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# Latest developments in wastewater treatment and biopolymer production by microalgae

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ABSTRACT

The use of microalgae is nowadays recognized to be an efficient and eco-friendly strategy for the removal of contaminants from wastewater. Thanks to their versatility, these photosynthetic organisms can grow in a broad spectrum of wastewaters, including those from agricultural, animal, municipal, and industrial sources, while converting nutrients such as nitrogen and phosphorus into useful products. Currently, microalgae are beginning to be exploited at large scale for the treatment of agricultural and municipal wastewaters. However, novel applications for specific types of wastewater, such as from petrochemical sources, while producing promising results, are still in their early stages. Thus, further work should be performed to optimize microalgal technology in light of its application to industrial contexts.

Currently, there is also a growing interest in making these technologies even more economically and environmentally sustainable by using microalgal biomass, obtained during wastewater remediation processes, to produce novel bioplastic materials, potentially replacing petroleum-based counterparts and reducing the adverse impact of human activities and manufacturing on the environment.

The present review will encompass the latest developments in algal technologies for environmental remediation, with a specific focus on novel applications in the field of petrochemical wastewater treatment. Then, a literature review of bioplastics production via microalgae and its integration into the wastewater treatment process will be conducted. Information gathered in this review can be used to identify research topics that need to be addressed in order to optimize the use of microalgae-based technology for wastewater remediation.

## 1. Introduction

Microalgae are microscopic organisms or plants living in marine, freshwater, and soil environments. Phylogenetically, microalgae differ from terrestrial plants. Since less than half of the 72.500 currently identified algal species have been studied [1], the potential of algal

*List of abbreviations:* ATS, Algal turf scrubber; APS, Advanced pond system; BOD, Biological oxygen demand; COD, Chemical oxygen demand; CSG, Coal seam gas; CWs, Constructed wetlands; DWW, Dairy wastewater; EIA, Energy information administration; EPA, Environmental protection agency; EPS, Extracellular polymeric substances; FAO, Food and agricultural organization; FLA, Fluoranthene; FW, Flowback water; GHS, Greenhouse gases; HM, Heavy metals; HHV, High heating value; HRP, High rate pond; HRPAP, High rate pond for algal treatment; HRT, Hydraulic retention time; IUPAC, International union of pure and applied chemistry; OD, Oxygen demand; PAHs, Polycyclic aromatic hydrocarbons; PBAT, Polybutylene adipate-co-terephthalate; PHA, Polyhydroxyalkanoates; PHB, Polyhydroxybuthyrate; PHBV, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PHE, Phenanthrene; PE, Polyethylene; PLA, Polylactic acid; PP, Polypropylene; PVC, Polyvinyl chloride; PW, Produced water; PYR, Pyrene; ROS, Reactive oxygen species; SWW, Swine wastewater; T-IPL, Intense pulsed light; TFS, Total dissolve solids; TOC, Total organic carbon; WW, Wastewater; WWTP, Wastewater treatment plant.

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technologies for a diverse range of applications is indisputable. Many algae strains are among the most efficient plants that can convert solar energy into chemical energy. Microalgae can accumulate a wide range of commercially important products, including carbohydrates, oil, sugar, protein, cellulose, various polymers, and high value functional bioactive compounds. Algae produce oxygen ($O_2$), sequester carbon (C), remove nutrients such as nitrogen (N) and phosphorous (P), and absorb many pollutants during their photosynthetic growth in wastewater (WW). Because of these capabilities, microalgae are ideal for effluent treatment applications. Moreover, microalgal biomass can be used as a feedstock for manufacturing many products in strategic markets. Hence, there are tremendous opportunities for utilizing algae-based technologies in various environmental and product development applications.

Algal WW remediation and use of the resulting biomass to produce valuable bio-products, have been studied by many industrial and academic research groups [2,3]. Removal of inorganic contaminants such as nitrates, ammonia, sulphates and phosphates as well as sodium (Na), calcium (Ca), and heavy metals (HMs), has been the focus of many investigations [4–6]. Algal treatment of agricultural WW has been limited to tertiary treatment, de-nitrification, and de-phosphation (Fig. 1).

