

Advanced Techniques in Wastewater Treatment: A Comprehensive Review

Abstract: This comprehensive review explores advanced techniques in wastewater treatment, addressing the necessity for effective wastewater management due to increasing water scarcity and pollution from various sources such as households, industries, and agriculture. Conventional wastewater treatment methods, which include preliminary, primary, secondary, and tertiary stages, are increasingly being supplemented or replaced by advanced technologies due to their limitations in efficiency and capability. This review covers innovative approaches such as membrane filtration processes, advanced oxidation processes (AOPs), and biological treatments like membrane bioreactors (MBRs) and constructed wetlands (CWs). These advanced techniques demonstrate superior capabilities in removing complex contaminants including metals, organic and inorganic chemicals, and pathogens. The review also highlights the environmental benefits and potential for resource recovery and conservation offered by these advanced methods. By enhancing the quality of effluents beyond the capabilities of conventional methods, these advanced techniques play a crucial role in addressing the challenges posed by urbanization, industrialization, and population growth, ultimately contributing to sustainable water management and environmental protection.

Keywords: Wastewater treatment, advanced techniques, membrane filtration, advanced oxidation processes, membrane bioreactors, constructed wetlands, water sustainability.

INTRODUCTION

Wastewater is defined as water that has had specific substances added to it that have altered its physical, chemical, or biological characteristics and made it unfit to drink. The daily activities of humans are primarily reliant on water, and as a result, they discharge "waste" into the water. Body wastes (feces and urine), hair shampoo, hair, food scraps, fat, laundry powder, fabric conditioners, toilet paper, chemicals, detergent, household cleansers, dirt, and microorganisms (germs) are among the substances that can cause illness and harm the environment. It is widely recognized that a significant portion of the water that is supplied is disposed off as effluent, which underscores the significance of its treatment (Amoatey *et al.* 2011). Wastewater treatment refers to the systematic use of processes and technologies aimed at eliminating the majority of pollutants present in wastewater, with the ultimate goal of safeguarding the environment and promoting public health (Metcalf and Eddy 1991). The primary objective of

wastewater treatment is to extract pollutants, remove coarse particles, eradicate toxicants, and kill potential pathogens. This process is intended to allow the remaining clean water, which is referred to as effluent, to be discharged back into the environment for a variety of purposes (Alagha *et al.* 2020). According to World Vision, over 770 million individuals worldwide lack access to clean and secure water for domestic and drinking purposes (Villarín *et al.* 2020). Wastewater treatment is also designed to increase the availability of water for human consumption and alleviate the strain on natural water resources. Wastewater treatment is one of the most viable alternatives for improving water sustainability as water scarcity intensifies due to increased demand and encroaching drought conditions (Tortajada 2020). According to Al-Juaidi *et al.* (2014) the increasing human population will continue to place a greater burden on natural resources, such as pure water, for industrial and domestic purposes. The world is at risk of experiencing acute water shortages and diseases associated with polluted water in the absence of a sustainable water source. There are numerous sources of water contamination, including households, industry, mines, and irrigation. However, the largest source of water contamination is the extensive use of water by industry (Hai *et al.* 2007). The types of treatment of wastewater rely on its nature and the required quality of water after the treatment. Wastewater treatment (Figure.1) consists of four primary stages: preliminary (physical and mechanical), primary (physicochemical and chemical), secondary (chemical and biological), and tertiary (physical and chemical). Additionally, there is a stage for treating the sludge formed, which involves supervised tipping, recycling, or incineration. The aforementioned techniques have been implemented to eliminate chemical and biological contaminants that pose significant threats to the environment and public health (Sharma *et al.*, 2021).

While there are different types of conventional technologies that have been acknowledged for the purpose of treating water in homes and industries, these approaches have their limitations, as indicated by research (Oller *et al.* 2011; Gil *et al.* 2009; Gavrilescu 2004; Fomina and Gadd 2014; Gleick and Palaniappan 2010). Conventional methods exhibit a relatively high degree of automation. Typically, they necessitate power and stimulation. These systems necessitate specialized labour for their operation and maintenance. Further, the use of traditional methods has become restricted due to various challenges. These challenges include a growing public awareness of the negative effects of water pollution, a demand for higher quality water, a decrease in water resources due to rapid population growth and industrial development, and advancements in manufacturing industries that offer more advanced wastewater treatment processes. Eliminating contaminants such as diverse metals, organic and inorganic chemicals, and pathogens from water is more challenging. Therefore, researchers have introduced a range of innovative methods, including membrane filtration processes, Advanced oxidation Processes (AOPs), UV irradiation, carbon nanotubes (CNTs), magnetic techniques, and numerous others. Water is a critical natural resource; consequently, it must be safeguarded. It is imperative to prevent contamination by organic and inorganic contaminants in order to preserve the reserve's prevailing flora and fauna. Nevertheless, the environment is further polluted by the discharge of secondary contaminants or byproducts by certain technologies that are employed for this purpose (Bartolomeu *et al.* 2018). Consequently, there is an imperative need for wastewater treatment technologies that are both cost-effective and efficient (Bueno *et al.* 2017). Water scarcity is a global issue that underscores the urgent necessity for year-round

food production to combat starvation, deprivation, and malnutrition. This necessitates the reuse of wastewater for irrigation purposes (Inyinbor *et al.* 2019). As individuals, communities, and industries seek to ensure that essential resources are accessible and appropriate for use, advanced waste water treatment techniques have garnered global attention. This is essential as society addresses the consequences of urbanization, industrialization, population growth, and the depletion of potable water. Wastewater treatment is not always capable of effectively treating wastewater, which can result in a variety of issues, such as health problems and odours. New methods are employed to address these challenges in the treatment of waste water. The quality of effluent can be enhanced beyond the constraints of conventional technologies through the implementation of these advanced treatment technologies, thereby achieving the objective of resource recovery or resource conservation. The available domestic water supply can be increased by recycling advanced wastewater treatment plant effluents, either directly or indirectly. The primary scope of this comprehensive review is to explore advanced techniques in wastewater treatment. Given the increasing water scarcity and pollution from various sources such as households, industries, and agriculture, there is a pressing need for effective wastewater management. The review addresses the limitations of conventional wastewater treatment methods, which are often insufficient in handling complex contaminants, and highlights innovative approaches that demonstrate superior capabilities. These approaches include membrane filtration processes, advanced oxidation processes (AOPs), and biological treatments like membrane bioreactors (MBRs) and constructed wetlands (CWs) etc.

MEMBRANE FILTRATION PROCESSES

A membrane is a selective barrier that restricts the passage of components through it, thereby separating two phases (Ravanchi *et al.* 2009). In the process of filtering impurities, salts, heavy metal ions, viruses, and other particles from water, scientific membranes function similarly to the cell walls in our bodies. The membranes are the selective barriers in wastewater treatment that permit the passage of water while preventing the passage of undesirable substances (Chadha *et al.* 2022). Membranes can be classified as either organic (polymeric) or inorganic (ceramic or metallic) based on their composition. The morphology of the membranes is determined by the characteristics of the material. Figure 2 illustrates a membrane-separation system that divides an influent stream into two outgoing streams: the permeate and the retentate or concentrate. The permeate refers to the fraction of the fluid that has successfully traversed the membrane. The retentate, also known as the concentrate, comprises the components that have been excluded by the membrane (Chen *et al.* 2006).

In recent decades, the utilization of membranes as a filtration technology has experienced advancements and has been adopted in several sectors, including large-scale enterprises, textiles, and domestic applications. A notable characteristic of membrane filtration is its compact spatial requirement. The chemicals employed in this procedure are very minimal, hence rendering it more desirable and feasible compared to traditional pre-treatment techniques. The membrane filtration process can vary in size based on the size of the pores. The four types of filtration are Microfiltration (MF), Nanofiltration (NF), Ultrafiltration (UF),

and Reverse Osmosis (RO). These four processes operate when pressure is applied (pressure-driven). Firstly, let's delve into Microfiltration, examining its intricacies.

