2
Review of Literature

2.1 WASTEWATER AND WATER POLLUTION

The twenty-first century is critical for ensuring clean water access, as nearly 2.6 billion people lack safe drinking water and sanitation in developing countries [Bain *et al.*, 2018; Lakshmi and Reddy, 2017]. The industrial sector uses 22% of freshwater, with consumption varying between high-income and low-income countries [Lakshmi and Reddy, 2017]. Around 70% of freshwater withdrawals are used for agriculture, and only 24% of wastewater undergoes treatment before disposal and reuse [Lakshmi and Reddy, 2017]. Urbanization and lifestyle changes are contributing to an increased volume of wastewater discharge, which poses a significant threat to aquatic ecosystems [Pratap *et al.*, 2023]. Wastewater contains various chemicals, toxic metals, hazardous substances, aromatic compounds, and dyes, which risk contaminating natural resources and disrupting their normal functioning [Pratap *et al.*, 2023]. With a population of 17% and the potential to surpass 1.5 billion by 2050, India faces significant pollution issues in farmland and aquatic ecosystems due to natural geological processes, agricultural methods, and industrial discharges [Kaur *et al.*, 2012]. Various wastewater treatment methods are currently employed globally, but large-scale implementation is not feasible due to operational and maintenance costs and capital costs.

2.2 SALINE WASTEWATER CHARACTERISTICS

Saline wastewater contains high levels of salts and organic contaminants, making it difficult to treat as salt interferes with the activity of many heterotrophic bacteria [Siman'kova and Zavarzin, 1992]. The predominant components of organic matter in wastewater are nitrogen, phosphorus, and sulfur [Yang *et al.*, 2022].

Saline wastewater is a prevalent issue in the US, Australia, India, Argentina, Sudan, Israel, and Central Asia [A. Martínez-Huitle and Ferro, 2006]. Salinity in water can be primary or secondary. Primary salination refers to the natural process of moving salts in the environment, whereas human activities cause secondary salination. Primary salinization refers to the significant movement of salt in water during seasonal cycles from precipitation, wind, mineral decomposition, and salt accumulation (Figure 2.1). The primary factors contributing to the saline waste generation are agriculture, livestock farming, and the discharge of high-salt domestic sewage. In certain regions, water softeners and salts are employed to mitigate the formation of mineral deposits in appliances, but this practice contributes to the generation of saline wastewater.

Treating saline wastewater efficiently and comprehensively with conventional methods is challenging due to inorganic salts and various organic pollutants. Incineration technology [Ma *et al.*, 2014; Yang *et al.*, 2022] and advanced oxidation methods are commonly recommended for treating saline wastewater. In the incineration method, all organic matter is oxidized through high-temperature combustion in a specialized incinerator [Ma *et al.*, 2014]. The disadvantages of this technique include increased energy consumption and carbon emissions. Moreover, this process would necessitate substantial investment, prompt corrosion of equipment, and obstruction of pipes by salts [Yang *et al.*, 2022]. The advanced oxidation process employs Fenton oxidation, photocatalytic oxidation, electrochemical oxidation, sono-chemical oxidation, and additional oxidation techniques to decompose organic matter in wastewater [De Laat and Le, 2006; Ma *et al.*, 2021]. However, these chemical processes are expensive and

produce toxic byproducts. Thus, effectively managing saline wastewater with organic contaminants remains an ongoing challenge, representing a considerable environmental risk.

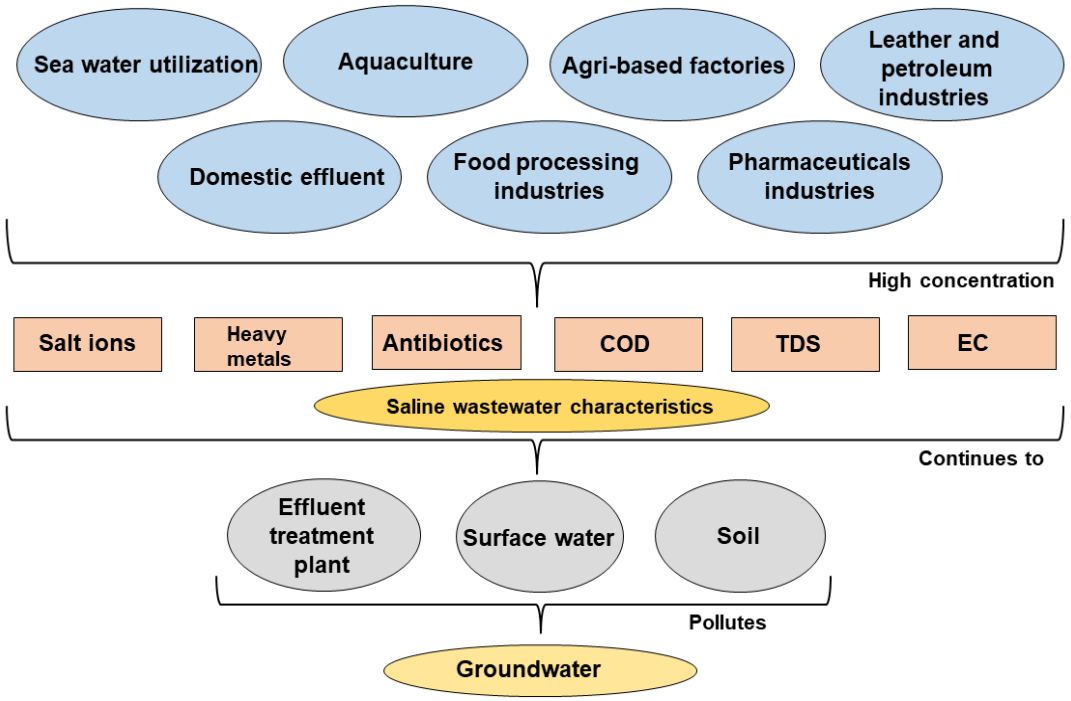


Fig. 2.1: Factors contributing to secondary salinization as well as groundwater contamination.

A group of researchers [Martín-Queller *et al.*, 2010] found that urban activity and livestock farming caused a substantial rise in salty waste and observed an increase in nitrate concentration from 8.5 to 20.8 mg/l during the months of irrigation. Additionally, the nearby metropolitan areas increased the phosphorus levels in the river from 0.19 to 0.42 mg/l, also reported that the use of pig manure as fertilizer for soils, subsoils, surface water, and groundwater increases the salinity of the water with the addition of organic matter [Martín-Queller *et al.*, 2010].

Applying salts directly to the roads and sidewalks of the nation during the cold weather to dissolve ice and snow contributes to the generation of saline wastewater. A study by Meriano *et al.* [2009] discovered that paved roads contribute 50% of road salt to catchment streams and Frenchman's Bay Lagoon through surface runoff in Ontario, Canada. Stream water quality is consistently destroyed throughout the year due to the presence of salt and organics from runoff and baseflow.

2.3 CLASSIFICATION OF SALINE WATER

The salt concentration of water resources can be categorized based on the ranking system established by the Food and Agriculture Organization of the United Nations (FAO) [Rhoades *et al.*, 1992], summarized in Table 2.1. This categorization aids in comprehending the potential applications of saline water and wastewater in crop cultivation, as only crops with a high tolerance can thrive when irrigated with water that has an electrical conductivity (EC) exceeding 10 mS/cm.

Table 2.1: The classification system established by the FAO, as outlined by Rhoades *et al.* [1992], for the saline water categorization.

Water type	**EC (mS/cm)**	**TDS (mg/l)[a]**	**Water use**
Normal water	Less than 0.7	Less than 450	Drinking
Slightly saline	0.7-2	450-1300	Irrigation only
Moderately saline	2-10	1300-6400	Primary effluent and groundwater
Highly saline	10-12	6400-16000	Secondary effluent
Extremely saline	25-45	16000-28800	Extremely saline wastewater
Brine	More than 45	More than 28800	Sea and lake water

[a] The conversion factor for EC to TDS is typically assumed to be K = 0.64.

