Review

A Review on Eco-Restoration of Rivers with Special Focus on Industrial Wastewater Treatment

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Abstract: Rivers are the lifeline of an ecosystem, since every member of the ecosystem depends directly or indirectly upon them for their sustenance. Changes in the riparian conditions would strongly impact the ecosystem-to-organism interactions and inter-organism interactions. Due to lack of regulations and widespread use of technology for industrial wastewater treatment, most of the industrial discharge ends up in the river. This leads to increased toxicity and river pollution and can be remedied only through restoring the ecological conditions of the river. Eco-restoration of rivers is meaningless without addressing the reason behind river pollution hence feasible industrial wastewater treatment methods are discussed in this study, with emphasis on their practicality and effectiveness.

Keywords: River Pollution, Industrial Wastewater Treatment, Sustainability, Ecological Restoration

Introduction

Rivers, by themselves, can be termed small- scale bio diversity hotspots since they sustain and support a lot of ecological communities and inter-species interactions. Human civilization originated on the banks of rivers and till date, humans are directly or indirectly dependent on rivers for all their daily needs. Rivers and the riparian ecosystems are dynamically evolving in nature. They are controlled and deeply influenced by both natural and human activities. Over the years, many regions across the world are reeling under water stress-where the demand for water is higher than that available. Water scarcity is not merely about the lack of water, but the lack of good quality water. All over the world, rivers are either polluted and turning unfit for usage, or are simply drying up due to unpredictable, extreme climate. A 2016 assessment of the water quality situation in rivers in Latin America, Africa and Asia, *A Snapshot of the World's Water Quality*, estimates that one- third of the regions' major rivers are severly affected by pathogenic pollution, one-seventh polluted by organic contaminants and one-tenth facing moderate to severe salinity pollution (UNEP, 2016). Still today, 80% of global wastewater goes untreated, containing everything from human waste to highly toxic industrial discharges. The nature and amount of pollutants in freshwater determines the suitability of water for many human uses such as drinking, bathing and agriculture. Even in India, the situation is far from ideal (CPCB, 2009).

In 1995, many severely polluted stretches on 18 important Indian rivers were identified in a report by the Central Pollution Control Board (CPCB). The negative impact that increased BOD and pathogenic activity had on water quality was inferred from the results of the water quality monitoring tests (CPCB, 2009).

During 1995-2009, the number of observed samples with BOD values less than 3 mg/l was between 57-69%; in 2007 the proportion of observed samples was 69%. There was a gradual decrease in the BOD levels and in 2009, 17% had BOD value higher than 6 mg/1. The unnerving aspect of the trend was that either the discharge sources where not compliant with prevalent pollution control standards or the prevalent pollution control standards had to be modified (Rajaram and Das, 2008).

The main cause for such contamination is discharge of untreated domestic and industrial effluent in water bodies from urban areas. About 70% of the total effluent treatment capacity in India, which amounts to 8040 MLD is concentrated in 35 metropolitan cities. However, metropolitan cities are found to treat only 52% of their total wastewater generated every year. This indicates that smaller towns and cities have very little wastewater treatment capacity (Rajaram and Das, 2008).

In the industrial sector only 59% of the large and medium industries performed proper effluent treatment in 1995. 1.5 million Indian children below 5 years die each year due to water related diseases and the country loses about Rs 366 billion each year due to the same (Parikh, 2004).

60% of river pollution in India happens due to untreated sewage, out of which, 40% is contributed by industries alone. Industrial waste not only causes water pollution, but also thermal pollution (Parikh, 2004). When untreated, hot industrial wastewater that is not subjected to cooling operations in cooling towers and such like, is released into the river, it greatly damages the riparian ecosystem. Fishes lose their ability to reproduce and the eggs laid by many marine organisms are destroyed. Many plants and small riparian animals cannot withstand the heat and toxicity of wastewater and they succumb to it. This may lead to mass extinction of various species and the ability of the river to clean itself and sustain life will be destroyed. Analysis of the trends observed in the lives of those organisms will give a clear picture about the quality of the river water. Rivers exchange materials, water, nutrients and energy with the surrounding environment. River water quality, sediment characteristics and biological communities, all reflect characteristics of the upstream and even the downstream environment. Soil deposition by rivers onto their floodplains has influenced the course of human agriculture and the distributions of human populations since antiquity. In the name of urbanization and industrialization, we have destroyed large portions of riparian vegetation and have isolated rivers from their floodplains. Unless the ecology of the river is restored, fatalities and dire consequences owing to river pollution will continue to increase.

Ecological restoration (or) eco-restoration is the act of enhancing and preserving bio-diversity, health and the nature of the ecosystem by restoring and rectifying certain factors that have led to an imbalance and discord in ecological relationships. Through there are multiple processes in eco-restoration, they can be broadly classified into 4-an interplay of hydrological, geomorphic, ecological and biogeochemical processes (Yarnell *et al*., 2015). The way restoration engineers regard the process of eco-restoration is purely utilitarian, since millions around the world are dependent on rivers for food (irrigation for cultivation), potable water, transportation, electricity and running industries. This extensive dependence on the river by humans is also the reason behind various political, diplomatic and legal disputes. Rivers and similar freshwater bodies are protected by law in the regions they are situated hence the design and implementation of eco- restoration projects will greatly depend on the regulatory, political and legal lobbying that may occur (Iovanna and Griffiths, 2006).

Eco-restoration of rivers can be broadly classified into three categories:

1. Eco-Restoration through design: This form of eco-restoration focuses heavily on the flow rate (i.e.,) discharge rate of the river since flow is an important variable in controlling the sediment levels, biota and the ecology of the river (Doyle *et al*., 2005; Yarnell *et al*., 2005). It also includes Channel Reconfiguration. Channel reconfiguration is usually found in urban and agricultural regions where river channels are reshaped and the speed of the river flow is brought down using wood and rock deflectors. In addition, banks are fortified with material to minimize erosion caused due to unprecedented, strong and excessive runoff (like floods) (Levell and Chang, 2008). It is based on the assumption that once the channel gets attuned to the current flow rate and the level of accumulation of sediments, species would begin reassembling and all other ecological processes like nutrient processing, decomposition would be ‘restored’. This approach leads to the restoration of the physical, chemical and biological functions of a river that is self-regulatory and possesses stable channels (Rosgen, 2011)
   However, this form of eco-restoration does not focus on ecological or chemical processes. Any improvement or restoration in the ecological/chemical processes is considered to be the byproduct of the project undertaken to modify the morphology of the channel. Yet, ecologists have pointed out that though restoration of hydrogeomorphology is important, it is inadequate for degraded channels and it can even lead to damage of the stream’s ecological conditions. For example, in restoring channel morphology, if trees along the river are removed from a previously closed-canopy stream, the energy regime may change to one dominated by primary production (like algal domination). Further, true ecological recovery cannot be achieved until the source of pollutants is removed (Doyle *et al*., 2005)
2. Eco-restoration through ecological functions: This is a more comprehensive process-based restoration method that goes beyond hydrogeomorphic processes to include ecological processes’ restoration. Functional ecological restoration consists of efforts specifically targeted at restoring critical ecosystem features (e.g., riverside vegetation) and critical ecological processes, such as nutrient flow, the input of organic matter and productivity (Beechie *et al*., 2010). The idea of functional restoration is relatively new and many governments and regulatory agencies still rely on channel design measures because of the relatively recent nature of functional restoration and the immense amount of involvement it requires from the stakeholders (Yarnell *et al*., 2005)
3. Preventive Ex-situ eco-restoration of rivers: Both functional restoration and eco-restoration through channel design are localized operations (i.e.,) carried out on or near the river, at the reach level, which is 1 km away from the river. However, this does not help in

fully combating river pollution. Eco-restoration of rivers is carried out to preserve the ecology of the rivers and pollution is one of the biggest threats faced by the riparian ecosystems. Hence to prevent degradation of rivers and destruction of ecosystems through non-native species (both biotic and abiotic components like toxic chemicals and heavy metals), eco-restoration must begin at the 'source' level-where the pollutants are being released into the river. This means, one must prevent illegal discharge of runoff, particularly industrial runoff, into the river since it contributes the most to the toxicity of the river water and significantly increases the BOD and COD of the water (Beechie *et al*., 2010). This form of eco-restoration is deemed to be the best by ecologists and researchers, because it helps prevent degradation of water quality and destruction of riparian ecosystems by keeping a check on the source(s) of river pollution and is the most sustainable solution to the problem of river degeneration. In the rest of the review, certain existent and emerging wastewater treatment technologies are discussed with special focus on their utility