Microfiltration (MF)

Microfiltration (MF) is a method of filtering fluids using a membrane to eliminate particles that are in the micron size range. The MF membrane possesses hole diameters that span from 0.1 to 10.0 μm , effectively preventing the passage of microbes. Microfilters are effective for sterilizing water solutions. For instance, the *Pseudomonas diminuta* bacteria, which has a diameter of 0.3 μm , can be effectively disinfected using a microfiltration (MF) membrane that has hole diameters smaller than its size. However, both organic and inorganic molecules can permeate through MF membranes. The primary process for conventional depth filtration involves adsorption and trapping, whereas MF membranes utilize a sieving mechanism that relies on specific pore sizes to hold particles larger than the diameter of the pores. Therefore, this technique provides membranes that have an absolute rating, making them highly desirable for crucial tasks like as filtering sterile parental fluids, filtering sterile air, and producing particulate-free, extremely pure water for the electronics sector. MF membranes are often composed of natural or synthetic polymers, including cellulose acetate (CA), polyvinylidene difluoride, polyamides, polysulfone, polycarbonate, polypropylene, and polytetrafluoroethylene (PTFE) (Mulder 1996). Several recently developed MF membranes include ceramic membranes made from alumina, membranes generated through the anodization of aluminum, and carbon membranes. Glass is employed as a membrane material. It is possible to apply zirconium oxide onto a carbon tube that has pores. Sintered metal membranes are produced using stainless steel, silver, gold, platinum, and nickel materials, in the form of disks and tubes. The characteristics of membrane materials are directly manifested in their final uses. The selection criteria include mechanical strength, temperature resistance, chemical compatibility, hydrophobicity, hydrophilicity, permeability, permselectivity, and the cost of the membrane material and production process. Microfiltration commonly employs two process modes: dead-end and cross-flow modes (UN.ECE 1990). In the dead-end mode, the entire solution is compelled to pass through the membrane. The compounds to be separated are accumulated on the membrane, resulting in an increase in the hydraulic resistance of the deposit. The membrane should be replaced promptly when the filtrate flux no longer meets the minimum values required at the maximum operating pressure. This mode is mostly utilized for solutions that have a minor level of contamination, such as in the creation of water that is extremely pure. In the cross-flow mode, the solution moves horizontally across the surface of the membrane at a velocity ranging from 0.5 to 5.0 m/s. This prevents the creation of a layer on the membrane surface. A circulation pump generates the cross-flow velocity or shear force required to regulate the thickness of the cover layer. The system is mostly utilized for periodic back flushing, a process in which a portion of the filtrate is forcefully directed in the opposite direction at specific intervals, thereby disrupting the cover layer. The standard operational pressure for this mode is 1–2 bars (Noyes 1994). A MF has a broad spectrum of uses in the treatment of water and wastewater. An extremely advantageous prospect for MF lies in the field of municipal water treatment, enabling the disinfection of water without the need for

disinfectants such as ozone and chlorine. A recent study demonstrated that MF membranes has the capability to effectively eliminate viruses from surface water that is polluted. The reason for this discovery is that viruses are smaller than the pores in an MF membrane. It is believed that the viruses are being absorbed onto the clay particles, which are large enough to be trapped by the microfilter (Madaeni *et al.* 1995). MF has the potential to be used in the treatment of municipal sewage. Engineers are investigating the implementation of distributed processing, which entails the utilization of multiple small sewage treatment plants. MF can effectively eliminate heavy metals from waste streams by employing pretreatment chemicals to induce the precipitation of the metals into particles that can be easily filtered. Although conventional wastewater treatment includes pretreatment, its use of gravity settling for solid/liquid separation is less efficient compared to membrane filtration. An effective technique for eliminating heavy metal ions entails the attachment of the metals to a specific agent, followed by the separation of the laden agents from the effluent. Blocher and co-workers (Blocher *et al.* 2003) have developed a unique hybrid process that combines flotation with MF. This process involves integrating specially built submerged microfiltration modules directly into a flotation reactor for the separation step. This enabled the integration of the benefits of both flotation and membrane separation, while surpassing their constraints.

Nanofiltration (NF)

In 1984, Dr. Peter Eriksson introduced a new type of membranes for commercial use, which he dubbed NF membranes. NF is characterized by its capacity to selectively isolate minute solutes from a solution through two distinct methods. The first mechanism, widely accepted in the scientific community, involves the separation of molecules depending on their charge in water, a process known as ionic separation of NF. The second mechanism involves the process of separating uncharged solutes based on their molecular weight by sieving. The NF membrane types are categorized based on the membrane structure and pore shape, including isotropic micro-porous, nonporous, dense, electrically charged, asymmetric, ceramic, and liquid membranes (Trivunac and Stevanovic 2006; Krantz 2008; Baker 2004). Nanofiltration (NF) is a filtration technique in which a portion of the feed solution is allowed to flow through a semi-permeable membrane (Figure.3).

The incoming stream is separated into two parts: the permeate, which is the filtered fraction, and the retentate or concentrate, which is the non-filtered portion that is discarded. NF has demonstrated excellent elimination of organic matter. Chlorine disinfection is crucial for eliminating microbial growth that has been observed in NF distribution systems. In order to minimize the growth of microorganisms, the use of NF membranes that have a low capacity to retain inorganic elements and a high ability to remove organic materials can result in water of optimal quality. Membrane systems typically have two distinct flow configurations: Cross-flow with concentrate recycle (CFCR) and Flow system with a dead-end (Abdel-Fatah 2018) as depicted in Figure 4.

Cross-flow filtration, also known as tangential flow filtration, involves the use of a high-pressure flow of feed water over the membrane. The solution is separated into two components: the permeate, which passes through the membrane and is filtered, and the reject or concentrate, which flows along the membrane surface without undergoing separation or filtering. The

concentrate consists of all discarded salts and is typically concentrated with all unwanted substances. The flow system that includes a terminal unit with no outlet is being run by accumulating refuse until the process of backwashing becomes necessary. The backwashing procedure eliminates and removes all the collected concentrate by utilizing a washing liquid volume that is 2-5% of the total inflow solution. The cross-flow mechanism maintains a consistent flow rate of permeate and extends the lifespan of the membrane by preventing irreversible fouling.

Ultrafiltration (UF)

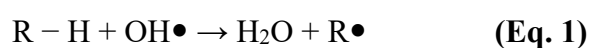
Ultrafiltration (UF) is a membrane-based separation technique that effectively separates, filters, and concentrates fluids with a size range between microfiltration and nanofiltration. The defined range of molecular weights for this domain is from 500 to 500,000 Daltons. The diameter of the corresponding aperture is approximately between 0.001 and 0.1 micrometers. The working pressure difference typically ranges from 0.1 to 0.8 megapascals, and the diameter of the separated component is roughly 0.005 to 10 micrometers. Figure 5 displays the schematic diagram of the ultrafiltration process. The technique can be conceptualized as utilizing the pressure difference between the two sides of the membrane as the impetus. Driven by static pressure, the ultrafiltration membrane acts as the filtering material to allow the solvent and small-molecular-weight solute, which have a smaller pore diameter, to pass through from the high pressure side to the low pressure side. Meanwhile, the large molecular weight solutes are retained on the high pressure side. When water passes through the membrane surface, only water, inorganic salts, and small molecules can go through the membrane. This prevents large molecules like suspended solids, colloids, proteins, and microorganisms from passing through. The objective is to purify, separate, and concentrate the solution (Taotao *et al.* 2008; Liu *et al.* 2016; Bray *et al.* 2021).

Ultrafiltration membranes are mostly retained by physical screening. Nevertheless, the pore size of ultrafiltration membranes may occasionally exceed that of solvents and solute molecules. Despite its intended purpose of not trapping, it surprisingly exhibits a noticeable effect of separation. The chemical properties of the membrane surface, such as electrostatic effects, may be the cause. In conclusion, the retention of ultrafiltration membranes is facilitated by three primary mechanisms: adsorption on the membrane's surface and in the pores, retention in the pores, and the elimination of mechanical pores on the membrane's surface (Polyakov *et al.* 2013).

Reverse Osmosis

Reverse osmosis (RO) is acquiring global acceptance in both water treatment and desalination applications. The process is pressure-driven, and a semi-permeable membrane is used to reject dissolved constituents that are present in the feed water. This rejection is the result of physical–chemical interactions between the solute, solvent, and membrane, as well as size exclusion and charge exclusion (Radjenovic *et al.* 2008; Bellona and Drewes 2005). A pressurized feed solution is passed over one surface of the membrane during the procedure. The water will

migrate from the more concentrated solution to the more dilute solution through the membrane as long as the operation pressure, which varies from 10 to 70 bars depending on its application, is greater than the osmotic pressure of the feed solution. In a typical procedure, the semipermeable membrane allows solvent (e.g., water) to flow from a dilute concentration to a more concentrated solution until equilibrium is achieved (Noyes 1994). This process will be reversed by applying high pressure to the concentrated side. A higher concentration of solute is left behind as a result of the solvent flowing away from the concentrated solution. In application, the waste stream passes through the membrane; however, the solvent (e.g., water) is driven through the membrane, while the remaining solutes (e.g., organic or inorganic components) do not pass through and become progressively concentrated on the feed side of the membrane. The majority of RO membranes are composed of polymers, including cellulosic acetate and matic polyamide varieties, and are rated for NaCl rejection at 96–99%. Two varieties of RO membranes are typically used: thin film composite membranes and asymmetric or skinned membranes. The thin film is composed of a variety of polyamines and polyureas, while the support material is typically polysulfones. The pore structure of RO membranes is the tiniest, with a pore diameter that ranges from approximately 5 to 15 Å (0.5 to 1.5 nm). The semipermeable membrane permits only the smallest organic molecules and unchanged solutes to pass through, with the water. This is due to the extremely tiny size of RO pores. The membrane will also reject a greater than 95–99% of inorganic compounds and charged organics as a result of the charge repulsion set up at the membrane surface. The primary benefit of RO for the treatment of process effluents is its capacity to concentrate diluted solutions for the recovery of salts and compounds with minimal power consumption. The primary energy requirement for separations is a high-pressure pump; no latent heat of vaporization or fusion is necessary. Additionally, it necessitates comparatively limited floor space for compact, high-capacity units and demonstrates favorable recovery and rejection rates for a variety of conventional process solutions. Advanced oxidation processes (AOPs) are a class of chemical treatment techniques that can be used to break down organic materials that are resistant to conventional methods. These techniques involve oxidation reactions with a strong, non-selective hydroxyl radical (OH•), which can break down organic pollutants that are resistant to conventional methods and improve the biodegradability of wastewater (Rekhate and Srivastava 2020). AOPs have the potential to totally mineralize organic molecules into carbon dioxide and water (Eq. 1).



