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# Treatment of Water and Wastewater for Reuse and Energy Generation-Emerging Technologies

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## Abstract

Fresh water quality and supply, particularly for domestic and industrial purposes, are deteriorating with contamination threats on water resources. Multiple technologies in the conventional wastewater treatment (WWT) settings have been adopted to purify water to a desirable quality. However, the design and selection of a suitable cost-effective treatment scheme for a catchment area are essential and have many considerations including land availability, energy, effluent quality and operational simplicity. Three emerging technologies are discussed, including anaerobic digestion, advanced oxidation processes (AOPs) and membrane technology, which holds great promise to provide integrational alternatives for manifold WWT process and distribution systems to mitigate contaminants and meet acceptable limitations. The main applications, basic principles, merits and demerits of the aforementioned technologies are addressed in relation to their current limitations and future research needs in terms of renewable energy. Hence, the advancement in manufacturing industry along with WWT blueprints will enhance the application of these technologies for the sustainable management and conservation of water.

**Keywords:** anaerobic digestion, advanced oxidation processes, membrane technology, renewable energy

## 1. Introduction

Wastewater, which is the biggest waste stream from municipalities, petrochemical, pharmaceuticals, food, textile, agricultural, polymer and paper industries and so on contain high contaminants of oil and salts of organic and inorganic compounds [1–5]. This strikes as a major ecological problem with high environmental impacts when discharged into the ecosystem without proper treatment. Furthermore, the industrial revolution associated with demographic growth have increased the demand for freshwater supply, which is depleting the natural fresh water supply sources [3, 5], although wastewater can be treated through various physical, chemical and biological strategies [1–3]. Unfortunately, the current conventional wastewater treatment methods cannot eliminate the contaminants. In addition conventional wastewater treatment can be expensive. Therefore, the quest for clean water and

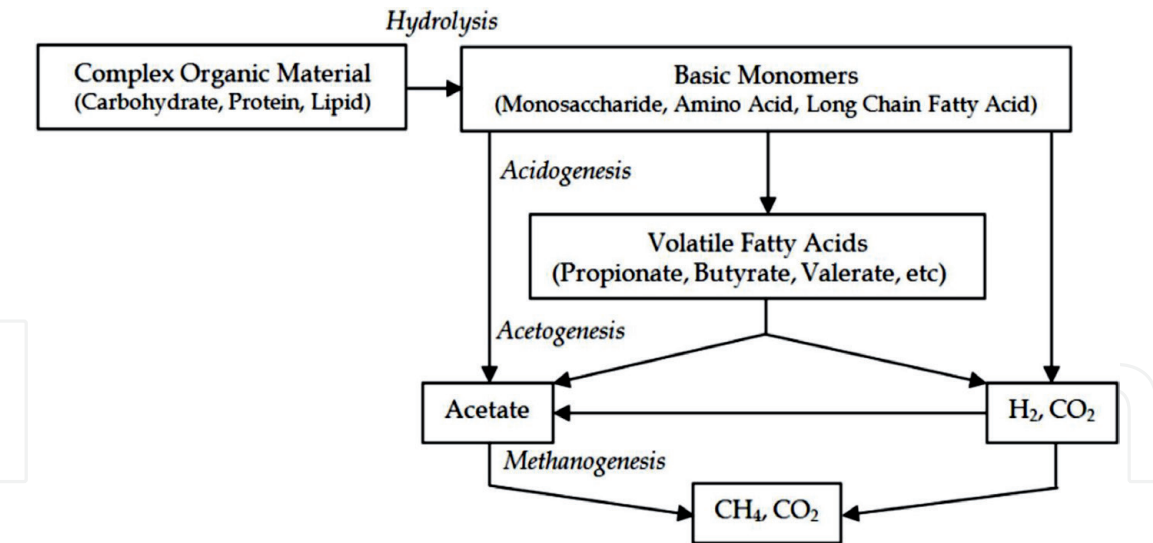
clean environment has resulted in various environmental protection agencies setting stringent discharge limits [3, 4]. Conversely, there are always variations in wastewater qualities which have different impacts on the environment [2–4], where a proper wastewater treatment incorporated with primary, secondary and advanced treatment strategies seems to more viable [1, 3, 4]. The primary treatment involves separating the solids from the liquids via filtration or sedimentation, whereas the secondary treatment removes the dissolved solids and other contaminants through chemical precipitation and biological process [4, 6, 7]. Then UV light or membranes are used for further treatment [1, 2, 5]. After which, the treated water can be profitable to farmers as well as the environment positively in sustainable manner viz. irrigation, and agricultural purposes. In this study, evaluating the streamline flow of innovative wastewater treatment technologies for reuse and subsequent sludge generation as an energy source is being addressed. The biological treatment is presented in section one, followed by membrane technology and lastly the advanced oxidation process. The current limitations and future prospects of each technology are also presented.

## 2. The biological wastewater treatment process

Municipal solid wastes are attracting more obstructive legislation with respect to landfill disposal of the biodegradable fraction [4, 8]. The treatment process for these organic fractions is biological wastewater treatment. These technologies maximises the recycling and recovery processes of waste components. The biological treatment is regarded as an important and vital aspect of wastewater treatment and is a technique employed for municipal or industrial use for soluble organic components [9]. Among all, the most widely employed method for sludge treatment is anaerobic digestion [9, 10].

### 2.1 Anaerobic digestion (AD) process

In this process, a large fraction of the organic matter (cells) is broken down into carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ), and this is accomplished in the absence of oxygen. About half of the amount is then converted into gases, while the remainder is dried and becomes a residual soil-like material. Kougias and Angelidaki [11] reported that the end products of organic assimilation in anaerobic treatment of waste are  $\text{CH}_4$  and  $\text{CO}_2$  as depicted in **Figure 1**. The AD technology has encountered significant recognition in the last few decades with the applications of separately configured high rate treatment processes for industrial wastewater streams. In the wastewater treatment settings, the AD has been employed in several instances throughout the world for bioremediation and biogas production [8, 12, 13]. Biogas, a well-known and common renewable source of energy, is produced via the AD process, consisting largely of  $\text{CH}_4$  and  $\text{CO}_2$ . As an alternative source of energy, the AD process produces biogas that can be chiefly used as fuel in combined heat and power gas engines [11, 12, 14]. There has also been a rapid adoption of anaerobic co-digestion, where two or more different feed stocks are digested together in anaerobic biodigesters with the core aim of improving the biogas yield [8, 11–13, 15–17]. Other advantages ensured in the anaerobic systems include lower energy requirements, a safer and more convenient way of converting “waste” to useful products associated with urbanisation, being a predictive tool for the fulfilment of the UN Sustainability Goal to meet Global standards, having excellent nutrient recovery and high organic removal efficiencies. Drawbacks include longer hydraulic retention times (2–4 months) and high alkalinity requirements [11, 18, 19]. The aerobic system presents merits such as high organic removal efficiencies, excellent effluent quality