2.4 SOURCES OF SALINE WASTEWATER

The growing consumption and reliance on seawater for various purposes in coastal areas have resulted in a significant contribution of saline wastewater; for example, a country like Hong Kong utilizes seawater for firefighting and toilet flushing [Li *et al.*, 2018]. Aquaculture plays a crucial role in the economies of many nations, serving as a significant source of seafood and contributing to their overall food security and economic development. It also leads to saline wastewater generation because these activities emit pollutants such as inorganic salts, organic compounds, and nutrients that harm the environment [Xiang, 2007]. Moreover, tanneries, fish processing plants, oil and gas industries, textile factories, and pharmaceutical companies discharge significant saline wastewater (Figure 2.2), which contaminates the soil and groundwater [Zhao *et al.*, 2020]. Table 2.2 shows the contribution of saline sewage generation by various industries.

2.4.1 Industrial effluent

Sodium chloride has traditionally been employed to preserve and enhance food taste. It reduces the amount of moisture in food and inhibits microbial growth. Food industries use this technique to preserve meat, dairy products, pickled vegetables, and fish by incorporating a substantial amount of salt [Alam *et al.*, 2022]. The primary application of salt in the pickle industry is for canning and pickling purposes. Saline water is primarily utilized to remove nitrogen and organic matter from seawater fish [Alam *et al.*, 2022]. The tanning process in leather production is intricate and time-consuming, and salt is used to produce finished leather, creating a significant amount of saline waste [Lefebvre and Moletta, 2006]. Industrial effluent with 1-3% salty waste is classified as high-saline wastewater. The concentration of a particular salt species in the saline wastewater is a determining factor in selecting an appropriate treatment method. The natural processes of plant water absorption and salt exclusion lead to a rise in soil salinity. Nevertheless, irrigation and fertilization practices are the primary source of

agricultural saline wastewater. Applying synthetic fertilizers and using manure from livestock facilities can lead to elevated levels of nitrates in water bodies. Suboptimal irrigation systems result in significant water leakage, heightening the likelihood of salinization and flooding. Approximately 70% of the total volume of wastewater generated is utilized for agricultural fertilization and irrigation [Barbera and Gurnari, 2018]. Effluent from wastewater treatment plants and septic systems, along with excessive irrigation of lawns and residential areas, are major sources of saline wastewater. In 2015, 6% of the total water withdrawals in the United States were saline, with the thermal industry accounting for 97% of these withdrawals [Dieter *et al.*, 2017].

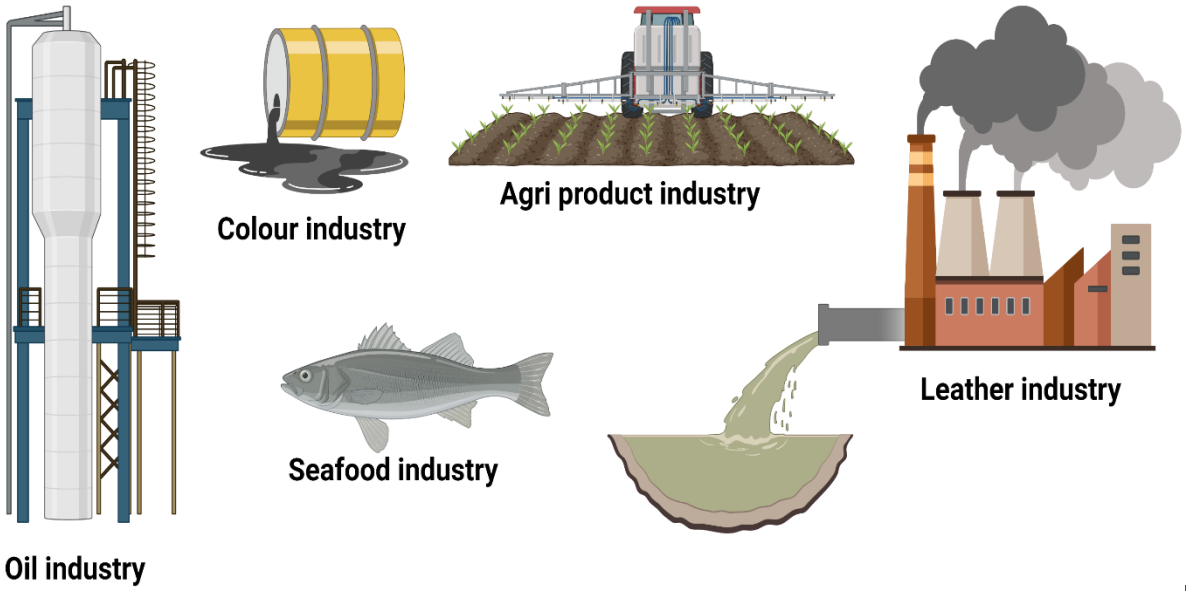


Fig. 2.2: Industries responsible for the generation of the saline sewage.

2.4.2 Domestic effluent

Household wastewater exhibits elevated salinity compared to freshwater due to the utilization of water softeners, detergents, cleaning goods, soaps, and shampoos. The EC of spent water is often 70-100 mS/cm more than that of potable water [HWT, 2020]. Traditional methods of water treatment may not effectively eliminate organic content from these types of wastewater, as shown in fig.2.3 that the traditional method is only effective up to 1-1.5% of salinity [Levlin, 2010].

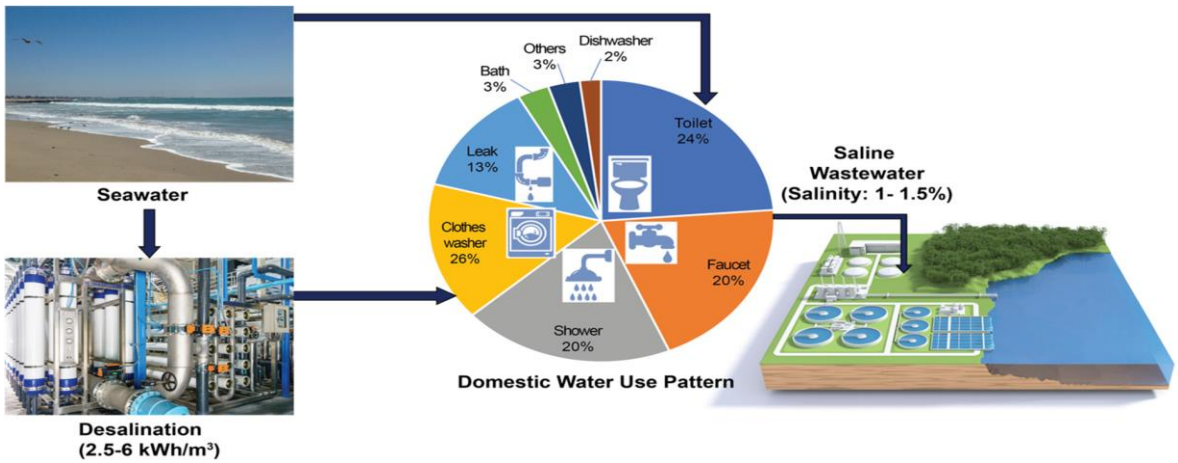


Fig 2.3: Domestic effluent generation and treatment [Ali *et al.*, 2022].

2.4.3 Petroleum effluent

An oil refinery produces saline waste, which consists of the recycling of oil containing sulfur, the processing of petroleum products, and the techniques used to eliminate salt and moisture during oil refining [Radelyuk *et al.*, 2019]. The wastewater generated from these refineries contains solid particles, dissolved minerals, hydrocarbons, nitrogen-containing chemicals, and other substances like toxic metals and phenolic compounds. To satisfy the requirements for waste disposal, a complex series of treatment procedures is essential. The prescribed treatment procedure comprises pre-treatment screens, sand traps, equalization tanks, primary treatment with oil traps, coagulation-flocculation, dissolved air flotation, and electrocoagulation flocculation [Radelyuk *et al.*, 2019]. The secondary treatment employs activated sludge and a moving bed biofilm reactor. During the post-treatment phase, wetlands, advanced oxidation processes, and membrane technologies are used to enable the reuse of water. The characteristics of the wastewater, such as high salinity levels and other chemical substances, pose challenges for biological processes.