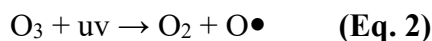
Hydroxyl Radical (•OH) is a very effective oxidizing agent that can be used to break down organic pollutants that are resistant to widely utilized oxidants like O₃, O₂, and Cl₂. The hydroxyl radical plays a crucial role in the elimination of harmful compounds. The hydroxyl radical, formed through a chemical reaction, initiates a cascade of reactions that ultimately results in the full breakdown of organic contaminants (Munter 2001). AOPs can lead to the complete mineralization of pollutants to CO₂, water, and inorganic compounds, or at least their transformation into more benign products, through chemical wastewater treatment. In addition, the partial decomposition of non-biodegradable organic contaminants can result in biodegradable intermediates. Therefore, combined AOPs were implemented as pre-treatments, followed by biological processes are both cost-effective and highly economically viable

(Cañizares *et al.* 2009). Despite the fact that AOPs employ a variety of reagent systems, such as photochemical degradation processes (UV/O₃, UV/H₂O₂), photocatalysis (TiO₂/UV, photo-Fenton reactives), and chemical oxidation processes (O₃, O₃/H₂O₂, H₂O₂/Fe²⁺), they all generate OH[•] radicals. These radicals are highly reactive, attack the majority of organic molecules, and are not highly selective (Skoumal *et al.* 2006; Rosenfeldt *et al.* 2007).

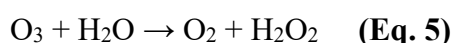
OZONE BASED AOPS

Ozonation and UV radiation (O₃/UV)

The combination of ozonation and UV-radiation (O₃/UV) is a highly effective catalytic system for breaking down persistent contaminants in wastewater. The process begins with the decomposition of ozone through photolysis, which is then followed by the generation of OH[•] radicals through the reaction of O[•] with water (Emam, 2012). The combined impact of O₃ and UV light enhances the breakdown of ozone through direct mechanisms described in equations (2)-(4), as well as the indirect generation of hydroxyl radicals as described in equations (5) and (6). The hydroxyl radicals produced in a water-based solution react with the aromatic ring in the dye molecule, leading to the creation of smaller aliphatic molecules such organic acids, aldehydes, and ketones (Khare *et al.* 2007). Ultraviolet (UV) light accelerates the breakdown of recalcitrant dyes by producing more free hydroxyl radicals (OH[•]), which in turn enhances the rate at which the dyes lose their color (Tichonovas *et al.* 2017). The production of hydroxyl radicals can be illustrated using equations (2) to (6).



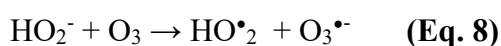
The indirect production of OH[•] by the following reaction is also possible.



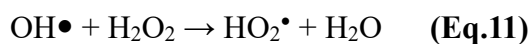
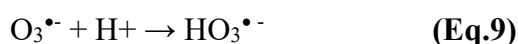
The combination of O₃ and UV increases the degradation of azo dye at all pH levels (Wu 2008).

O₃/H₂O₂

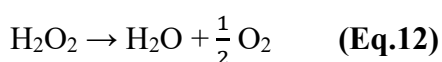
H₂O₂ in conjunction with ozonation is a highly effective catalytic system for the degradation of refractory pollutants in wastewater. Peroxone AOP, which is also known as the O₃/H₂O₂ process, is characterized by a radical chain mechanism that is initiated by the ozone decomposition of the hydroperoxide anion HO₂⁻. The synthesis of OH[•] radicals is facilitated by the synergistic effect of O₃ and H₂O₂.



It is probable that O_3 reacts with the excess HO_2^- that is produced from Eqs. (7)-(8), resulting in the production of OH^\bullet through Eqs. (9-11).



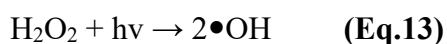
Nevertheless, the formation of the hydroperoxide ion (HO_2^\bullet) is a consequence of the scavenging of OH^\bullet by excess H_2O_2 , as illustrated in Eq. (11). It is not advisable to have a hydrogen peroxide concentration that is too low, as H_2O_2 effectively competes with hydroxyl radicals (Eq. (11)) and decomposes without oxidizing the pollutants, as demonstrated in Eq. (12) (Rodríguez *et al.* 2013).



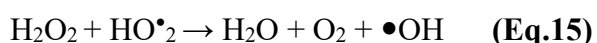
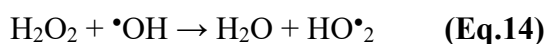
Below a certain level of ozone dosage, the addition of H_2O_2 did not result in any significant increase in the rate of OH^\bullet formation (Barry *et al.* 2014). The initiators/promoters H_2O_2 undergo a reaction with ozone until they cease to have an impact on ozone degradation. The researchers Barry *et al.* (2014) defined the ozone dose at which reactions with the initiators/promoters chemicals are completely depleted as the ozone dose threshold. Beyond this threshold, the addition of H_2O_2 enhances the rate of HO^\bullet formation. The authors noted that the addition of H_2O_2 does not significantly affect the exposure to HO^\bullet during ozonation, unless doses exceeding the threshold ozone doses are applied.

UV/H₂O₂ (Ultraviolet/Hydrogen Peroxide Processes)

In general, the combination of UV light radiation with hydrogen peroxide can effectively generate OH radicals. Additionally, UV light serves as a natural disinfectant for various organic contaminants and wastewater systems. The utilization of these systems has been documented in numerous sectors, ranging from the pharmaceutical business (Bobu *et al.* 2013; Jamil *et al.* 2017) to the textile industry, as well as in the removal of organic pollutants, and so on (Pandis *et al.* 2022). Modeling the mechanisms and processes (Imoberdorf and Mohseni 2012) has allowed for an investigation into the chemistry of this technique. The results suggest that substituting expensive H_2O_2 with chemicals like Cl_2 could be a beneficial alternative. This substitution is particularly effective at low pH levels and low UV doses (38). The primary chemical process taking place in these systems is outlined as follows (Zoschke *et al.* 2012):

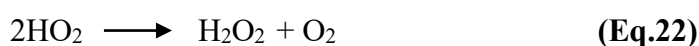
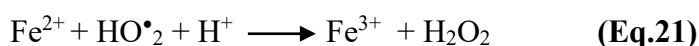
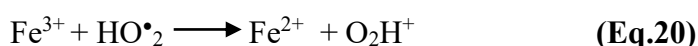
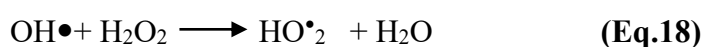


Under the influence of radiation, hydrogen peroxide molecules generate OH radicals. The decomposition is ascribed to a Haber-Weiss mechanism, which is triggered by the breaking of the O-O bond. The creation of additional OH molecules is initiated by the following chemical reactions (Oppenlaender 2007):



Fenton-Related AOPs

Iron is the most commonly utilized metal among those capable of activating H₂O₂ and generating hydroxyl radicals in water. The Fenton process involves the reaction of H₂O₂ with Fe²⁺ to produce highly reactive species. The reactive species generated are commonly identified as hydroxyl radicals, however other compounds including ferryl ions are suggested. The Fenton-related chemistry for water and wastewater treatment has been extensively examined in previous literature (Pignatello *et al.* 2006). The Fenton radical processes predominantly encompass the subsequent reactions:



The generation of OH· is facilitated by electron transport, as described in Equation 16. Nevertheless, the OH· generated can be eliminated by either of the Fenton reagents, as seen in Equations 17 and 18. Hence, it is necessary to empirically establish the ideal molar ratio between iron ions and hydrogen peroxide in order to minimize the undesired scavenging. Despite the fact that Equation 17 suggests that the Fe³⁺ created from Equation 16 can be converted to Fe²⁺, the iron cannot function as a catalyst in the Fenton system due to the significantly lower rate constant in Equation 17 compared to Equation 16. As a result, Fe³⁺ precipitates as iron sludge under normal water and wastewater treatment conditions. The sludge must be disposed of separately, which leads to increased complexity in treatment and higher operational expenses. It is important to mention that the production of hydroxyl radicals is most efficient during the Fenton reaction when the pH is acidic (Deng and Zhao 2015).