Electrocoagulation

Most industrial wastewater treatment methods can be classified into 3 categories-physical, biological and chemical. Electrocoagulation is an electrochemical process that is used to separate contaminants from the rest of the influx. An electric field is applied onto the incoming wastewater and the charge on the suspended heavy metals gets neutralized. The neutralized particles bond with each other to create large floating masses called flocs, which is similar to sludge, upon aggregation.

The following mentioned mechanisms occur during an electrocoagulation process (Mollah *et al*., 2004):

(1) Reactions occur near the electrodes to produce metal ions from electro dissolution of the anode and at the cathode, hydrogen gas is produced
(2) Breaking and destabilizing emulsions between pollutants, suspended particulates and the rest of the influx
(3) Coagulation of the destabilized phases and their aggregation as flocs, in the aqueous phase
(4) Elimination of coagulated contaminants through sedimentation, where coagulated solids are scattered through bubbles of hydrogen gas evolved and reach the top of the reactor
(5) Electrochemical and chemical reactions increasing the cathodic reduction of organic pollutants and metal ions
Anode:

$$Fe(s)\,yields \rightarrow Fe^{+2} + 2e^{-}$$
$$Al(s)\,yields \rightarrow Al^{+3} + 3e^{-}$$

Cathode:

$$2H_2O + 2e^{-}\,yields \rightarrow H_2 + 2OH^{-}$$
$$8H^{+} + 8e^{-}\,yields \rightarrow 4H_2$$

Overall:

$$Fe(s) + 2H_2O\ yields \rightarrow Fe(OH)_2 + 2H_2$$
$$3H_2O(l) + 3e^{-}\,yields \rightarrow 1.5H_2(g) + 3OH^{-}$$
$$3H_2O(l) + Al(s)\,yields$$
$$\rightarrow 1.5H_2(g) + Al(OH)_2(s)$$
$$4Fe(s) + 10H_2O(l) + 10O_2(g)\,yields$$
$$\rightarrow 4Fe(OH)_3(s) + 4H_2(g)$$

EC can also be applied in the removal of tannins, dyes, other metals from wastewater, with the reaction mechanism almost unaltered. The applied potential between the metal electrodes generates the coagulant species from the dissolution of the electrodes and hydrogen is simultaneously developed at the cathode, which takes the contaminants to the top surface of the treated solution. The coagulant species added-transition metal salts like Ferrate (VI), spinel ferrites, polymers cause the aggregation of the suspended particles, which leads to adsorption and contaminant precipitation. Though different electrodes have been reported in literature, Fe, Al electrodes are most commonly used because of their efficiency and low cost. The EC process could thus be summarized by anode oxidation and formation of coagulants, the destabilization of the contaminants and breaking of emulsions and finally the formation and sedimentation of the heavy flocks and flotation of light flocculated flocks (Hendaoui and Ayari, 2020).

Here are some parameters affecting the removal of contaminants from the influx:

- Effect of initial pH: The maximum TOC elimination at pH = 5 was 65%. Elimination efficiency decreases when pH is increased, which can be attributed to evolution of hydrogen gas at the cathode. In phosphate removal, when there is no control over pH, low pH is preferred for reducing energy requirements and when the pH of the system is controllable, the optimal value is between 6 and 7 because solubility of $Fe(OH)_2$ formed is minimal in this range (Darban *et al*., 2020)
- Electrolysis time: When electrolysis time increases the amount of metal hydroxides generated also increases and the efficiency of the process increases till it becomes constant (Bener *et al*., 2019)
- Current density: Current density determines the cumulative floc-growth, which has an impact on

the effectiveness of electro-coagulation. As the current density increases, anodic dissolution and dissolution of metal hydroxide flocs increases, resulting in increased efficiency in contaminant removal (Bener *et al*., 2019). When the current density increased from 50 to 100 mA/cm^2, the results showed that the efficiency of TOC removal increased from 28.5 to 34.42%. (Bener *et al*., 2019)

- Distance between the electrodes: For effluents with high electrical conductivity, which are supplied with constant current, distance between the anode and cathode must be increased (Bener *et al*., 2019)
- Effect of applied voltage on metal removal: The result at 8 V showed that the maximum removal of metals was found to be 96, 98 and 99.5% for Cr, Cu and Pb, respectively (Bener *et al*., 2019)

Comparison with other Treatment Methods

Under optimal operating conditions for the EC method (50 A/m^2, 45 min and pH = 6), the removal efficiencies of 79% for TOC, 83% for COD, 73% for total phosphate and 95% for color were obtained, while under the optimal conditions for the electro-Fenton method (50 A/m^2, 45 min, 25 mM H_2O_2 and pH = 3), the removal efficiencies 87% for TOC, 91% for COD, 96% for total phosphate and 99% for color were obtained. Operating costs per m^3 effluent treated were measured. Results obtained for EC and EF methods were 0.74 and 1.23 V/m^3, respectively. Hence the EF method is more efficient than the EC method but is also more expensive than the same (Darban *et al*., 2020).

Though CC has brought a considerable decrease in the percentage of COD, suspended solids and chlorides, the extent of decrease in the total dissolved solids is only 14.05% using alum and 26.3% with $FeCl_3$, whereas the EC method which has reduced both COD and TDS to 92.3 and 91.5%, respectively, proving to be more efficient with Fe-Al assembly using a minimal current of 0.04 A at a time interval of 15 min. The coagulant consumption is also less in EC than in CC rendering it as a cost-effective technology (Darban *et al*., 2020). Variation of TOC removal extent with current density and pH when subjected to electrocoagulation is shown in Fig. 1.

