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Phycoremediation: A future aspect of wastewater treatment

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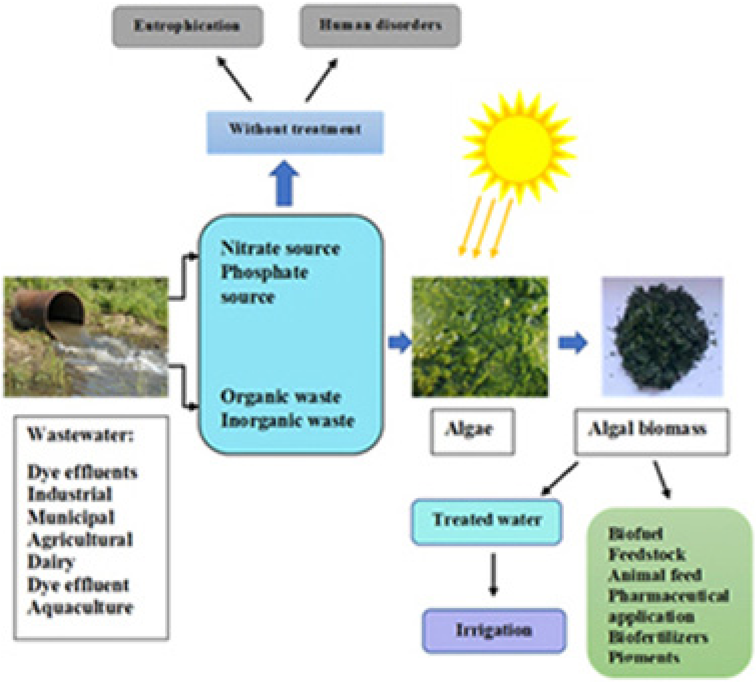
Abstract

The increase of industrial activities has led to the production of toxic pollutants such as heavy metals, dyes, pesticides, phenols, organic compounds, etc., in the aquatic system leading to water pollution. This increase in water pollution has become a threat to humankind and a matter of concern for protecting aquatic flora, fauna, and other living organisms. The classical treatment of wastewater include physical, chemical, and biological methods. These known chemical and physical methods require a lot of energy and induce secondary pollutants into the environment. Phycoremediation is a biological process of removing waste from wastewater using algae, which have played a crucial role in removing nutrients such as nitrogen (N), phosphorous (P), sulfur (S), and minerals that act as feed for the growth of these algae rather than being contaminants. Algae have also been found to be efficient in removing toxic elements such as mercury, cadmium, arsenic, etc, as well as radionuclides as a bio absorbent. These algae are not only capable of removing the nutrients but are also capable of reducing the BOD and COD of the wastewater. Another significant advantage of utilizing algae in bioremediation is that it produces a large amount of biomass and absorbs and accumulates heavy metals. Thus, phycoremediation is now an emerging technology for wastewater treatment and can be a sustainable biomass feedstock for biofuel production.

Key words: BOD; COD; heavy metals; phycoremediation; wastewater.

Graphical abstract



Introduction

Water constitutes about 70% of the living organisms, making it a basic need and a valuable national asset. The anthropogenic activities have affected the entire ecosphere by changing the global cycle of elements or releasing effluents and pesticides into the environment. An alarming increase in water pollution in the present time is a threat to living organisms and the coming generation. The leading source of the water pollution is the release of untreated wastewater which includes household and industrial waste (Nasr and Ismail, 2015; Gupta *et al.*, 2014).The environmental pollution caused by the release of a wide range of compounds, i.e., persistent organic pollutants (POPs), inorganic pollutants such as heavy metals from industries, and medicinal waste from the pharmaceutical industries, have created a disturbance to the ecosystem (Gursahani and Gupta, 2011). This has indirectly led tothe reduction of water levels in the ground and increased ocean water levels with the melting of ice caps, climatic changes, global warming, and ozone layer depletion due to photochemical oxidation (Sharma *et al.*, 2011), which has made ecologists focus more on the impacts of pollution and its reduction (Khan and Ansari, 2005). The wastewater consists of a high concentration of organic and inorganic nutrients such as nitrogen (N) and phosphorous (P), which lead to eutrophication, algal blooms, uncontrolled spread of certain aquatic macrophytes, oxygendepletion, and loss of various floral and faunal species resulting in total degradation of the water bodies (Schindler *et al.*, 2008). The appropriate and adequate policy measure needs to be enforced and practiced, which otherwise would lead to an increase in the water crisis in the agricultural sector (Seckler *et al.*, 1998; Vörösmarty *et al.*, 2005; Lobell *et al.*, 2008; Bekunda *et al.*, 2009).