ADSORPTION USING CARBON NANOTUBES (CNTs)

Since its discovery in 1991, carbon nanotubes (CNTs) have been widely recognized as an exceptional material for various environmental applications. Carbon nanotubes (CNTs) possess a cylindrical hollow structure, a large specific surface area, a high pore volume, a high aspect ratio (i.e., a high length-to-width ratio), hydrophobic walls, good electrical conductivity, stable chemical properties, and are more mesoporous than activated carbon (AC). These characteristics make CNTs an exceptional adsorbent for the removal of organic compounds (Kanel *et al.* 2016; Wang *et al.* 2015). Furthermore, carbon nanotubes (CNTs) have been demonstrated to possess significant adsorption capabilities for heavy metals, phenols, natural organic matter, methyl orange, and red dye (Joseph *et al.* 2011). In addition, carbon nanotubes

(CNTs) are utilized as an adsorbent in water and wastewater treatment procedures to eliminate pharmaceuticals, personal care products (PPCPs), and endocrine disrupting compounds (EDCs) (Jung *et al.* 2015). CNTs have demonstrated significant potential as adsorbents for various organic pollutants, including 1, 2-dichlorobenzene, polycyclic aromatic hydrocarbons (PAHs), dyes such as methylene blue, methyl orange, and rhodamine B, phenols, and isonicotinic acid. This is due to their porous structure, large specific surface area, and strong hydrophobicity. Several studies have confirmed their effectiveness in adsorbing these pollutants, as reported by Bhatia *et al.* (2019), Li *et al.* (2020), Saxena *et al.* (2020) and Pete *et al.* (2021). The organic pollutants can be captured within the pores or adhered to the surfaces of carbon nanotubes (CNTs) through various types of interactions, including hydrophobic interactions, π - π interactions, van der Waals forces, electrostatic attraction, and hydrogen bonding. Typically, these interactions occur simultaneously (Pyrzynska 2008). CNTs can be classified into three basic types: single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs), and functionalized SWCNTs. A single-walled carbon nanotube (SWCNT) is composed of a single layer of rolled graphite sheet, while a multi-walled carbon nanotube (MWCNT) is made up of many SWCNTs with varying diameters arranged concentrically (Pan and Xing 2008). Functionalized carbon nanotubes (CNTs) possess oxygen-containing functional groups, including hydroxyl groups ($-\text{OH}$), carbonyl groups ($-\text{C}=\text{O}$), or carboxylic groups ($-\text{COOH}$) (Jung Son *et al.* 2015). Acids, such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3), can be utilized to oxidize CNTs, leading to the incorporation of functional groups (Celik *et al.* 2011). Heat treatment is frequently employed to reverse the process and eliminate the functional groups (Takagi *et al.* 2007). CNTs possess exceptional adsorption capacity and can be regenerated rapidly without any loss in their adsorption capability, making them a highly adaptable adsorbent.

MEMBRANE BIOREACTORS (MBRs)

The activated sludge process (ASP), which has been the conventional municipal wastewater technology for the past century, has been replaced by membrane bioreactor (MBR) technology as the preferred wastewater treatment technology. MBR is, in fact, one of the most significant innovations in wastewater treatment (Meng *et al.* 2009; Drews, 2010; Lin *et al.* 2012), as it addresses the shortcomings of the traditional ASP, such as the need for a significant amount of space for secondary clarifiers, the production of excess sludge, and the challenges associated with the removal of recalcitrants (Mutamim *et al.* 2013). MBRs have been employed for the treatment and reclamation of effluent in both municipal and industrial settings (Friha *et al.* 2014; Chu *et al.* 2006). MBR is a wastewater treatment process that integrates membrane technology with biological treatment (anaerobic, aerobic) (Eddy *et al.* 2014). In contrast to conventional biological procedures, which employ clarifiers for gravity settling, this process employs microfiltration or ultrafiltration to separate sludge generated by biological processes. MBR provides numerous advantages over the conventional activated sludge (CAS) procedure. An MBR typically consists of two primary elements: (1) the biological unit, responsible for the biodegradation of wastewater; and (2) the membrane module, which physically separates treated water from the mixed wastewater (Van Houghton *et al.* 2022; Chang *et al.* 2022). MBRs

can be classified into two groups based on their configuration: integrated MBR systems and recirculated MBR systems. The first group of bioreactors, generally referred to as integrated MBR systems, includes those that are equipped with internal membranes (Figure 6). The driving force across the membrane is generated by either generating negative pressure on the permeate side or pressurizing the bioreactor. The membrane is cleaned by regular back-pulsing and occasional chemical backwashing. A diffuser is placed right below the membrane module to aid in the cleaning of the filter surface. Simultaneously, the diffuser serves the dual role of mixing and aerating. Additional anaerobic or anoxic compartments can be incorporated to facilitate the concurrent biological degradation of substrates (Li *et al.* 2018; Zhao *et al.* 2022).

The second form is referred to as a recirculated (external) MBR system, where the membrane module is assembled externally to the bioreactor (Figure 7). This application can make use of membranes for both the inner and outer layers of the skin. A rapid crossflow velocity of the feed across the membrane surface creates a pressured environment, which serves as a driving factor for the separation process. Currently, the utilization of MBRs for commercial purposes has been on the rise. This can be attributed to the advancements in polymeric membranes, such as polyvinylidene fluoride (PVDF), polyether sulfone (PES), polyethylene (PE), and polysulfone (PSF), which are now more affordable and durable. These membranes offer lower pressure requirements and higher permeate fluxes (Erkan *et al.* 2018). A Membrane Bioreactor (MBR) system has several advantages compared to conventional activated sludge (CAS) and other wastewater treatment technologies. The bioreactor's capacity to effectively retain both suspended matter and a majority of soluble elements leads to a remarkable effluent quality that meets stringent discharge criteria and enables direct water reuse.

AEROBIC GRANULATION

The selection of microorganisms with the appropriate metabolic capabilities and their efficient separation from the treated effluent are necessary for successful wastewater treatment. A substantial amount of research has been conducted to reduce the settling time of activated sludge. This is accomplished through the use of biofilm reactors or the formation of dense flocs. Biogranules, a condensed form of biofilm that is produced through self-immobilization, are a significant advancement in this field. These granules are compact conglomerates of a variety of bacterial species, with each gram of biomass containing millions of organisms. (Lee *et al.* 2010). Aerobic granules are compact clusters of microbial cells that occur spontaneously in aerobic wastewater treatment systems. These objects are distinguished by their round shape, robust structural strength, and capacity to quickly sink. The formation of these granules occurs by a self-immobilization process, in which many microbial species come together to break down both organic and inorganic substances present in wastewater (Zeng *et al.* 2024). The mechanism behind microbial aerobic granulation is still a topic of considerable controversy due to the complex nature of aerobic granulation. Based on the concept outlined by Zeng *et al.* 2024, aerobic granulation initiates with the clustering of microbial cells. Fungi utilize glucose as their carbon source and release H^+ ions to decrease the pH, so producing a favorable environment for their growth while inhibiting the growth of competing bacteria (Tay *et al.* 2002). Filamentous fungi undergo growth from spores to mycelia in response to shear stresses,

functioning as a focal point for the attraction of other microorganisms and as a supporting framework. Certain bacteria adhere to inorganic precipitates located inside the granule's core, where these precipitates serve as a central point for the bacterium's development and reproduction. Some bacteria utilize cations such as Ca^{2+} and Mg^{2+} to facilitate aggregation by decreasing electrostatic repulsion and increasing van der Waals forces. The application of shear pressures during the granulation process induces the release of extracellular polymeric substances (EPS), which then adhere to organisms and bind them together within the granule. The elevated cell surface hydrophobicity and intense hydraulic stress, along with the constrained settling time, promote the attachment of microorganisms to aggregates, resulting in the formation of aerobic granules. Granules are initially formed from small microbial clusters that expand through additional aggregation. These dense granules settle rapidly as a result of the selection pressure in the reactor, which favors biomass that settles quickly and eliminates biomass that settles slowly. Diverse microbial communities are able to contribute to the structure and function of granules by establishing distinct aerobic and anaerobic zones within the granules due to the oxygen and nutrient gradients. Microbial proliferation, EPS production, and shear forces that could potentially cause disintegration are all balanced by the maturation and growth of granules. The reactor's operation, which encompasses the feed composition, aeration, and cycle management, is essential for the maintenance of granulation.