In general, the photo-autotrophic route has been exploited for algal WW treatment. Many algae species can grow using organic carbon as an energy source instead of light through heterotrophic or mixotrophic metabolism [7]. Increasing the biomass and lipid productivity of microalgae via heterotrophic or mixotrophic growth strategies has been investigated [8]. Degradation of organic pollutants, such as hydrocarbons, in WW using heterotrophic or mixotrophic algae, further expands the applications of algal WW remediation [9]. There are only a few studies examining the use of algae to remove organic contaminants from WW produced by the petroleum industry.

This article reviews aquatic microalgae. Considering that fresh water is a scarce resource and current industrial or agricultural WW management and disposal practices can create human health issues as well as environmental and economic challenges, an integrated system approach involving the use of the algal biomass generated during WW remediation for high value product development is addressed in this review. The main reasons for featuring municipal, agricultural and industrial WW include their very diverse chemical compositions, large production volumes, and their adverse environmental impact. The production of algae-based polymers is also discussed as an example of the potential viable utilization of the algal biomass generated during WW remediation for product production within a biorefinery system. Indeed, use of chemical feedstocks from non-renewable sources, such as fossil fuels, combined with the current plastic pollution problem, makes the plastic industry unsustainable in its current form [10–12]. Hence, there is an immediate need for new renewable feedstock sources and environmentally benign technologies for polymer production. This review highlights several algal technologies as alternative approaches to current polymer production methods.

## 2. Methodologies for microalgae cultivation

Several methodologies have been developed for microalgae cultivation [13,14]. The first step in designing an algal production system is the decision on the type of system that need to be built, which can either be an open or a closed system. Open systems, such as tanks, ponds, and lakes, are the most common and widely commercialized outdoor systems. These systems are simple to construct, easy to manage, and preferred for their low energy demands. Usually, the depth of water in the system is kept in the range of 0.2–0.4 m to allow light to penetrate. Since the open systems are exposed to outdoor environmental conditions, cultures are prone to contamination and changes in growth medium composition due to nutrient dilution (because of precipitation or rain) or concentration (because of evaporation), reducing productivity [15].

Closed systems, also referred to as photobioreactors (PBRs), are isolated from the external environment, thus avoiding contamination and other adverse external influences. Therefore, PBRs often exhibit a higher productivity compared to open systems. Tubular or flat-plate PBRs made of plastic or glass are the most common designs used in industry. Air supplemented with other gasses, usually carbon dioxide ($CO_2$), is bubbled through the water column in the PBR [16]. The most important PBR design features for high productivity and low energy consumption are reactor diameter and culture mixing mechanism [17]. The main disadvantages of PBRs are high energy demands, limited volume, and reduced light penetration due to fouling of the reactor walls and difficulty cleaning the system, resulting in higher operational costs [16].