2.4.4 Mining effluent

Water is essential for various activities and processes in the mining industry, such as exploration and mineral processing. The waste products generated by these activities consist of various dissolved ions, such as sodium, calcium, magnesium, potassium, chloride, sulfate, and organics, depending on the geographical area and the specific methods used [Thiruvenkatachari and Su, 2017]. The water consumption and EC of waste materials in the mining sector depend on the extraction of minerals [Thiruvenkatachari and Su, 2017]. The coal mine site in the Czech Republic produces pollutants such as organic matter (comprising primarily fossil material along with lesser amounts of carbonized and recent organic matter altered by weathering and erosion processes) and elevated levels of Mn, Sr, and Ba in the sediments which constitutes the saline waste [Vörös *et al.*, 2021].

Table 2.2: An overview of the critical characteristics of saline wastewater in the effluents discharged by various industrial sectors.

Source of saline wastewater	TDS	TOC	COD	EC	Salt ions	pH	References
Petrochemical industrial effluent	30000 mg/l	60 mg/l	-	-	5320.2 mg/l	5-6	[Osman *et al.*, 2019]
Industrial effluent	48000-80000	-	53000-89000 mg/l	-	-	-	[Tuin *et al.*, 2006]
Municipal wastewater	1703 ± 236 mg/l	-	2302 ± 269 mg/l	2886 ± 157 µS/cm	-	7.67 ± 0.18	[Cartagena *et al.*, 2013]
Industrial effluent	54526 mg/l	-	-	76800 µS/cm	-	7.14	[Hashim and Hajjaj, 2005]
Gulf (brine) water	45000 ppm	-	-	-	45750 ppm	8.2	[Al Mutaz and Wagialia, 1990]
Brine water	79660 mg/l	-	-	85200 µS/cm	79659.99 mg/l	7.5	[Melián-Martel *et al.*, 2013]
Brine wastewater	48510 mg/l	-	-	61100 mS/cm	48617.8 mg/l	6.94	[Ahmed *et al.*, 2001]
Industrial effluent	80000-100000 mg/l	-	100 mg/l	-	-	8-9	[Tun and Groth, 2011]

Reverse osmosis brine	19200 mg/l	50-70 mg/l	-	15 mS/cm	18806 mg/l	7.5	[Tun and Groth, 2011]
Inorganic industrial wastewater (ceramic)	1605 mg/l	-	-	3210	1390.043 mg/l	8.01	[Moosavirad *et al.*, 2015]
Coal washing	1490 mg/l	-	-	2980 µS/cm	1700.463 mg/l	7.23	[Moosavirad *et al.*, 2015]
Polyethylene factory effluent	2565 mg/l	-	-	5130 µS/cm	1825.636 mg/l	8.79	[Moosavirad *et al.*, 2015]
Coal mining	14500 mg/l	-	-	29000 µS/cm	10934.079 mg/l	7.19	[Moosavirad *et al.*, 2015]
Ferromolybdenum factory effluent	2300 mg/l	-	-	4600 µS/cm	2034.99 mg/l	7.76	[Moosavirad *et al.*, 2015]

2.5 EFFECT OF WATER SALINITY

Water salinization impacts approximately 7% of the Earth's land surface and more than 20% of agricultural land, causing disturbances to ecosystem function and effects on living organisms and the economy [Schuler *et al.*, 2018]. The adverse impacts on living organisms encompass compromised renal function, heightened arterial pressure, and an elevated prevalence of disease vectors exhibiting salt tolerance. Saline wastewater constrains economic and social development, adversely affecting agriculture, livestock, households, public services, and industrial activities (Fig. 2.4). The repercussions are interrelated, leading to decreased economic growth and welfare. The social ramifications encompass the displacement of individuals and the scarcity of employment opportunities resulting from insufficient access to water and food for the entire population [Schuler *et al.*, 2018].

Salinization exacerbates environmental and soil degradation, resulting in elevated food production expenses and the onset of diseases. Saline wastewater is a major environmental problem that accumulates residues and causes equipment damage and economic expenses. Payen *et al.* [2016] examined the impacts of salinization in a life cycle assessment. They determined four pivotal factors: land use conversion, irrigation, brine disposal, and excessive water consumption. Human activities can increase the salt content of soil and water, a phenomenon known as secondary salinization. The concept of the circular economy promotes strategies to enhance water efficiency, minimize the consumption of natural resources, and maximize water recycling. Salinity also impacts green-house gases (GHG) emissions-related air pollution [Ardón *et al.*, 2018]. Research indicates that methane emissions are insignificant in brackish [Ardón *et al.*, 2018]. One study has shown that salt reduces chemical oxygen demand (COD) removal efficiency and is inversely related to nitrogen removal, leading to increased N_2O emissions [Shao *et al.*, 2020].

Water salinization additionally contributes to the occurrence of acid rain and desertification. This is because saline wastewater, which contains sulfur compounds, has the potential to generate hydrogen sulfide [Malone Rubright *et al.*, 2017]. H_2S can then undergo oxidation to form SO_2, resulting in acid rain [Malone Rubright *et al.*, 2017]. Australia and Asia have the largest soil areas impacted by salinity and sodality, with many experiencing desertification [Singh, 2009]. The primary cause of this phenomenon is the irrigation techniques employed in semi-arid regions, which accumulate concentrated salts from fertilizers in the soil [Singh, 2009].

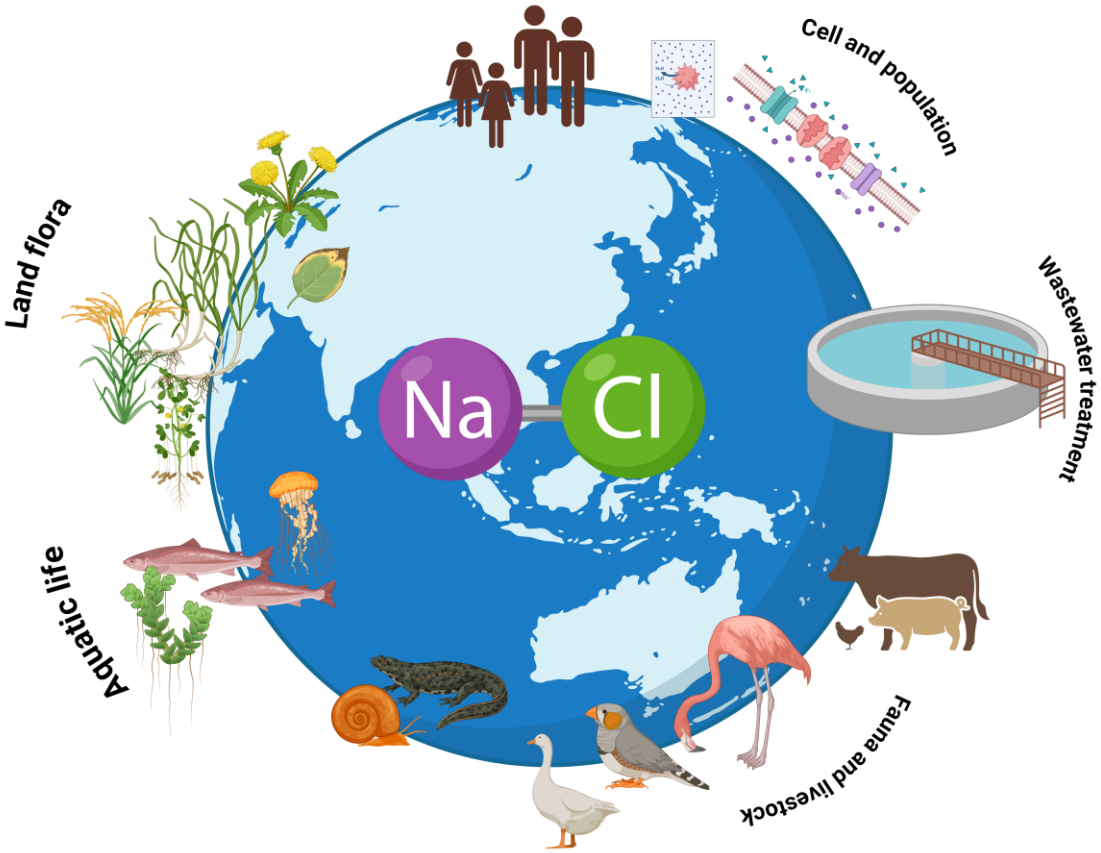


Fig 2.4: Effect of salinity on the ecosystem.

