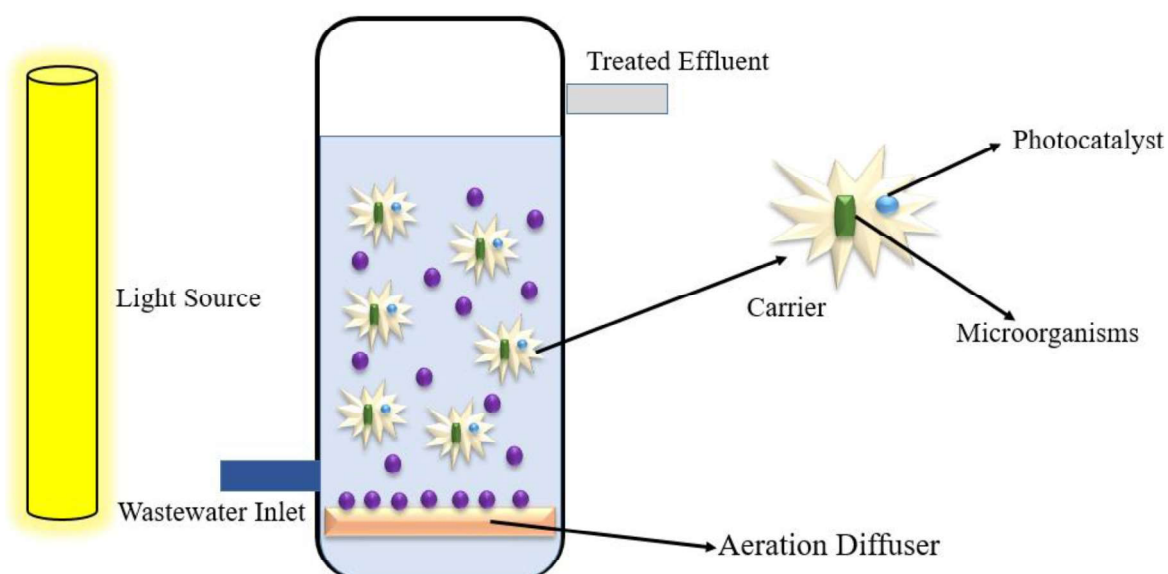


Figure 1.13. A schematic illustration of Intimate coupling of photocatalysis and biodegradation (ICPB)

1.6.3 Advantages and limitations of ISPB and ICPB techniques

ISPB and ICPB are usually used for the complete mineralization of recalcitrant organic compounds. However, both techniques exhibit numerous process advantages along with their

limitations. The choice between the two techniques depends on the specific wastewater treatment requirements and the nature of the pollutants to be removed. ISPB provides flexibility and versatility, while ICPB offers enhanced treatment efficiency and a more compact system. A comparative study of key features and limitations of both the ISPB and ICPB techniques is summarized in **Table 1.4**.

Table 1.4 A comparative analysis of the advantages and limitations of ISPB and ICPB techniques.

Techniques	Advantages	Limitations
ISPB	<ul style="list-style-type: none"> • ISPB allows for independent optimization of photocatalysis and biodegradation parameters, enabling the use of specific photocatalyst and microorganisms most suitable for each process. • It is effective in degrading complex and recalcitrant pollutants since photocatalysis initiates the breakdown, and biodegradation further degrades the resulting smaller compounds. • It enables precise control over reaction conditions, facilitating the optimization of individual processes for maximum efficiency. • It can be applied to a broader range of pollutants and wastewater types, making it a versatile approach for various industrial and municipal applications. • Both photocatalysis and biodegradation are well-established technologies, making ISPB easier to implement and scale up in existing wastewater treatment systems. 	<ul style="list-style-type: none"> • Since ISPB involves sequential reactions, the overall treatment time may be longer compared to ICPB, which conducts simultaneous reactions. • During the sequential treatment, some intermediate products generated during photocatalysis may not be efficiently degraded during biodegradation, leading to the accumulation of residual pollutants. • Implementing two separate treatment steps may increase the complexity of the system and require additional operational and monitoring efforts.