There are many conventional methods for treating wastewater, including physical, chemical, and biological processes (Fig. 1). Depending on the pollution, type of pollutant(s), and the volume to be treated, they may be used together or separately. The World Health Organization (WHO) has framed the guidelines to improve wastewater management regimes and mitigate health risks at all stages of treatment. The expected level of pollutant exclusion can be attained by wastewater treatment methods categorized into primary, secondary, and tertiary treatment. The primary treatment involves temporarily storing waste in a container, where lighter material (oil, grease, and solids) floats on the upper level while heavy materials settle at the bottom. According to Rawat *et al.* (2011), water-borne micro-organisms often undertake secondary treatment in a well-maintained environment. It may be essential to separate the microbes from the treated water before discharge. Tertiary treatment is performed in addition to primary and secondary treatment. Both physical and chemical methods are more expensive when compared to the biological methods of wastewater treatment. The chemical methods used for the treatment of wastewater raise the total dissolved matter, pH, and conductivity of the treated water. The conventional remediation techniques are inefficient and eco-hazardous compared to the non-conventional, which are cost-effective, reliable, and eco-friendly. To solve this environmental issue, there is a need for an economical and sustainable method to tackle the problem of wastewater treatment, which can be achieved by using biological methods of treatment. One of these includes bioremediation because of its low cost and eco-friendly nature.

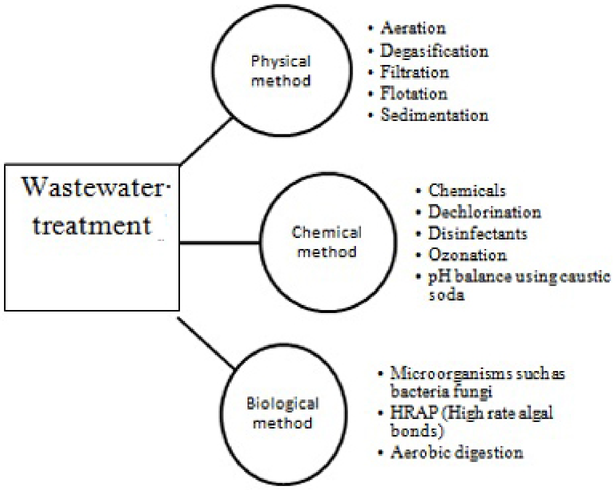


Fig. 1: Physical, Chemical, and Biological methods of wastewater treatment.

Bioremediation uses living organisms to degrade the environmental contaminants into less toxic forms by bacteria, fungi, algae, and plants (Vidali, 2001). Phycoremediation is the process that involves algae in the bioremediation of the environment, which leads to the reduction or biotransformation of toxic compounds from wastewater and appears to be a sustainable technique (Rao *et al.*, 2011; Koul and Taak, 2018; Upadhyay *et al.*, 2019a). The most promising attributes of the algae are higher photosynthetic capabilities as compared to the higher plants (Bhatnagar *et al.*, 2011), its capacity to incorporate nutrients such as nitrogen (N) and phosphorous (P) from sewage water for its growth, and its tolerance to extreme conditions (Ahmad *et al.*, 2017). Algae are an excellent sink for carbon dioxide as it contributes to reducing greenhouse gases (Bhola *et al.*, 2014), which has broad applications for the harvested biomass (Gupta *et al.*, 2013), carbon dioxide sequestration (Becker, 1994), and as a bio-absorbent. Another significant advantage of utilizing algae in bioremediation is that it produces a large amount of biomass and absorbs and accumulates heavy metals (Baghour *et al.*, 2002). Apart from being a carbon sink, algae play an essential role in bioabsorption (due to metal-binding groups on cell surfaces), bioconcentration, and biotransformation of pollutants as it has a significant surface-to-volume ratio.

After bioremediation, the algal biomass consists of many proteins, carbohydrates, carotenoids, chlorophyll, fatty acids, and vitamins that can be used as animal feed and supplements in medicines in the pharmaceutical industries (Kay and Barton, 1991). Algae has also been found to produce secondary metabolites that have been reported of antibacterial, antifungal, anti-inflammatory, anti-diabetic, and antioxidants properties (Sarkar *et al.*, 2006). Due to the low cost and high performance of the algal species, the method can be used as an alternative to the physical and chemical methods of wastewater treatment. The main objective of the review is to understand the potential of algae in removing excess nutrients, BOD, COD, organic, and inorganic wastes from the wastewater. Also, the valorisation of algal biomass for biofuel production after phycoremediation is discussed.

Mechanism of phycoremediaton

Heavy metals, plant nutrients, organic and inorganic contaminants, pesticides, and radioactive substances can all be accumulated and assimilated by microalgae in their unicellular bodies (Gani *et al.*, 2016). Sedimentation, Flocculation, and rhizofiltration are the basic mechanisms by which algae remove contaminants (Renuka *et al.*, 2015; Stauch-White *et al.*, 2017; Yadav *et al.*, 2011). Rhizofiltration with algae is a technique in which algae concentrate, absorb and precipitate metals in their biomass from contaminated water (Yadav *et al.*, 2011). Several inorganic and organic contaminants (Ni, Zn, Pb, Cr, Cu) are extracted through rhizofiltration. Rhizofiltration has been documented in unicellular algae such as *Chlamydomonas* sp., *Chlorella* sp., *Spirogyra* sp., blue-green algae-*Phormidium* sp., marine algae, such as *Ascophyllum* sp., *Fucus* sp. and *Sargassum* sp. (Srinivasa Rao *et al.*, 2005, Yadav *et al.*, 2011). This potential of reducing N, P, and heavy metals has enhanced the water quality and provides a simpler, convenient and economical alternative compared to other environment clean-up strategies. This biochemical approach includes cation and anion exchange, absorption, precipitation, and oxidation/reduction.