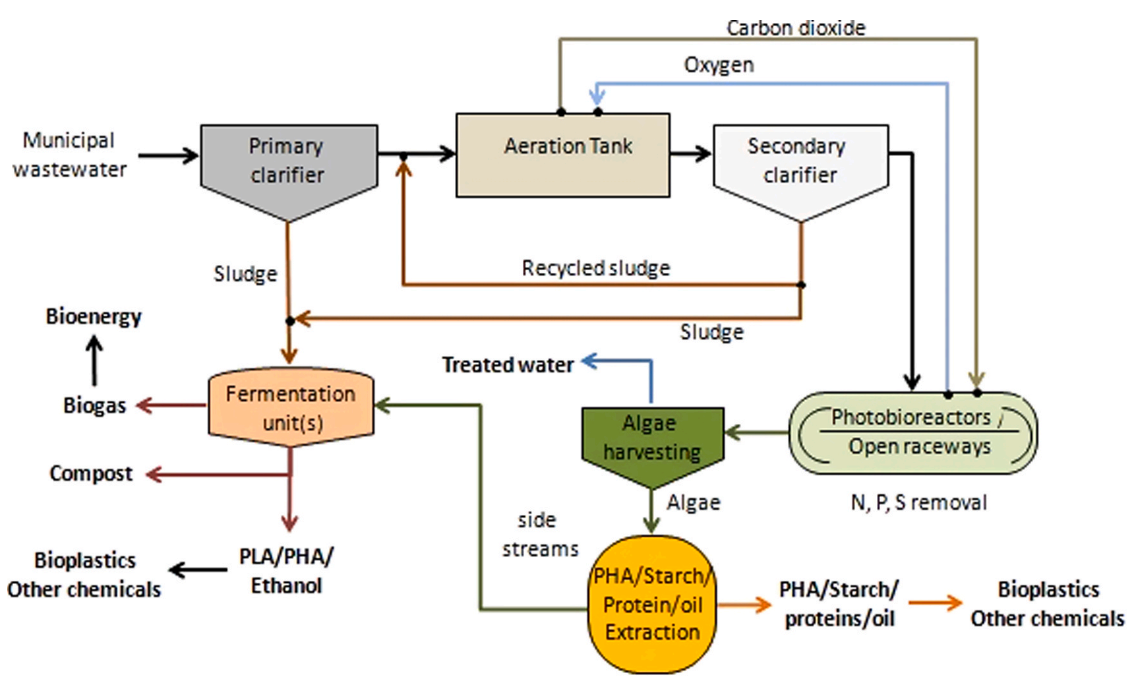


**Fig. 1.** Example of a possible wastewater treatment process integrated with microalgae cultivation and bioplastic production [5].

Batch, semi-continuous, or continuous operational modes are the main strategies used for algal culture systems [14]. A closed batch system requires less management than a continuous system, and thus represents a lower-cost strategy. The main characteristics of a batch system are as follows: culture medium does not have to be renewed frequently, microalgae continue to grow until all the nutrients are depleted and cell self-shading occurs or pH variations and contamination impede further growth. In batch systems, agitation of the culture is critical to ensure nutrient availability and gas exchange at the interface between cells and growth medium. Artificial or natural light can be provided to the cells. In some cases, an external $CO_2$ supply is used to enrich the air and facilitate faster cell growth [18].

Cultivation in semi-continuous mode is similar to batch operation, except periodical renewal of the culture medium and continuous removal of effluents are necessary. The main advantages of a semi-continuous system are high biomass productivity and simplified operation [18].

Suspended or immobilized cell cultures can be used to grow microalgae [19]. Polysaccharides from natural sources (calcium or barium alginate, agar, carrageenan) or synthetic polymers (acrylamide, photo-cross linked resin, urethane) are some of the materials used for algal cell immobilization to improve their stability and productivity [18]. Immobilized-cell cultures enhance process efficiency by retaining the cells in the reactor [20,21]. The high cost of the polymers used for immobilization are the main disadvantages of this technique [22]. Furthermore, the need to separate cells from the immobilization support material before further downstream processing occurs increases the cost.

One of the interesting new approach is microalgae cultivation in the form of a biofilm for WW treatment. Biofilms can be described as complex structures of different types of microorganisms embedded in extracellular polymeric substances (EPS) that form on solid surfaces under specific light and humidity conditions. Microalgae and cyanobacteria are the prevalent organisms forming a symbiotic relationship in microalgal biofilms [23]. However, in most cases bacterial cells and protists are the dominant organisms in the biofilms. The use of microalgal biofilm-based cultivation can enhance biomass productivity at a reduced operational cost [24]. Berner and colleagues [25] described three different methods of microalgal biofilm formation for WW treatment: continuously submerged systems, intermittently submerged systems and perfused systems. Gross and colleagues [26] classified microalgal biofilms as stationary or rotating based on their movement in the liquid medium. It has been demonstrated that biomass productivity and rate of pollutant removal from WW varies with the microalgae strains and biomass matrices used for biofilm formation [26,27].

## 3. Algal wastewater treatment

### 3.1. Algal municipal wastewater remediation

The 2030 Agenda developed by the United Nations (UN) [28] identified improvement of water quality as one of the most important goals for sustainable development in member countries around the globe. Treatment of effluents before they are discharged is mandatory in many countries, because they often contain inorganic and organic compounds that can adversely affect aquatic flora and fauna and can indirectly interact with the food chain, leading to serious issues with human health. Moreover, contaminants can adversely affect the physicochemical properties of water, causing damage to coastal waters, lakes, rivers and aquifers [14]. Most of the contaminants present in aqueous effluents derive from domestic, agricultural and industrial activities [24].

Municipal WW mainly consists of human feces, urine, and WW generated during domestic washing, bathing, and cooking, also referred to as "gray water". Some industrial WW may also enter municipal WW channels in certain areas [29]. The main objective of a municipal WW Treatment Plant (WWTP) is to reduce Biological Oxygen Demand (BOD) of the WW. Aerobic microorganisms deplete dissolved oxygen in WW and reduce its organic material load [29].

