Chapter 11
Wastewater Remediation: Emerging Technologies and Future Prospects

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Abstract Treatment of industrial effluent combining sustainability and high efficiency is the need of the hour. Conventional effluent treatment techniques suffer from energy-intensiveness, low output efficiency, risks of secondary contamination apart from bearing an array of treatment steps. This makes it imperative for a paradigm shift in the process development and design of wastewater treatment plants to cater to the stringent environmental conditions and challenges of the future. Novel technology solutions like integrated membrane separation, photocatalysis, nanotechnology focusing on complete pollutant degradation without generation of toxic residues and scoring high on the eco-friendliness aspect offers promising options to deliver broad-spectrum effluent remediation. This chapter explores novel green alternatives. The chapter also studies the pros and the cons of conventional ETP and evaluates their newage modifications. This is followed by an in-depth discussion of the crux of emerging novel technology solutions, scope of their application and possible integration with prevailing separation techniques. Finally, strategies like waste valorization patterns of process intensification in design were discussed for sustainable and cost-effective technology development.

Keywords Sustainable · Effluent treatment · Process intensification · Waste to wealth · Membrane separation · Photocatalysis

11.1 Introduction

Remediation of wastewater and its reclamation represent one of the most pressing research challenges in today's world, at the backdrop of water scarcity in different regions coupled with an increase in the environmental hazards associated with the

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discharge of toxic industrial effluents. There is a dire need to treat and recycle industrial effluent to decrease freshwater consumption and prevent depletion of water resources. This can be achieved by purification of effluents and grey water recycling. Wastewater treatment (WWT) is often perceived as a necessary expenditure towards the environment. The emergence of the waste to wealth techniques, incentivising the treatment process by the formation of value-added products is one of the approaches towards greater implementation of the wastewater remediation guidelines and standards by all and sundry.

While understanding the process of wastewater remediation, it is very important to understand that industrial effluents are a highly variable matrix with widely varying characteristics. The parameters of BOD, COD, heavy metal loading, total dissolved solids, total suspended solids, microbial content are present in varying concentrations apart from the contaminants particular to the production processes particular to the respective industries. For example, steel plants effluent apart from high loadings of the aforesaid contaminants also contain toxic ammonia, cyanide, phenol in high concentrations produced during coke quenching and water scrubbing of the coke oven gases (Das et al. 2018). Similarly, effluents emanating from tanneries contain high of toxic hexavalent chromium used during chrome tanning, or pharmaceutical effluents contain active pharmaceutical ingredients (API's, drug residues) (Gadipelly et al. 2014). This makes selection of the right removal technique critical for degrading the specific and generalized components. Hence, any Wastewater Treatment Plant (WWTP) is often a blend of different separation processes to handle varied categories of contaminants. The most common unit operations found in any Effluent Treatment Plant (ETP) include aerators, clarifiers, screens, chemical dosing and disinfectant. Some of the units are described in the schematic in Fig. 11.1.

The conventional wastewater treatment plants include bulky infrastructure comprising of primary, secondary and tertiary stages. This makes the capital and operating costs expensive. These large installations are often tailor-made for a narrow range of operating conditions making them unsuitable for handling fluctuating contaminant loadings. Hence undesirable phenomenon like washout of the microbial columns takes place. The conventional WWT plants are often highly energy-intensive

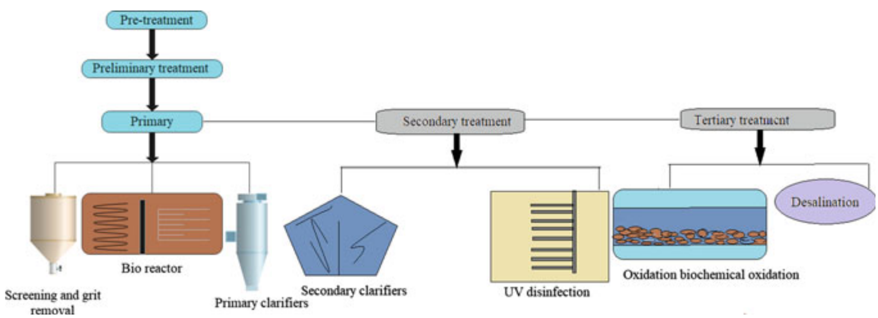


Fig. 11.1 WWT treatment stages in conventional treatment plants

which increases the cost of production of clean water. This puts budget constraints for moving towards the zero liquid discharge techniques. The design strategies to meet the most stringent environmental norms also necessitate provision of sludge disposal, concentrate management, prevention of generation of toxic residues, minimization of any form of secondary contamination. The curent techniques cannot cater to all of the aforesaid requirements.

This calls for a paradigm shift in the process design and WWT plant operation perspectives. There is a worldwide focus on the selection of sustainable, environment-friendly techniques that also guarantee high treatment efficiency. This has led to the development of operationally flexible, modular process intensified systems that integrate sustainability and high output efficacy. Novel technological developments in the field of advanced separation techniques like membrane separation, photocatalysis and nanotechnology are constantly changing the conventional mindsets in wastewater remediation. Integration of the novel technologies with conventional technologies are also being researched upon to prevent scraping of existing infrastructure for implementation of new treatment options. Hybrid technologies like membrane adsorption or photo-Fenton's are being developed to ameliorate the drawbacks of the conventional WWT methods while cutting down cost of the advanced WWT options. Process intensification is also being explored to develop multi-functional systems like the nano-bubbler ozonators that perform multifarious functions of disinfection oxidation, precipitation, aeration in one single assembly. The research in this domain is crucial for development of remediation techniques keeping in mind the future constraints of water and energy that are bound to arise.