2.6 CONVENTIONAL METHODS FOR SALINE WASTEWATER TREATMENT AND CHALLENGES

Saline wastewater treatment methods encompass membrane technologies, thermal operations, and chemical, biological, and electrochemical technologies (Table 2.3). However, concentrated waste requires meticulous handling for proper disposal. Surface water discharge, sewage discharge, deep-well injection, and evaporation ponds are frequently used for saline wastewater disposal. Conventional methods for treating saline wastewater face significant challenges, and these methods can be energy-intensive, generate large volumes of sludge, and have limited capacity to handle fluctuations in salinity levels of water.

To overcome the limitations of conventional approaches is crucial as industries and municipalities grapple with the growing need for sustainable saline wastewater management solutions. Innovative technologies that efficiently treat saline wastewater and recover valuable resources from this challenging waste are becoming increasingly important.

Table 2.3: Different methods are used to remove contaminants from wastewater

Pollutant		**Treatment process**	
	Physical	**Chemical**	**Biological**
Solids	Settling, flotation, and filtration	Oxidation reaction	Aerobic, anaerobic
Greases	Flotation		
Colloids	Coagulation, flocculation, filteraion		
Organic compounds	Adsorption	Oxidation reaction	Aerobic, anaerobic
Volatile compounds	Desorption		
Inorganic compounds	Desorption		
Heavy metals		Precipitaion	Aerobic
Toxicants	Filtration, adsorption	Oxidation	
Microorganisms	UV radiation, filtration, adsorption	Oxidation	Aerobic, anaerobic

2.6.1 Membrane technologies

Membrane technologies are widely recognized for their effective elimination of contaminants, user-friendly nature, and capacity to retrieve resources in the process of treating wastewater. Semi-permeable membranes, such as hollow fibers, spiral wounds, and flat sheets, are used to improve the effectiveness of newly developed membranes [Liang *et al.*, 2021].

A. Reverse osmosis

Reverse osmosis is a membrane-based technology that employs pressure to effectively remove organic and inorganic contaminants from industrial wastewater [Brehant *et al.*, 2003]. It achieves a high level of effectiveness, with a ~70% recovery rate for water [Ahmad *et al.*, 2018]. Nevertheless, the system's efficiency declines as the salt concentration rises, as observed in the case of high-saline wastewater generated by the petrochemical sector [Ahmad *et al.*, 2018]. The elevated energy demand associated with treating saline wastewater also leads to higher expenses, rendering reverse osmosis a more expensive alternative.

B. Forward osmosis

Forward osmosis processes involve the transfer of solvents from regions of lower solute concentrations to areas of higher solute concentrations, requiring minimal energy for circulation. Forward osmosis is an effective method for treating saline wastewater as it achieves a water recovery rate of ~50%, removes ~90% of organic compounds and ~ 97.7% of divalent ions, and allows a flow rate of 5 liters of water per square meter per hour [Ezugbe *et al.*, 2021]. Integrating various membrane processes can improve system performance by reducing energy consumption, increasing the recovery rate, and enhancing pollutant removal. However, there is still a requirement to strengthen compact forward osmosis systems with significant surface areas for utilization in various fields and large-scale applications [Roy *et al.*, 2016].

C. Membrane bioreactor

The membrane bioreactor is a well-established technology that effectively removes a broad spectrum of organic and inorganic substances from wastewater, including ammonia and organic compounds [Patsios *et al.*, 2021]. The reduction of organic matter is dependent upon the

salt concentration of wastewater in the membrane bioreactor, resulting in a ~50% decline of organics at the optimal salt concentration [Jang *et al.*, 2013]. Adsorbents such as activated carbon, zeolite, and cation and anion exchangers facilitate the removal of both inorganic and organic waste, resulting in improved effluents [Hazrati *et al.*, 2018].

D. Membrane distillation

Membrane distillation has been used to treat saline wastewater containing salt, proteins, and polysaccharides [Alam *et al.*, 2022; Madalosso *et al.*, 2021]. As a result, there have been favorable outcomes, such as the retrieval of water and the elimination of all organic substances, which can be reused in various industrial processes [Alam *et al.*, 2022]. Consequently, there have been favorable results, such as water retrieval and elimination of all organic compounds. Membrane fouling poses a substantial challenge in membrane distillation, requiring optimization specifically for saline wastewater [Alam *et al.*, 2022].

2.6.2 Thermal power-based technologies

Thermal processes, such as evaporation and crystallization, treat saline wastewater by causing a phase change that aids in eliminating contaminants [Alam *et al.*, 2022]. The thermal process involves three distinct processes: multi-stage flash, multi-effect distillation, and mechanical vapor compression. All the techniques involve high-temperature evaporation systems and the use of a compressor to condense the vapor [Subramani and Jacangelo, 2014]. However, higher thermal energy demands can be mitigated by employing low-temperature evaporation systems and utilizing waste heat [Stengler *et al.*, 2018].

2.6.3 Chemical methods for saline waste treatment

Chemical processes are used to treat saline wastewater, with ion exchange processes being the predominant method. Magnetic ion exchange resins, a type of ion exchange technology, offer improved efficiency and cost-effectiveness for saline waste treatment [Sahu, 2020]. Advanced oxidation processes employing hydroxyl radicals have been widely used to remove phenol, ammonia, and organic compounds from saline wastewater [Pérez-González *et al.*, 2012; Seid-Mohammadi *et al.*, 2016]. The combination of UV irradiation and persulfate has been used to eliminate phenol with a removal efficiency of ~93% [Seid-Mohammadi *et al.*, 2016].

Furthermore, the utilization of coupling agents has been investigated to remove pollutants and salts from wastewater. Alyssum mucilage, a type of natural coagulant, has been utilized to treat oily wastewater containing salt. Under optimal conditions, they achieved a COD removal efficiency of 92.30% and a surfactant removal efficiency of 99% [Fard *et al.*, 2021]. The drawback of the chemical method is the use of toxic/hazardous chemicals as well as the process is heavily costly and cannot be scaled up at a large-scale treatment process.

2.6.4 Biological treatments

Elevated levels of salt hinder the efficiency of biological processes in the treatment of saline wastewater. However, halophilic bacteria can survive in environments with high salinity levels and can be eradicated using advanced biological methods. Halophilic microorganisms can be categorized as mild, moderate, or extreme microbiota. These halophilic bacteria regulate osmotic pressure and hydration by retaining inorganic solutes and synthesizing hydrolytic enzymes [Zhao *et al.*, 2020]. Researchers have effectively formed granules from halophilic sludge to treat saline wastewater, removing ammonia and COD [Huang *et al.*, 2019].