MICROALGAE BASED WASTEWATER TREATMENT

The process of microalgae-based wastewater remediation is feasible by utilizing wastewater as a source of nutrients for microalgae growth. This approach enhances the sustainability of the process and promotes the concept of a circular economy. In recent years, a variety of effluent types have been utilized to cultivate algal biomass for phytoremediation purposes (Srimongkol *et al.* 2022). Microalgae-based systems are capable of bioremediating wastewater to a high degree, and they can remove 45–65% of BOD and COD (Al-Jabri *et al.* 2020; Geremia *et al.* 2021). Conventional waste water treatment (WWT) methods have the disadvantages of high operational costs and unavoidable secondary pollution from chemical processes, while microalgae-based WWT systems exhibit natural disinfection capabilities and are more effective in reducing nutrient contamination (El-Sheekh *et al.* 2021). In contrast, microalgae are the most prospective decontaminating agents for a variety of pollutants due to their high surface-to-volume ratios, which result in high biosorption capacities. They are capable of eliminating harmful substances and can transition between photoautotrophic, heterotrophic, and mixotrophic growth (Laraib *et al.* 2020). Microalgae-based bioremediation is regarded as a reliable alternative for the enhancement of conventional WWT systems, as it provides a solution to the liquid or solid residues generated by conventional methods (Figure. 8) and also converts them into value-added products (Figure. 9). Coupling the microalgal cultivation with other prevalent WWT systems is an effective approach to decrease the cost of microalgae production (Kalra *et al.* 2021). The commercial efficacy of microalgae has been the subject of increasing research due to their high capacity for nutrient uptake and the production of substantial biomass. In comparison to vascular plants, microalgae exhibit a significantly higher growth rate, and the cultivation of microalgae as a component of WWT does not have any adverse environmental effects. Microalgae biomass can double its original biomass within 13 hours of cultivation (Mohsenpour *et al.* 2021; Aron *et al.* 2021). Microalgae are capable of

withstanding harsh conditions and require only a limited amount of land for cultivation. This reduces the competition for land among other uses, including agriculture, livestock farms, industry, and human residential areas. The sustainable use of microalgae in wastewater treatment has been extensively researched for over 50 years in terms of the production of useful chemical compounds, such as biofuels, and wastewater treatment. This is due to the fact that microalgae can efficiently convert carbon dioxide (CO₂) into biofuel products and chemical substances without generating pollution, which can result in a reduction in greenhouse gas emissions. Additionally, these procedures surpass the drawbacks of conventional wastewater treatment, including the production of secondary pollution from chemical operations and the high operational costs (Rasoul-Amini *et al.* 2014; Aketo *et al.* 2020; Chai *et al.* 2021).

CONSTRUCTED WETLANDS (CWs)

CWs are engineering systems that are designed and constructed to control water pollution by utilizing the natural processes of emergent/floating/submerged wetland plants, saturated or unsaturated substrates/soils, and associated microbial communities (Saeed and Sun 2012; Almeida *et al.* 2017). They are synthetic systems that have been engineered to mimic the biological, chemical, and physical processes that occur in natural wetlands (Zhang *et al.* 2014). The utilization of CWs enables the more cost-effective, sustainable, and effortless remediation of wastewater, with a high rate of nutrient recovery and minimal maintenance/operation costs (Kamilya *et al.* 2022; Klomjek 2016) in an environmentally responsible manner (Moreira and Dias 2020; Dan *et al.* 2011). CWs are capable of treating effluent from a variety of sources, including municipal, livestock, industrial, agricultural, domestic, acid-mine waste, storm runoff, and landfill leachate (Rajan *et al.* 2020; Chang *et al.* 2022). The phytoremediation technique is capable of removing or degrading a variety of harmful compounds, such as antibiotics, heavy metals, landfill leachate, textile dyes, pesticides, hormones, petroleum, and explosives (Markou *et al.* 2018). Microbial degradation, plant absorption, substrate adsorption, and filtering by the packed media and biological predation are all methods by which a diverse array of pollutants, such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SSs), total Kjeldahl nitrogen (TKN), total phosphorus (TP), total coliforms (TCs), and metals, can be eliminated from wastewater with the assistance of CWs (Saeed and Sun 2011). Surface water flow CW (SCW), subsurface water flow CW (SSCW), and hybrid CW (HCW) are the primary classifications of constructed wetlands (CW). The first two classifications are primarily determined by their hydrological structure, while the third system is a combination of various CW types (Kumar *et al.* 2020).

1) Surface Water Flow CW (SCW)

SCW are in general shallow water flow channels or basins with some vegetation that is established on the soil layer (Vymazal 2014). In SCW, water travels horizontally at a minimum velocity, resulting in a water column depth of up to 80 cm. This category of CWs is partially exposed to sunlight and the atmosphere. The pollutants are efficiently removed through a variety of physicochemical or biological processes as the wastewater travels through the wetland and interacts with the vegetation (Wang *et al.* 2017). The upper surface of the wetlands functions as aerobic zones as a result of atmospheric diffusion, while anoxic and anaerobic zones are present in close proximity to the residues. However, the anoxic zone is present near

the water surface in high-loading SCW. This form of CWs is employed as an advanced wastewater treatment process, which is followed by secondary or tertiary treatment. The nitrification/denitrification process is the most effective method of removing nitrogen in SCW. The schematic representation of a surface flow constructed wetland (SCW) is depicted in Figure 10.

2) Subsurface Flow CW (SSCW)

Subsurface flow CW (SSCW) is a type of CW that is characterized by the growth of either saturated or unsaturated vegetation on the sediment. In these CWs, wastewater circulates either vertically or horizontally, causing pollutants to interact with microbes that inhabit the rhizosphere zone (Saeed and Sun 2012). According to Saeed and Sun (2017), the SSCW's contaminant removal mechanism involves the following steps: filtration and settling, precipitation and chemical conversion, adsorption on the media surface, plant uptake, organic matter removal by microbes, and nutrient conversion. The microbial reaction in SSCW is more pronounced than SCW during the removal of the contaminant. Water flows beneath the media in SSCW, and it can be classified into two categories based on the flow pattern: (a) vertical subsurface water flow CW (VSSCW) and (b) horizontal subsurface water flow CW (HSSCW).

Horizontal Subsurface Flow CW (HSSCW)

The effluent is horizontally introduced into the gravel media of CW in horizontal subsurface flow CW (HSSCW) and undergoes treatment. The water is not exposed to air and is fed into CW below 5 cm from the top stratum as a result of subsurface flow. The effluent enters aerobic, anoxic, and anaerobic zones. The oxygen is drained into waste water by aerobic zones located near the roots (Vymazal 2014). The dissolved oxygen (DO) in the upper zone of HSSCW is increased as a result of the oxygen released by plant roots. The lower zone continues to be anaerobic as a result of the inadequate oxygen supply. Vegetation activity is influenced by temperature, and DO content is low in winter but elevated in summer (Huang *et al.* 2013). Horizontal flow decreases DO levels due to high oxygen consumption during degradation. Despite low nutrient removal, HSSCW effectively removes solids and organics (Mburu *et al.* (2013a, b)). The horizontal subsurface flow constructed wetland (HSSCW) is illustrated in Figure 11.

Vertical Subsurface Flow CW (VSSCW)

VSSCW comprises of a flatbed topped with gravel and macrophytes planted on its surface. The upper layer of the CW is fed with wastewater, which then permeates the subsequent layers of the CW. The effluent then percolates through the gravel media to reach the outlet as a result of the gravitational force. The aeration of the bed is improved as a result of the vertical movement of effluent, which propels it out of the confined air and draws fresh air from the atmosphere. The purified water is collected in VSSCW, where the bed depth ranges from 0.45 to 1.20 m and the slope is 1–2% (Stefanakis *et al.* 2014). For improved oxygen transfer in constructed wetlands (CW), the gravel media is fully drained to allow fresh air to occupy the media. Atmospheric oxygen contributes more to bed oxygenation than oxygen from plants. In vertical

subsurface constructed wetlands (VSSCW), macrophytes help maintain hydraulic conductivity. Figure. 12 illustrates a schematic representation of a vertical subsurface flow-constructed wetland (VSSCW).

3) Hybrid Constructed Wetlands (HCW)

Hybrid CWs are formed by combining CWs in order to achieve effective effluent treatment. The arrangement of VSSCW and HSSCW is the primary component of HCW. The most frequently employed varieties of HCW are (a) VSSCW and HSSCW systems in series and (b) HSSCW combined with VSSCW systems (Stefanakis *et al.* 2014). In a combined system of VSSCW and HSSCW, the VSSCW unit is installed first to remove suspended solids and organic matter, as well as to provide nitrification. Initially, HSSCW is implemented in conjunction with HSSCW–VSSCW to eliminate organic matter, and subsequently, denitrification is obtained. Subsequently, VSSCW is implemented to optimize organic removal and establish favourable conditions for nitrification. According to Nguyen *et al.* (2018), HCW is a highly effective treatment procedure for the removal of all pollutants.