Cation/anion exchange

The occurrence of several functional groups on the algal cell wall (–COOH, –OH, $-NH_2$, PO_3^{2}, $-P_2O_3$, –SH, carboxyl, aromatic, alkyl, and amide) provides a negative charge, which facilitates metal adsorption (cations) and absorption (Upadhyay *et al.*, 2019b). Thus, these serve as a strong metal cation binding site and are involved in metal exchange via the ion-exchange mechanism. This biochemical method of heavy metal removal (through cation/anion exchange) from aquatic systems is very effective as it has the potential for remediation and the recovery of metals from wastewater.

Absorption

Inorganic ions such as PO_4^{3-}, NO^{3-}, and heavy metals are abundant in wastewater and in order to convert inorganic N to organic N, microalgae use the assimilation mechanism. During this process, inorganic nitrogen translocates into the cytoplasm and a sequence of oxidation and reduction reactions occurs, when NO_3^- and NO_2^- reductase are present in the cytoplasm. There is a conversion of inorganic N to NH_4, which is then absorbed into the cytoplasm (Upadhyay *et al.*, 2019b). Algae transform PO_4^{3-} present in the water into an organic compound through phosphorylation process. Algal biomass quickly absorbs metal ions with increased electronegativity and lower ionic radii (Mehta and Gaur, 2005).

Precipitation

According to De-Bashan and Bashan (2004), algae cause a drop in the surrounding pH and facilitate the precipitation of different harmful contaminants in wastewater as they secrete various chemicals, including organic acids and secondary metabolites, which help phosphorus reduction by soluble Fe, Ca, or Al in wastewater. The active sites of the cell wall are bound with protons at low pH, leaving no open sites for metal cations to bind. As a result, as pH rises, the number of negatively charged sites (hydroxyl groups of polysaccharides, PO_4^{3-} and $-NH_2$ groups of nucleic acids, structural polysaccharides, and carboxyl groups of proteins) rises, causing metal cations to adsorb on the cell surface, which further decreases their bioavailability (Leong and Chang, 2020).

Algae for removal of organic pollutants

The various nitrogenous and phosphatic compounds are added to the wastewater because of anthropogenic activities. According to Barsanti and Gualtieri (2006), ammonium ion (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), or nitrogen (N_2) are the most abundant form of nitrogen in the wastewater. The presence of excess unionized ammonia or nitrate/nitrite leads to eutrophication and is very toxic to aquatic animals and humans. Ward *et al.* (2005) reported that ingestion of more than 20 mg/L of nitrate uptake could increase the risk of cancer, gastric problems, malfunctioning of thyroid glands, and non-Hodgkin's lymphoma, whereas less than 10 mg/L of nitrates can cause methemoglobinemia in infants (Fig. 2). So it is necessary to remove excess nitrates present in the ecosystem. Rahimi *et al.* (2020) reported that the conventional methods are not suitable for removing the excess nitrates from the wastewater because of the high solubility and stability of nitrates which is not feasible by adsorption and co-precipitation treatment. This indirectly results in high energy and cost for the treatment of nitrate-contaminated water (Rezvani *et al.*, 2019).

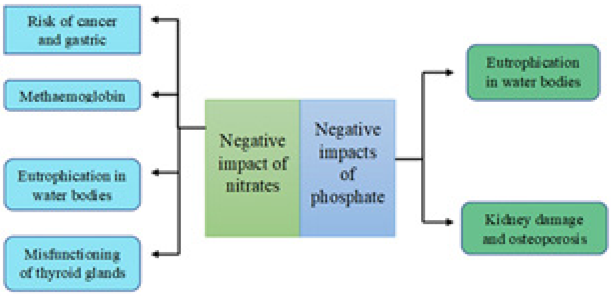


Fig. 2: Negative effects of nitrates and phosphates in humans and aquatic ecosystem.

The biosynthesis of peptides, proteins, ribonucleic acid (RNA), deoxyribonucleic acid (DNA), etc., require nitrogenous compounds (Cai *et al.*, 2013; Conley *et al.*, 2009). Microalgae assimilate nitrogen by converting inorganic form to organic form. However, ammonium ion is the most preferred form of inorganic nitrogen, which is assimilated by the microalgae as it can be easily converted into amino acid glutamine without any involvement of redox reaction, which utilizes less cellular energy (Cai *et al.*, 2013; Flynn *et al.*, 1997). Microalgae also assimilate nitrate and nitrite by reducing them to ammonium ions, but the pathway requires various enzymes and is complex with intermediate products (Dortch *et al.*, 1984). Enzyme nitrate reductase mediates the reduction of nitrate to nitrite, followed by enzyme nitrite reductase, which reduces nitrite to ammonium (Cai *et al.*, 2013; Flynn *et al.*, 1997).