Various biological WW treatment strategies have been developed in response to the increasing need for alternative eco-friendly and economically-sustainable solutions to the conventional chemical WW treatment methods used during the last few decades. In the new WWTPs, various microorganisms are used to remove nitrates [30], sulfates [31], phosphates [32], as well as BOD and COD (Chemical Oxygen Demand). Although bacteria are the dominant organisms in WWTPs, fungi [33], protists [34], and microalgae [35] also play significant roles in contaminant removal. The first use of algae for WW treatment to remove pollutants and excess nutrients (mainly nitrates and phosphates) goes back to the late 1950's [36]. Utilization of microalgae in the secondary and tertiary treatment steps in WWTPs has been extensively investigated [13,24,37].

Municipal WW is potentially a good medium for microalgae growth because of the presence of high concentrations of nutrients such as nitrate and phosphate, as well as organic matter and other carbon sources needed for cell growth [38]. Microalgae are able to significantly reduce the amount of nitrate and phosphate, and consequently reducing BOD of the WW [22]. Microalgal removal of metals present in municipal WW due to the pesticide and agricultural amendment applications is well documented [39]. It has been also reported that microalgae can efficiently remove contaminants originating from pharmaceuticals [40] and personal care products [41]. Municipal WW to be used for algal treatment can be withdrawn from three different points at a WWTP: 1) raw sewage, 2) effluent from an aeration tank after activated sludge treatment, and 3) water generated during sludge dewatering, which contains high amounts of nutrients [42].

Microalgae-based WW treatment systems have a number of advantages over conventional WW treatment processes including: 1) very high pathogen reduction (i.e. efficient removal of total coliform organisms [13]), 2) efficient nutrient recovery from the biomass and 3) significant reductions in $CO_2$ emissions [43].

Selection of the algal species and strains to be used in WW treatment is based on their biological and physiological characteristics as well as other factors such as availability of cultivation area, light and nutrients, pH, temperature, and the physical and chemical characteristics of the WW [24,44]. The criteria to consider during the microalgal screening are fast growth rate, high contaminant removal rate, adaptability to different types of WW and local environmental conditions, and high biomass productivity. Unfortunately, one single strain cannot always meet all these conditions. In such cases, fast growth and rates of high contaminant removal would be the main selection criteria [24].

WW treatment can be coupled with other production methods [45]. For example, algal biomass grown in WW can be processed to extract lipids and produce biofuel [46,47], or anaerobically digested for biogas production [48]. Furthermore, depending on the chemical composition of the biomass generated, it can also be used in the production of antioxidants, pigments, carbohydrates, or other high value bio-products [49]. A promising option is the use of biomass produced in a WWTP for biopolymer production, which will be discussed in detail in this article.

Recently, Emparan and colleagues [22] reported a list of the most common microalgae strains used in WW treatment since 1997 and compared their contaminant (BOD, COD, phosphate, nitrate) removal efficiency. Among them, several *Chlorella* (*C. sorokiniana, C. minutissima*), *Scenedesmus* (*S. acutus, S. quadricauda, S. rubescens*), *Botryococcus braunii*, *Oscillatoria*, *Nostoc*, *Chlorococcum*, *AuxenoChlorella protothecoides* species have been highlighted as the most efficient in municipal WW treatment. *Chlorella sorokiniana*, *Chlamydomonas acidophila* and *Galderia sulphuraria* isolated from an extreme environment, were also successfully used in WW treatment [50]. Lipids protein and carbohydrate contents, as well as BOD, COD, phosphate and nitrate removal rates for a number of microalgal species used in WW treatment have also been published [16,51].

Table 1 briefly summarizes some of the most relevant studies performed on algal treatment of municipal WW coupled with other industrial processes during the last three years (2017–2020).

In summary, the use of microalgae for municipal WW remediation offers many options for optimizing efficient removal of a broad range of pollutants using microalgae strains and/or microbial communities comprising various organism, i.e. bacteria, fungi etc. Integrated technologies exploiting microalgae have been demonstrated to be efficient, low-cost and environmentally friendly tools for the treatment of municipal WW [24].