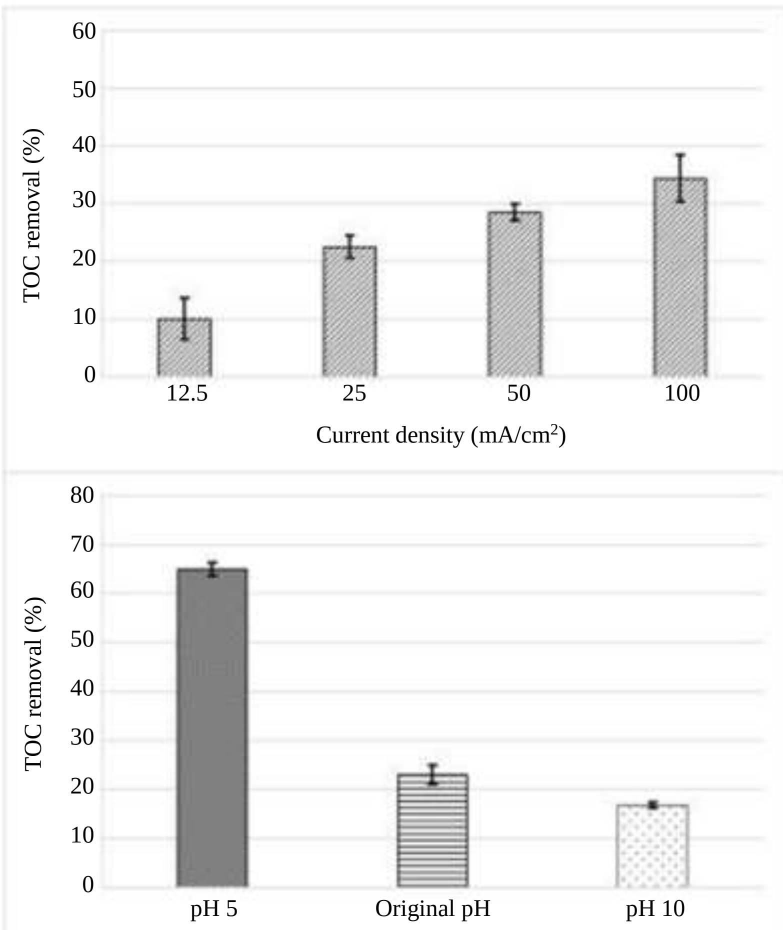

Fig. 1: Variation of TOC removal with current density and pH (Bener *et al*., 2019)

To sum up, EC, when used in combination with other treatment methods, is an environment-friendly and economical strategy in industrial wastewater treatment. It is highly recommended for toxic effluents that contain a lot of heavy metals, dyes and paints. Since it does not require additional chemicals, secondary pollutants are not generated. It can be operated on low current hence can also be used in combination with alternate sources of electricity like solar cells, fuel cells etc. It generates lesser sludge and shows higher performance than chemical coagulation. However, it incurs high maintenance costs and the electrodes turn passive over usage and need to be replaced often, which tends to increase the cost (Bener *et al*., 2019).

Nanoremediation of Wastewater

Various eco-friendly and efficient nanomaterials have been developed over the previous decades for industrial wastewater treatment. Having shown high removal percentages, which translates to high sedimentation efficiency, these nanomaterials can be divided into 3 categories: Nano-adsorbents, nano-catalysts and nano-membranes (Tyagi *et al*., 2017).

Nano-adsorbents: They are generally produced from chemically active substances with high adsorption capacity on the given surface area (Kyzas and Matis, 2015). Hence certain heavy metals like Cu, Pd, Ti, which were removed as heavy metal contaminants during electrocoagulation, can also be used to fabricate nanocomposites, transition metal complexes. Apart from these, materials that can be used for developing nano-adsorbents include activated carbon, silica and metal oxides (El Saliby *et al*., 2008).

Nano-catalysts: In industrial wastewater treatment, metal oxides and semiconductors are used as electrocatalysts to inprove the performance of the fuel cells and Fenton based catalysts are used for improving chemical oxidation of organic pollutants (Chaturvedi *et al*., 2012).

Nano-membranes: Here, separation of pollutants is driven by osmotic pressure.

Adsorptions of heavy metals from wastewater by using the nano-adsorbents are affected by many factors such as temperature, pH, adsorbent dose and incubation/contact time. The surface of the adsorbents are generally modified, like in case of Fe_2O_3 nano-particles through the addition of 3-aminopropyltrimethoxysilane. This increases affinity, which enhances simultaneous removal of different pollutants such as Cr^{3+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and As^{3+} from wastewater (Tyagi *et al*., 2017). MnO nanoparticles show high adsorption ability due to polymorphic structure and high BET surface area and are generally used in the removal of As(V) from wastewater (Wang *et al*., 2011).

ZnO non-rods, nanoplates, nanowires, nanocubes, nanorods, nanobelts, miscrospheres and nanosheets show high Pd based nano-particles are used in combination with carbon nanotubes to overcome the limitations associated with using elements like Pt, Zr in manufacturing nanocatalysts. Pd is flexible, versatile and can also form nanocomposites with carboxylated MWCNT, pristine Multi-Walled Carbon Nanotubes (pMWCNT), amine-modified MWCNT, hydroxyl-modified pristine multi-walled carbon nanotubes, carbon black and carboxylated graphene, showing high removal efficiencies for Cu(II), Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} and As^{3+} (Singh *et al*., 2013).

However, noble metals are now being used with cheaper transition metals to manufacture bimetallic nanocatalysts (Ma *et al*., 2015). Since nanocatalysts are very selective, they must be fabricated keeping in mind the kind of pollutant that ought to be efficiently removed. Among all materials used as nanocatalysts and nanocomposites, the Fenton-based nanocatalysts are some of the most established and evolving entities in terms of industrial wastewater treatment, especially with reference to treating organic pollutants and microbial contaminants in industrial discharge. Though the Fenton process has been used for over 200 years in removing organic contaminants from industrial discharge, the biggest drawback of this process is the continuous loss in the amount of catalyst and the need to main acidic conditions (pH = 3) for optimum function, since Fe(III) becomes about 100 times less soluble than Fe(II) during near-neutral and basic conditions, causing the precipitation of Fe(III) into $Fe(OH)_3$, which slows down the treatment process. Hence Fenton's reagent is used as an effective replacement to the Fenton reaction (Kurian and Nair, 2015). Fenton reagents consist of spinel ferrites of Zn, Ni, Cu and Co and are manufactured through auto-combustion and sol-gel method. Transition metal ferrites are used in the manufacture of Fenton reagents to modify the stability and redox properties, which increases efficiency of catalysis. Cu-Fenton systems are extensively used because Cu is one of the most easily obtained transition metals. They are comprised of organic and inorganic homogenous Cu-complexes (whose catalytic performance depends on the coordination state of their co-ordination numbers and steric configuration) for treating discharge from dyeing and pharmaceutical industries (Inchaurrondo *et al*., 2014), heterogeneous reaction systems which are reported to show higher catalytic efficiency, decreased sludge production, Cu-inorganic composites-made my mixing of Cu with inorganic substances (to produce bi-metallic Cu-Fe alloys for instance) or doping with inorganic materials lie silica, using co-precipitation or sol-gel methods (Xue *et al*., 2016). Out of all the Cu-Fenton systems discussed above, heterogenous $CuFe_2O_4$ is used extensively due to it exhibiting high thermal and chemical stability (Kurian and Nair, 2015). $NiCo_2O_4$-grapheme modified nanocomposites are also used in microbial fuel cells to produce hydrogen upon electrolysis, with Coloumbic efficiency 66.2%, Cathodic hydrogen recovery 27.9%, Overall hydrogen recovery 18.4% and COD removal efficiency 58.1% respectively (Jayabalan *et al*., 2020).

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Table 1: Surface area, removal capacity and maximum adsorption capacity of particular ions for select nanomaterials

Nanomaterial	SA	RP	A_{max} Ion	References
Polymer-modified Fe_3O_4 (a)	NA	85	Pb(ll)-166.1, Cd(ll)-29.6	Yavuz *et al*. (2010)
CeO (a)	72	NA	As(V)-22.4, Cr(VI)-15.4	Luo *et al*. (2010)
TiO2 NPs (a)	185.5	99.2	Cd(II)-135.2, Ni(II)-115.6	Engates and Shipley (2011)
ZnO (a)	15.75	46.21	Pb(II)-160.7	Kumar *et al*. (2013)
Homogenous Cu Fenton complexes (with EDTA, CN^- as ligands) (b)	29.7	99.75	-	Chen *et al*. (2014)
*Cu Fe_2O_4 spinel (heterogenous Cu-inorganic Nanocomposite) (b)	27.6	94.87	Acetaminophen-126.13	Sharma *et al*. (2015)

a- Nanoadsorbents
b- Cu-Fenton nano catalysts
SA- Surface Area (m^2/g)
RP- Removal Percentage
A_{max} Ion-Maximum adsorption capacity of ion (mg/g)
*- Cu Fenton spinels nanocomposites are generally used to treat effluents with organic (dye- based) pollutants

However, nanoremediation techniques are still plagued by high manufacturing cost of nanomaterials and high operational costs, the need to develop suitable techniques to prevent noble metal wastage while being used as catalysts, decreasing environmental impacts associated with them being used for effluent treatment, amongst many others (Table 1). These issues can be addressed by focusing on control of metal leaching, which will decrease the nanocatalytic efficiency and pose environmental risks if the metals used in the catalyst are found to contaminate the industrial discharge; developing robust, multi-purpose, cost-effective catalysts that can operate over a wide range of pH; and designing and developing novel processes and reactors for treating specific industrial wastewaters so the burden does not lie solely on nanoremediation.