In this chapter, a step by step discussion of the crux of different conventional WWT techniques which forms the core of any WWTP has been undertaken. The process fundamentals, merits and demerits of various conventional and novel techniques have been discussed. The future research perspectives for each technique have been evaluated along with discourse on the newer technological modifications. The novel and emerging separation technique, their areas of application, innovation and sustainability quotient and research perspectives for implementation was studied in detail followed by a discussion of the integrated options for complete WWT technology development. Finally, the possibility of value-added product recovery and process intensification in WWTP design as tools for sustainable technology development was also briefly evaluated.

11.2 Conventional Effluent Treatment Techniques

The conventional effluent treatment techniques can be broadly divided into physico-chemical and biological processes. Each class can be further subdivided depending on the mechanism, applicability and raw materials used.

11.2.1 Physico-chemical Treatment Processes

The conventionally applied techniques represent distinct classes that can be broadly grouped under the physico-chemical treatment processes.

11.2.1.1 Adsorption

Adsorption is perhaps the most ubiquitously used and researched technology option in the domain of wastewater treatment. The crux of the process is based on the selective mass transfer of the target contaminants from the bulk phase to the surface of the adsorbents, based on their relative affinity. The term adsorption loosely refers to the accumulation on the surface and is often used in conjunction with sorption which indicates the ability of the compound to load adsorbate in its entire internal structural matrix.The adsorbents have a3D porous surface structure which imparts a high degree of interfacial mass transport and accumulation characteristics. They are characterized by interstices and capillary-like micro-channels which enables rapid accumulation of the selected ions/components on the surface.

The most widely used adsorbent is activated carbon and its analogous forms like activated carbon, charcoal due to its large surface area and porous structure. Both powdered and activated variants are used to treat different contaminants present in wastewater like heavy metals, toxic anions like fluoride, cyanide and also dissolved organics (Mavrov et al. 2003; Demirbas 2008). Activated carbons are used in two variants: Powdered activated carbon (PAC) and Granular Activated Carbon (GAC). The former is commonly used to treat low volumes of wastewater while the latter is preferred in packed beds and activated carbon filters (Johnson 2014). The important factors that govern the adsorptive removal of contaminants include solution pH, adsorbent dosage, adsorbate concentration and physical state, interfering ions present in the feed, and hydrophobicity of the adsorbate. The optimum performance of the adsorbent is determined by attainment of the equilibrium, which in turns depends upon the adsorption kinetics and isotherm.

Different classes of adsorbents have been developed for removal of different contaminants like chitosan complexes, activated alumina, and also polymeric adsorbents. The biggest USP of the process is the simplicity and the cost-effectiveness of the operation. However, one problem faced in this process is that of sludge disposal after the exhaustion of the adsorbent beds. While using adsorption process for the mitigation of heavy metals and other toxic contaminants, the passivation of sludge is of utmost priority to prevent any secondary contamination. Nevertheless, the process of adsorption and adsorption integrated with filtration has proven to be efficacious for treatment of waters catering to the domestic sector and also small industrial installations.

11.2.1.2 Coagulation–Flocculation

The key focus of these treatment techniques is to precipitate/settle the contaminants by dispersing their surface charge.

In the process of coagulation, chemical compounds are added to introduce opposite charges into the medium. This dispelling of surface charges aids in the coalescence of smaller particles. Subsequently, their weight increases and they precipitate at the bottom due to the difference in the densities. Coagulation is often accompanied by mixing which promotes the interparticle collision and quick growth of the microflocs (Prakash et al. 2014). Commonly available chemicals like ferric chloride, aluminum sulfate (alum) act as coagulants binding ions, organics and also colloidal sols from feedstreams (Zhanpeng and Yuntao 2006; Bratby 2015).

In the process of flocculation, modification of surface tension and particle density is induced by flocculent dosing. Here growth of the microflocs takes place resulting in the formation of visible flocs. This growth process continues till a particular floc size is attained before it can be separated by filtration, floatation or sedimentation. Flocculants are more often polymeric in their chemical structure than coagulants which adsorb small particles on its surface (Otsuka and Ohishi 2013). In comparison to the sludge generated by inorganic flocculants, polymeric flocculants generate lesser sludge volume sinc ethey are driven by ionic solvation. In fact chemical modification by grafting of naturally available polymers like starch, guar gum, has yielded efficacious flocculants for wastewater treatment. They act by a bridging mechanism where the polymer binds the particles by forming a loop or a bridge. Ionic charges are also incorporated into the synthetic flocculants for increasing the celerity of the separation process. Some commonly used cationic flocculants include quaternary ammonium compounds, while the anionic polyelectrolyte flocculants comprising of carboxylic or sulfonic groups are also used for the pupose. (Brostow et al. 2009).

Coagulation and flocculation are techniques that are commonly used in conjuction. The mode of action includes charge destabilization, interparticle collision and floc formation which occurs simultaneously for speeding up the process of wastewater treatment. The coagulant also in many cases serves as flocculation promoters strengthening the flocs. This enhances the ease of separation (Zhanpeng and Yuntao 2006). Inorganic coagulants bearing aluminum or iron forms multi-charged polynuclear complex in solution. This is a function of the solution pH. These hydrolyzed species bind with the contaminants. These are also polymeric and pre-polymerized class of coagulants which have a higher resistance to solution pH and temperatures (Bratby 2016).

While coagulation-flocculation represents a relatively simple and efficacious technique for water treatment, it is often not sufficient to be used as a standalone option. There are also considerations of sludge disposal, cost (especially for polymeric coagulants flocculants), secondary contamination which needs to be weighed upon to ascertain technological feasibility in the long run. Research and development focusing on biodegradable, non-toxic natural polymeric coagulants flocculants are a right step in this direction and merits more pilot trials for long term applications.