CONCLUSION- In conclusion, the comprehensive review of advanced techniques in wastewater treatment highlights significant progress and innovative methods developed to address the limitations of conventional wastewater treatment technologies. Traditional methods, while effective to an extent, face challenges such as high operational costs, extensive energy requirements, and the inability to remove certain persistent pollutants. Advanced treatment technologies such as membrane filtration, advanced oxidation processes, carbon nanotubes, and membrane bioreactors offer promising solutions. Membrane filtration processes effectively separate contaminants with high efficiency, while AOPs utilize strong oxidizing agents to break down complex organic pollutants into less harmful substances. Carbon nanotubes demonstrate exceptional adsorption capacities for various organic and inorganic pollutants, enhancing the overall treatment process. MBRs combine biological treatment with membrane filtration, addressing the shortcomings of traditional activated sludge processes by offering higher effluent quality and better handling of sludge. Constructed wetlands present a sustainable and cost-effective approach, leveraging natural processes for water purification. These systems are particularly beneficial for treating effluents from diverse sources, including municipal, industrial, and agricultural wastewaters, with low operational and maintenance costs. The review underscores the importance of integrating these advanced techniques to achieve efficient, cost-effective, and environmentally sustainable wastewater treatment solutions. As water scarcity becomes an increasingly critical global issue, the implementation of these advanced methods is vital for enhancing water reuse and conservation efforts, thereby ensuring the availability of clean water for future generations. Overall, the continuous development and optimization of these advanced wastewater treatment technologies are essential to meet the growing demand for high-quality water and to protect public health and the environment.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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Graphical Abstract