Photocatalytic Treatment of Wastewater

This method focuses on reducing COD levels by mineralizing target pollutants (Fig. 2). Organic pollutants are degraded by Ultraviolet (UV) light radiation below 400 nm absorbed by TiO_2 semiconductors is to form oxidative agents like the Hydroxide ion (OH-). UV light is absorbed by TiO_2 to produce electrons close to the conduction band and holes close to the valence band (Hoffmann *et al*., 1995). Decomposition of organic pollutants occurs in two ways- direct oxidative destruction at the holes or indirect oxidative destruction via (OH-) radicals. Various organic pollutants like dyes, pesticides, organic compounds containing halogens, Polychlorinated Biphenyls (PCB), detergents and phenols have been removed (EL-Mekkawi *et al*., 2016; Zhang *et al*., 2014):

- Just like any other photocatalysis process, this can also be generalized into (El-Mekkawi *et al*., 2016)
- Contact establishment between the contaminants and the catalyst surface
- Absorption by the catalytic surface (semiconductor surface)
- Photocatalytic reactions and product formation
- Movement of products from the semiconductor surface to the solution volume

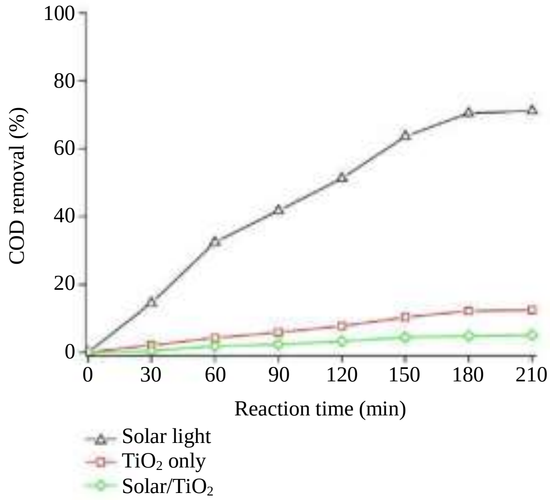

Fig. 2: COD removal percentage over reaction time

This process is generally carried out in Compound Parabolic Collector (CPC) reactors. They are static reactors composed of tubular photoreactors looking like transparent pipes that are connected in series. Each pipe is placed on a collector made of 2 halves of a parabola, allowing the incident radiation from the sun to get concentrated on the photoreactor. To make the pollutant recovery process easier, the photocatalyst can be loaded into the medium, which is supported by solid materials like ceramic and stainless steel, for high temperature annealing. The TiO_2 photocatalyst can be loaded onto polymeric sheets, which will minimize the overall cost of the photocataytic implementation. TiO_2 catalyst is bound to the polymeric sheets inside the CPC reactor through silicon based adhesives. The reactor is mounted on a platform and a centrifugal pump circulates wastewater inside the reactor (El-Mekkawi *et al*., 2016) (Fig. 3).

Since the idea of photocatalytic treatment of wastewater is very recent, the system can be regularly monitored for noting changes and making alterations. COD measurements can be performed using a COD meter and a multiparameter photometer. Variation of UV radiation, absorbance and decolorization with time is given.

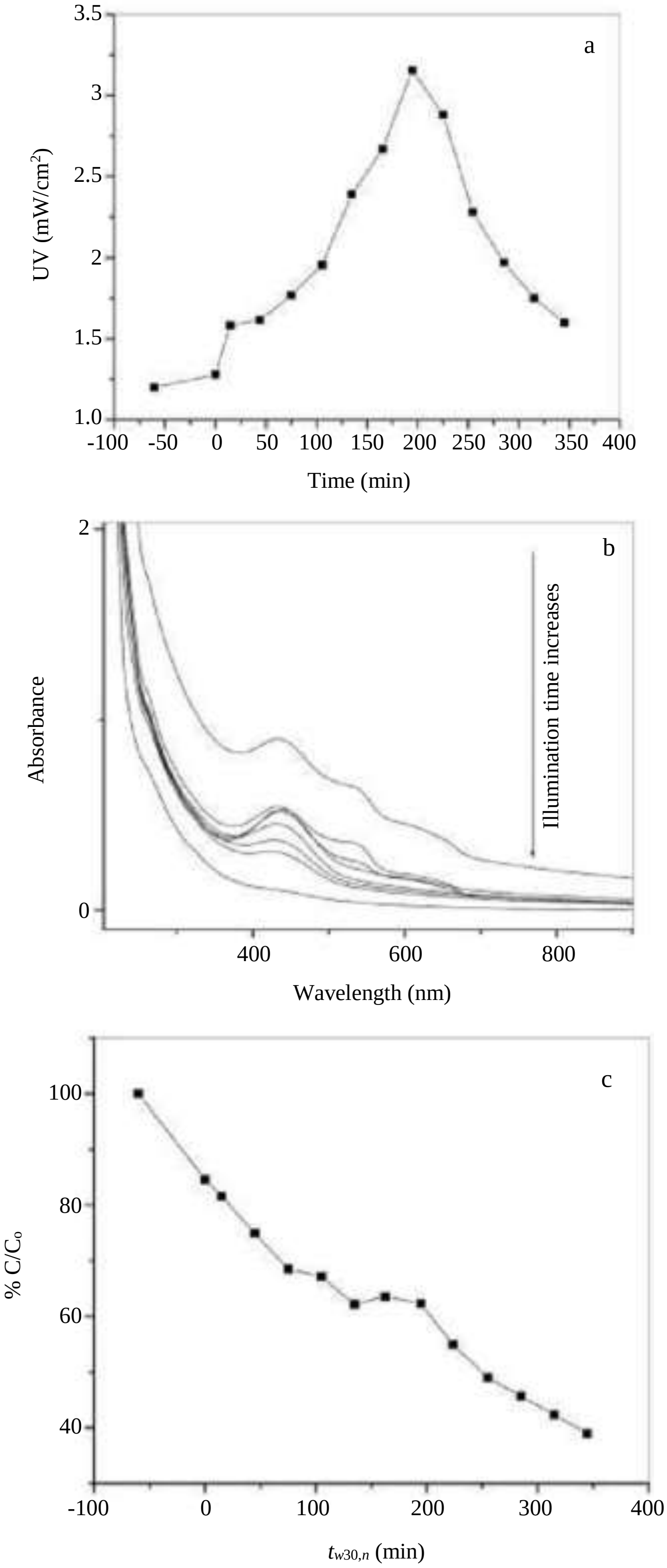

Fig. 3: (a) Measures solar UV at different time instances of the experiment. (b) change in absorption spectrum after 6 h of photocatalytic treatment (c) Decolorization of wastewater as a function of $t_{w30,n}$ (normalized solar illumination time) (El-Mekkawi *et al*., 2016)

The Total Suspended Solids (TSSs), Biological Oxygen Demand (BOD), total dissolved solids, total sulfides (H_2S), Settle-able Solids (SSs), total nitrogen, total phosphorus and oil and grease can be measured periodically to check whether the CPC reactor is functioning properly and to ensure the safety of the treated wastewater. Changes in the color of water during the degradation experiments can be observed using a UV-visible (UV-Vis) spectrophotometer (El-Mekkawi *et al.*, 2016).