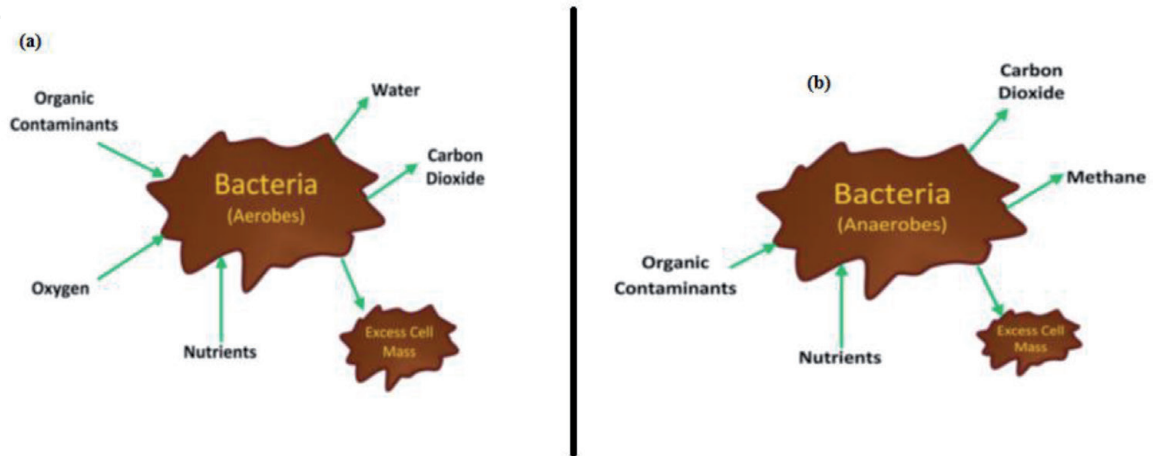


**Figure 1.**  
Modified stages of the anaerobic digestion process, adapted from [11, 12].

and shorter start-up times (2–4 weeks). Demerits include longer hydraulic retention times, pretreatment requirements for delignification of lignocellulosic biomass, odour built-up in bioreactors, costs associated with  $CO_2$  upgrading, no nutrient recovery and high energy requirements [8, 12, 17]. Research conducted by Kainthola et al. [19] details the major differences between the anaerobic and aerobic systems of wastewater treatments, as depicted in **Figure 2**, demonstrating the mechanism with species required and products formed. The anaerobic/aerobic systems have also been employed largely at both municipal and industrial levels as a method for wastewater treatment for many years. It presents advantages such as a lower consumption of energy, low chemical consumption, low sludge production, its enormous potential for the recovery of resources, simplicity of the operation and the requirement of less equipment. Some advantages of the biological treatment method over other treatment techniques such as thermal and chemical oxidations are capital investments required and costs in operation of the processes [8, 11, 12, 14].

2.1.1 Operating parameters of AD process

Some operating parameters which are usually monitored and optimised to maximise the performance and operation of AD include organic loading rate, pH, hydraulic



**Figure 2.**  
Schematic diagrams of (a) aerobic treatment principle and (b) anaerobic treatment principle, adapted from [11, 12].

retention time, temperature, carbon to nitrogen ratio and many more [15, 20]. As a result, any sharp variation in these parameters could adversely affect the substrate concentration in the biodigesters. Some of the operating parameters are discussed in Sections 2.2.1–2.2.4.

#### 2.1.1.1 Organic loading rate (OLR)

This is generally expressed in terms of the amount of chemical oxygen demand (COD) or volatile solids (VS) of digester volume in a day and denoted as  $\text{KgCOD/m}^3 \text{ d}$  or  $\text{KgVS/dm}^3 \text{ d}$ . Most favourable COD removal of the canning industry effluent was found to be between 89 and 93% at OLRs of 9.8 and  $10.95 \text{ kgCOD/m}^3 \text{ d}$  at an HRT of 10 h at a pH of 5.5 [15, 18, 19]. This prediction becomes viable during the selection of the reactor-type and other process parameters such as pH control. OLR has been found to increase with decreasing biodegradation of the volatile solid and the subsequent bioenergy produced. The performances of bioreactors decrease when the OLRs increase with energy production [10, 15, 17].

Furthermore, the pH range suitable for AD is reported to be within the range of 6.8–7.2 [13]. This is achieved by charging the AD at an optimum OLR to obtain a higher yield of biogas. There is usually a variation in pH during AD especially during acidogenesis where volatile fatty acids such as propionate, butyrate and acetates are produced [19]. The presence of phosphates ( $\text{PO}_4^-$ ) in most wastewater treatment facilities renders the pH adjustment with calcium hydroxide possible to a pH of about 7.2, even at high concentrations. The growth of microorganisms in AD is largely dependent on the pH of the substrates undergoing the overall biodegradation [8]. In the treatment of wastewaters, the observed pH range of 6.0–7.1 was been reported in a study where a mixed batch reactor produced larger quantities of biogas at an average value of  $0.405 \text{ m}^3/\text{d}$  [11].

#### 2.1.1.2 Temperature

Temperature conditions during the AD process for bioenergy production includes psychrophilic ( $<30^\circ\text{C}$ ), mesophilic ( $30\text{--}40^\circ\text{C}$ ) and thermophilic ( $50\text{--}60^\circ\text{C}$ ) [8, 12]. The anaerobes are found to be more active under both mesophilic and thermophilic temperatures as compared to psychrophilic temperatures. Comparatively, thermophilic temperatures are considered suitable for the enhancement of biomethanation by accelerating the hydrolysis of the polymeric feedstock and other metabolic pathways [12, 13]. However, several studies have shown that thermophilic digesters suffer from poor process stability due to volatile fatty acid accumulation during the acidogenesis process, most especially propionate [13, 17].

#### 2.1.1.3 Hydraulic retention time (HRT)

This is the measure of the time required to achieve the complete biodegradation of an organic matter associated with process parameters such as the temperature of the medium and the waste composition [12]. The HRTs observed in AD under mesophilic and thermophilic temperatures are 15–30 days and 12–14 days respectively [13, 17]. Temperature and HRT effects on the methanogenesis process have been observed in a study by Shah et al. [13]. In the same study, the working temperature was adjusted from 30 to  $55^\circ\text{C}$  following an HRT of 8–12 days.