Phosphorus is another essential macronutrient present in nucleic acid (DNA, RNA), proteins, and lipids and also participate in their biosynthesis. It is also known to play a vital role in cellular metabolic processes (Tiessen, 2008). At the same time, an excess amount of phosphate has been found to cause kidney damage and osteoporosis in humans (Goswami *et al.*, 2022). Phosphorus is found in wastewater in the form of orthophosphate, polyphosphate, or organic phosphates (Schindler, 1977). The primary source of phosphorus in the wastewater is agricultural and domestic wastes (Bennett *et al*.. 2001; Soranno *et al.*, 1996). Powell *et al.* (2009) reported phosphorus from wastewater by microalgae in the form of orthophosphates and utilizing them in various metabolic processes. It forms the primary part of ATP and ADP used in different metabolic processes that utilize ATP/ADP as an energy source.

Removal of organic pollutants from domestic wastewater

Boonchai *et al.* (2012) have shown algae to efficiently utilize nitrogen and phosphorous from municipal wastewater as a nutrient source. Yang *et al.* (2008) also reported that the presence of nutrients, especially nitrogen (N) and phosphorous (P) in the form of nitrite, nitrate, ammonia/ammonium, or phosphorous, leads to eutrophication in water bodies. The nutrient removal from wastewater has been effectively seen in *Chlorella* sp., a unicellular green alga, by Lim *et al.* (2010); Cho *et al.* (2011) and Malla *et al.* (2015), stating that the microalgae to be cost-effective and environmentally sustainable for the wastewater treatment as well as biofuel production. Samori *et al.* (2013) studied the growth and nitrogen removal capacity of *Desmodesmus communis* and a natural algal consortium for wastewater treatment. Silva-Benavides and Torzillo (2011) reported a comparative study of nitrogen and phosphorous removal using microalgae *Chlorella* and *Planktothrix* in municipal wastewater.

Removal of organic pollutants from industrial wastewater

The food and milk processing industries consume a large volume of water then characterized by high BOD and COD, oil fats, and other nutrients such as nitrogen and phosphorous (Ji *et al.*, 2015). *Chlorella pyrenoidosa* cultivated in soybean processing wastewater was able to remove 89 and 70% of total nitrogen and total phosphate, respectively (Hongyang *et al.*, 2011). Pathak *et al.* (2015) studied the potential of the algae *Chlorella pyrenoidosa* for the removal of phosphate and nitrate from the textile industry. Liu *et al.* (2016) also reported the removal of phosphates and nitrates by 87 and 82% respectively by alga *Diplosphaera* sp. in dairy and winery wastewater.

Reduction in COD and BOD

According to Singh and Pandey (2018), biological oxygen demand (BOD) is the amount of oxygen present in the water needed by aerobic micro-organisms to breakdown organic compounds. Chemical oxygen demand (COD) measures the organic compound that can be chemically oxidized rather than just the level of biodegradable pollutants (Abdel-Raouf *et al.*, 2012). Excess of BODisa reason for depletion of dissolved oxygen in water bodies, fish death, and anaerobiosis (Abdel-Raouf *et al.*, 2012) and microalgae are known to reduce the level of BOD and COD from wastewater.

Reduction of BOD and COD from domestic wastewater

Sahu (2014) analyzed about 70% reduction in BOD and 66% reduction in COD in the sewage wastewater after treatment with the microalga *Chlorella vulgaris.* In contrast, Ahmad *et al.* (2013) reported 98% reduction in BOD and COD in *Chlorella vulgaris* and *Rhizoclonium hieroglyphicum* in domestic wastewater. Riaño *et al.* (2011) studied the removal of COD by 71% from fish farm wastewater using microalgae *Oocystis* sp. Sengar *et al.* (2011) also reported an 82% reduction in COD level and 96% reduction in BOD while treating sewage wastewater using *Synedra affinis* and *Euglena viridis. Chlorella minutissima* showed a reduction in BOD and COD by 95% and 90%, respectively, in primary treated wastewater (Malla *et al.*, 2015). There was a reduction in COD and BOD by 80 and 95% from the domestic wastewater using *Spirulina* sp., *Nannochloropsis* sp.,

Table 1: COD and BOD removal efficiency of various algae from wastewater.