Upon observation, it is seen that photobleaching of water occurs. The COD, that implies the amount of organic pollutants decreases significantly. The mineralization percentage was calculated to be 39%. The BOD/COD ratio increases, which means fresh bio- degradable species have been formed which can be removed by normal biological treatment (El-Mekkawi *et al.*, 2016). The process can be made more sustainable, using waste produced from other manufacturing industries as apt support. Solid waste like iron scrap (from battered second hand cars that are going in for an overhaul), construction debris, slag from the fertilizer industry and steel industry can be used to provide the mechanical support which is required during the loading and functioning of the photocatalyst. Instead of fabricating fresh polymeric sheets, waste fabric (fabric that has been made in excess) from the textile industries can be used. They can be made into suitable substrates for the binding of TiO_2 composite, using melt processing in-situ cross linking and heat pressing (Zhang *et al.*, 2014).

The advantage of photocatalytic industrial wastewater treatment using TiO_2 in CTC reactor is that sunlight, a perennial source of energy, is used. Hence it is suitable for tropical countries. TiO_2 is non-toxic and apart from this, no other chemical is used hence it is safer than chemical coagulation processes. Further, even waste materials can be used in the fabrication of the waste management system and since it is safe and the products can be removed by normal biological processes, it is a very sustainable solution. The biggest advantages of this treatment strategy are the simple design of the CTC and low operating costs. But the CTC, at present, is capable of treating only small amounts of wastewater that does not contain a lot of toxic impurities, which can ideally be found in small-medium scale industries. Hence unless the design and implementation are tweaked, it will continue to have only limited applications.

Constructed Wetlands

Constructed wetlands are artificially designed systems. They function on natural processes that depend on wetland vegetation, soil and associated microorganisms that are present in the wetland ecosystem, to purify industrial wastewater. Constructed wetlands are often termed as natural bio-reactors and are a cost effective choice for industrial wastewater treatment due to simple operational mechanisms. Wastewater passes through an intricate network of plant roots, media and bio-films, where various chemical, biological and physical routes influence pollutant removal. The most common type of wetlands used for industrial wastewater treatments are hybrid wetlands, which are a combination of both Horizontal Flow (HF) and Vertical Flow (VF) wetlands. (Vymazal and Kröpfelová, 2008).

HF systems can perform denitrification but have very limited oxygen transport capacity. VF systems higher oxygen transport capacity but negligible denitrification occurs in VF systems (Vymazal, 2007). Hence, hybrid systems are constructed to complement each other.

Heavy metal concentration of the inflow and out flow in a constructed wetland and its cleansing efficiency is depicted based on data from (Khan *et al.*, 2009) in Fig. 4. Treatment efficiency based on various parameters is discusses in Fig. 5. Hybrid wetlands and their efficiency in treating various typesof industrial wastewater is mentioned in Table 2.

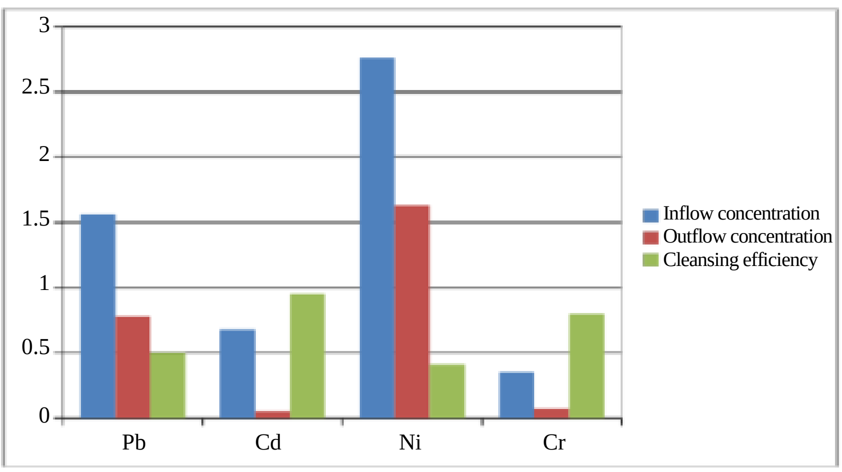

Fig. 4: Heavy metal concentration of the inflow and out flow in a constructed wetland an d its cleansing efficiency. Based on data from (Khan *et al*., 2009)

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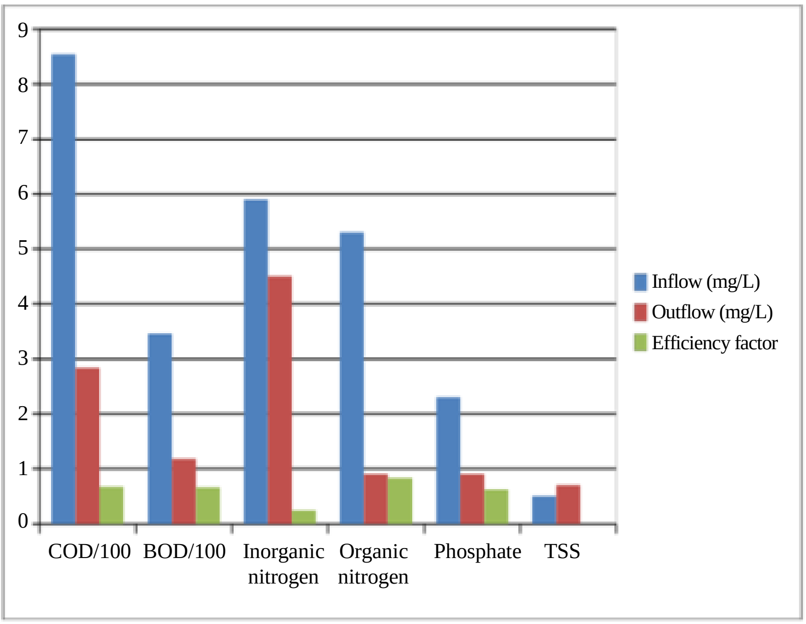

Fig. 5: The COD, BOD, amount of inorganic and organic nitrogen, phosphate and TSS levels before and after treatment of mixed industrial wastewater using hybrid constructed wetlands and the efficiency, based on data from (Justin *et al*., 2009)

Table 2: The usage of hybrid wetlands in treating select types of industrial wastewater has been depicted in the form of a table, with TSS, BOD, COD being the governing parameters

Industry	*TSS*	*TSS*	*COD*	*COD*	*BOD*	*BOD*	References
Petrochemical	82.8	4.5	250	89	38.6	8.1	Hawkins *et al.* (1997)
Distillery	129.0	17.0	1558	448	942.0	279.0	Serrano *et al.* (2011)
Textile	129.0	9.0	771	122	198.0	66.0	Bulc and Ojstrsek (2008)
Food processing (Meat)	561.0	34.0	3188	100	2452.0	84.0	Soroko (2005)
Mixed industrial wastewater	0.5	0.7	854	284	346.0	118.0	Justin *et al.* (2009)

a-Parameter in inflow (mg/L)
b-Parameter in outflow (mg/L)
BOD_5^i -Same as BOD, only indicates the fact that the BOD value has been obtained after testing for 5 days

Macrophytes have few desirable properties that make them a crucial part of Constructed Wetlands. They can adapt easily to survive in the harsh, toxic conditions of the wastewater pumped into the constructed wetlands. These features range from mode of reproduction, rapid growth, apical dominance, mechanical alterations, distinctive gaseous exchange mechanisms and special morphological growth structures, such as rhizomes, knees and air-filled roots that aids in extra root aeration. All these features make the microphytes capable colonizers of the wetland wastewater environment. They make the surface of the beds steady, aid physical filtration, prevent clogging in the vertical flow system, maintain appropriate temperature, protect against ice deposited during winter and give great surface area for microbial development. They significantly improve the transfer of oxygen into the rhizosphere (SSWM, 2020).