ICPB

- ICPB provides a synergistic effect in which photocatalysis and biodegradation occur simultaneously, leading to enhanced treatment efficiency and faster pollutant removal.
 - The combined action of photocatalysis and biodegradation facilitates the degradation of more complex dyes that are difficult to remove with individual processes.
 - The photocatalytic oxidation generates smaller and more biodegradable compounds, making them more accessible and attractive to microorganisms, thereby promoting faster and more efficient biodegradation.
 - It requires a single reactor, resulting in a smaller footprint, and needs lower operational and maintenance costs compared to ISPB.
 - It can lead to the complete mineralization of pollutants into non-toxic by-products, ensuring complete mineralization and reducing environmental impact.
- Integration of photocatalysis and biodegradation needs optimization of reaction conditions, such as light intensity, photocatalyst loading, and microbial activity, to attain maximum efficiency.
 - The presence of ROS may affect the activity of certain microorganisms, and affect the biodegradation process.
 - The stability of photocatalysts in the presence of microorganisms is crucial to achieving long-term performance, as some catalysts may be susceptible to degradation or fouling.
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1.7 Graphene-based Nanomaterials

Graphene-based nanomaterials have emerged as a promising class of materials due to their unique properties, including high surface area, excellent mechanical strength, and outstanding electrical and thermal conductivity (Gusain et al., 2020). These materials are composed of single or few layers of graphene, which is a two-dimensional carbon allotrope arranged in a honeycomb lattice. Graphene, Graphene Oxide (GO), Reduced Graphene Oxide (rGO), Graphene Nanoplatelets (GNP), Graphene Quantum Dots (GQDs), Graphene Aerogels, and Graphene Nanoribbons (GNRs) are commonly used nanomaterials for a wide range of applications including environmental remediation (Ferrand et al., 2020; Zhang et al., 2022). In the context of textile wastewater treatment, graphene-based nanomaterials have shown gigantic potential for organic pollutant removal from wastewater. They can be utilized as catalysts, adsorbents, and support materials for immobilizing microorganisms (viz. Nanobiocatalysts) to enhance the biodegradation of organic pollutants (Banerjee et al., 2018).

1.7.1 Graphene

Graphene is a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice (Sharma and Kamalesu, 2023) (**Figure 1.14**). It is the basic building block of other carbon-based materials such as graphite, carbon nanotubes, and fullerenes. It possesses exceptional properties, such as high thermal and electrical conductivity, a large surface area, and excellent mechanical strength (Du et al., 2023). Due to these unique characteristics, it finds a versatile nanomaterial for a wide range of applications comprising electronics, biomedical devices, energy storage, and water purifications. Recently it gains a significant research interest worldwide among researchers as having a potential impact on scientific research and multiple industries.

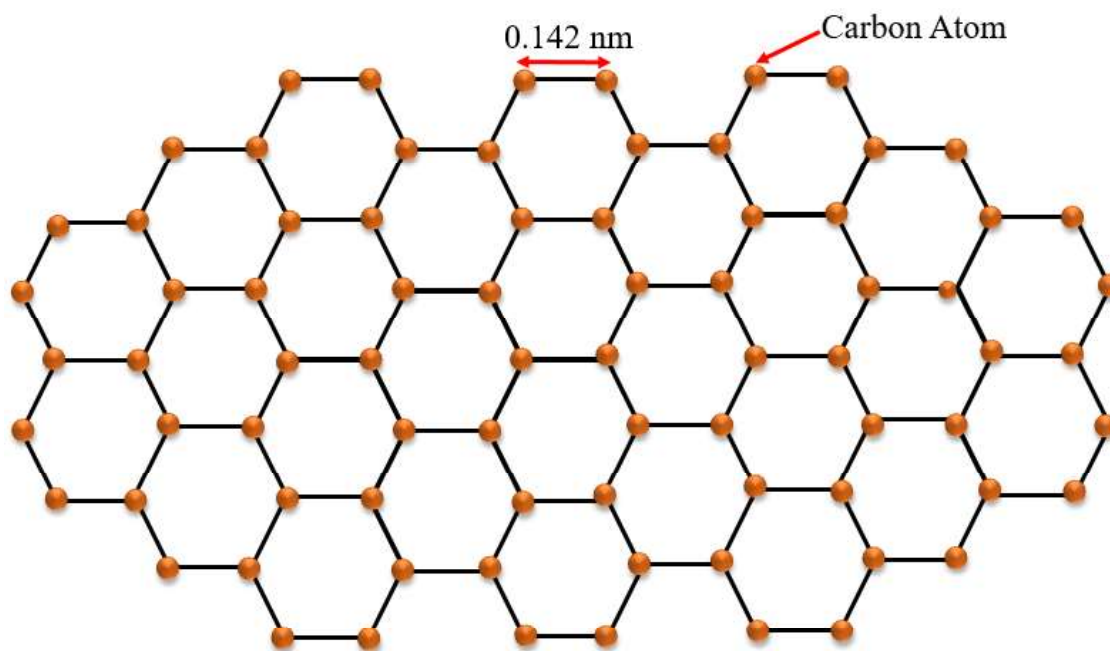


Figure 1.14. Schematic illustration of Graphene sheets

1.7.2 Graphene Oxide

Graphene Oxide (GO) belongs to the family of graphene-based nanomaterials and is derived from graphite through chemical oxidation (Wu et al., 2023). It is a single-atom-thick layer of carbon having a two-dimensional honeycomb lattice structure (Priyadarsini et al., 2018). It has numerous oxygen-containing functional groups including epoxy, hydroxyl, and carboxyl groups on its edges and at basal planes (Aliyev et al., 2019) (**Figure 1.15**). Its high surface area, hydrophilic nature, and presence of abundant functional groups are liable for the strong interactions with various pollutants including heavy metals and organic compounds (de Araujo et al., 2022). It exhibits excellent adsorption capabilities, and due to this feature, it has been remarkably employed for the removal of textile dyes from wastewater (Li et al., 2018). Its exceptional mechanical strength and electrical conductivity along with various applications in the field of environmental remediation has garnered significant attention in recent years.