Name of algae	Source of wastewater	Parameter	Removal efficiency	References
Scenedesmus sp	Municipal wastewater	COD BOD	93% 84%	Sahu (2014)
Chlorella vulgaris, *Rhizoclonium hieroglyphicum*	Domestic wastewater	COD BOD	98.3% 98.7%	Ahmad *et al*. (2013)
Scenedesmus sp	Fertilizer wastewater plant	COD BOD	93% 84%	Pham *et al*. (2020)
Chlorella zofingiensis	Piggery wastewater collected from the private farm	COD	79.84%	Zhu *et al*. (2013)
Scenedesmus sp	Pulp and paper mill effluents	COD BOD	75% 82%	Usha *et al*. (2016)
Spirulina sp. *Nannochloropsis* sp. *Chlorella* sp.	Domestic wastewater	COD BOD	80% 95%	Sofiyah *et al*. (2021)
Oocystis sp.	Fish farm wastewater	COD	71.10%	Riano *et al*. (2011)
Pithopora sp.	Thermal wastewater	COD BOD	87.23% 87.75%	Murugesan and Dhamotharan (2009)
Synedra affinis, *Euglena viridis*	Sewage wastewater	COD BOD	82% 96.20%	Sengar *et al*. (2011)

and *Chlorella* sp. as a consortium (Sofiyah *et al.*, 2021) (Table 1).

Reduction of BOD and COD from industrial wastewater

As mentioned above, industries are also one of the main sources of the addition of nutrients into the water bodies, which leads to an increase in the COD and BOD levels. A reduction in 70% COD and 61% BOD was observed in wastewater collected from the food processing industries using microalga *Botryococcus* sp. (Gani *et al.*, 2016). Chokshi *et al.* (2016) reported that the level of COD was reduced by 90% after four days of cultivation, whereas ammonical nitrogen was consumed entirely after six days of cultivation of microalgae *Acutodesmus dimorphus* in dairy wastewater. Hende *et al.* (2014) found significant removal of BOD and COD to about 96 and 87%, respectively, from the industrial wastewater after treating with microalgal bacterial flocs and *Scenedesmus* sp. showed 93 and 84% reduction in COD and BOD from fertilizer-based wastewater (Pham and Bui, 2020).

Algae as a source of removal of Persistent Organic Pollutants (POPs)

According to Pandey *et al.* (2019), persistent organic pollutants (POPs) are a carbon-based heterogeneous set of toxic compounds that adversely affect human health and the environment. Polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), petroleum hydrocarbons (PHCs), insecticides, pesticides, phenolics, and antibiotics pose significant public and environmental threats. Many studies have reported microalgae as an effective bioremediating agent for phenolic derivatives and many polyaromatic hydrocarbons (Dosnon-Olette *et al.*, 2010). Algae are omnipresent in nature and are present widely in the photic zone of the aquatic ecosystem and may be considered a major sink for the transformation of PAHs (Cerniglia *et al.*, 1980). Soto *et al.* (1975) found that *Chlamydomonas angulosa* bio-accumulated naphthalene within the cell but was unable to metabolize the pollutant. *Chlorella* sp. effectively removed 2,4-dinitrophenol (2,4-DNP) by degradation and the possible mechanism of metabolizing phenols and their derivatives involves intracellular enzymes such as laccase and polyphenol oxidase (Klekner and Kosaric, 1992).

Phenol (hydroxybenzene) and its derivatives are aromatic hydrocarbons categorized under alcohol which are also considered persistent organic pollutants. Phenol serves as an important raw material in a wide range of industries, including pharmaceuticals, chemical industries, leather, and oil refinery (Senthilvelan *et al.*, 2014). There are several reports of phenol biodegradation ability by algal strains such as *Scenedesmus obliquus, Chlorella* sp., and *Spirulina maxima* (Klekner and Kosaric, 1992), *Ankistrodesmus braunii* and *Scenedesmus quadricauda* (Pinto *et al.*, 2003; Pinto *et al.*, 2002), *Ochromonas danica* (Semple and Cain, 1997), *Chlorella* VT-1 (Scragg, 2006), *Chlorella vulgaris* (Scragg, 2006; El-Sheekh *et al.*, 2012), *Lyngbya lagerlerimi, Volvox aureus, Oscillatoria rubescens,* and *Nostoc linckia* (El-Sheekh *et al.*, 2012). Phenolics such as 4-hydroxybenzoate, tyrosol, caffeic acid, p-coumaric acid, and vanillic acid were removed efficiently (70%) when *Scenedesmus quadricauda* and *Ankistrodesmus braunii* were grown under dark conditions (Pinto *et al.*, 2003).

Benzo[a]pyrene (BaP) is considered a dangerous pollutant because of its toxicity, carcinogenicity, and teratogenicity (Pandey *et al.*, 2019). Benzo[a]pyrene (BaP) was removed by unicellular green microalgae *Scenedesmus capricornutum* and *S. acutus* from an aqueous environment, and it was observed that the physical sorption and degradation were the basic mechanism used by algae to remove these pollutants (García de Llasera *et al.*, 2016).