11.2.1.3 Ion-Exchange

Ion-exchange is a physico-chemical treatment process that commonly finds usage in water softening applications. As the name suggests, the process functions by replacing ions from the contaminated water with an ion of the same charge. The replaced ion gets incorporated onto the ion exchange resin matrix and can be released on regeneration. The ion-exchange resins are available in the form of microbeads, columns or porous ion-exchange membranes, wherein the loosely bounded ions are replaced (Figueiredo et al. 2017).

The resins can be broadly categorized into 2 categories; cation exchange resins and anion exchange resins for removal of cationic and anionic species respectively. The ion-exchangers may be of polymeric (resin) composition or of inorganic, zeolite origin. The microporous beads of ion exchange resins that are synthesized industrially usually consist of polystyrene or polyacrylate as base materials. Into that gel matrix, water and the resin are dispersed in a 1:1 ratio (Neumann and Fatula 2009).

The charged functional groups present in the monomers are the key building blocks for the ion-exchange process. The binding forces between the functional groups and ions are relatively weak and can be reversed by ionic interactions with a stronger electropositive or electronegative potential in the electrochemical series. This allows for the regeneration of the ion exchange resins or zeolite columns. However, it is observed that the ion exchange capacity diminishes progressively with each regeneration cycle (Das et al. 2017).

The most common example of application of ion exchange and its regeneration is found in water softening when supersaturated polystyrene beads are used to remove calcium and magnesium ions. The exhausted resin beds are subsequently flushed with brine when sodium ions once again replace the loosely bound Mg^{2+}/Ca^{2+} cations and regenerate the resin (Leonard 2000). One of the drawbacks faced in the conventional gel-based ion-exchange polymeric beads is the relatively lesser surface area, and fouling propensity. To counteract these shortcomings, macroreticular resins with a large porous structure have been developed which are resistant to organic fouling. The cross-linked structure gives rise to a 3D maze with increased surface area. Furthermore, cross-linked structure of polystyrene divinylbenzene offers chemical resistance. The chemical structural formations are demonstrated in Fig. 11.2 below:

In the domain of industrial wastewater treatment, the ion exchange resins are broadly divided into four categories depending upon the application:

(a) Strong acid cation
(b) Weak acid cation
(c) Strong base anion
(d) Weak base anion.

In recent years there has been commercial level implementation of resin technology for treating wastewater as well as saline water. However, their ionic specificity is often a hurdle which increases the cost and necessitates different ion exchanger formulations for separate ionic species.

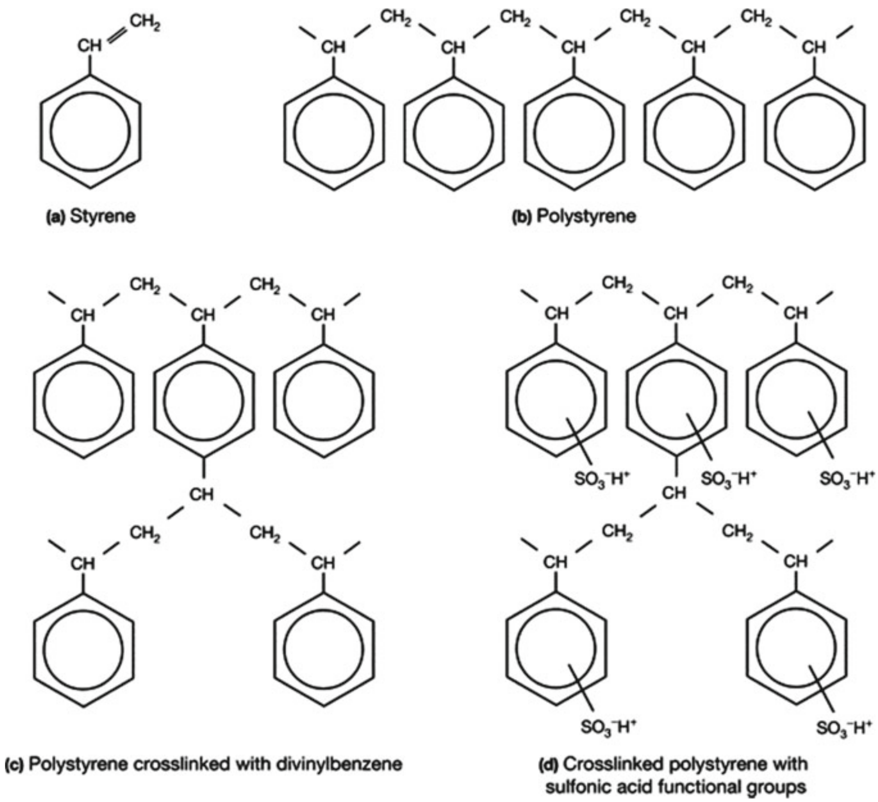


Fig. 11.2 Porous cross-linked resin structure (Schönbächler and Fehr 2014)