Halobacter halobium can effectively treat saline wastewater containing ~3.5% NaCl and 4,500 mg COD/l. Meanwhile, *Staphylococcus xylosus* can remove ~93% of COD at ~3% NaCl [Kargi *et al.*, 2000]. Martínez-Espinosa *et al.* [2007] investigated the potential of utilizing *Haloferax mediterranean*, a halophilic bacterium with denitrification capabilities, to remove nitrate and nitrite from saline wastewater. Ali *et al.* [2020] demonstrated the utilization of a novel marine anammox bacteria in a membrane bioreactor to purify saline sewage, and these

microorganisms exhibited a nitrogen removal rate of 0.3 kg/m^3d and achieved an efficiency of approximately 90%.

Amezaga *et al.* [2014] suggested the use of photosynthetic organisms to treat saline wastewater, like halophilic cyanobacteria. These cyanobacteria exhibit rapid growth, can tolerate a broad spectrum of salt concentrations, and can undergo genetic transformation. Hülsen *et al.* [2019] proposed the utilization of purple phototrophic bacteria to eliminate organic compounds and extract nutrients from saline and marine-like wastewater. These organisms showed swift acclimatization to high-salt environments and displayed promise for a synergistic approach to treating wastewater and recovering resources, especially saline industrial sewage. Shen *et al.* [2015] emphasized marine microalgae's usefulness and economic significance in treating saline wastewater. They demonstrated that these microalgae are highly effective in removing nitrogen and phosphorus from saline wastewater and can produce large amounts of lipids.

2.7 ELECTROCHEMICAL TREATMENT TECHNIQUES

2.7.1 Electrochemical oxidation

Electrochemical oxidation is a process in which a catalyst-coated anode facilitates a chemical reaction that produces active oxygen, leading to the oxidation of pollutants present in saline wastewater [Mousazadeh *et al.*, 2021]. The movement mechanism of electrochemical oxidation can be either direct or indirect [A. Martínez-Huitle and Ferro, 2006]. Direct mechanisms directly remove pollutants that interact with active oxygen, whereas indirect mechanisms involve the presence of highly reactive ions such as hypochlorous acid and chlorine [A. Martínez-Huitle and Ferro, 2006]. Electrochemical oxidation techniques have effectively eliminated organic compounds from saline wastewater, and their conductivity is elevated due to cationic and anionic salts [Dindarloo *et al.*, 2015]. However, hypochlorite ions can produce detrimental intermediate compounds during the treatment process when these ions react with organic pollutants [Sun *et al.*, 2021].

2.7.2 Electrofloatation

Electroflotation is an electrochemical process used to eliminate insoluble or dispersed pollutants in saline wastewater [Alam *et al.*, 2022]. The process entails water electrolysis, which produces hydrogen and oxygen gas bubbles that attach to contaminants and create a stable layer of floating sludge [Alam *et al.*, 2022]. Few past works have demonstrated that elevated salinity and conductivity levels enhance efficiency, although the electrodes may experience corrosion, which can impede the rate of the process [Alam *et al.*, 2022]. Oil field saline effluent treatment has demonstrated a 90% oil removal efficiency within 30 minutes at a salinity concentration of 4 mg/l [Bande *et al.*, 2008]. Electroflotation performs effectively under optimal salinity conditions [Kolesnikov *et al.*, 2019].

2.7.3 Electrodialysis

Electrodialysis is a technique that employs direct current to break apart and isolate dissociated ions from wastewater [Seid-Mohammadi *et al.*, 2016]. It is efficient in the treatment of saline water, including wastewater from industries that use brine and brackish water [Campione *et al.*, 2018]. The process can be either simple or multi-chamber electrodialysis. An electrodialysis system comprises three compartments separated by porous membranes with anodic and cathodic electrodes [Alam *et al.*, 2022]. Electrochemical deposition has been used to eliminate pollutants from different types of wastewater, such as heavy metal-based wastewater, sanitary sewage, textile wastewater, and industrial effluents [Alam *et al.*, 2022].

2.7.4 Electrocoagulation

Electrocoagulation technology is a sophisticated method for isolating pollutants, specifically heavy metals, pharmaceuticals, organic compounds, dyes, and salts [Mateen *et al.*, 2020]. The process entails the electro-dissolution of sacrificial electrodes, commonly made of aluminum, iron, or a combination of both, to generate coagulant species [Alam *et al.*, 2022; Mollah *et al.*, 2004]. The process involves the generation of metal ions by the anode, the production of hydroxyl ions and hydrogen gas from water by the cathode, electrolytic reactions occurring at the electrode surface, the adsorption of contaminants by the coagulants produced, and the separation of colloids through sedimentation or flotation [Alam *et al.*, 2022].

Traditional electrochemical processes encounter significant expenses in operation, electrode material, mass transfer limitations, and catalytic fouling accumulation. Nano-enhanced electrodes, such as reduced graphene, ordered mesoporous carbon, carbon aerogel, carbon cloths, and multi-walled carbon nanotubes, provide enhanced electrochemical methodologies, significantly increased surface area, stability, and cost reduction. However, it is necessary to consider operational parameters, appropriate membrane and electrode materials, and optimize the electrodialysis techniques with others in combination [Alam *et al.*, 2022].

2.8 MFC

MFC uses electrogenic anaerobic microbes to produce energy by oxidizing the organic substrate at the anode and producing electrons, protons, and CO_2 as products. A conventional two-chamber MFC design contains an anodic chamber and a cathodic chamber separated by a proton exchange membrane (PEM) or an ion-selective membrane [Logan *et al.*, 2006]. Microorganisms oxidize the organic matter in the anodic chamber to produce electrons, protons, and CO_2. The electrons are transferred onto the anode surface, from where they flow across an external circuit to the cathode, constituting the flow of current. Movement of the electrons and protons from the anode to the cathode, where electrons are captured and reduced with the help of a terminal electron acceptor, maintaining redox potential differences. The protons migrate to the cathode through the PEM. At the cathode, molecular oxygen reduction to water depletes electrons and protons.

Applications of MFCs include the production of bioelectricity, the treatment of wastewater, the sequestration of CO_2, the removal of heavy metals, and bioremediation. The power output of an MFC is influenced by variables such as electrode spacing, temperature, and ion concentration in the electrolyte. As the ion concentration in the electrolyte rises, the resistance in the system decreases, leading to a boost in power output.

Salinity in wastewater increases power generation efficiency in MFCs, provided a specific group of bacteria capable of decomposing organic substances is identified. Studies have investigated how higher levels of salinity and conductivity affect the power generation of MFC systems [Lefebvre *et al.*, 2012]. These experiments have primarily focused on using freshwater bacteria. The power output of single-chambered MFCs has been observed to reach 400 mM NaCl concentrations [Liu *et al.*, 2005]. However, the main goal was to enhance the power generation capacity of the MFC system rather than prioritizing the treatment of saline water. Previous research has also utilized extremophiles and halophilic bacterial populations obtained from natural salty marshlands to treat wastewater with high salt content [Vijay *et al.*, 2018]. However, the tolerance and activity of halophilic bacteria can vary depending on their natural habitats, which highlights the need for further research to identify more effective microbial communities. Here are some examples of the treatment of saline wastewater in MFC mentioned in table 2.4.

Table 2.4: Use of MFC for the saline wastewater treatment.