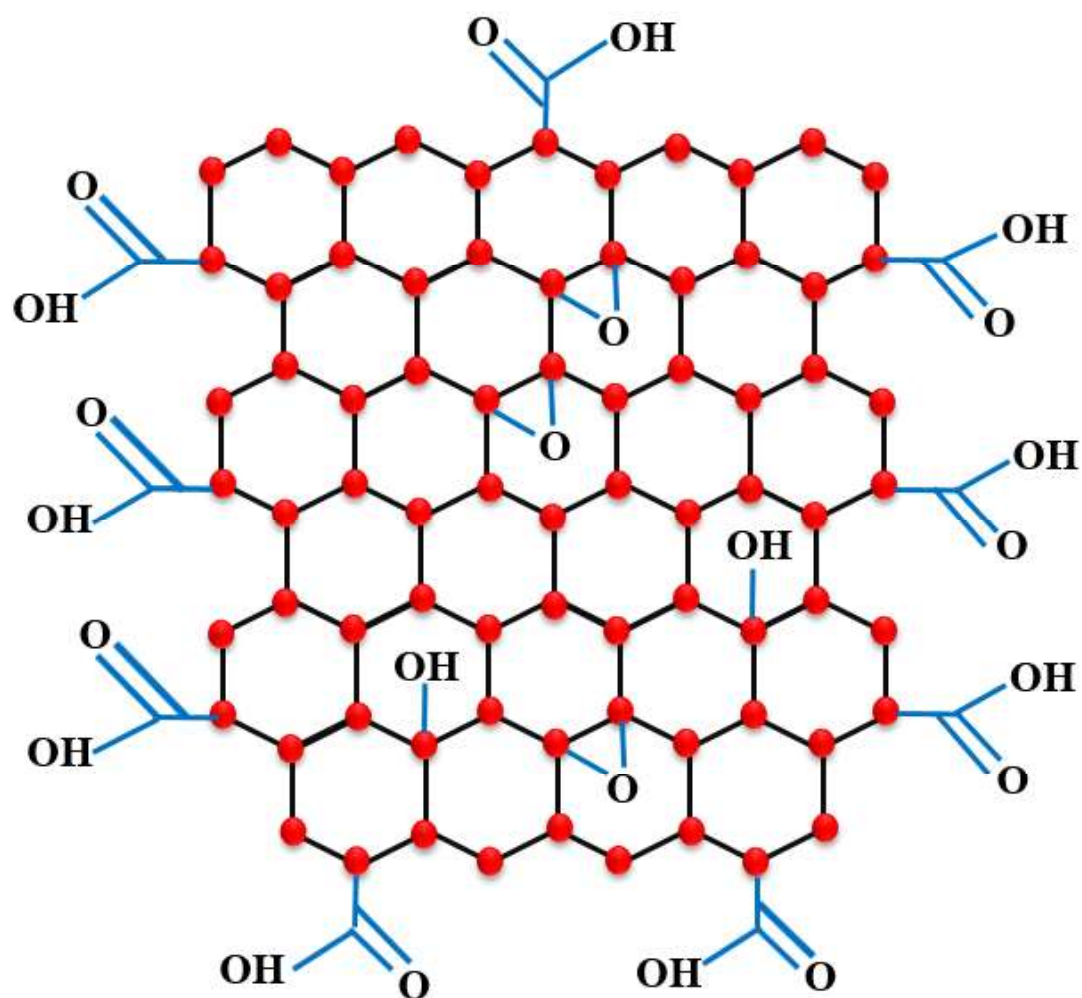


Figure 1.15. Schematic illustration of Graphene Oxide

1.8 Microbial cell entrapment: GO-based polymer hydrogel

Microbial cell entrapment is an innovative technique that involves enclosing living microbial cells within protective matrices or carriers (Shen et al., 2019). This process enhances the stability and viability of the microorganisms, allowing them to thrive and function effectively in various applications. In this approach, biocompatible materials like alginate are commonly used as matrices for microbial cells entrapment (Nezamdoost-Sani et al., 2023) (**Figure 1.16**). Alginate, a natural polysaccharide derived from seaweed, forms a gel-like structure when exposed to divalent cations like calcium ions. This gel matrix acts as a shield, safeguarding the

enclosed microbial cells from harsh environmental conditions, such as temperature fluctuations and chemical stresses.