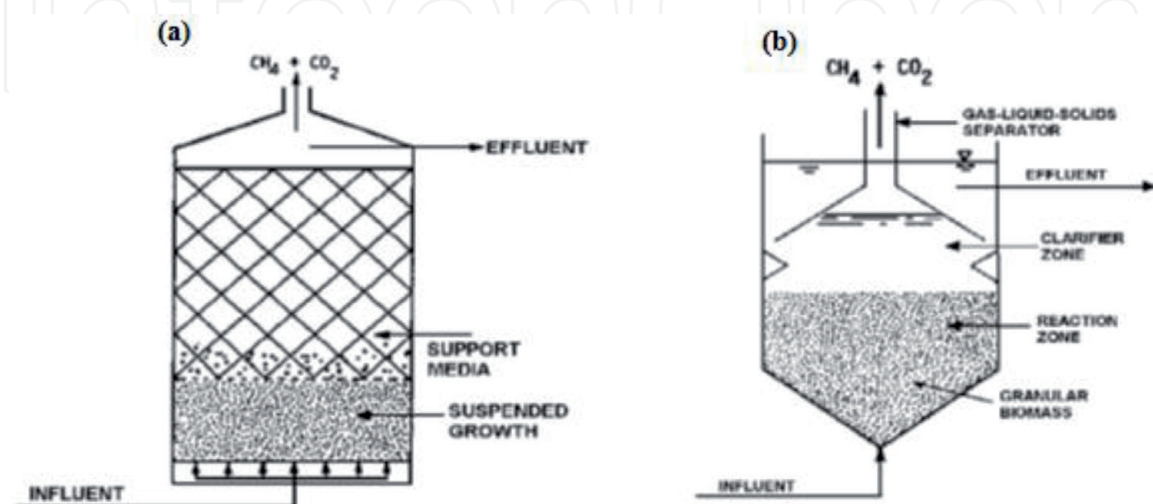


### 2.1.2 Applications of the anaerobic digestion process

The full-scale application of the AD technique in the treatment of industrial wastewater depends on the hydrodynamic configuration of the AD reactor. There have been different types of AD reactors applicable in the wastewater treatment settings, which includes continuous stirred tank reactor (CSTR), the anaerobic sequencing batch reactor (ASBR), upflow hybrid anaerobic sludge-filter bed (UASFB), upflow anaerobic sludge blanket reactor (UASBR), expanded granular sludge bed (EGSB), anaerobic baffled reactor (ABR), anaerobic fixed-bed reactors (AFBR) and integrated bio-membrane reactors [8, 13, 15–17]. For instance, **Figure 3** depicts schematic cross section view of the upflow hybrid anaerobic sludge-filter bed and the upflow anaerobic sludge blanket reactor. The integrated anaerobic-aerobic bioreactors have been most preferred in the past few decades due to its ability to meet stringent constraints in terms of mitigating odorant compound release and minimising sludge production.

#### 2.1.2.1 Limitations of adapting AD process in large scale

Research has shown that among the various reactors used in the performances for the treatment of wastewaters, the UASBR configuration is the most widely used with a high-rate anaerobic reactor for the treatment of high-strength wastewater [8, 12]. Several modifications have been carried out in the design of bioreactors to enhance both the consistency and the efficiency of the reactors. The AD process does encounter failures causing serious environmental hazards [8]. In addition, some of the aforementioned operating parameters as previously discussed (Section 2.2) can affect the performances of the microbes responsible for the biodegradation of organic matter in the wastewater settings. Further drawbacks observed in AD large scale operation include microbial shift, process instability, low yield of biogas production and poor water quality [8, 10, 12, 14, 19]. For instance, monodigestion of energy crops still struggle to meet the reduction targets concerned with the drawbacks in AD compared to anaerobic co-digestion (AcoD) such as a mixture of slurry and energy crops [5, 20]. In response, pretreatment techniques for cellulose enhancement and the use of energy crops as feed stocks have been found to increase the efficacy of biogas production via AD [12]. Some of the improvement techniques which have gained attention in terms of research for the betterment of AD process design and the optimisation includes



**Figure 3.**  
(a) Upflow-hybrid anaerobic sludge-filter bed and (b) upflow-anaerobic sludge blanket reactor [8].

evaluating the AD process kinetics and dynamics, nitrification-denitrification, recycling of the centrate back to the AD reactor, wastewater characterisation, optimisation of operational and environmental parameters, and microbial community shift.

2.1.3 Future prospects of AD application

According to the United Nations Sustainability Development Goal of 2030, the use of renewable energy is expected to reach 100% by the year 2050. The seventh goal focuses on the production of affordable and clean energy globally which is environmentally friendly [21, 22]. Renewable energy has gained attention to cater for the ever-increasing use and over-reliance of non-renewable forms of energy. This arises because of the emission of greenhouse gases compelling researchers in the past decades to search for an alternative means of sustainable energy production [17, 23–25]. The reserve for energy has become necessary for global concern in maintaining a sustainable way in lieu of the resources available especially at WWTPs. Aside the protection of the environment, wastewater treatment plants (WWTPs) also serve as a source of generating renewable forms of energy such as biogas. In a WWTP, the dumping of sewage sludge produced as a by-product is a problem of growing significance representing up to 50% of the entire operating costs of all WWTPs [8, 12, 14]. Also, wastewaters with a high content of nitrogen can be treated with the nitrification and denitrification technique form of AD generally known as Anammox [26]. Constructive government policies have shown Germany as being the dominant global biogas energy generation country globally for the future [23, 25]. Latest reports predict that biogas production could increase from 18,244 Gigawatt hours (GWh) in 2012 to 28,265 GWh in 2025, indicating a compound annual growth rate (CAGR) of 3.4%. In 2011, Germany contributed the largest share of the world’s cumulative installed capacity as the country accounted for approximately a quarter of the global biogas biogas [23, 25, 27].