### 3.2. Agricultural and animal wastewater

#### 3.2.1. Dairy wastewater

The dairy industry around the world has undergone profound changes over the last decade and technological innovations have made possible to develop dairy products with health benefits [64]. In recent years share of the dairy products in human diet has been on the rise in many countries. The Food and Agricultural Organization (FAO) predicts a 13.7% increase in world dairy product consumption by 2023 [65].

The dairy industry exploits large quantities of water throughout the processing lines. According to a recent estimate the amount of WW generated by the dairy industry (DWW) is almost three times the amount of the milk processed [64]. About 0.2–10 L of DWW are generated for each liter of milk produced [66]. Due to the serious threat DWW poses to the environment and public health, large quantities of DWW need to be treated prior to disposal [67,68]. DWW contains a complex mixture of several inorganic nutrients (phosphates, nitrogen-ammonia) at high concentrations, BOD, COD, fats, oils and both suspended and dissolved solids [69,70]. The main challenges in DWW treatment are the reduction of oxygen demand (OD), which can be as high as 2000–2500 mg $L^{-1}$ COD and 800 mg $L^{-1}$ BOD, and the reduction of the contaminants with potential adverse health effects i.e. antimicrobial, antibiotics, hormones used in livestock production [71–73]. Organic materials such as fats, lactose and proteins (mainly casein) contained in DWW are particularly

**Table 1**
Summary of the most relevant studies coupling municipal WW treatment with other industrial processes.

| Microalgal strain | Type of wastewater | Processes analyzed | Efficiency | Reference |
|---|---|---|---|---|
| *Botryococcus braunii* | Domestic WW | Optimization of algal productivity during WW treatment in order to provide biomass rich in high-quality oil for biodiesel. | 100% removal of P 61–65% removal of N | [52] |
| *Nannochloropsis oculata, Tetraselmis suecica* | Municipal WW | To test the influence of WW on different types of microalgae and the microalgae productivity on biofuel production. | The highest bioethanol yield of *N. oculata* was 3.68%. The highest bioethanol yield of *T. suecica* was 7.26%. | [53] |
| *Botryococcus* sp. | Domestic WW | Screening of microalgae for WW treatment and biofuel production. | Up to 61.7% lipid production for biofuel and up to 64.5%, 89.8% and 67.9% of N, P and TOC removal respectively. | [54] |
| *Chlamydomonas reinhardtii, Chlorella* sp., *Parachlorella kessleri, Nannochloropsis gaditana* | Municipal WW | The comparative evaluation of four microalgae for their potential to grow in WW and the simultaneous production of feedstock for biodiesel. | *P. kessleri* showed the highest growth rate and biomass production removing up to 98% of phosphate after 10 days of growth in 100% municipal WW. | [55] |
| *Scenedesmus* sp. | Municipal WW | Microalgal biomass production treating WW effluent and digestate, and quantification of the methane yield of harvested microalgae biomass co-digested with waste activated sludge after an autohydrolysis pretreatment (biogas production). | Complete removal of $N\text{-}NH^{4+}$ and $P\text{-}PO_4^{3-}$ and 58% $N\text{-}NO^{3-}$ and 70% COD; a constant production of 1.1 g TSS $L^{-1}$ of algal biomass was achieved. | [56] |
| *Scenedesmus dimorphus, Selenastrum minutum* | Municipal WW | Evaluation of stresses on two microalgal strains during WW treatment in order to enhance lipid content for biodiesel production. | Lipid concentrations were higher in *S. dimorphus* (35% and 34%) under nutrient deprivation, and in *S. minutum* (40% and 39%) at 5% salinity. | [57] |
| *Scenedesmus obliquus* | Domestic WW | Secondary treated domestic WW was used to cultivate *S. obliquus* for the biomass and lipid production as a renewable feedstock for biodiesel. | *S. obliquus* utilized 95.2% and 78.5% of P and N contents.<br>The highest percentage of C16-C18 fatty acids (54.76% from total lipids) were recorded in algae cultivated in 100% WW. | [58] |
| *Spirulina platensis* | Domestic WW | Treated WW was used for *S. platensis* cultivation, and the harvested biomass was used for biodiesel and biogas production. | Removal efficiency of 2.86 gCOD $day^{-1}$, 0.12 g $PO_4$-P $day^{-1}$, 0.82 g $NH_4$-N $day^{-1}$, 0.13 g $NO_3$-N $day^{-1}$ and 0.88 g total N $day^{-1}$.<br>The biomass contains 26.65% (dry weight) of lipids with C:16 and C18:1 fatty acids. Residual biomass can produce 165.0 ± 5.39 mL of biogas per g Volatile Solids with 62.38 ± 2.12% average methane content. | [59] |
| *Chlorella* sp. *Scenedesmus* sp. | Municipal WW | Municipal WW treatment and evaluation of P and N recovery by microalgae in order to use their biomass as potential bio-fertilizers. | Recovery of total N was ≥ 95% for the microalgae cultures; P recovery was less than 15% of the initial concentration. Both the microalgae biomass were used as bio-fertilizer to grow the wheat plant, and the number of leaves and the average size of the leaves of the plants were higher compared to conventional fertilizer. | [60] |
| *Scenedesmus obliquus* | Municipal WW | Examination of growth characteristics, lipid production and nutrient removal capability of *S. obliquus*, in order to enhance its biofuel production. | N and P removal rates over 99% Lipid accumulation: 31.45–35.74% of dry weight. | [61] |
| *Scenedesmus* sp. ISTGA1 | Municipal WW | Treatment of municipal WW and biodiesel production | Biomass and lipid production were 1.81 g $L^{-1}$ and 452 mg $L^{-1}$ respectively. Significant removal of heavy metals and organic contaminants was observed; a balanced mixture of saturated and unsaturated fatty acids mainly (C16 and C18) indicated an appropriate quality of biodiesel produced by the alga. | [62] |
| *Parachlorella kessleri, Tetraselmis* sp., *Chloroidium saccharophilum* | Municipal WW | Screening for microalgae useful in WW treatment and lipid production for biofuel applications | *P. kessleri* removed 99% of N and 82% of P. Lipid productivity was 56 ± 1 mg $L^{-1}$ $day^{-1}$ in *P. kessleri* and 35 ± 10 mg $L^{-1}$ $day^{-1}$ in *C. saccharophilum*. | [63] |