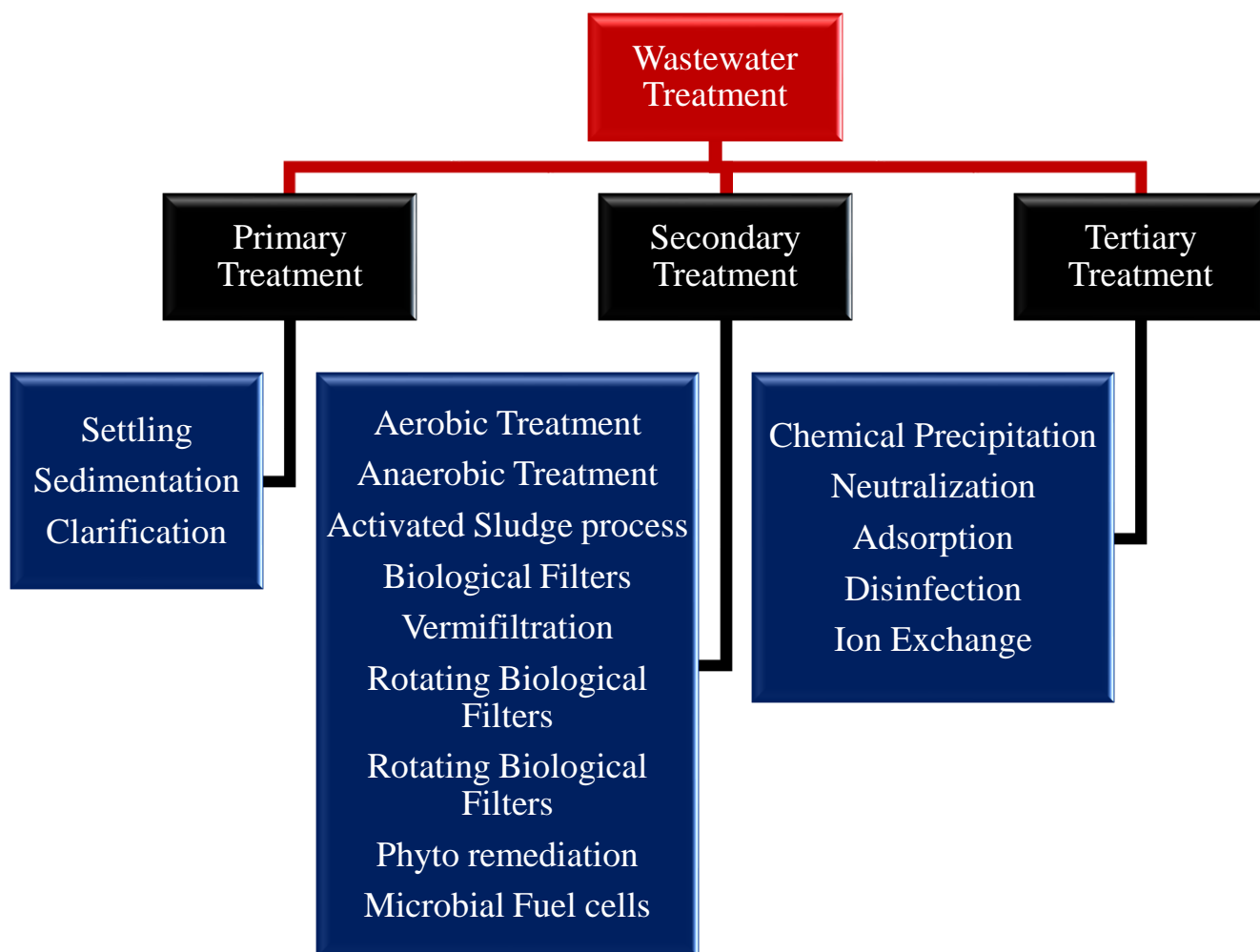


Figure 1. Stages of wastewater treatment

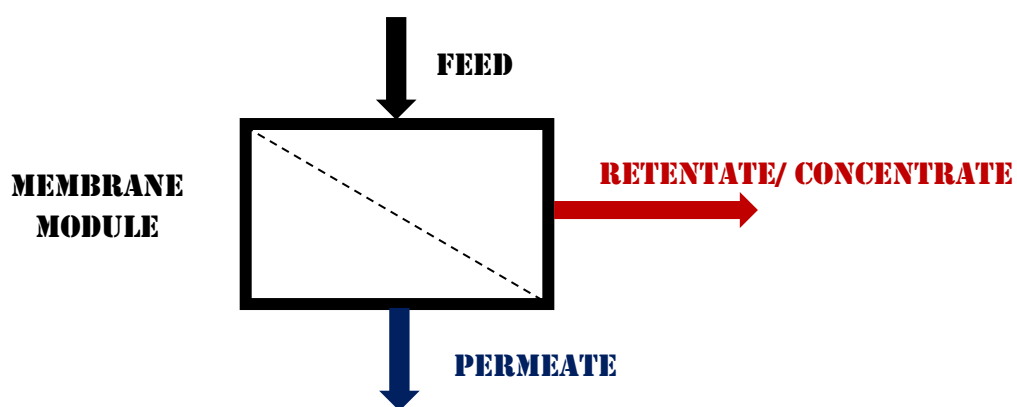


Figure 2. Diagram of a membrane separation system

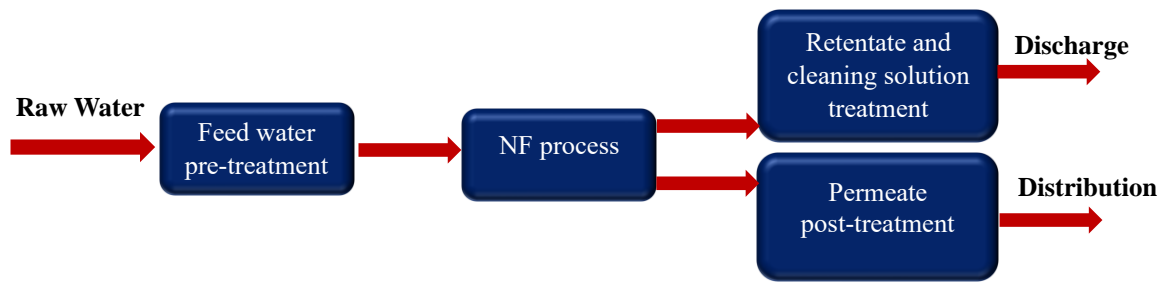


Figure 3. Illustration of Nanofiltration process

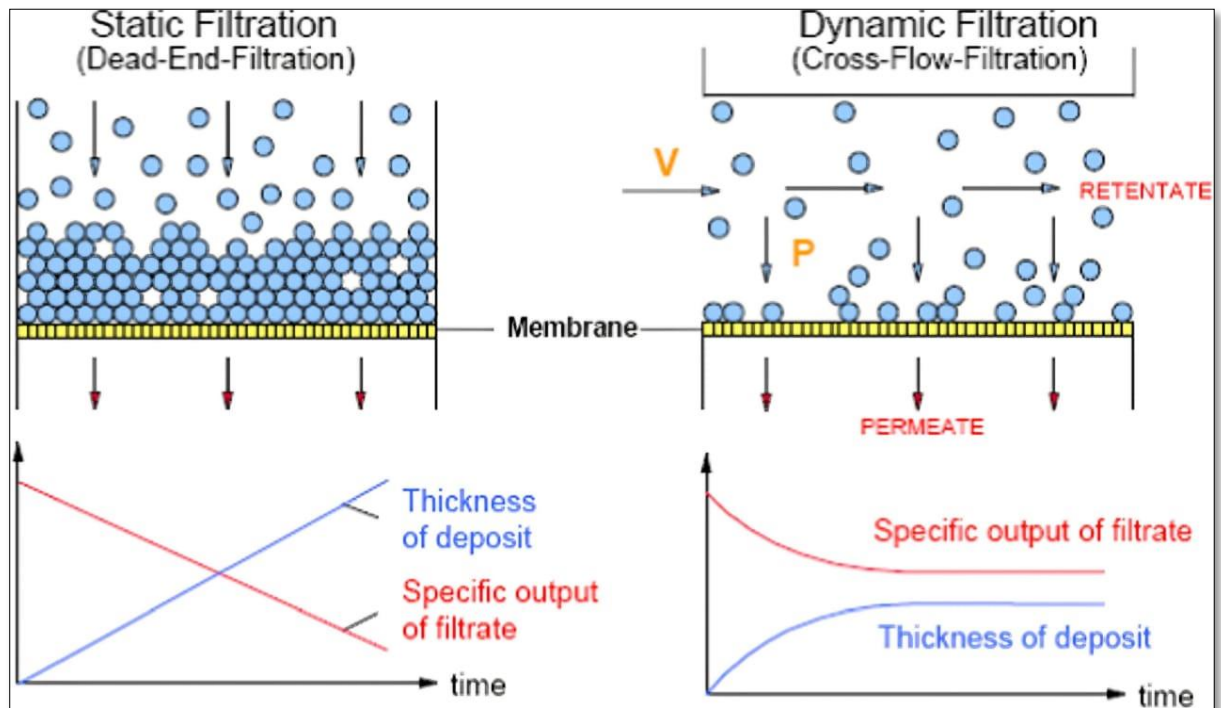


Figure 4: Membrane flow configurations

Cross-flow filtration, also known as tangential flow filtration, involves the use of a high-

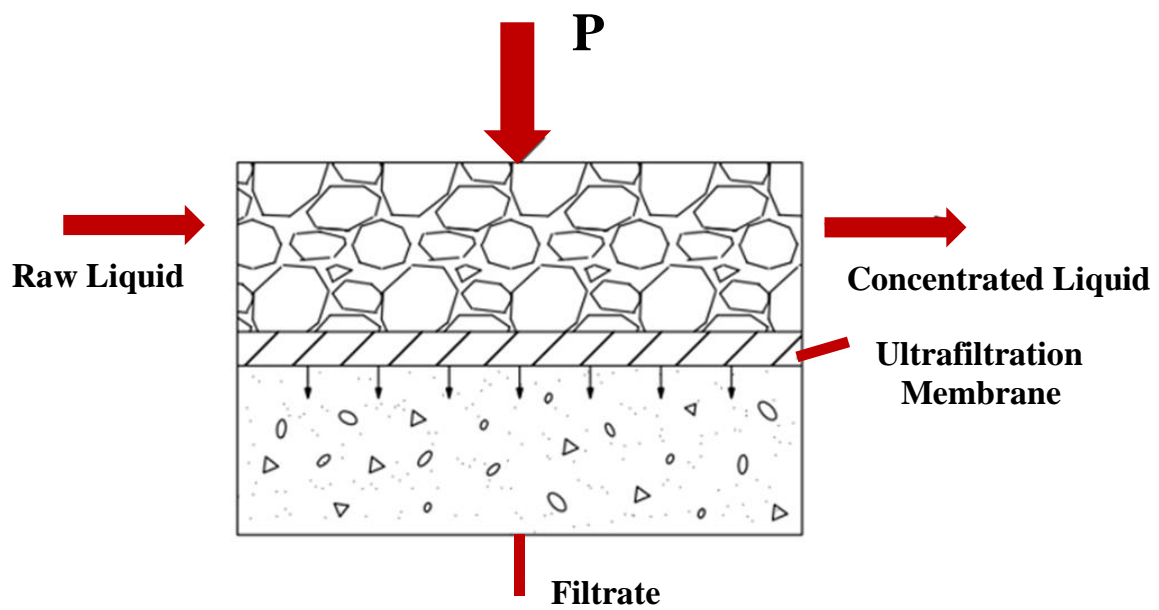


Figure 5. Illustration depicting the ultrafiltration process

ADSORPTION USING CARBON NANOTUBES (CNTs)

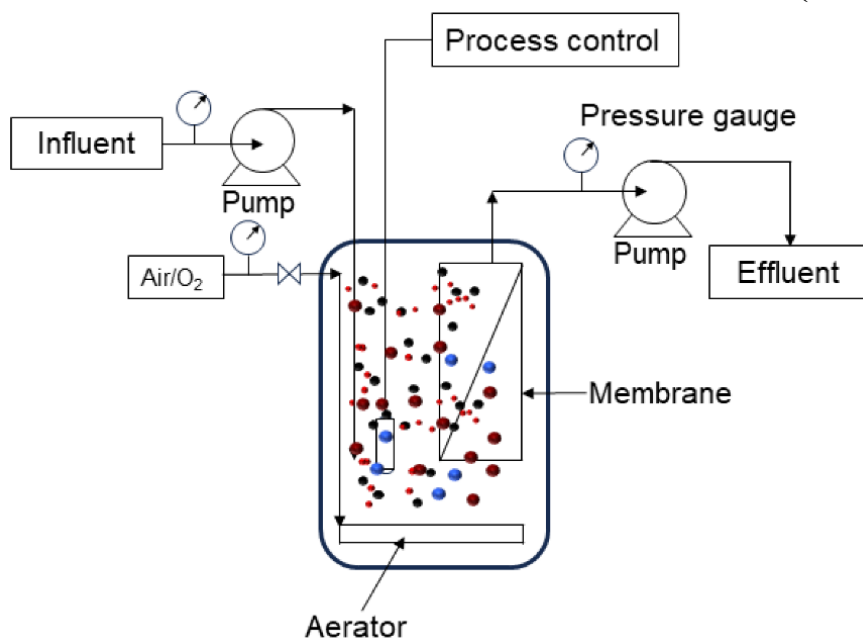


Figure 6. An integrated (internal) MBR system (Song *et al.* 2018).

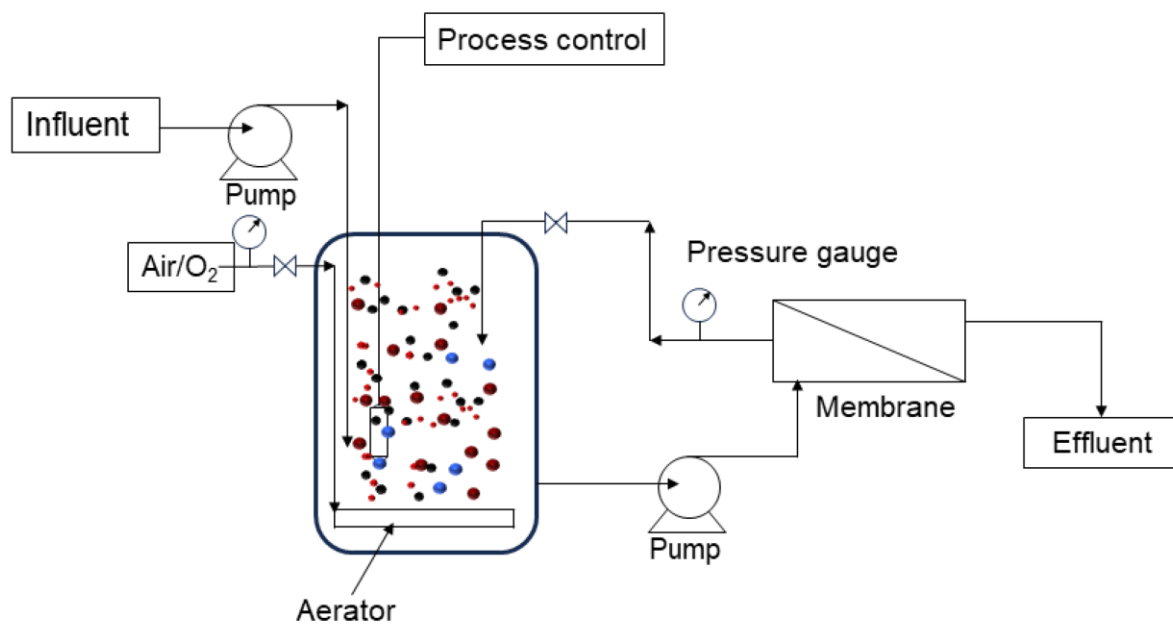


Figure 7. A recirculated (external) MBR system (Song *et al.* 2018).