3. Membrane technology

Membranes, as a thin layer barrier for size differential separation, are usually integrated with chemical and biological treatment or standalone systems in secondary treatment of wastewater settings [28–30]. In a typical membrane mechanism, there is usually a driving force, such as a semi-permeable barrier which controls the rate of movement of components by fractional permeation and rejection through pores of different sizes as depicted in **Figure 4** [32]. The permeation and selective rejection is a function of the membrane pore size and chemical affinity, which helps

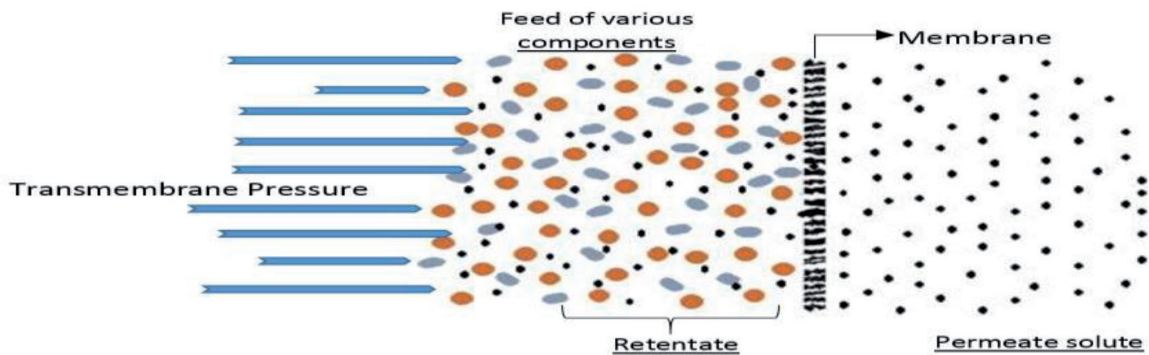


Figure 4. Membrane selective permeation for various solutes adapted from [31].

to have a product stream devoid of target components [33]. Due to the relatively low energy requirement and wastewater treatability efficiency, membrane technology has tremendously improved by the development of new materials and configurations for industrial applications. Some of these applications include microbial fuel cells, removal of organic and inorganic components, disinfection, pathogen removal and desalination [30, 33, 34].

### 3.1 Types of membrane technologies

Generally, the major driving force for selective filtration is a potential gradient of variables such as hydrostatic pressure, electrical voltage, temperature, concentration or a combination of these driving forces [29, 32]. These variables including nature (natural and synthetic) and structure (porous or non-porous and heterogeneous or homogenous) have been used in the classification of membranes [28, 31, 32, 34]. However, most commercially available and industrially used membranes are pressure-driven and energy driven (electrodialysis and electrodialysis reversal) membranes [35]. Pressure driven types are namely microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF). These are also classified by their pore sizes or molecular weight cut-off (MWCO). MWCO is expressed in Daltons ( $1 \text{ Da} = 1 \text{ g mol}^{-1}$ ) and is the minimum or smallest component that can be retained with at least 90% efficiency [28, 30, 32, 35]. It should be noted that as the pore size of these membranes decrease, the driving force for the operation increases. For instance, the MF and UF are referred as low pressure driven processes while RO and NF are high pressure driven processes [28, 29, 34].

### 3.2 Applications of membrane technology

#### 3.2.1 Microfiltration (MF) application

Microfiltration utilises a sieving mechanism to retain macromolecules or particles more than  $0.1 \mu\text{m}$ , specifically in the range of  $0.1\text{--}10 \mu\text{m}$  [30]. Unlike UF, RO and NF, the transmembrane pressure (TMP) for both sides of the membrane as a result of the small particle retention is puny, hence requiring a relatively small TMP lower than 2 bar but varies from 0.1 to 2 bar [28, 30]. As indicated, the larger pore sizes of MF membranes limit removal to suspended solids, bacteria, some viruses (up to 2-log), protozoan cyst, turbidity and on a lesser extent, organic colloids within the region [28, 29, 32].

#### 3.2.2 Ultrafiltration (UF) application

The role of UF is increasing as a pretreatment for desalination and membrane bioreactors. Ultrafiltration (UF) like MF utilises physical sieving as a separation mechanism. The pore size, MWCO and pressure for a UF membrane ranges from  $0.05 \mu\text{m}$  to  $1 \text{ nm}$ ,  $1\text{--}500 \text{ kDa}$  and operating pressure of  $1\text{--}7 \text{ bar}$  [30, 33]. As such, UF with a definite MWCO are impermeable to compounds with molecular weights exceeding the MWCO and have shown a 3–6 log removal of chlorine resistant protozoan cysts, active *Giardia lamblia*, colloids, viruses and coliform bacteria. The use of MF and UF as pretreatment to RO has gradually emerged as an industry standard. Both are often used as pretreatment for NF and RO processes to reduce membrane fouling and is also applied as a post treatment to chemical precipitation for organic chemical removal and pH adjustment, phosphorus, hardness and metals [29–31, 33, 34]. Fouling is highly eminent in UF due to the high molecular weight of fractions retained in relations with the small osmotic pressure differentials and



liquid phase diffusivity. However, this does not negatively influence the demand for UF's as any design, configuration and application will be fouled [28, 30, 36]. The configuration for application is influenced by the mechanical stability, hydrodynamic requirement and economic limitations.

### 3.2.3 Nanofiltration (NF) application

Nano filtration is a pressure related process where the mechanism of separation is based on molecular size for the removal of dissolved micro pollutants and multivalent ions. The NF is a complex process characterised by solvent diffusion, transport and electrostatic repulsion effects at the membrane surface and within the nanopores [29, 30]. The difference between the pore diameter and particle size forms the basis of the sieve effect. Based on the membrane pore size, NF is often referred to as 'loose RO' with separation taking place at the lower end of UF and upper end of RO as it covers a MWCO of 100–500 Da, a pore size of 0.5–5 nm and operates at relatively low pressure of 5–35 bar [28, 30, 34]. The NF is usually deployed in the removal of polyvalent cation, reduction in colour, tannins, turbidity and disinfection by-product precursors such as organic matter as their potency lies in the high rejection of divalent ions (98%), permeation of monovalent ions (20–80% rejection) and high flux. Nano filtration is often used as a post treatment or polishing step in conventional treatment processes. Although it is not advisable to be used in desalination processes, it is used to reduce the salt content of slightly saline water. Recent applications have used NF as a pretreatment to RO reducing the operating pressure in RO providing savings in operational and maintenance costs [31, 32, 35]. Second stage fouling is usually reduced in NF systems through ozone pretreatment and non-thermal crystallisation while cleaning is done using suitable alternatives that also exist for MF and UF [30, 33].

### 3.2.4. Reverse and forward osmosis

Reverse osmosis, often referred to as tight membrane has been widely used in brackish water and wastewater treatment with its effectiveness in desalination against conventional thermal Multi stage flash. High external pressure of 15–150 bar which is a function of the hypertonic feed and greater than the osmotic pressure is applied to retain dissolved solute and solvent permeation at a MWCO around 100 Da through diffusion mechanism [37–39]. Using concentration gradient as the driving force, separation and concentration in forward osmosis (FO) occurs as the concentrated solution (e.g., salts such as NaCl) draws water from a less concentrated feed solution. Characteristic advantages include low energy consumption, simple configuration and operation, low membrane fouling tendency and high rejection of a wide range of contaminants. The use of FO operates at ambient conditions, hence irreversible fouling is low [37, 39]. However, FO technology is faced with the lack of recyclable and economical drawing solutions, internal and external concentration polarisation and a difficulty of developing effective large scale plants [37]. To achieve desired process flow and optimum configuration, ROs are arranged in stages and passes. The sequence of the stages has the concentrate stream of the first stage as the feed inlet of the second stage. Permeate streams from both streams are summed into one discharge channel. However, passes involve either a one path recovery of permeate or the rechanneling of permeates from the first RO into the second RO to improve quality [40, 41] as summarised in **Table 1**.