11.2.1.4 Advanced Oxidation Processes (AOP)

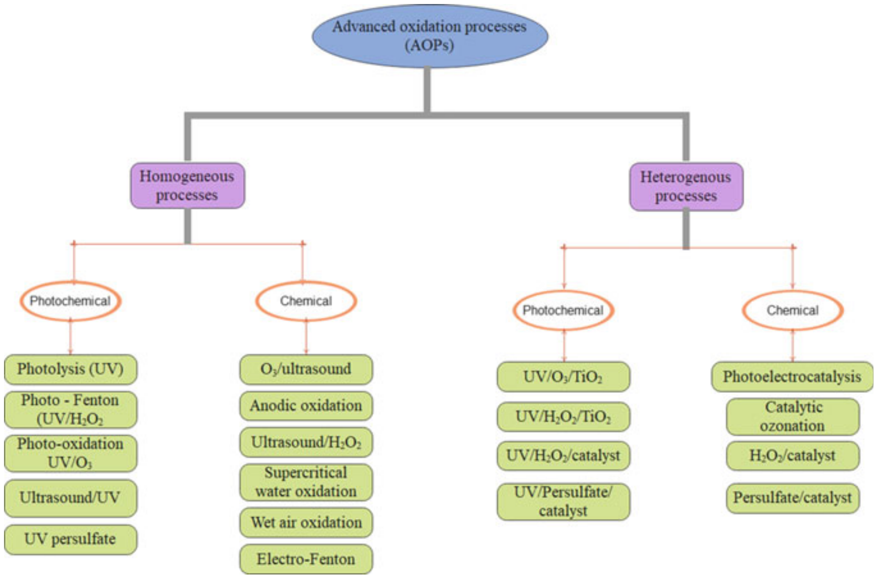
The class of treatments is a group of accelerated, contaminant degrading techniques that are used for the removal of hazardous chemicals, dissolved organics and micropollutants from effluents. There are different classes of AOP's like Ultra-violet oxidation, H_2O_2—Fenton's, photocatalysis, ozonation, chemical oxidation via ferric or titania and their hybrid variations. Other variants include microwave and other electromagnetic wave-based wastewater treatments. Infact UV based treatments due to their efficacy in hydrolyzing the microbial content have become a common household name (Babuponnusami and Muthukumar 2014; Liu et al. 2006; Wang and Chen 2020). Common industrial AOP'S include wet air oxidation, photolysis, UV treatment. Their common pathway of action is oxidation and hydrolysis through free radical formation (Kaur et al. 2020).

The AOP'S have demonstrated successful mitigation of hazardous water pollutants like microbes, API'S such as diclofenac, carbamazepine, dissolved organics like polyaromatic hydrocarbons and heavy metals (Oh et al. 2014; Kowalska et al.

2020; Du et al. 2020). The other benefits include in-situ treatment, no or very less, benign residue generation; and fast reaction times (Singh and Garg 2021). AOP's also include innovative and greener options like sonolysis where soundwaves of different frequencies are used to generate the reactive oxygen species (ROS) without the use of any additional chemicals. Sonolysis harnesses a physical phenomenon called acoustic cavitation where the growth and adiabatic collapse of bubbles are involved that generates heat to split the water molecules into reactive $O^{\cdot}$ species (Balachandran et al. 2016; Rayaroth et al. 2020).

$$H_2O \rightarrow O^{\cdot}H + H^{\cdot}$$
$$O^{\cdot}H + H^{\cdot} \rightarrow H_2O$$
$$2O^{\cdot}H \rightarrow H_2O_2$$
$$2^{\cdot}H \rightarrow H_2$$
$$^{\cdot}H + O_2 \rightarrow HO_2^{\cdot}$$

The AOP'S are divided into photochemical and non-photochemical process based on the reaction pathway. The photochemical AOP'S can be further subdivided into homogenous and heterogenous categories based on physico-chemical mechanisms. Hybrid options like electro fenton's or electro photo-fentons are usually classified in the heterogenous photochemical AOP category (Verma et al. 2021). The different classes of AOP'S are shown in figure below.



Apart from acting as standalone options, AOP'S have also demonstrated increased efficiency when integrated with other treatment options like biochemical degradation or fluidization (Ghime and Ghosh 2020).

Despite the overwhelming high removal efficiencies demonstrated by AOP'S, novel processes like sonolysis, electro photo-fentons has still not been implemented industrially. In recent years research in the process intensified system developments such ozonation with nanobubbles targeting broad-spectrum contaminant removal are finding industrial applications. Another impedicament is the high cost associated with fabrication and installation of such systems. The cost economic analysis and design intensification are required for commercial level implementaion.

11.2.2 Biological Treatments

Bioremediation techniques can be broadly categorized into three groups:

(i) Aerobic processes,
(ii) Anaerobic processes,
(iii) Phytoremediation.

Each of the categories have been serially described below.

11.2.2.1 Aerobic Effluent Treatment Processes

In the simplest terms, aerobic bioremediation is the use of oxygen to treat effluents in the presence of oxygen. As such most of the common substrates on which microorganisms act include dissolved organics. The organic compounds serve as sources of carbon and electrons that can be harnessed for the growth of the microbes. The molecular oxygen acting as electron acceptors are used to oxidize the carbon into CO_2 and new cell mass. The combined processes of oxidation–reduction where the microbe acts as electron receptors and the contaminant as a source of electron donors break down the organic foulants and colloidal matter present in the effluents.

Oxidation

COHNS (Organic matter) + O_2 + Bacteria → CO_2 + NH_3 + Other end products + Energy (Samer 2015).

The microbes are also capable of degrading inorganic constituents including heavy metals (Fernandes et al. 2008). Aerobic degradation technology focuses on introducing microbe culture in the form of columns of sludge or sludge blankets in which the effluent is fed for the biological remediation processes to take place. In such systems, stoichiometric ratio of 1:3 of hydrocarbon: oxygen is maintained. The rate-controlling step is the O_2 transport to the microbial cells. Based on the location of the sludge blanket and the mechanism of O_2 transport and associated reaction, aerobic treatments are classified into in-situ and ex-situ technologies. The growth kinetics of those microbial enzymes catalyzed reaction can be described with the help of Monod's equation (Russel 2006).

$$\mu = \frac{\lambda S}{K_s + S}$$

μ Specific growth rate coefficient
λ Maximum growth rate coefficient
S Concentration of the limiting nutrient
K_S Monod coefficient.