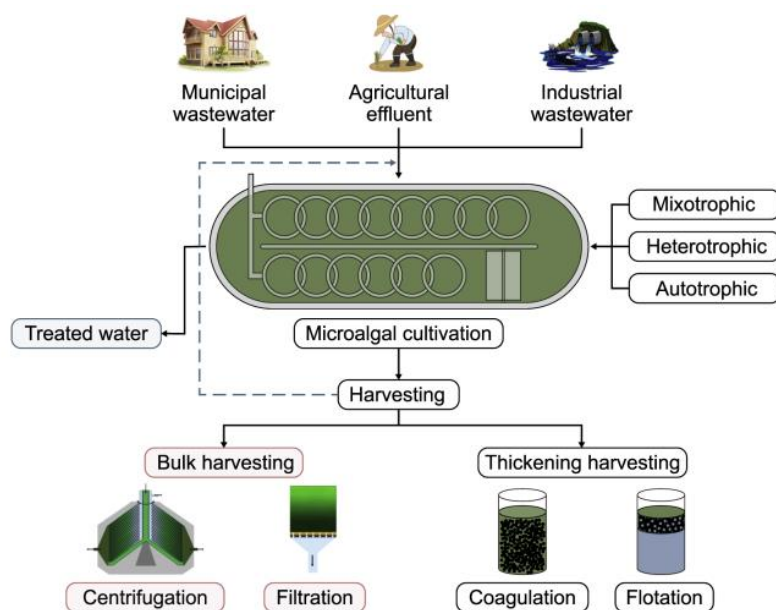


Figure 8. Microalgae-based wastewater treatment (⁹³Abdelfattah *et al.* 2022).

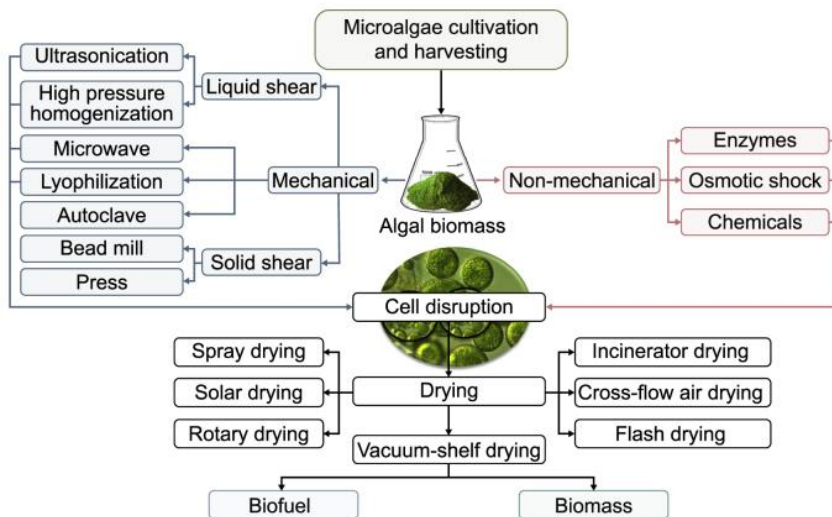


Figure 9. Methods for producing biomass and biofuel while treating wastewater with microalgae (⁹³Abdelfattah *et al.* 2022).

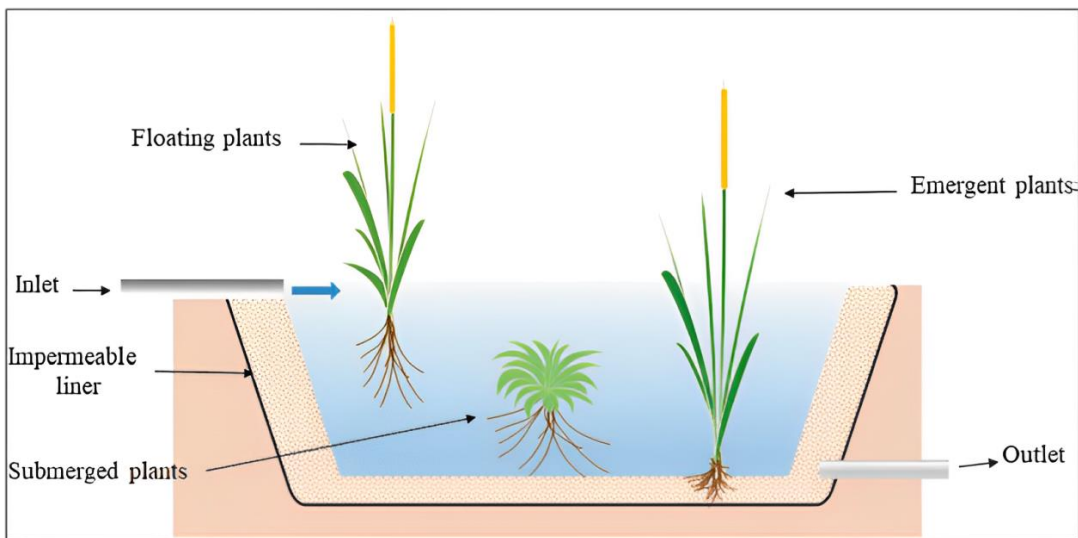


Figure 10. Surface flow constructed wetland (SCW)

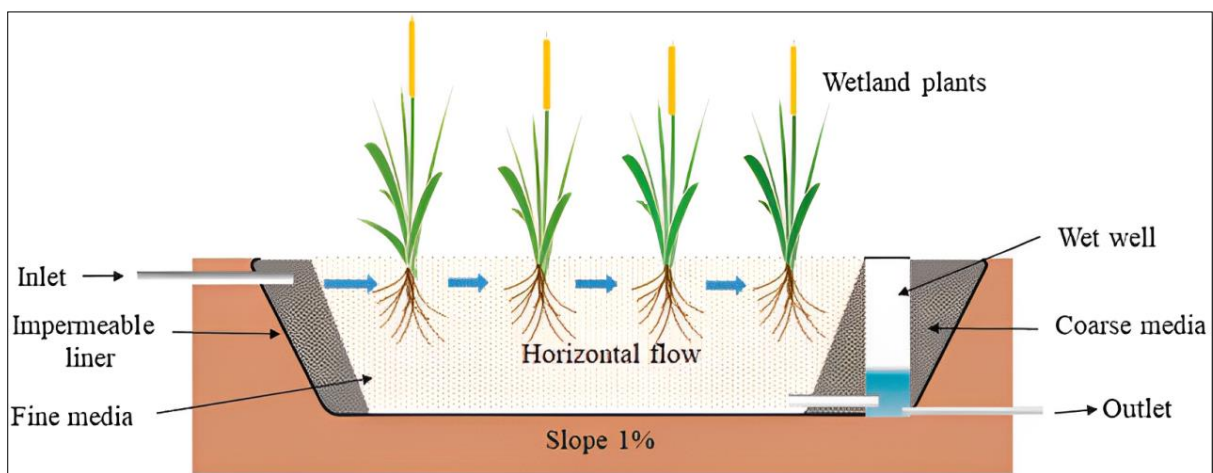


Figure 11. Horizontal subsurface flow constructed wetland (HSSCW)

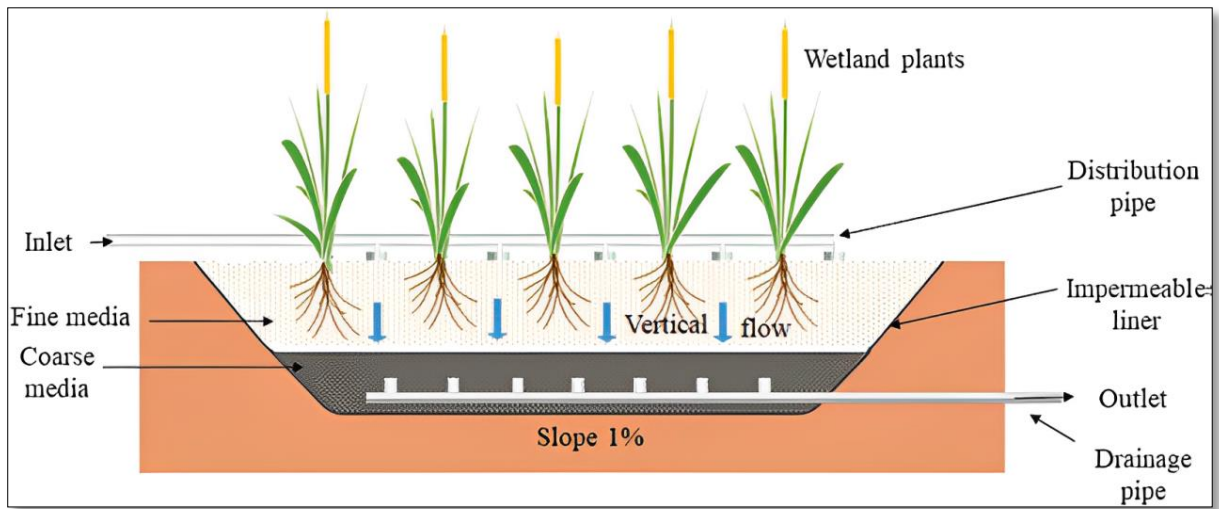


Figure 12. Vertical subsurface flow constructed wetland (VSSCW)