Membrane	Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
Structure	Asymmetrical (thickness 10–150 µm)	Symmetric (thickness = 10–200 µm) or asymmetric (thickness = 0.1–0.5 µm and supported by sublayer of 50–150 µm)	Asymmetric 150 µm	Asymmetric 150 µm
Material	Ceramic, PP, PSO, PVDF	Ceramic, PTFE, PSO, CA, PVDF, thin film	PA,CA, PES, SPSF, PI, PVA, CS, organic/inorganic hybrids: thin film	Zeolite, PVDF, PES, PBI, TFC
Transport Laws	Darcy' Law	Darcy	Fick's	Fick's
Module	Dead end: flat sheet or spiral wound Cross flow: capillary, hollow fibre or tubular	Capillary, spiral wound, others: tubular, plate and frame, rotary modules, vibrating modules and dean vortices	Tubular, spiral wound, plate and frame	Tubular, spiral wound, plate and frame
Configuration	Dead end, cross flow, transverse flow	Dead end, cross flow, transverse	Shell-side feed, bore-side feed, cross flow	Cross flow in various stages and passes

*PBI, polybenzimidazole; CA, cellulose acetate; PSO, polysulfone; PP, polypropylene; PVDF, polyvinylidene fluoride; PES, polyethersulfone; TFC, thin film composite.*

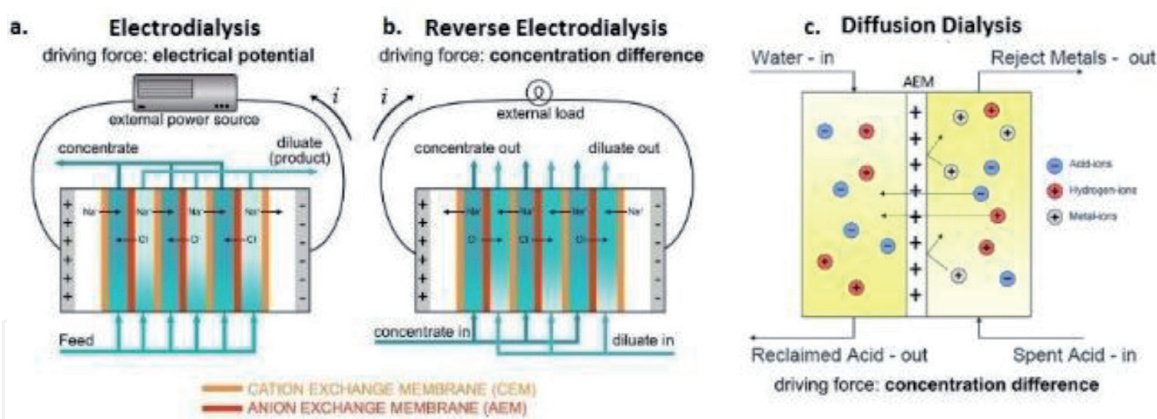
**Table 1.**  
*Summary of pressure-driven membranes [39–41].*

3.2.5 Membrane bioreactors

Low-pressure driven MF and UF used for critical solid-liquid separation has been integrated with biological treatment into a hybrid activated sludge process termed as membrane bioreactors (MBR) for wastewater treatment. Unlike conventional wastewater treatment processes with treatment limitations, MBRs have shown wide range treatment efficiency in the removal of organic and inorganic emerging micro pollutants including pesticides, antibiotics, analgesics, anti-epileptic, biodegradable organic compounds, microplastics, industrial chemicals and nutrients [30, 42, 43]. The MBRs can be configured into gravity or submerged vacuum driven systems by using hollow fibre or flat sheet modules, while pressure driven membranes on the other hand are mostly configured with external pipe cartridge systems. The MBR is usually combined with conventional systems including thermophilic or mesophilic bioprocesses, AOPs, powdered activation carbon to enhance improve the water quality and treatability efficiency [39, 40, 42, 44]. Some of the advantages of MBRs include small foot-print requirement, simple transport configuration and the ability to handle high biomass concentrations [45].

3.2.6 Ion exchange membrane

Ion exchange membranes are classified as anion exchange membrane (AEM) if the polymer matrix is embedded with fixed positive charge groups and vice



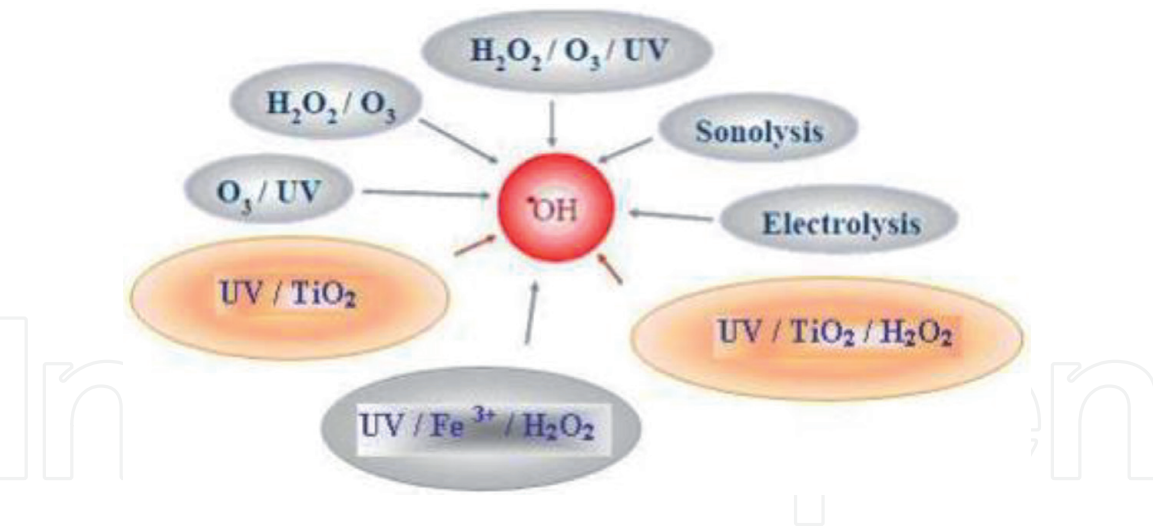
**Figure 5.** Configurations of (a) electrodialysis, (b) reverse electrodialysis and (c) diffusion dialysis [35].