Wastewater source	Salinity	Types of MFC	Biological/Chemical	Power/ current output	COD Removal (%)	References
Pharmaceutical	4%	air cathode MFC	*Ochrobactrum, Marinobacter, Bacillus, Rhodococcus*	505 mW/m^2	68%	[Pugazhendi *et al.*, 2022]
Olive oil industry	-	Upflow MFC	*Ochrobactrum, Marinobacter, Rhodococcus, Bacillus*	439 mW/m^2	89%	[Pugazhendi and Jamal, 2023]
Tannery industry	4%	Upflow MFC	*Ochrobactrum, Marinobacter, Rhodococcus, Bacillus*	385 mW/m^2	72%	[Ghorab *et al.*, 2022]
Fish market wastewater	4.6%	Air cathode MFC	*Ochrobactrum, Marinobacter, Bacillus, Rhodococcus, Flavobacterium, Alicyclobacillus, Pseudomonas, Martelella, Stenotrophomonas, Xanthobacter, and Microbacterium*	420 mW/m^2	63%	[Jamal and Pugazhendi, 2021]
Petrochemical industrial	-	Dual chambered MFC	Chemical	270 mW/m^2	80%	[Tamilarasan *et al.*, 2024]
Saline wastewater	2%	Heterotrophic ammonia assimilation coupled MFC	*Marinobacter*, *Halomonas*	29.93 mW/m^2	96.4 %	[Zhao *et al.*, 2024]
Seafood processing	209 g/m^3	Tubular upflow MFC	*Stenotrophomonas* sp.	222 Mw/m^2	83%	[Jayashree *et al.*, 2016]
Saline wastewater	5 g/l	Constructed wetlands MFC	*Ochrobactrum*	16.4 mW/m^2	64.79 ± 1.15%	[Xu *et al.*, 2019]
Simulated starch saline wastewater	500 mM-3000 mM	Dual chambered MFC	*Bacillus* sp. *Staphylococcus* sp. *Virgibacillus* sp. *Staphylococcus* sp.	207.05 mW/m^2	-	[Vijay *et al.*, 2018]

2.9 PMFC

PMFCs offer a process that can provide high CO_2 concentrations for algae growth, has a mechanism to prevent high inhibitory oxygen concentrations, and can meet a fraction of the process electricity requirements (Figure 2.5). PMFCs are a modified form of MFCs and are considered promising systems for wastewater treatment and power generation. In such systems, microorganisms convert organic matter into electricity [Khandelwal *et al.*, 2018]. In PMFCs, the CO_2 produced at the anode is fed to the cathode for fixation by algae which in turn produces O_2 as an electron acceptor to complete the MFC circuit [Wang *et al.*, 2011]. Wang *et al.* [2011] reported proof of using PMFCs for algae cultivation at the cathode with simultaneous anodic CO_2 fixation and generation of oxygen as an electron acceptor. The power output from the device was 5.6 W/m^{3,} with algae growth in the cathode chamber linked directly with power generation. The cathode dissolved oxygen concentration was found to be 6.6 mg/l. The power generation from the MFC depends on the oxygen concentration at the cathode, and a concentration level of 6.6 mg/l is considered suitable [Kang *et al.*, 2003]. The device was demonstrated to be an efficient carbon capture device for algae biomass production.

De Schamphelaire and Verstraete [2009] reported an integrated system consisting of an algal biomass production unit, an anaerobic digester to convert algae biomass to biogas, and an MFC to generate electricity while treating digester effluent. They estimated their system results in an about 9 kW/ha capacity power plant, with 23 kW/h prospects. The study of Khandelwal *et al.* [2018] showed that the algae biomass degradation at the anode was coupled with algae biomass production at the cathode. The algae biomass harvested from the cathode was used for oil extraction and fed back into the system at the anode for degradation by a microbial consortium. The replacement of costly fuels like glucose/acetate at the anode with algae biomass and capture of O_2 generated by the photosynthesis process via cathodic reduction to water was achieved, as high O_2 concentrations are inhibitory to the growth of algae, particularly in closed systems.

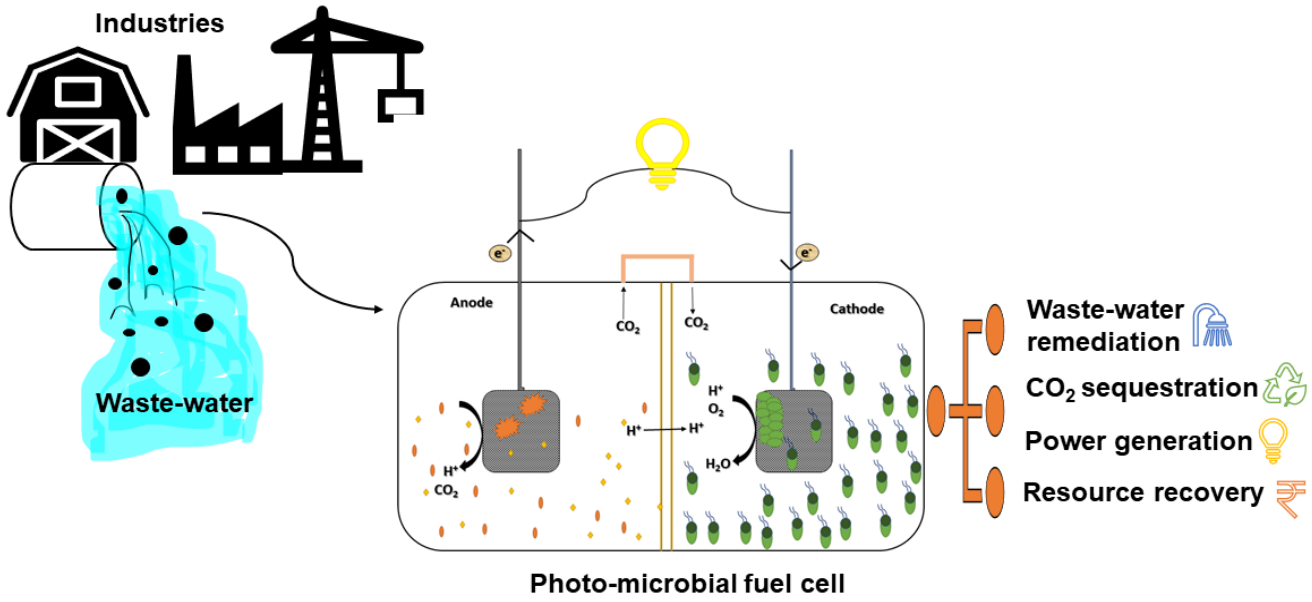


Fig. 2.5: A typical photosynthetic microbes assisted PMFC showing power generation with various applications [Mishra and Chhabra, 2023].

2.9.1 Mechanism of bioelectricity generation in PMFC

The energy-generating redox reaction is separated into two chambers of a PMFC, with oxidation happening at the anode and reduction at the cathode. The oxidation generates electrons that travel from the anode to the cathode, constituting the current. The protons diffuse through the proton exchange membrane to balance the moving charges. The electrons, protons, and oxygen combine at the cathode surface to produce water. The main steps in PMFC are 1) photosynthesis by algae at the cathodic chamber, 2) oxidation of organic matter under anaerobic conditions by electrogenic bacteria at the anode chamber, 3) transfer of protons and electrons from the anode to the cathode chamber, and 4) reduction of oxygen at the cathode.

In the case of anodic electrogenic bacteria, oxidation of NADH to NAD^+ during the mitochondrial respiration process plays a principal role in voltage generation [Logan *et al.*, 2006]. Many dehydrogenases are an integral part of the plasma membrane of algae and have an essential role in the electron transport chain [Shukla and Kumar, 2018].

$$CH_2O \text{ (Organic matter)} + H_2O \longrightarrow 4\,e^- + 4\,H^+ + CO_2 \qquad (2.1)$$

In algae, photosystems comprise several pigments, including chlorophyll. The pigments are arranged in a fashion that harvests maximum solar energy and transmits that to the reaction

center. The carotenoids are at the outer surface, and chlorophyll forms the reaction center. Algal photosynthesis is completed in two steps: light and dark reactions. The light mediates electron ejection from the two reaction centers of the P680 and P700 photosystems during the light reaction. The oxidized P680 splits water into oxygen, protons, and electrons. The electrons fill the hole and stabilize the reaction center for the next cycle. The splitting molecule breaks water molecules into oxygen, protons, and electrons. Meanwhile, the ejected electron transports through the Z-scheme from photosystem (PS) II (P680) to PS I (P700), resulting in a proton gradient that generates ATP. In non-cyclic photophosphorylation, $NADP^+$ accepts the electron generated through the oxidation of PS I, producing NADPH. In cyclic photophosphorylation, only ATP is generated as the electron flows in a cycle coming back at the same reaction center.

$$2\ NADP + 2\ H_2O + 2\ ADP + 2\ P_i \xrightarrow{\text{light energy/chlorophyll}} 2\ NADPH_2 + 2\ ATP + O_2 \quad (2.2)$$

During the dark reaction, NADPH and ATP reduce CO_2 through the Calvin-Benson cycle (C_3 cycle). The first step of this cycle is catalyzed by Ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) [Taiz and Zeiger, 2015] as shown in the equation below:

$$CO_2 + 4\ H^+ + 4\ e^- \xrightarrow{2NADPH2;3ATP} CH_2O + H_2O \quad (2.3)$$

The Rubisco enzyme shows a higher affinity for O_2, thereby dropping the rate of carbon dioxide fixation and algae growth [Hopkins, 1999]. Since oxygen inhibits the process of photosynthesis, continuous/periodic deoxygenation of the algae growth medium is essential to sustain healthy algae growth.