The design of the hybrid system consists of two stages of several parallel vertical flow beds (usually planted with *Phragmites australis*), followed by two or three horizontal beds (planted e.g., Typha or Carex). In these systems, the vertical flow beds are loaded with pre-treated wastewater for 1-2 days and then allowed to dry out for 4-8 days. The thin crust of solids formed on top of the vertical flow beds gets mineralised during the rest. Nitrification takes place in the vertical flow stage at the end of the process sequence. If nitrate removal is needed, it is necessary to pump the effluent back to the front end of the system where denitrification can take place in the less aerobic horizontal flow bed using the raw feed as a source of carbon needed for denitrification (Vymazal and Kröpfelová, 2008).

The two-stage horizontal-vertical-flow constructed wetland system consists of three basic units:

- Mechanical pre-treatment through of a two or three-chamber settler, for removal of large particles and settleable materials
- A horizontal subsurface flow sand or gravel-based constructed reed bed for BOD removal and Total suspended solid removal
- A loaded vertical flow wetland system for denitrification

Compared to other faster aerobic treatment options (e.g., activated sludge), constructed wetlands are natural systems, where treatment may require more land and time, but the operating costs are lesser since constructed wetlands consume little to no energy, do not require sophisticated equipment, chemicals or expensive spare parts or chemicals (SSWM, 2020).

Hybrid systems are more expensive than non-hybrid systems like horizontal and vertical flow constructed wetlands or free surface-flow constructed wetlands. They require a larger are, are more complex in operation especially when dealing with monitoring and adjustment of input load (SSWM, 2020). The operation and maintenance of constructed wetlands is tricky. A skilled operator must always ensure that the filters are loaded and placed properly, do not get clogged and the system shows good overall performance. Further the wastewater influx must be pretreated and sent to the wetlands to ensure the filters do not get damaged. Also, the wastewater must not be stored for a long time in an open, artificial pond so as to prevent the wetland from being a breeding ground for mosquitoes and the origin for contagious diseases. The discharge must be thoroughly checked for the presence of pathogens, its DO, BOD, COD must be analysed based on intended reuse (SSWM, 2020).

Hence Constructed wetlands are generally used as a secondary treatment process, with pretreatment performed to remove suspended solids Primary treatments, such as anaerobic reactors, septic tanks, biogas settlers are the most suited to lower the BOD and prevent clogging of the constructed wetland. Therefore they are most suited to small communities where thorough planning and regular maintenance can be ensured. Constructed wetlands are best suited to warm climates but can be modified to handle freezing and the ensuing levels of sub-par microbial activity (SSWM, 2020).

Microalgae

Microalgae cultures have shown great capacity in cleansing industrial wastewater, especially in case of wastewater that contains a lot of heavy metals (Salama *et al*., 2019).

Microalgae cultures' rapid metal uptake capability, energy- saving potential, eco-friendly usage, low cost of implementation and availability to absorb both high and low concentration levels of metals are some of its unique advantages (Salama *et al*., 2019) (Fig. 6).

The cell wall and membrane of microalgae usually is made up of polysaccharides, proteins and lipids. The membrane transporters are vital in facilitating the interaction between microalgae and the heavy metals in the wastewater influx. The mechanism for heavy metal bioremediation includes non-metabolism dependent uptake and metabolism-dependent uptake (Luo *et al*., 2019). The non-metabolism-dependent processes mainly consist of cell surface adsorption (ion exchange, physical adsorption and complexation) and extracellular adsorption (precipitation).

The presence of essential nutrients like carbon, nitrogen and phosphorus makes wastewater a suitable medium for microalgae cultivation (Luo *et al*., 2018). Nitrogen is important for microalgae growth as it aids formation of proteins, enzymes, ATP/ADP etc.

In recent years, researchers have reported the nitrogen and phosphorus removal efficiency by various microalgae species from municipal, agricultural, industrial and other types of contaminated wastewater. The cultivation of Chlorella vulgaris in anaerobically-treated piggery wastewater in an open raceway pond led to a nitrogen and phosphorus recovery of 85.3 and 89.5%, respectively (Wang *et al*., 2016). Nitrate (NO_3^-), Nitric Acid (HNO_3) and ammonium (NH_4^+), could be transformed into organic nitrogen through assimilation. The inorganic phosphorus (e.g., $HPO_4^{2-}/H_2PO_4^-$) in wastewater could be easily assimilated by microalgae (El-Sheekh *et al*., 2016). ATP and glutamate were transformed into ADP and PO_4^{3-} by phosphorylation during microalgae metabolism, with phosphate emoval rate varying with the concentration of phosphorus in effluent and the type of the microalgae used (El-Sheekh *et al*., 2016).

The algae, after removing a substantial amount of heavy metal from the wastewater influx, can be subjected to hydrothermal treatment to produce biofuel and bio-char. However, one must take care that the heavy metals present in the feedstock for hydrothermal treatment remain in the aqueous phase alone and don't get transferred to the organic phase that contains biofuel, during hydrothermal processing. Still, such migration occurs during thermochemical conversion. This is a severe problem, because heavy metals can increase corrosion and wear in engines. Additionally, metal emissions from the combustion of such biofuel produced have an adverse effect on human health and the environment. In the isolation of heavy metals, a lot of factors like temperature, pH and the type of metal, are involved (Li *et al*., 2018).

This method helps in effective nutrient recovery and removal of heavy metals from industrial discharge. Further, the algae are also valorized since it can be used to produce biofuel. The bio-char obtained can also be used as an adsorbent (Ahmad *et al*., 2014). However, this process is very expensive when it comes to industry-level implementation. The development of a large-scale, efficient hydrothermal reactor (to convert microalgae into biofuel) still remains a challenge. Further, microalgae cannot be directly cultured on industrial wastewater that contains a high concentration of COD, total nitrogen, total phosphorus and other toxic compounds.