In terms of process design, the aerobic bioremediation technologies can be segmented into aeration lagoons, oxidation ponds, trickling filters. In these systems different forms of bioventing are used for oxygen supply into the unsaturated zone by using oxygen sparger, aerators or oxygen radical generating compounds like ozone, hydrogen peroxide to increase the speed of the process. One of the side reactions that are observed especially in oxidation ponds is the growth of the algae due to the conducive environment. The selection of the appropriate technology depends upon the organic loading of the effluent volume, interfering ions present and solution pH. For example, effluents originating from food processing industries are treated in aeration lagoons while activated sludge reactors are widely used for the treatment of municipal sewage and allied effluents (Tenore et al. 2018; Khazaei et al. 2009) The design parameters include hydraulic retention time, aeration and/or bubble generation rates, microbial biomass growth, BOD and COD of the effluents. The advantage of the aerobic process is that it can treat a wide range of biodegradable contaminants. It also demonstrates higher biomass yields than anaerobic processes and relatively low CAPEX. However, there are drawbacks like low temperature and pH tolerances, operational difficulties like sludge overflow, BOD and COD overload, necessity of larger reactor size which entails higher energy experience. These trade off's need to be carefully addressed for cost-effective treatment technology development.

11.2.2.2 Anaerobic Bioremediation

This class of treatments utilize anaerobic bacteria to degrade the contaminants in the absence of oxygen. They are typically used for systems with a BOD > 500 mg/L (Samer 2015). The two principal bacterial classes that are used for the anaerobic digestion process are acidogenic bacteria and methanognic bacteria using thermophilic or mesophilic pathways (Stams 1994; Moset et al. 2015). These bacteria and chemosynthetic autotrophs or semi-autotrophs and are more resistant to feed pH, temperature and toxicity levels (Lin and Chen 1999).

The efficacy of these processes can be determined by plotting biosorption isotherms which helps ascertain optimum removal rates under equilibrium conditions. The chief sources of inorganic nutrients are nitrate, phosphates and sulfates which get converted to ammonia and nitrogen, hydrogen sulfide and ATP + H_2O

respectively (Russel 2006). The systems that are used for this purpose include anaerobic lagoons, anaerobic sludge blanket reactors anerobic methane reactors which function by development of an anaerobic biofilm driven by co-metabolism and fermentative pathways. The process does not need any external energy source like oxygen requirement in the aerobic counterparts. Moreover, the calorific values of the gases that are released like methane, hydrogen sulfide are utilized as energy sources. The residual sludge from the process can also be used as a fertilizer or soil conditioner leading to a win–win situation (Nriagu 2011).

The anaerobic reactors are capable of treating large effluent volumes in shorter residence time. Apart from treatment of complex industrial wastewater like dye processing effluents, dairy processing wastewater, steel plant effluents the anaerobic processes are particularly effective for lipid breakdown which is not possible in the aerobic reactors due to inhibitory lipid kinetics (Ma et al. 2015). However, one fundamental drawback of the anaerobic reactor system is the failure to completely stabilize the contaminants. This necessitates a secondary treatment step or combination with aerobic reactors. Despite this shortcoming, anaerobic bioremediation techniques find multifarious applications due to their low reactor volume, lower energy consumption and lesser sludge generation. The energy yield from the evolved gases serves as additional value addition to the process.

11.2.2.3 Phytoremediation

Phytoremediation encompasses different processes of phytoextraction, phytostabilization, phytodegradation, phytodesalination, phytovolatilization all of which uses different plant species for contaminated effluent treatment. As the name indicates, this process offers a sustainable green treatment option that minimizes the production of toxic residues or any forms of secondary contamination. Primarily plant roots are utilized for biosorption of nutrients, heavy metals and other contaminants from wastewater. The different phytoremediation techniques discussed above often use aquatic plants like free-floating *azollapinnata*, *spirodelapolyrhiza, eichhorniacrassipes*, submerged (*hydrophilla corymbesa, vallisneria americana, hyriophylum aquaticum* as well as emergent plants like *nuphurlutea*, *Nymphaea* species) (Mustafa and Hayder 2021). Plant species have demonstrated particularly high efficiency for uptake of heavy metals such as lead, chromium, among others (Chanu and Gupta 2016; Kassaye et al. 2017).

The aquatic plants have shown heavy metal removal from complex systems like municipal wastewater, textile industry effluents which contain high BOD, COD, heavy metals, organic and inorganic nutrients, pathogens and a host of other contaminants (Mojiri 2012; Dulawat 2017). The heavy metal uptake by the plants can also be recovered using hyperaccumulator plant species that yield a large amount of biomass such as *Alyssum bertolenii* (Robinson et al. 1997). This has given rise to an entire new research domain called phytomining which is being used to clean up metal contaminated sites, old abandoned heavy metal mine sites by bio-harvesting of metals (Sheoran et al. 2009). The process of phytoremediation can be used for simultaneous remediation of contaminated water and soil with very less or no energy inputs. Here also, removal techniques can be divided into ex-situ and in-situ subcategories both of which offers the scope of utilization of the produced biomass. Interestingly, it is seen that the mechanisms of phyttoremediation processes often resemble their physico-chemical counterparts (such as ion-exchange, hydroxide condensation, precipitation and ionic complexation) (Gardea-Torresdey et al. 2004).

The plant body exhibits two distinct defence mechanisms of avoidance and tolerance to cope with the toxicity of the heavy metals (Hall 2002). Interestingly certain species of plants display broad-spectrum heavy metal sorption like *Sedum alfredii* which has demonstrated uptake of Zn^{2+}, Pb^{2+} and Cr^{3+}species (Yang et al. 2004). This can help in practical application by reducing the surface area requirements for plant growth. Through this process. the toxic microbial content can be minimized. Studies have shown the complete removal of faecal*Streptocci*and *pseudomonas* after receipt of algae treatments (Rajhi et al. 2020). Apart from contaminant mitigation, nutrient recovery of $NO_3^{(-)}$ and $PO_4^{(3-)}$ compounds are also possible resulting in the formation of slow-release fertilizers like struvite. A crucial factor is the uptake time and resistance of the plant species to fluctuating levels of pH, toxicity which will decide the viability of the phytotoremediation process.