Algae as a source of remediation of medicinal pollutants

The active pharmaceutical compounds are one of the emerging environmental pollutants because of their increased ecological risks and widespread presence from the medicinal industries, which are of great concern. The main source of these pollutants in the pharmaceutical industry which include chemicals commonly used to prevent human and animal disorders for health and beauty purposes, pharmaceuticals, and personal care items (PPCPs). Silva *et al.* (2019) stated that the environmental protection agency (EPA) recently identified and added about 12 compounds from the personal care products, pharmaceuticals, and endocrine-disrupting elements due to their excess existence and toxicity level to the environmental ecology. Therefore, there is an urgent need for reliable and cost-effective methods of removing these PPCPs for wastewater treatment (Ebele *et al.*, 2017). Microalgae have played an essential role in the bioremediation of these pollutants. Villar-Navarro *et al.* (2018) reported the biodegradation of analgesic and anti-inflammatory drugs, lipid regulators, and psychiatric drugs using the algae *Coelastrum* sp. Microalgae *Selenastrum capricornatum, Chlorella vulgaris,* and *Chlamydomonas reinhardtii* have shown the removal of β-estradiol and ethinylestradiol in synthetic media conditions (Wang *et al.*, 2017; Hom daiz *et al.*, 2015). *Chlorella sorokiniana* showed about 69 and 98% removal efficiency for paracetamol and salicylic acid, respectively, as shown in Table 2.

Industrial production and overuse of antibiotics in clinical practices in humans, horticulture, animals, and the flesh industry, as well as inappropriate disposal of used medicine containers and wastewater treatments, have emancipated a huge amount of antibiotics into the environment. Once released, these pharmaceuticals are transported and distributed to water, air, soil, or sediment (Pruden *et al.*, 2013; Boxall, 2004). Freshwater cyanobacteria *Aphanizomenon gracile, Microcystis aeruginosa, Planktothrix agardhii,* and *Chrysosporum bergii* have the ability to grow on different concentrations of antibiotics (amoxicillin, kanamycin, ceftazidime, gentamicin, ceftriaxone, nalidixic acid, norfloxacin, tetracycline, and trimethoprim). The increased resistance of these cyanobacteria to antibiotics suggests that they are naturally resistant to antibiotics (Dias *et al.*, 2015). Ge and Deng (2015) observed the removal of fluoroquinolone antibiotics, ciprofloxacin hydrochloride and enrofloxacin by two marine algae *Isochrysis galbana* and *Platymonas subcordiformis,* in a photo induced system.

Inorganic pollutant removal from wastewater

Heavy metals are the main inorganic pollutants present inside the wastewater released from the industries that have high toxicity and bioaccumulation in living species and the food chain. Heavy metal exposure is a significant threat to living organisms and leads to environmental degradation. According to Rigueto *et al.* (2020), it is a public concern as

Table 2: Phycoremediation potential of algae for medicinal pollutants.

Medicinal pollutants	Source	Algae used for remediation	Mechanism of remediation	References
17β-estradiol and 17α-ethinylestradiol	Synthetic media for medicinal test	*Selenastrum capricornutum* *Chlorella vulgaris*	Biotransformation	Wang *et al*. (2017)
		Chlorella vulgaris	Biotransformation and Bioconcentration	Lai *et al*. (2002)
17α-Estradiol, 17β-estradiol, estrone, and estriol	Synthetic media for medicinal test	*Scenedesmus dimorphus*	Bioabsorption	Zhang *et al*. (2014)
β-estradiol and 17α-ethinylestradiol	Synthetic media	*Selenastrum capricornutum* *Chlamydomonas reinhardtii*	Biodegradation	Hom-Diaz *et al*. (2015)
Anti-inflammatory and analgesic drugs, lipid regulators		*Coelastrum* sp	Biodegradation	Villar-Navarro *et al*. (2018)
Paracetamol Acetylsalicylic acid, Caffeine,	Synthetic media for medicinal test	*Spirulina platensis* *Chlorella homosphaera,* *Scenedesmus obliquus.*	Bioconcentration	Rempel *et al*. (2021)
Paracetamol, Salicylic acid Diclofenac, Ibuprofen, Paracetamol and Metoprolo	Synthetic media for medicinal test	*Chlorella sorokiniana*	Biosorption	Escapa *et al*. (2017) de Wilt *et al*. (2016)
Bisphenol A	Synthetic media for medicinal test	*Monoraphidium braunii* *Pseudokirchneriella subcapitata,* *Scenedesmus acutus,* *Scenedesmus quadricauda,* *and Coelastrum reticulatum*	Biodegradation	Gattullo *et al*. (2012) Nakajima *et al*. (2007)

different industries specifically or indirectly drive heavy metals into rivers and the sea in the form of liquid waste. The heavy metal present in the water includes chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), nickel (Ni), mercury (Hg) and zinc (Zn), which are categorized as toxins of environmental priority owing to their extreme toxicity (Berthiaume *et al*., 2020).