versa for cation exchange membranes (CEM) [35]. This involves the permeation of anions/cations and rejection of cations/anions in the effluent. Electrodialysis (ED), reverse electrodialysis (RED), diffusion dialysis (DD) and Donnan membrane process (DMP) are examples of these, which usually involves the exchange of ions between the solutions across the membrane as shown in **Figure 5**. The application of these processes is usually based on the type of effluent and is reported to be non-fouled and energy resourceful as mechanism of separation is by potential gradient. The DD is applied to reclaim free mineral acids and alkalis while DMP is used in recovery of toxic and valuable metals from various feeds. In both DD and DMP, a Donnan equilibrium is established hence their difference lies in application areas. Unlike ED and RED, DD and DMP are being applied on bench scale, have osmotic limitations and therefore kinetic studies are being considered for various effluents. However, ED and RED constructions require compatibility of feed stream and stack materials, electrical safety consideration and larger footprint to produce equivalent water quantity and quality [30, 32, 33, 36].

#### 4. Advanced oxidation process

Basically, there are two stages which are usually employed in wastewater treatment settings via a pre-treatment step involving mechanical and physicochemical systems to reduce the heterogeneous components of the effluents followed by an advanced treatment process. The physicochemical process enhances the efficiency of the advanced treatment by agglomerating the contaminants into a larger size for easy filtration or removal [46, 47]. However, degradation of emerging recalcitrant components with membrane and bioremediation in advanced treatment processes attests to be complex. So, in addressing this problem, advanced oxidation process (AOP) has gained much attention due to its potential to degrade a wide range of organic micro-pollutants [47, 48]. This process involves the generating of potent reactive hydroxyl radicals ( $E_0 = 2.8 \text{ eV}$ ) with photon energy and without further additional chemical treatment. Examples are chemical oxidation ( $\text{O}_3$ , Fenton reagents), photochemical oxidation (Ultraviolet-UV/ $\text{O}_3$ , UV/ $\text{H}_2\text{O}_2$ ), heterogeneous photocatalysis (UV/ $\text{TiO}_2$ ), electrolysis and sonolysis [46, 49–52] as shown **Figure 6**. These technologies use UV-A with long wavelengths of 315–400 nm, and UV-C with short wavelength radiation of 100–280 nm for degradation of most environmental contaminants. Generally, UV/ $\text{O}_3$  and UV/ $\text{H}_2\text{O}_2$  processes consume large amounts of oxidant, which makes them uneconomical to operate [43]. On the other hand,



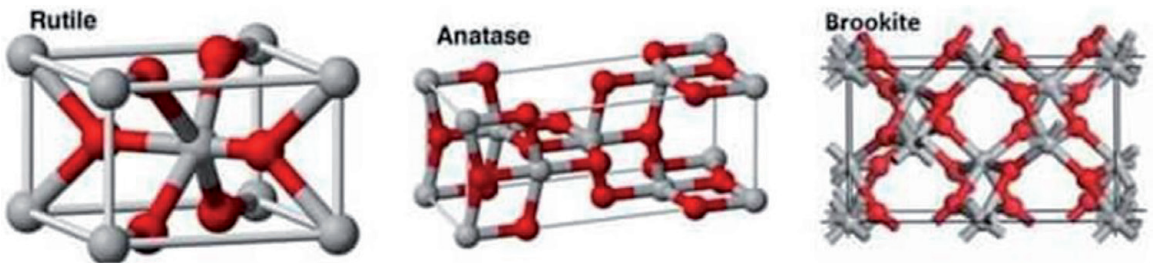


**Figure 6.**  
*Types of advance oxidation process (AOPs) adapted from [46].*

the hazards associated with ozone being an unstable gas limits its application and is usually coupled with an ozone-water contacting device to convert the ozone into its liquid phase thus increasing the cost of production. However, the considerable operational conditions of ambient temperature and pressure and the use of a low-cost and chemical stable catalyst ( $\text{TiO}_2$ ) are predominantly attractive for complete mineralisation of contaminants and by-products. This makes heterogeneous photocatalysis techniques to be advantageous over other AOP's. Other advantages include no sludge production, quick reaction rate, low cost and operating well at ambient temperature and pressure conditions [46, 49].

#### 4.1 Photocatalysis

There are several semiconductors favourable for water treatment such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CdS}$  and  $\text{ZnS}$ , which are active within a band gap energy of 2.3–3.2 eV and wave length of 413–539 nm [53, 54].  $\text{TiO}_2$  has been the most widely used photocatalyst and exists in three major crystalline polymorphs such as anatase, rutile and brookite (**Figure 7**). There have been intensive studies to determine the crystalline structure, surface area, density of surface hydroxyl groups and adsorption/desorption characteristics of  $\text{TiO}_2$  [46, 49]. As mentioned, the surface hydroxyl group concentration has been documented to play a vital role in the photocatalytic degradation process, such that an increase in concentration of the hydroxyl groups on the catalyst surface might have a positive effect on the reaction rate [46, 49, 51]. Thus, the hydroxyl radicals produced ( $\text{OH}^\bullet$ ) are a very combative species and are therefore able to oxidise a wide range of organic pollutants in a swift and effectual means.