2.9.2 PMFC design parameters

A. Dual v/s single chambered MFCs

PMFCs can be single or dual-chambered. In both types, an anode and a cathode are immersed in two redox environments. In sediment MFCs, the upper layers are suitable for cathode placement as these are exposed to light and support photosynthesis and oxygen generation [Shukla and Kumar, 2018]. Anaerobiosis prevails in the lowermost layers of the water column and sediment where the anode can be placed. In dual chambers, the electrodes can be on the same plane but separated into different compartments via a selectively permeable membrane. Both systems can be operated in batch or continuous mode. The shape of the chambers can vary. Dual-chambered PMFCs are difficult for industrial scale-up due to their complex design and high operational costs. Hence, single-chambered PMFCs are preferred over the dual-chambered design.

B. Construction materials, electrolytes, electrodes, and separators

MFCs can be made of glass, concrete, acrylic, polyvinyl chloride, polycarbonate, perspex, stainless steel, polymethyl methacrylate, plastic, and ceramics [Shukla and Kumar, 2018]. In the case of PMFC, the cathodic chamber has to be transparent for light penetration. Ceramics are the most sustainable for anodic compartments amongst the said materials as these are cost-effective, use renewable materials, and do not create pollution. The most common ceramics are earthenware pots, terra-cotta pots and cylinders, and goethite cylinders [Behera and Ghangrekar, 2011].

C. Electrode material

The MFC electrode should have high conductivity, higher surface area, non-toxic, non-polluting, and have a low charge transfer resistance. The latter often requires the modification of electrodes with electrode catalysts that accelerate the rate of charge transfer reactions. Researchers attempt to enhance MFC's power output by changing the electrodes' shape and material. Carbon-based electrodes such as carbon cloth, carbon felt, carbon brush, carbon paper, graphite plate, graphite rod, and graphite foil are commonly used as base electrodes [Shukla and Kumar, 2018]. The electrode catalysts can be platinum black or metal oxides as well as their

nanoparticles coated on/dispersed in carbon materials. Similarly, carbon nanotubes, graphene, N doped graphene/graphene oxide find applications as electrode material. Other less commonly used electrode materials include gold, silver, copper, nickel, cobalt, aluminum, titanium, and stainless steel [Zhao *et al.*, 2008]. Baudler *et al.* [2015] found that carbon electrodes are better than other electrodes as they offer low internal resistance, are cheap, recyclable, non-corrosive, and usable for a long time. The drawback of carbon electrodes, particularly for PMFC applications, is the dark and opaque appearance that blocks light or has a shading effect. In addition, these have low thermal conductivity, resulting in low power output. Therefore, transparent metal electrodes are suitable for PMFC applications [Baudler *et al.*, 2015].

The disadvantages of metal electrodes include low surface roughness that reduces charge transfer rates and the absence of well-defined pores that prevents proper microbial attachment [Logan *et al.*, 2006]. Moreover, metal electrodes may corrode over time resulting in background currents and lower conductivity. Literature studies suggest that the nanoscale surface morphology of electrodes decides the conductivity and ability to interface with microbes [Bacakova *et al.*, 2011; Cao *et al.*, 2009; Legeay *et al.*, 2010; Sekar *et al.*, 2004]. Even with electrodes made of similar carbon material, differences in conductivity, surface area, space, and size of carbon microfiber can result in variable MFC performance [Sanchez *et al.*, 2015].

D. Separator

The electrolyte and separator should have high conductivity. The anions and cations flow in opposite directions in closed circuits with flow rates proportional to the magnitude of the current. The separator has two roles: (1) to prevent the mixing of anodic and cathodic substrates and (2) to allow the movement of ions across the chambers. Separators like electrodes should be non-toxic, have high ionic conductivity, and be impermeable to oxygen. The most commonly used separators are proton exchange membranes that wear negatively charged groups like $-PO_3^-$, $-PO_3^{-2}$, $-COO^-$, $-C_6H_4O^-$, and $-SO^{-3}$ that successively protonate and deprotonate [Rodenas Motos *et al.*, 2015]. The lower ion/proton conductivity increases the internal resistance, lowers conductivity, and creates a pH gradient with low pH at the anode. Low pH disrupts microbial growth and lowers power output [Winfield *et al.*, 2013]. MFC can be operated without any separator, but this decreases the coulombic efficiency of the system due to the diffusion of oxygen to the anode and electron donor to the cathode [Ghangrekar and Shinde, 2007]. The anion exchange membranes with positively charged groups like, $-PR^+$, $-SR^+$, $-NH_3^+$ help exchange negative ions creating an ionic balance [Zhuang *et al.*, 2012]. Separators like salt bridges, glass fibers, glass wool, clayware membranes, and ceramic membranes can exchange cations and anions primarily due to their high water-holding capacity. The separator needs periodic replacement/cleaning as they tend to clog in long-term operations lowering the MFC performance. Separators made of non-biodegradable materials are undesirable. Thus, ceramic separators like clayware hold promise for scale-up MFC systems. Behera and Ghangrekar [2011] demonstrated the efficiency of the terracotta separator that has a wall thickness of 4 mm. Similarly, rock phosphate blended clayware can be used as a separator showing maximum power density, 5% RP blend gives 890 ± 95, 10% RP blend gives 960 ± 120, and CW gives 1200 ± 152 mW/m^3 of power density [Khandelwal *et al.*, 2018].

E. Effect of light intensity, temperature, dissolved oxygen (DO), CO_2, pH, and salts

Light is essential, and the photoperiod's duration determines the power output. High light intensity increases the temperature, enhancing the reaction rate and the substrate utilization rate up to a certain temperature [Shukla and Kumar, 2018]. A light intensity of 3500–100,000 lux with a light/dark regime of 18/6, 12/12, and 16/8 h was reported as optimum for PMFC operation [Reddy *et al.*, 2019]. The optimum temperature for PMFC operation is 30 ºC but may vary from organism to organism. DO also increases with light intensity. However, as mentioned in the previous sections, high DO inhibits algae growth. The DO content also depends on the types of algal species used at the cathode. The PMFCs can provide a DO content as high as 18-19 mg/l for cathodic reactions [Taşkan *et al.*, 2021]. A minimum DO of 2.2 mg/l is required for the continuous operation of PMFC [Jang *et al.*, 2013]. The DO content also goes down with salinity [Kim and Chung, 1984].

A neutral pH range of 6.8-7.5 is optimal for algae growth. Carbon dioxide dissolves well in alkaline pH, and algae absorb better bicarbonates [Reddy *et al.*, 2019]. The CO_2 concentration at the cathode plays an essential role in MFC performance, with an optimum value of about 5% CO_2-air mixture [Reddy *et al.*, 2019]. There are two methods for supplying CO_2 to the PMFC: *in-situ* and *ex-situ*. In the *ex-situ* method, the catholyte is purged or supplied with pure CO_2 gas or bicarbonate generated elsewhere. In an *in-situ* way, CO_2 generated through anaerobic digestion of organic matter at the anode is used. There are benefits and drawbacks to both strategies. Microalgae grow faster with the *ex-situ* method, but the system requires additional units for the transport of CO_2. The *in-situ* method relies on the metabolic rate of microbes at the cathode, the partial pressure, and pH of the catholyte. Generally, anodic off-gas supports effective algae growth [Khandelwal *et al.*, 2018]. It directly affects how well the PMFC works, making the material more conductive.