According to Reddy and Lee (2012), adsorption is one of the most effective advanced wastewater treatment processes. Algae have received a great deal of attention for decontamination of water as a biological method of biosorption process, which is economical. The adsorption of lead and uranium cations has been observed by the brown alga *Cystoseira indica* (Moghaddam *et al*., 2013). Vijayaraghavan *et al*. (2006) reported that *Sargassum wightii* could be used as a potential biosorbent to treat nickel polluted electroplating industrial effluents. The dead algal biomass also removes heavy metals from wastewaters through biosorption, although this process is less effective than the live algae cells (Salama *et al*., 2019). Lyamlouli *et al*. (2014) reported mercury biosorption by *Ulva lactuca, Jania rubens, and Sphaerococcus coronopifolius*. The biosorption of copper by *Spirulina platensis* from synthetic media was reported by Al-Homaidan *et al*. (2014).

Gupta *et al*. (2010) studied the biosorption of nickel using alga *Oedogonium hatei,* and biosorption of lead and copper was reported in *Spirogyra* sp. (Gupta *et al*., 2006; Singh *et al*., 2007; Gupta and Rastogi, 2008). Pavasant *et al*. (2006) studied the biosorption potential of alga *Caulerpa lentillifera* in removing copper, cadmium, lead, and zinc from water. Heavy metals are transferred through the cell membrane into the cytoplasm by diffusion and their subsequent binding with the internal binding sites of proteins and peptides (metal transporters, GSH, Oxidative stress-reducing agents, and phytochelatins) is studied by Pradhan *et al*. (2019).

Algae also immobilize heavy metals by following methods (a) exclusion by membrane-bound transporters, (b) chelation, and (c) generation of reducing enzymes or antioxidants that reduce heavy metals by redox reaction are all genetically controlled mechanisms. (Gómez-Jacinto *et al.*, 2015). According to Priatni *et al.* (2018), the cell wall of microalgae is made up of lipids, organic proteins, and polysaccharides (cellulose and alginate) with heavy metal-binding functional groups (-OH, single bond -COOH, PO_4^{3-}, $-NH_2$, imidazole, single bond -SH, single bond SO_3^-, and others) along with cell polymeric substances like exo-polysaccharides and peptides with uronic groups. Because metal ions in water exist in the form of cation, they are adsorbed onto the negative-charged cell surface due to different functional groups (Pradhan *et al.*, 2019).

Algae as a novel bio-absorbent of radioactive elements

Cesium is one of the radioactive elements used in nuclear fission and is one of the most hazardous elements for human consumption (Ahmed *et al.*, 2017). Azizkhani and Faghihian (2019) prepared a magnetized absorbent by impregnating *Spirulina platensis* with potassium nickel hexacyanoferrate (KNiFC) and obtained the maximum adsorption capacity for uptake of cesium by the absorbent. Al-Masri *et al.* (2003) reported tolerance towards cesium and lead in *Sargassum vulgare.* Zalewska and Saniewski (2011) investigated the bioaccumulation ability of red algal species *Polysiphonia fucoides*, and *Furcellaria lumbricalis* for radionuclides ^{51}Cr, ^{54}Mn, ^{57}Co, ^{60}Co, ^{65}Zn, ^{85}Sr, ^{109}Cd, ^{110m}Ag, ^{113}Sn, ^{137}Cs and ^{241}Am under laboratory conditions, where *P. fucoides* demonstrated better bioaccumulative properties towards most of the investigated radionuclides.

Transgenic algae for phycoremediation

Various biotechnological approaches have been deployed to enhance algae potential for bioremediation. One of the strategies to enhance the efficiency of algal strains is genetic engineering**.** The chloroplast, mitochondrial and nuclear genomes of several microalgal strains have been sequenced, and expressed sequence tag databases have been created (Zeng *et al.*, 2011). The genes (MTP genes) involved in the metallo regulatory proteins from various algal species such as *Spirulina* sp, *Microcystis aeruginosa, Synechococcus* sp., *Anabaena flosaquae, Fischerella* sp., and *Nostoc* sp. have been enumerated by the researchers. The MT-II gene inserted transgenic *C. reinhardtii* was found to possess more metal tolerance with high cell density in a higher cadmium concentration than the wild type *C. reinhardtii* (Cheng *et al.*, 2019).

Siripornadulsil *et al.* (2002) studied P5CS gene expression in transgenic *Chlamydomonas* increased the metal binding capacity of Cd by four times, whereas transgenic expressing HAL2 gene showed 2.5-fold greater Cd binding capacity compared to the wild-type. The proline content of the algae increased by introducing the P5CS (pyrroline5 carboxylate synthase) and HAL2 gene in another transgenic *Chlamydomonas.* The algae's heavy metal binding capacity gets enhanced with high proline content, which induces phytochelatin synthesis. At WRI gene from *Arabidopsi thaliana* enhanced the lipid biosynthesis in *Nannochloropsis salina* (microalgae) and the lipid content of *N. salina* increased by 36% compared to the wild-type strain (Kang *et al.*, 2017). RNA gene silencing approach was used for silencing the CrCO gene of *Chlamydomonas reinhardtii* and reported that the lipid and triacylglycerol levels could be increased up to 24% (Deng *et al.*, 2015).