**Figure 7.**  
*Crystal structures of  $\text{TiO}_2$  adapted from [51, 52, 55].*

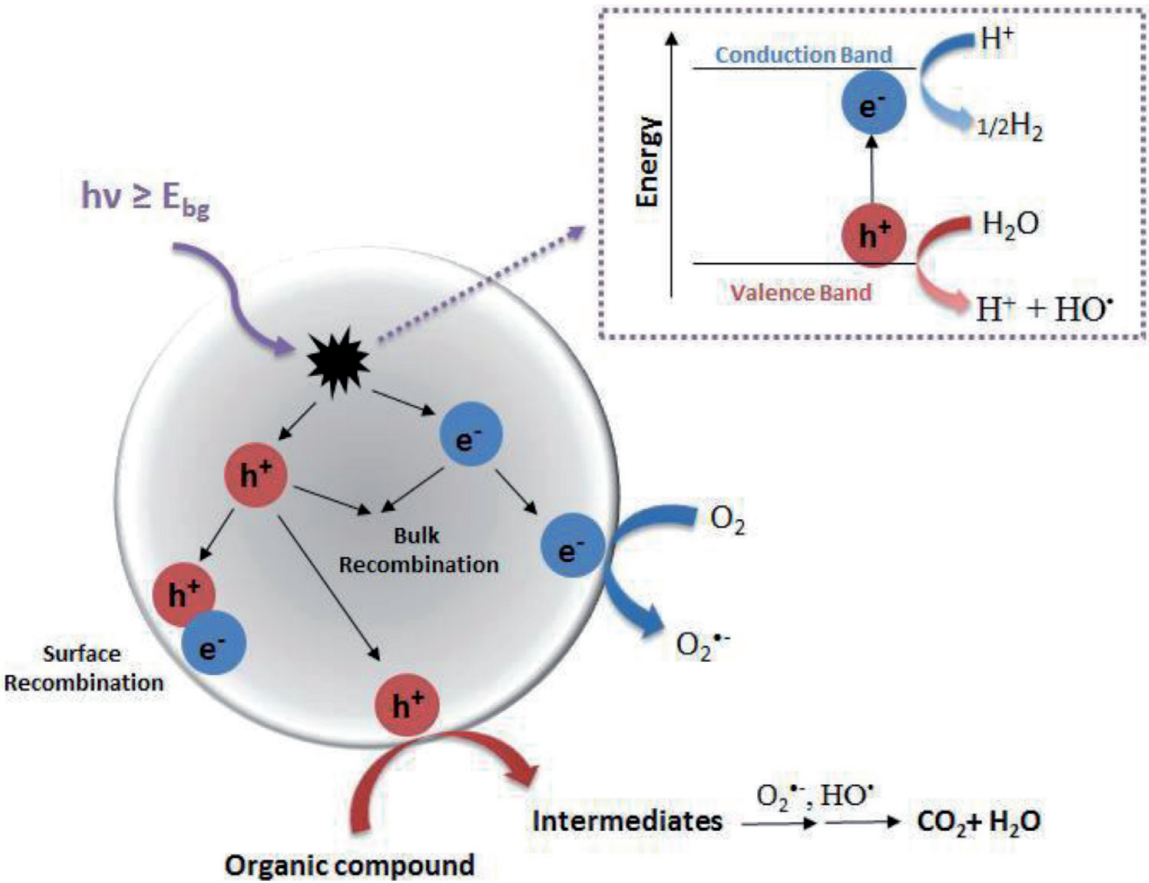


4.1.1 Principles of heterogeneous photocatalysis

The heterogeneous photocatalysis process involves series of reactions such as oxidation, dehydrogenation, hydrogen transfer and metal deposition, among others [55]. Besides, the normal thermal and chemical catalytic actions that ease any distinctive chemical reaction require simultaneous activation of the molecules. As such, in photocatalysis, a light source with energy equal to or higher than the band-gap energy of the catalyst is employed to stimulate the catalyst to be active during the reaction bringing about the reduction or oxidation of the adsorbed species on the surface, for instance, oxidation of organic compounds into their subordinates until carbon dioxide and water are formed [56, 57]. This results in charge separation as the electron ( $e^-$ ) moves from the valence band to the conduction band of the semiconductor catalyst, resulting in a hole ( $h^+$ ) in the valence band as shown in **Figure 8**.

4.1.1.1 Selection of catalysts

Some of the parameters to consider in selecting a photocatalyst to enhance the degradation capacity include the nature and intensity of light source, the amount of photons to activate the catalyst, the reaction medium and the water chemistry to generate the hydroxyl radicals, and the nature and concentration of the pollutants [46, 51, 55]. However, the relationship between the energy levels of conduction and valence bands with respect to the energy for reduction and oxidation is one of the cardinal points to consider in selecting a photocatalyst [46, 47]. The chemical capacity of the photo-generated electrons and holes has high influence on the conduction band energy level of the photocatalyst. Thus the photo-generated electron of a catalyst should be able to



**Figure 8.** Schematic illustration of the photocatalytic mechanism in the presence of a water contaminant adapted from [46, 49, 52].

have essential energy to ease the mineralisation of the micro pollutants. The conduction band energy level of the photocatalyst in terms of mineralisation has to be more negative, while the valence band has to be more positive with respect to the energy for oxidation of water. This makes semiconductors with large band gaps to be considered as suitable for photocatalytic activities [46, 47, 50]. Thus, semiconductor materials are able to provide adequate negative and positive redox potentials in conduction bands and valence bands, respectively. In addition, the wider the band-gap of semiconductor material the higher the energy input to enhance its efficiency. Furthermore, the poor photo-corrosion stability of many semiconductors limits significantly the number of potential photo-catalytic materials for mineralisation in wastewater settings [55, 57].

#### *4.1.1.2 Modification of catalyst*

Photocatalytic activity of a distinctive semiconductor, such as  $\text{TiO}_2$ , can attract light energy equivalent to or higher than the band gap energy, resulting in generating electrons and holes. This electron-hole pair then migrates to the  $\text{TiO}_2$  surface and amalgamates with the adsorbed reactants to hasten the reduction and oxidation process. The lack of such an energy transfer leads to recombination of the pairs, which then competes with the desirable redox process with a high loss of energy. Therefore, to increase photocatalysis efficiency, suitable modification of the semiconductor band gap is essential to attract the recombination charge carriers which might hinder the photocatalytic efficiency. Some of these processes include (i) doping with metal cations and anions, (ii) coupling with other semiconducting oxides, (iii) sensitization with light harvesting compounds/dye molecules and (iv) plasmon resonance induced by specific metals [49, 51].

#### *4.1.2 Parameters affecting photocatalysis*

As with most processing techniques, several parameters affect the performance of the photocatalytic degradation process. Photocatalytic activities are being influenced by experimental conditions such as the amount of catalyst, light intensity, lighting area, reactor volume, pH type of reactor, temperature and pressure. Likewise, the inherent structural and properties of semiconductor photocatalyst influences its performance. This includes the particle size, phase composition, surface area, surface hydroxyls, lattice defects and the type of dopants (metals and non-metals) [46–48, 52]. The amount of light radiation absorbed is the driving force for semiconductor with threshold wavelength to provide the appropriate photon energy to overcome the band gap between the valence and conduction bands. This threshold wavelength is very important to promote electrons to be in an excited state corresponding to the band gap energy as depicted in **Table 2**.

#### *4.1.3 Applications of photocatalysis*

With the current greenhouse emission problems and energy deprivation situation, photocatalysis emerges as one of the alternative ways of providing feasible solutions to the global front in relation to energy and the environment. For instance (**Figure 9**), in the phenomenon of photosynthesis, green plants trap the solar energy from the sunlight and with a series of enzyme catalysed redox processes, converts the  $\text{CO}_2$  into water and carbohydrates by releasing oxygen into the atmosphere where most living organisms depend on to survive. In this scenario, photocatalysis which works with the same principle has gained incredible status and hence can be explored for divert applications in seeking sustainable energy, social economic growth and environmental impact.