11.3 Advanced Effluent Treatment Techniques

These represent the emerging technological developments in the field of wastewater treatment. In recent years membrane separation techniques have been touted as a panacea for WWT. Apart from the widely studied pressure-driven membrane processes, there are also interesting developments in terms of utilization of thermal and concentration gradients. Photocatalysts and nanotechnology also offer very rapid degradation of contaminants and have garnered widespread research focus. Some of the interesting and promising technologies are described below.

11.3.1 Membrane Distillation (MD)

It is an innovative application of membrane separation technique combining distillation with membrane separation and has been used for radioactive wastes resistant contaminants like arsenic and chromium. Here, nonporous hydrophobic membranes are used that allow preferential vapour transport. The contaminated feed solution is heated, to generate vapours which are transported through the hydrophobic membrane impervious to any solvent flow in the liquid state. Resultantly the contaminant remains behind in the residual concentrate while the vapours containing pure solvent undergo separation. In order to ensure rapid separation of the vapours and to condense them to yield pure water, a coolant is circulated in the permeate side. This creates a thermal gradient between the feed and the permeate sides, enhancing the driving force for the separation and providing a medium for impingement of the vapour molecules. Mechanisms such as air gap, sweep gas or vacuum are also increased to further enhance the separation flux.

Membrane distillation technologies have demonstrated 90% removal of contaminants like arsenic, phenols, (Kiai et al. 2014; El-abbassi et al. 2012) and has also been applied for seawater desalination (Alobaidani et al. 2008). MD offers advantages over conventional thermal separation techniques by reducing the temperature requirements and also by initiating vapour transport at temperature less than the boiling point temperature. This allows the flexibility of coupling renewable energy sources like solar energy, geothermal energy sources and also low-grade waste heat to power the energy requirements of the process (Wang et al. 2019; Sarbatly and Chiam 2013). Compared to the other membrane-based processes, the use of hydrophobic membranes entails lower fouling propensity than the hydrophilic counterparts. This also decreases the stringent pre-treatment conditions needed for the maintenance of the membrane (Alobaidani et al. 2008). MD systems equipped with the provision of heat recovery demonstrates high-performance ratio of 8 due to the short diffusion path traversed by the vapour molecules through the compact, dense MD membrane (Schneider et al. 1988). In terms of process design, membranes module and template selection affect the process performance. Depending upon the operating conditions, plate and frame tubular shell and tube or spiral wound modules are used with flat sheet or hollow fibre hydrophobic membranes. PVDF (Poly Vinylidene Fluoride) and PTFE (Poly Tetra Fluoro Ethylene) are the mostly used membrane material for MD followed by composite membranes (Adnan et al. 2012; Boo et al. 2016). The distribution of pore size, tortuosity, selectively governs the separation and results in near-complete exclusion of different contaminants.

However, notwithstanding all the benefits of the process, there are several challenges faced by the MD membranes. The principal among them are membrane wetting resulting in the gradual loss of the hydrophobic character of the membranes and the low flux associated with the process (Rezaei et al. 2018). Another operational difficulty experienced in real-life condition is temperature polarization, analogous to the concentration polarization due to the imposition of the temperature gradient. Dedicated research efforts in this direction are needed to address the problems. The benefit of high separation efficiency can also offset the operating cost involved in counteracting the operational difficulties. MD has the potential to be developed into an ambitious technology for converting industrial effluents into potable water.

11.3.2 Forward Osmosis

Forward osmosis represents a nascent, highly promising technological niche where concentration gradient is used as a driving force for separation. It is a direct opposite of its popular counterpart Reverse Osmosis (RO). In this process, an additional synthetic solution termed as the draw solution (DS) at a higher concentration than the feed (WW) is circulated on one side of the membrane. These two solutions are separated by a semi-permeable membrane which allows selective solvent transport. The difference in the feed and DS concentrations creates a concentration gradient along the length of the membrane surface. Under the influence of the concentration gradient, the solvent moves from the feed side to the DS side and a dilute DS is produced. This DS is then subsequently treated to get pure water. Recovery of the DS is also possible further incentivising the process. The ideal forward osmosis process is driven solely by concentration gradient without the requirement of any external energy expenditure. However, to increase the speed a small amount of external pressure is applied in a popular variant of the process called pressure assisted osmosis. This technology has proven to be particularly efficacious for drawing clean water from complex industrial effluents.

The operating principle is analogous to MD where the focus is on drawing the clean solvent while the contaminants remain behind in the feed. Owing to the simplicity, high separation efficiency and competitive flux values from the process, numerous hybrid options like integrated RO-FO, FO-MD, FO-NF and other possible process combinations are being researched upon (Kim et al. 2019; Bamaga et al. 2011) Application of osmotic membrane separation in conjugation with RO is helpful for managing the problem of highly saline concentrates. It has also demonstrated efficacious hypersaline brine treatment by cutting down energy expenditure by reducing the external pressure requirements (Das and Singh 2021).

The membrane selection and the draw solution selection are key factors affecting the FO process dynamics. Cellulose acetate thin-film composites with a thinner support layer are mostly used for the FO processes (Das et al. 2020). A critical literature review reveals the exploration of different classes of draw solute and their regeneration strategies. These range from commonly used ionic salts like NaCl and $MgCl_2$, polyelectrolytes, chelating ligands like EDTA, stimuli-responsive hydrogels, magnetic draw solutes (Koetting et al. 2015; Ge et al. 2012). Direct reduction of the secondary draw solute purification step occurs when edible macromolecular draw solutes are used. In this case, there is a yield of dilute draw solution containng nutrients instead of water. This can also be drunk as a nutrient supplement. Similarly, research has also been undertaken for the use of the dilute DS as fertilizers using nutrient concentrates as draw solutions (Phuntsho et al. 2012).