Algae for biofuel production

Microalgae are found to have higher biomass productivity than the plant crops in terms of land required for cultivation and the potential to reduce greenhouse emissions through the replacement of fossil fuels (Dismukes *et al.*, 2008; Brune *et al.*, 2009; Chisti, 2007). Oswald and Golueke (1960) proposed green microalgae as a potential source of renewable biofuel. Kiran *et al.* (2014a) reported that *Chlorella* species had appreciable generation time resulting in high lipid content and enhanced biofuel production. The nutrient uptake capacity of *Chlorella* sp. IM-01, can be used for biofuel production and integrated with wastewater treatment (Kiran *et al.*, 2014b). Microalgae have been genetically altered to boost their lipid storage potential for biofuel production (Aratboni *et al.*, 2019; Poonia *et al.*, 2022). Fathi *et al.* (2013) reported the bioremediation of wastewater by the green alga *Chlorella vulgaris* and the biomass of the algae to produce sustainable biofuel. The production of algal oil and biodiesel was also reported in *Oedogonium* and *Spirogyra* sp. (Sharif *et al.*, 2008). The kinetic study of a cyanobacterial consortium of *Oscillatoria subbrevis* and *Gloeocapsa atrata*on chromium (Cr) removal showed that biomass and lipid production increased when the cyanobacterial consortium was more when cultured in wastewater containing Cr than in the pure media (Kushwaha *et al.*, 2014).

Chokshi *et al.* (2016) reported that the cultivation of microalgae *Acutodesmus dimorphous* obtained dry biomass from dairy wastewater which contained around 25% lipid and 30% carbohydrate, which could be further converted into biodiesel and bioethanol, respectively. The critical disadvantage of algal biofuel production is the absence of technologies that do not support algal biomass cultivation only for biodiesel production because of its cost. Much more research is to be done on its utilization. The integrated application of microalgae for wastewater treatment and biofuel production is wise to reduce the cost, increase nutrient supply, and overcome water scarcity problems.

Future microalgae insights

Algal bioremediation is a renewable treatment technique for polluted water. Several approaches have been developed in the last decade to increase the use of these bio-remediating agents. There are many challenges to the commercialization of biofuels comprising microalgae. Even with the improvement in technologies, the cost of algal biofuels is twice that of fossil fuels. Thus, there is an emerging need to study and concentrate on algal biomass production utilizing urban wastewater (Rosli *et al.*, 2020). Genetic engineering can help the inefficient development of selected microalgae for wastewater treatment and biomass production. Microalgae is a good source of protein, which has an excellent commercial application, and has a considerable price of protein compared to biofuel per weight; however, lipids are lost during protein recovery. So, there is a requirement fora technique for efficient co-extraction or sequential extraction from the algal biomass (Binda *et al.*, 2020).The applicatory part of the algal-based nanoparticles has to be studied in the way these are to be incorporated into medical devices to increase their efficacy and diminish any side effects.

Conclusion

The wastewater treatment industry faces challenges concerning the fate of pollutants such as metals, heavy metals, pharmaceuticals, dyes, etc., which require an alternative method for water treatment to be reused. Phycoremediation is one of the sustainable and eco-friendly methods for cleaning polluted areas. Phycoremediation is coming out with a good result in bioremediating the wastewater in an ecological and economical manner with the utilization of low energy and production of biofuels. When compared to conventional treatment regimes, it is one of the robust alternative strategies for treating wastes and wastewaters sustainably and has the added advantage of reducing the carbon footprint. The process needs to be implemented in a vast space. Algae provide an advantage in the process because of the fast growth rate and their efficiency in removing pollutants and nutrients, which can help in the tertiary treatment of wastewater.

The bioremediation and biosorption processes are cost-effective when compared to other conventional methods. The incorporation of the phycoremediation techniques along with the traditional methods enables the new secondary treatment systems, which can prove to be eco-friendly and profitable. The heavy metals absorbed by the algal biomass can be recycled in collaboration with the industries, leading to complete removal from the environment. It would also lead to the conservation of the disposal sites of such heavy metals, therefore reducing the risk of soil pollution.

In actual field applications, limited studies on phycoremediation have been done; thus, extensive research is needed to understand the complexity of the process while working on a commercial level. Although microalgae grow in wastewater, the nutrients usually do not match the optimal levels required for algal growth. To solve this problem, two strategies can be used; the first is the modification of wastewater to match the algal culture conditions, and the second is the utilization of specified trained algae species that adapt to the wastewater. Several other factors such as abiotic, biotic, chemical, physical, and mechanical operation can affect algal growth during treatment, thus limiting their efficiency. It is necessary to study the effect of the physicochemical factors, biological factors, and the mechanism involved to ensure high-efficiency removal of all kinds of pollutants from the water. Meticulous studies are required to screen or develop hyper accumulator algal strains which could treat the contaminant in an efficient manner. However, the widespread adoption of this technology under a circular economy requires synergistic and strategic implementation of ideas generated by R&D labs, academic institutions, NGOs, industries, and policymakers.

Conflict of interest

The authors declare that they have no conflict of interest.

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