Semiconductor	Band gap energy (eV)	Wavelength (nm)
TiO <sub>2</sub> (rutile)	3	413
TiO <sub>2</sub> (anatase)	3.2	388
ZnO	3.2	388
ZnS	3.6	335
CdS	2.4	516
Fe <sub>2</sub> O <sub>3</sub>	2.3	539

Adapted from [47].

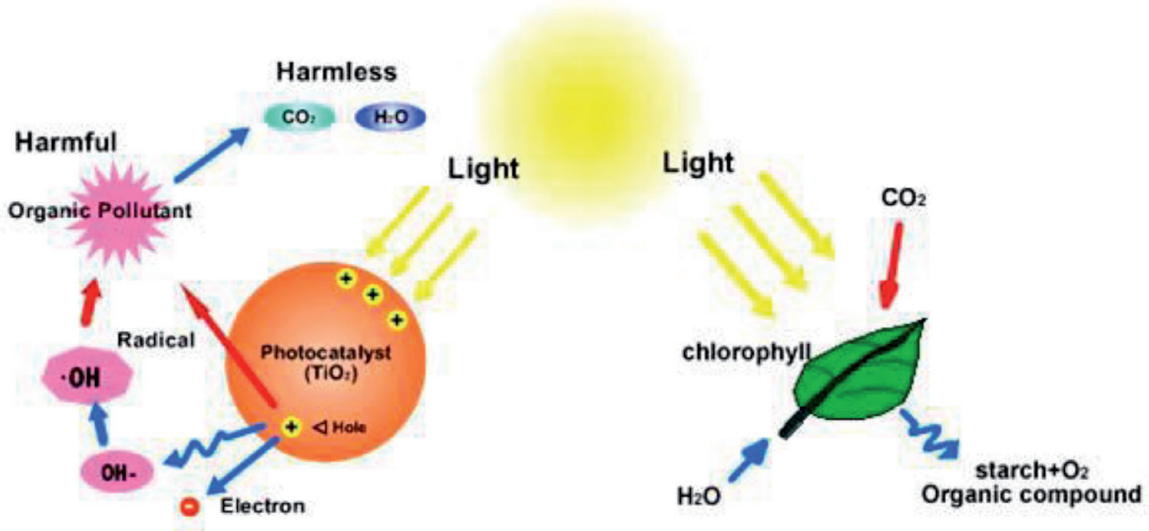
**Table 2.**  
*Semiconductors and their band gaps at specific wavelengths.*

4.1.3.1 Photocatalytic degradation in wastewater

The importance of photocatalytic degradation technology in pre- and post-treatment of water and wastewater using sunlight on a large scale is at the verge of development, with few of them like self-cleaning, anti-fogging and anti-bacterial applications currently being practiced. For instance, two slurry reactors coupled with TiO<sub>2</sub> were built in New Mexico (USA) and Almeria (Spain); however, the environmental conditions, low photonic yield and efficiency under the visible light make it challenging to be commercialised [27, 60–63]. There are numerous studies ongoing seeking to address some of these limitations in order to improve the photocatalyst, reactor design and light efficiency [55, 59]. Furthermore, the kinetics study to understand the mechanistic pathways of mineralisation of recalcitrant organic and micropollutants has also received attention.

4.1.3.2 Photocatalytic energy production

In the early 1900s, the photocatalytic techniques commonly referred to as “artificial photo-synthesis” was employed in reducing CO<sub>2</sub> into useful hydrocarbons (Figure 9). This has now attained incredible status on the global level. Currently researchers, scientists and engineers are exploring the mechanism to control the current atmospheric carbon dioxide levels (green-house gas effect) by altering it into fuels and useful chemicals, and the role of CO<sub>2</sub> as a source of energy. However, the



**Figure 9.**  
*Schematic comparison of photo-catalysis and photo-synthesis [58, 59].*

use of solar energy via chemical storage can be attained by photocatalytic or photo-electrochemical initiation of light-sensitive catalytic surfaces. Due to the simplicity of the photocatalytic process, it can be employed in converting solar energy into other useful forms of energy like hydrogen via splitting of water and hydrocarbons (methane, methanol, etc.), commonly known as solar fuels [52, 55, 59].

#### *4.1.4 Future prospects for photocatalysis*

There have been tremendous efforts dedicated to improving photocatalytic degradation efficiency, where some role of the aforementioned parameters on the AOPs performance have been studied with different types of wastewaters from the textile, oil refinery, slaughterhouses [46, 47, 59]. However, in relation to relative operational and energy utilisation costs, as well as the formation of unknown toxic intermediates from the parent compounds (semiconductors) and the pollutants remain unsolved. Although, this method is prone to shifting of hydroxyl radicals by non-target substances, but some are not suitable for certain varieties of toxic compounds that can counterattack the hydroxyl radicals rendering an increase in ecotoxicity when discharged into the environment. In response, there have been attempts to improve the semiconductor material performance by discovering the reaction mechanisms to develop commercial scale technology, but there are still some challenges which include mass transfer limitations, catalyst deactivation, generation of intermediate products and by-products, and the multi-complex optimisation of the materials and the reactor configuration [49, 55, 58]. Furthermore, due to the intrinsic nature of photocatalysis, it is very difficult to model photocatalytic reactors with a uniform light along the whole reactor volume [58, 59]. Therefore, a feasibility study on the irradiance distribution inside the reactor is required, especially with heterogeneous media such as  $\text{TiO}_2$  in suspension.

## **5. Conclusion**

The availability of a cost effective technology to ensure the economic viability of wastewater settings for domestic and industrial purposes is still limited. This chapter presented the insights in applicability of some of the cost-effective technologies in addressing the global water, energy and environmental concerns. The fate of biological systems (AD process), and some of its operating parameters essential for wastewater treatment and bioremediation to energy (biogas) were also discussed. Furthermore, limitations, applications and different configuration types of AD reactors, as well as the forthcoming of the AD process as the alternative technology for bioenergy production using wastewater as a source was discussed. The emerging membrane technologies such as Donnan membrane process are also spotted as the foreseen green and energy saving technologies for industrial and environmental applications. The future challenge for using AOPs in wastewater treatment could be addressed by developing a cost effective photocatalyst to enhance the wastewater treatment and coupled in reduction of carbon dioxide as a renewable energy source to fuels. Therefore, adapting strategies for processes integration and commercialisation of the aforementioned technologies will enhance sustainable social economy growth and development.

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