The successful exploitation of the concentration gradient has also yielded several interesting spin-off's like osmotic pumps, pressure retarded osmosis, osmotic bays, osmotic evaporators (Das et al. 2019a). Though they are challenges like internal and external concentration polarization, reverse salt diffusion, requirement of secondary purification step, FO is largely touted as the new-big thing in the domain of wastewater treatment possesing broad spectrum applicability.

11.3.3 Photocatalysis

It is a nascent technology that combines the efficacy of catalytic contaminant degradation with renewable solar energy as a source of energy. Broadly it can be classified as an advanced oxidation technology that is used to breakdown persistent organics like pesticides, textile dyes, oil as well as inorganic components like nitrates and heavy metals (Mboula et al. 2013; Prieto et al. 2005). Photocatalysis has also been used to breakdown pathogens like bacteria and viruses from contaminated wastewater (Martín-Sómer et al. 2019). The process of photocatalytic effluent treatment can be broadly divided into two parts homogeneous photocatalysis and heterogenous photocatalysis. The homogenous photocatalysis relies on the action of UV light to generate hydroxyl free radicals from water which in turn hydrolyze and breakdown metal ions and are accompanied by a formation of hydrogen peroxide.

$$\mathrm{MeOH^{n+} + h\upsilon \rightarrow Me^{(n-1)+} + OH^{\cdot}}$$
$$\mathrm{MeL^{n+} + h\upsilon \rightarrow Me^{(n-1)+} + L^{\cdot}}$$

(Prihodko and Soboleva 2013).

The heterogeneous photolysis as its name suggests includes composite phased materials, and also offer the flexibility of using visible light sources apart from UV waves. Critical analysis of research literature in this arena reveals large number of research dedicated to crystalline modification for improved catalytic material synthesis and the application of integrated photocatalytic systems with other advanced oxidation technologies. The fundamental principle of photocatalytic effluent treatment is derived from quantum chemistry where absorption of photonic packets equivalent to one quantum energy generates an electron-hole pair. The photogenerated holes drive thermodynamically spontaneous reactions catalyzed by hydroxyl cationic free radicals, by adsorptive mechanism on the surface of the photocatalysts.

$$\mathrm{H_2O_{ads} + h^+ \rightarrow HO^{\cdot}_{ads} + H^+}$$
$$\mathrm{OH^-_{ads} + h^+ \rightarrow HO^{\cdot}_{ads}OH^-_{ads} + h^+ \rightarrow HO^{\cdot}_{ads}}$$
$$\mathrm{R_{ads} + h^+ \rightarrow R^{\cdot +}_{ads}}$$

Similarly, spontaneous oxidative pathways are also catalyzed

$$\mathrm{O_{2ads} + e^{(-)} \rightarrow O_2^{\cdot -} ads}$$
$$\mathrm{O_2^{\cdot} ads + H^+ \rightarrow HO^{\cdot}_{2ads}}$$
$$\mathrm{O_{2ads} + 2e^{(-)} + 2H^+ \rightarrow H_2O_2 ads}$$

The oxidative mechanisms follows Langmuir-Hinselwood and Eley–Rideal pathways.

There are different classes of photocatalysts being researched upon. However, the vast majority of research publications as well as limited number of commercial ventures focused on using TiO_2anatase phase. TiO_2 nanomaterials are generally preferred due to the higher surface area of these processes (Hussain et al. 2010). Some of the process developments include nanosized TiO_2 embedded on zeolites or mesoporous supports for simultaneous oxidation and ion-exchange utilizing the molecular sieving properties. The TiO_2 is used as colloidal suspensions, solid nanoinjections or dispersed in carries suspended specially in the photoreactors.

However, while evaluating the market competitiveness of photocatalytic processes, their cost and photonic conversion efficiency are areas that demand further research before the competitiveness with other separation processes can be established. In a photocatalytic reactor one of the important design considerations is the depth of penetration, and depth of catalyst bed, which in turn depend upon catalyst synthesis and life of the active catalyst components. Application in real wastewater treatments often mandates pre-treatments to remove interfering ions which might poison the catalyst. Light storage and supply also poses veritable challenge. Comprehensive life cycle analysis covering catalyst synthesis, WWT efficiency and catalyst regeneration is necessary for cost-benefit assessment.

11.3.4 Nanomaterial and Nanotechnology

In recent years considerable research space in the domain of environmental technology in general and effluent treatment has been occupied by nanotechnology which represents a scaling down of the process to the nanolevel for increased speed, surface area and higher reaction efficiency. The nanomaterials that are used for wastewater treatment can be divided into metallic nanomaterials, metal oxides, carbon nanotubes and nanofibers and nanocomposites. The zero valent metal nanoparticle is the simplest to synthesize and widely used in the arena of effluent treatment. Silver nanoparticles are especially, used to degrade microbial contaminants due to the antibacterial and fungicidal properties of silver (Borrego et al. 2016; Kalhapure et al. 2015). Silver nanoparticles have also been combined with plant extracts in several green synthesis studies which have proven to be effective in the remediation of heavy metals (Shittu and Ihebunna 2017). Other prominent metal nanoparticles used in WWT include iron nanoparticles. Zero valent aluminium nanoparticles are also being researched upon due to their rapid surface reactions forming hydroxides and/or oxides (Rivero-Huguet and Marshall 2009).