2.9.3 Economic importance of PMFC

Algae accumulate a high oil content in their cells, and the oil composition is suitable for biodiesel production. The residual algae biomass is rich in proteins and carbohydrates. In a biorefinery, the residual algae are often subjected to biogas generation (Figure 2.6). However, the same can be used as an anodic substrate in MFC. Algae biomass is also bio-convertible to ethanol, biogas, and biohydrogen (Figure 2.6). Algae harvest and drying prior to lipid extraction is challenging. Therefore, wet algal biomass transesterification has been worked out. Direct or wet transesterification is the same as dry transesterification except that the extraction step is skipped, and the whole biomass is used as the reaction's feedstock [Shukla and Kumar, 2018]. Microalgae only require a little pre-treatment before fermentation because their cell walls have only a thin cellulosic fence and lack lignin.

Conversely, macroalgae must be treated first to get the stored carbohydrates out, while microalgal fermentation produces ethanol, acetate, hydrogen, and carbon dioxide. Hydrogen production from algal biomass can be accomplished through photobiological and fermentative processes [Shaishav *et al.*, 2013]. Hydrogenase is the main enzyme that speeds up reactions that lead to the production of biohydrogen. Some microbes can break down the organic compounds in algae without oxygen to make methane and carbon dioxide. Algal biomass can avoid the requirement of harvesting, dewatering, drying, or oil extraction to produce biogas [Shukla and Kumar, 2018].

Algae biomass is rich in carotenoids, terpenoids, xanthophylls, chlorophylls, phycobilins, polyunsaturated fatty acids, polysaccharides, vitamins, sterols, tocopherols, and phycocyanins [Ammar *et al.*, 2022]. Algae are frequently utilized as dietary supplements because of their nutritional value. *Spirulina* and *Chlorella* are two well-known algal species used as food sources. Algae aids in treating diseases like diabetes, rheumatic disorders, and high blood pressure in the arteries. Algae also benefit memory and concentration by providing omega 3 and omega 6 polyunsaturated fatty acids required for brain development. Additionally, they fight off bacterial, fungal, and viral infections. Algae are also rich in natural antioxidants and antimicrobials that improve shelf life and circumvent artificial preservatives [Gonçalves, 2021].

Algae, which can be unicellular, multicellular, filamentous, or saponaceous, are examples of organisms that produce their food through photosynthesis. With over 200,000 species, they are also the most prominent primary producers in the world. Microalgal production requires mass cultivation, biomass recovery, and downstream operations to ensure a consistent yield for food, chemicals, feed, biofuel, and biofertilizers, as shown in Figure 2.4 [Balasubramaniam *et al.*, 2021]. Blue-green algae (microalgae) can make plant growth hormones, polysaccharides, chemicals that kill bacteria, and other metabolites. They can also improve the fertility and quality of the soil [Ronga *et al.*, 2019]. According to Guo *et al.* [2021], the agroecosystem's primary sources of organic matter are cyanobacteria and green microalgae. In the case of constructed wetlands PMFCs, algae can make a big difference in the amount of

organic carbon in the soil by taking up carbon dioxide. Cyanobacterial heterocyst cells (e.g., *Nostoc*, *Anabaena*, and *Aulosira*) may fix atmospheric nitrogen to satisfy the needs of the soil's microbiota and plants [Fritsch, 1945]. Several studies have shown that injecting cyanobacteria or groups of cyanobacteria into crops has made a big difference in the nitrogen content of the soil. Inoculating the soil with cyanobacteria can reduce the soil nitrogen fertilizer requirement by 25 to 40 % [Ammar *et al.*, 2022].

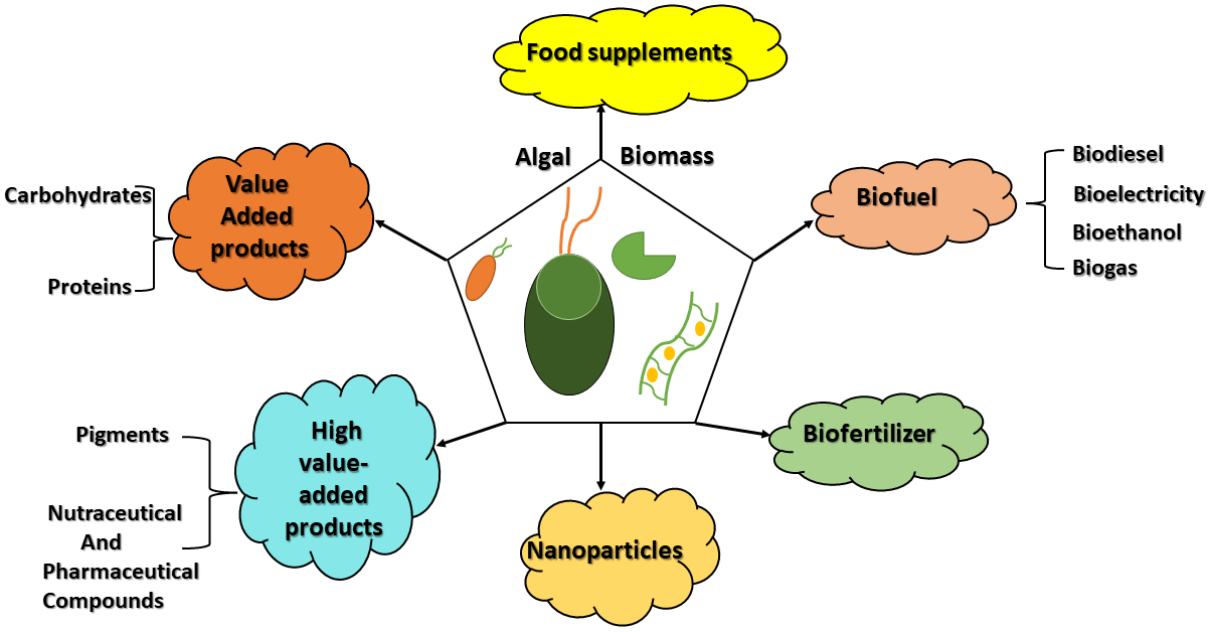


Fig. 2.6: Cultivation, value-added product generation, power generation, biofuel generation, and resource recovery of algae biomass [Mishra *et al.*, 2024].

2.10. USE OF PMFC IN THE TREATMENT OF SALINE WASTEWATER AND ORGANIC MATTER REMOVAL

A sediment MFC was built using a multi-anode reactor to treat saline wastewater and produces 2965 mW/m^2 of power density with a mixture of halophilic algae biomass as the anode substrate [Taşkan *et al.*, 2021]. Lakaniemi *et al.* [2012] used pretreated biomass of *Dunaliella tertiolecta*, which is a halophilic organism in dual chamber MFC, as an anodic substrate and observed the power density of 5.3 mW/m^2. The literature lacks studies on saline waste treatment using photosynthetic organisms or a combination of halophilic algae and halophilic bacteria. In light of the potential of algae-derived products, the energy production capabilities of algae-based PMFCs, the benefits of using PMFCs for saline wastewater treatment, and the need for exploration of the system at a mass scale, the following objectives were delineated for the present study:

1. Isolation of halophilic microalgae *D. salina* and its use at the biocathode of the saline PMFCs.

2. To study the effect of salt concentration on the PMFC performance.

3. Isolation of halophilic bacteria for the anode and operation of the PMFC with simulated saline wastewater containing starch and LEA as a substrate at the anode, operated outdoors.

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