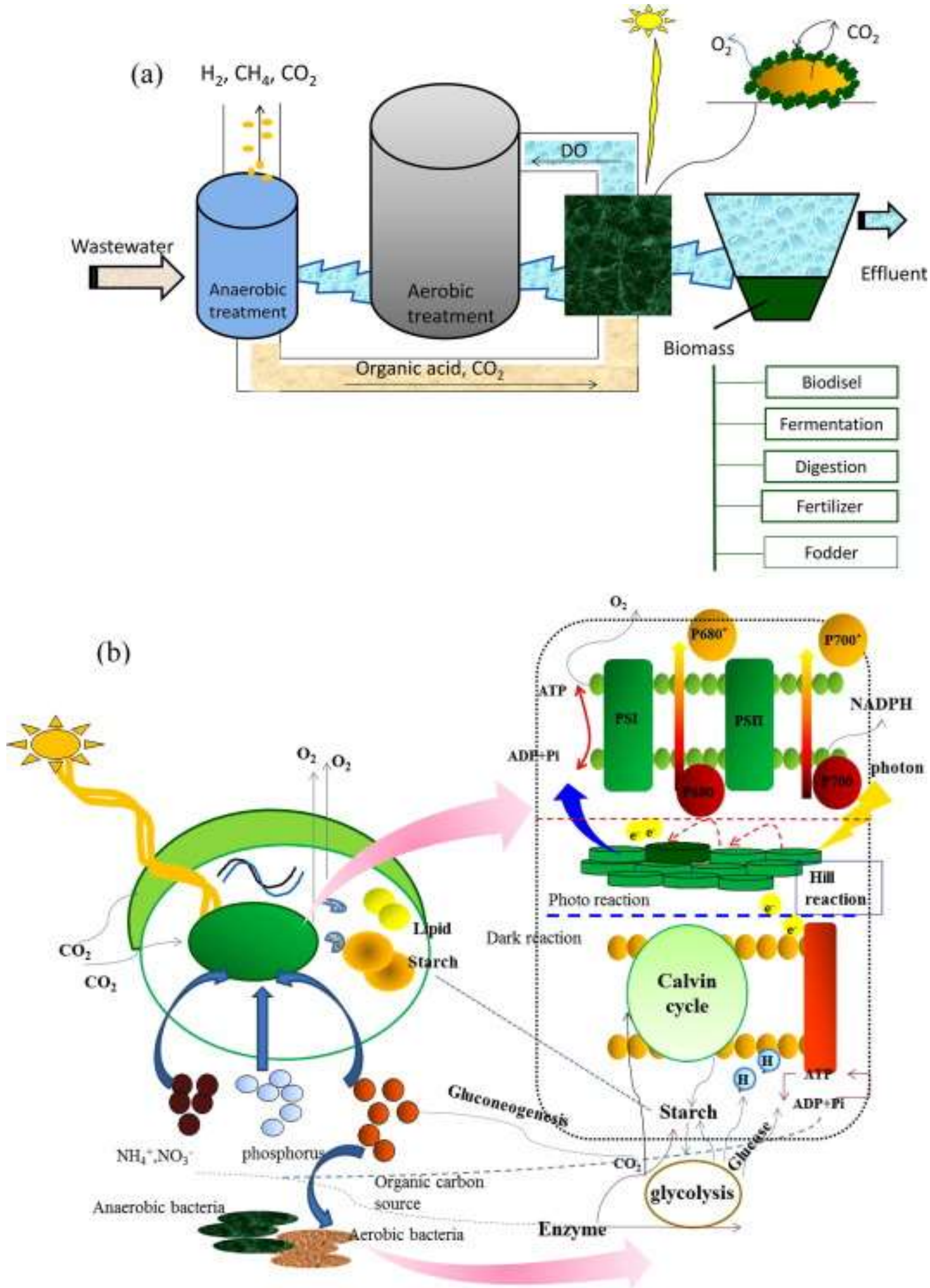

Fig. 6: Perspectives of using microalgae for industrial wastewater treatment (Wang *et al*., 2016)

Anaerobic-Aerobic Treatment

In comparison to other methods of wastewater treatment, it has the advantages of lower treatment costs with no secondary pollution. Aerobic biological processes are generally used for organic owing to high treatment efficiency while anaerobic systems show improved resource recovery and utilization with pollutant levels slightly above than those obtained after aerobic treatment.

Aerobic-anaerobic systems are designed to get the best features out of both the aerobic and anaerobic systems.

Types of bioreactors, HRT and COD% in Table 3.

Table 3: bioreactors, their hydraulic retention times and COD removal %

Name of bioreactor	Influent COD (mg/l)	Total COD removal (%)	Anaerobic COD removal (%)	Aerobic COD removal (%)	Hydraulic retention Time (hours)	Reference
RAAIB bioreactor (a)	345	84	-	-	1.2-15.5	Garbossa *et al*. (2005)
Upflow anaerobic/aerobic fixed bed reactor (b)	365-3600	95-98	27-70	37-92	9	Moosavi *et al*. (2005)
Anaerobic–aerobic granular biofilm reactor (b)	-	95-98	62-95	0-33	48	Shen and Guiot (1996)
Integrated anaerobic-aerobic fluidized bed reactor (b)	350	>80	-	-	24	Fdez-Polanco *et al*. (1994)

(a)-bioreactors with physical separation between aerobic and anaerobic zones
(b)-bioreactors without physical separation between aerobic and anaerobic zones

Some benefits of the anaerobic-aerobic process are listed below (Frostell, 1983; Cervantes *et al*., 2006):

- Most organic pollutants generated can get converted to biogas through anaerobic treatment
- The treatment process is efficient since aerobic post treatment enhances the quality of the process by reducing the toxicity of the products of anaerobic process Sludge generated during the aerobic process is utilized in the anaerobic process, hence less sludge is disposed. Consumes low energy (overall)
- Volatile organic compounds are degraded

Thus it can be inferred that anaerobic-aerobic treatment is economically and operationally promising in the treatment of high strength industrial wastewaters since it integrates the benefit of anaerobic digestion (i.e., biogas production) with the benefits of aerobic digestion (i.e., better COD and Volatile Suspended Solid (VSS) removal) (Chan *et al*., 2009). They have also been found to perform well for the following processes: Biodegradation of chlorinated aromatic hydrocarbons including sequential nitrogen removal including aerobic nitrification and anaerobic denitrification; anaerobic dechlorinations and aerobic ring cleavage; anaerobic reduction of Fe(III) and microacrophilic oxidation of Fe(II) with production of fine particles of iron hydroxide for adsorption of, phenols, carboxylic acids, ammonium ions, cyanide, radionuclides and heavy metals. The simplest approach towards incorporating the anaerobic-aerobic treatment is the use of systems such as aerated stabilization ponds, aerated and non-aerated lagoons, as well as natural and constructed wetland systems (Chan *et al*., 2009).

Conventional anaerobic-aerobic systems are usually composed of large ponds connected in series and are frequently characterized by low Organic Loading Rate (OLR), long Hydraulic Retention Time (HRT) as well as vast area of land or digesters. Aerobic treatment occurs in the upper part of these systems while anaerobic treatment occurs at the bottom end.

However, the conventional treatment plants suffer from problems related to their large space requirement, emissions from large open reactors, high energy consumption, low efficiency and heavy sludge production, which is actually surplus (Chan *et al*., 2009).

In order to meet strict restrictions with respect to odors, space occupied and minimal sludge production, conventional aerobic-anaerobic systems have evolved into the integrated anaerobic-aerobic bioreactors where both aerobic and anaerobic processes occur in a single bioreactor. Since bioreactors are simple to design and comprise of cheap, easily obtainable technology, research is going on to measure the efficacy of bioreactors in treating industrial and municipal wastewater discharge. However, most of the integrated bioreactors aren’t yet suitable for large- scale industrial implementation. Besides, further improvements such as installation of biogas capture system and utilization of suspended carrier or packing medium are considered essential (Chan *et al*., 2009).

Zero Liquid Discharge

Zero-Liquid Discharge (ZLD) is slowly gaining prominence as a viable solution for industrial wastewater treatment, since it increases the extent of water recycling and decreases the amount of water produced as industrial discharge. Water recycling is implemented in the form of a closed loop water cycle-where water that can be recycled does not go as industrial discharge and is recovered, to be treated and reused. This way, the extent of water efficiency is increased and the possibility of contamination in the industrial effluent decreases. (Barrington and Ho, 2014).

However, ZLD systems consume a lot of energy hence they are yet to be implemented everywhere (Barrington and Ho, 2014). Still, due to rampant water scarcity and aquatic pollution, ZLD has begun to garner a lot of attention (Oren *et al*., 2010).

Thermal processes are almost mandatory in ZLD systems. The wastewater is fed into a concentrator, which increases the concentration of brine. Then it is further fed into a crystallizer. The distillate is sent for reusal, where the sedimentized solids are either disposed of or reused.