The metal oxide nanoparticles include compounds that can also act as semiconductors for possible integration with photocatalyst TiO_2 nanoparticles which are widely used as a photocatalyst for effluent remediation falls under this category. Iron oxide nanoparticles doped with graphene is also an interesting technological development that intensifies process performance. The nanoparticles are potent scavengers breaking down radioactive elements, halogenated organic compounds, nitroaromatic compounds and other persistent pollutants (Ling and Zhang 2015; Liang et al. 2014; Xiong et al. 2015). Another novel development credited to advanced material science research is the discovery of carbon nanotubes. These are single layers of graphene bundled in a cylindrical shape which can be single-walled or multiwalled with interconnecting nanotubes. The multiwalled CNI'S can also be arranged in a hexagonal pattern forming a honeycomb structure. This greatly enhances the surface area and the fine diameters impart high selectivity to the nanoparticles. Their fast reaction kinetics and organic separation potential has been utilized in the area of pharmaceutical effluent management.

The contaminant mitigation mechanisms of the nanoparticles include adsorption and in some cases biosorption, oxidation and hydrolysis, ion-exchange. Due to the capability to exhibit more than one removal mechanism, nanoparticles can be used for broad-spectrum contaminant removal from complex industrial wastewaters like oil industry wastewater (He et al. 2021). Their fast kinetics and the nanolevel separation characteristics have been harnessed in the treatment of high salinity containing produced water (Kunduru et al. 2017). Another interesting class of heterogeneous nanomaterials are the nanocomposites. Nanoparticles embedded on polymeric membranes or ceramic/zeolite membranes have been used for the mitigation of particularly recalcitrant substances from effluents like catalysts residues, drug residues, volatile organic compounds (Zou et al. 2019; Li et al. 2019). Nanocomposites are multiphase substances consisting of porous media, gels, colloids and polymers (Rane et al. 2018). The nanomaterials are one fast-emerging technology that has the potential to develop as a standalone WWToption.

11.4 Sustainability and Value Addition in WWT

11.4.1 Recovery of Value Added Products from Effluent Streams

One of the important avenues of research in the domain of WWT is the recovery of value-added products from effluents streams this approach is a sustainable research perspective that considers wastewater as a rich source of underutilized compounds from which value addition may be derived. In recent years due to shrinkage of resources and implementation of stronger environmental norms, wastes to wealth technologies are receiving heightened research attention. Membrane separation techniques have been particularly studied for the recovery of value-added products, like brine and soda ash recovery, extraction of metallic values, chemical recovery and others. Niche areas of sustainable technology such as membrane-based crystallization have been harnessed for nutrient recovery (Das et al. 2019b).

While focussing on value-added product recovery from effluents, it is imperative to understand the compositions of the wastewaters and what are the products that can be recovered from it. Membrane crystallization and membrane extraction techniques have been successfully harnessed to recover organic acids like succinic acid, lactic acid and also pure lactose crystals from cheese whey (Wan et al. 2007; Guimarães et al. 2010; Tejayadi and Cheryan 1995). Ammonium and phosphate containing effluent streams have been reacted with magnesium dosing to isolate a slow release fertilizer magnesium ammonium phosphate; commonly known as struvite (Çelen and Türker 2001; Diwani et al. 2007). Several integrated membrane separation techniques have been utilized for struvite recovery (Diwani et al. 2007).

Biochemical and electrochemical technologies have also been studied for recovery of value-added products. For example, selective microbial action has been used for fumaric acid production or oven biogas production from organic effluents (Sebastian et al. 2019; Pogaku et al. 2015). Similarly, fruit and oil industry effluents have been exploited for bioethanol production via the bioreactor route. Physico-chemical techniques like accelerated carbonation, selective leaching have also demonstrated the potential of extraction of valuable components from effluent streams.

11.4.2 Process Intensification

The newer challenges of zero liquid discharge, highly toxic contaminants like emerging micropollutants necessitate a paradigm shift in the design of ETP units. It is imperative for the WWT techniques to be sustainable and environment friendly. In terms of design, these requirements translate into optimum raw material consumption, minimum energy expenditure, coupling with renewable energy resources, sludge management and high WWT efficiency. Process intensification is one research avenue that can meet those requirements. Process intensified systems are highly efficient, modular design units that are the product of compact process development, which aims to merge several unit operations into one. Another parallel focus is to make the systems sustainable without compromising on energy efficiency.

Research in the domain of advanced separation techniques has led to the advent of process intensified systems incorporating membrane separation, photocatalysis, and nanotechnology. All of these systems aim to replace the bulky, multicomponent traditional effluents systems with single staged multipass units that are essentially simple and highly efficient. The process complexity diminishes with scaling down of the process. The single membrane assembly/membrane bioreactor also allows operational flexibility of coupling and decoupling of additional membrane module to treat fluctuating feedstocks and variable contaminant loadings.

Integration of process intensification technologies with conventional treatment options and value-added product recovery will enhance the sustainability quotient and economic viability of the processes leading to more large-scale implementation.

11.5 Conclusion and Future Work

(1) There are a host of different classes of wastewater treatment techniques. It is imperative to select the technologies based on the contaminants, toxicity levels, concentration, effluent volume and overall process economics.

(2) The conventional effluents options often lack the operational flexibility to handle new age contaminants as well as fluctuating contaminant loadings. Research options to integrate these techniques or combine them with novel

techniques are needed for their applicability in the current effluent treatment scenario.

(3) Membrane separation techniques are being widely researched upon and practically implemented as a broad spectrum effluent treatment option. They can be easily coupled with nanomaterials or catalysts or with the conventional techniques leading to a win–win situation.

(4) In recent years, process intensification, recovery of value-added products and process sustainability are important attributes that are being increasingly incorporated in the new age effluents treatment techniques.

(5) Advanced novel techniques like photocatalytic membrane reactor, solar-driven membrane distillation are being explored to couple renewable energy sources thereby increasing the environmental friendliness quotients.

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