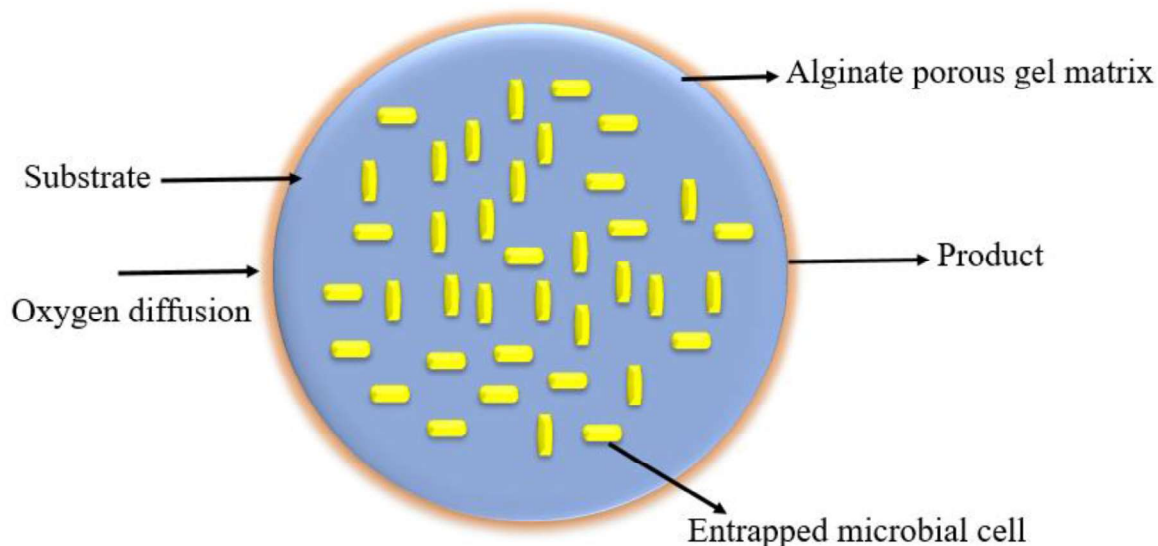


Figure 1.16. A typical illustration of microbial cell entrapment within an alginate-based polymer matrix

Microbial cell entrapment within GO-based polymer hydrogel has emerged as an innovative technique for the bioremediation of textile wastewater (Fares et al., 2020; Godiya et al., 2020). Bacterial cell cultures are allowed to immobilize within a three-dimensional network composed of GO and alginate polymers, which are formed by crosslinking alginate with GO. It provides a protective and supportive environment for the bacterial cells (Jia et al., 2020). The alginate component is liable for the formation of a gel-like structure, whereas the GO sheets are exfoliated and dispersed throughout the hydrogel network (Jiao et al., 2016). The three-dimensional network of hydrogel beads confines the bacterial cells within a defined space, akin to a physical barrier, maintains the spatial distribution of bacteria as also restricts their dispersal, and protects them from the external stressed environment (Bustos-Terrones et al., 2022). GO with diverse oxygen-containing functional groups with high surface area facilitate strong interactions with bacterial cells, adhere and immobilize them within the hydrogel matrix

(Lentz et al., 2022). Furthermore, the alginate component of the hydrogel beads provides a hydrophilic and biocompatible environment that supports bacterial growth and metabolism. Alginate is known for its high water-holding capacity and nutrient permeability, which can contribute to the sustained viability and functionality of the entrapped bacterial cells.

The entrapped microbial cells have immense potential for wastewater treatment and bioremediation. In wastewater treatment, entrapped microbial cells exhibit enhanced pollutant removal efficiency due to prolonged cell activity and protection from toxic substances. Moreover, the controlled release of entrapped microorganisms in targeted environment facilitate for sustained and efficient biodegradation processes. This technique have immense potential for developing eco-friendly and sustainable solutions to mitigate severe environmental challenges, making microbial cell entrapment a compelling avenue of research and application in diverse fields.

1.9 Brief Objectives

To address the challenges of textile wastewater treatment, this study aims to:

- i. Investigate the biodegradation potential of microbial consortia for recalcitrant dye removal.
- ii. Evaluate the effectiveness of advanced oxidation pre-treatment techniques to enhance wastewater biodegradability.
- iii. Develop and assess a hybrid system combining photocatalysis and bioremediation for efficient dye degradation.
- iv. Assess the performance of graphene oxide-calcium alginate-based hydrogels for microbial entrapment and dye mineralization.