Since ZLD systems consume a lot of energy, they are being combined with RO to reduce energy demand. However, RO systems can operate only with a short salinity range. Hence other techniques for salt concentration have emerged-such as Forward Osmosis

(FO), Electrodialysis (ED) and Membrane Distillation (MD) (Tong and Elimelech, 2016).

Thermal ZLD Systems

Here, wastewater is given pretreatment, sent into a brine concentrator, whose feed is further sent into a brine crystallizer followed by evaporation and recovery of solids. Pre-treatment comprises multiple processes like pH adjustment, filtration, anti-scaling treatment and de-aeration to reduce the fouling potential of the feed water. Distillates produced after crystallization and evaporation are recycled as clean water-either directly or after further treatment. The solids are recovered as by-products or sent to evaporation ponds, where they get processed and disposed (Tong and Elimelech, 2016).

Brine concentrators work based on the principle of Mechanical Vapor Compression (MVC), where feed water along with brine slurry travels through heat exchanger tubes present in the concentrator. The pumping is done as forced circulation with applied pressure, to prevent the fouling of heat exchanger tubes (Ghaffour *et al*., 2013).

Evaporation occurs and latent heat produced through the water vapor vaporizes the brine slurry. The concentrated brine is then fed into a crystallizer for further water recovery, whose working principle is similar to that of a brine concentrator (Mickley, 2008)

Since the feedwater is highly saline and viscous, the energy consumed by the crystallizers amounts to 52-66 kWh/m^3, which is almost thrice the amount of energy consumed during the brine concentration stage (Mickley, 2008). Evaporation ponds are a cheaper alternative, since they consume solar energy, especially for small applications. But they require a lot of space and the costs of land procurement may make the whole process expensive. The mechanical vapor compression step consumes a lot of energy, by itself. Further, the rate of recovery of water from evaporation ponds is also low (Tong and Elimelech, 2016).

Reverse Osmosis (RO) Incorporated Thermal ZLD Systems

Here, RO is combined with thermal ZLD systems to concentrate wastewater. The volume of brine slurry entering the concentrator and crystallizer decreases, hence less energy is consumed and operational costs decrease. As reported in previous studies, using RO to in a desalination plant conserves around 59-74% of energy and 47-69% of treatment costs compared to a concentrator-evaporation pond setup (Bond and Veerapaneni, 2008). But RO systems can operate only on a short salinity range and fouling may occur, which decreases the water which is actually being treated and brings down the lifespan of membranes. Therefore, various techniques that can be employed as pretreatment are pH adjustment, chemical softening and ion exchange. However, additional solid waste is produced due to intensive use of chemicals hence Ultra filtration can be preferred over RO for incorporation into the ZLD system (Bond and Veerapaneni, 2008).

Membrane based ZLD

Membrane based processes that are about to be reviewed under this title are Electrodialysis (ED), Forward Osmosis (FO) and Membrane Distillation (MD).

In MD, microporous membranes made of polypropylene, polyvinylidene fluoride or polytetrafluoroethylene are usually used. These are hydrophobic, less resistant towards mass transfer, have low thermal conductivity to avoid loss of heat, highly resistant to chemical degradation and show good thermal stability even at extreme temperatures. The membrane permits the passage of only the vapor that is produced due to temperature difference between the two sides of the membrane (Bush *et al*., 2016). MD is a rapidly developing technology that by utilizing waste heat, it has the potential to concentrate saline wastewater to such an extent that it almost becomes saturated. Using low-quality thermal energy, it can treat even highly saline feed. However, most of the recent MD applications are still in laboratory scale or at a pilot plant level (Zhao *et al*., 2012).

In FO, only water molecules pass through the semi-permeable membrane and not the solute, because of the osmotic gradient. A draw solution (a highly concentrated salt solution) is used as it has low water potential, it attracts water molecules from saline water which has a relatively higher water potential (Zhao *et al*., 2012). FO consumes less energy because the transport of water molecules through the membrane occurs due to difference in osmotic pressure and does not require external hydraulic energy. Moreover, the instances of membrane fouling are less and if they occur, can be easily reversed (Zhao *et al*., 2012).

ED technique which had previously been employed for the desalinating groundwater and surface water, can also be implemented in ZLD systems for feed pretreatment and brine concentration before being fed into the crystallizer. Ions dissolved in water are removed by passing the effluent through an ion-exchange membrane. These membranes prevent the carriage of co-ions but allow the transport of counter ions (Xu and Huang, 2008). As this process is driven by applied electric potential, cations pass through their respective membranes, move towards cathode while anions move in an anti-parallel manner via anion-exchange membranes, towards the positively charged anode. As a result, the diluate produced has less salt and brine streams, with higher brine concentrations are produced. Sethe enrgy consumed by each of them and the salinity range for operation are given in Table 4. When the polarity of the elctrodes is reversed, scaling and fouling on the membrane walls are removed. However, it is not viable for effluents with less salinity since the treatment cost would end up getting higher (McGovern *et al*., 2014).

Table 4: Separation techniques, salinity range of operation and energy consumed

Technology	Salinity range (mg/l)	Energy consumed B feed water (kWh/m^3)	References
MVC	>200,000	28-39	Mickley (2008)
RO	Approx. 70,000	4-16*	Tsai *et al*. (2017)
MD	>200,000	200-300	Charisiadis (2018)
FO	>200,000	21	Li *et al*. (2017)
ED	100,000<salinity<200,000	7-15	Loganathan *et al*. (2015)

Organic solid waste is produced through the ZLD process, which is difficult to dispose. The waste is chemically inert hence cannot be disposed using conventional biological methods. When it accumulates in the ZLD system, it causes fouling of the membrane and is a threat to the system's stability (Xiong and Wei, 2017). Firstly, the waste cannot be reused and when stored in evaporation ponds, it creates foul odors and has a detrimental impact on wildlife and involves leakage risks. Further, chemical leaching may occur if the waste gets disposed in landfills (Younos, 2005). High operating cost is a big concern in ZLD systems caused due to Moreover, complex system design leads to high cost of chemicals involved, heavy sludge production and marked salinity in the downstream wastewater. Pre-treatments such as acidification and degasification release CO_2 into the atmosphere and cause air pollution. Large amounts of energy are consumed, which significantly contributes in the release of greenhouse gases.

Conclusion

Ex-Situ treatment is a more effective solution to ecological restoration of rivers because it helps prevent and curb degradation of the riparian water quality and preserves the ecosystem of the river. Since many countries are grappling with deteriorating river quality due to illegal discharge of industrial sewage, the paper discusses current and emerging technologies in the domain of industrial wastewater treatment. However, each method has its own advantages and constraints and cannot be regarded as the only solution for preventing river contamination. Wastewater treatment strategies involving microalgae to produce biofuel, aerobic-anaerobic bioreactors must be scaled up and used in tandem with existing wastewater treatment strategies to bring down overall operation costs. Niche strategies like photocatalytic treatment must involve low cost, good quality, locally available materials and design to make them more industrially viable. Wetlands must follow sanitation and health guidelines and requisites for electrocoagulation which cost relatively higher (fuel cells, for instance) have to be tweaked or replaced be lower-cost, albeit high quality versions in order to make eletrocoagulation a standalone industrial wastewater treatment process.

Zero Liquid Discharge and even other strategies listed here must be clubbed with facilities for hydrothermal carbonization so that sewage sludge produced gets converted to electricity or is reused in the industrial complex.

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Author's Contributions

Godwin Glivin: Designed the research plan.

K Srividya: Planned the research outline and presented information in textual and graphical format.

V Sreeja: Guided in the research.

M Premalatha: Performed the overall supervision and checking.

Ethics

No potential conflicts of interest have been reported by the authors.

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