dangerous for the environment [74,75]. Bottling and packing, along with the cheese and ice cream production cycles are the main sources of organic materials present in DWW.

In general, the composition of the effluent determines if the DWW is treated using physical, chemical or biological methods [76]. One of the drawbacks of the physicochemical methods is that disposal of the physico-chemically treated DWW may lead to secondary contamination. For example, conventional treatment for P removal can cause high levels of aluminum (Al) in the sludge creating problems for safe disposal [77].

For many years, DWW treatment has been carried out with the use of conventional technologies like oxidation and settling ponds. The latter technologies are characterized by their high energy requirement and inefficient pollutant removal leaving substantial amount of nutrients in the treated water stream.

Novel algal technologies are being developed for WW treatment [78, 79]. For example, an advanced pond system (APS) [80] also called a high rate pond (HRP) which maintains aerobic conditions and high-rate aerobic conditions and high dissolved $O_2$ levels throughout the entire pond depth (30–45 cm) enhances treatment efficiency [81]. Craggs et al. [82] successfully employed an HRP for algal treatment (HRAP) and improved water quality compared to a traditional oxidation pond. Moreover, algal treatment of municipal, industrial and agricultural WW in HRAP could capture 660 kg of $CO_2$ per million L of WW by photo assimilation while a traditional APS releases 550 kg of $CO_2$ per million L [83]. Since microalgae can assimilate high amounts of nutrients due to the fast cell growth rate, algal removal of organic and inorganic compounds from dairy effluents has been studied extensively [84].

Recently, the use of two microalgae, one freshwater and one marine water strain, *Scenedesmus quadricauda* (Sq) and *Tetraselmis suecica* (Ts) was investigated by Daneshvar et al. [85] for DWW treatment. Biomass productivity for Sq and Ts in DWW were 0.47 and 0.61 g $L^{-1}$, respectively. Sq exhibited 86.21% Total Nitrogen (TN), 64.47% phosphate ($PO_4^{3-}$) and 42.18% Total Organic Carbon (TOC) removal efficiency, while Ts removed 86.21% of TN, 44.92% of $PO_4^{3-}$, and 40.16% of TOC. Sq and Ts were also able to remove tetracycline from water, 295.34 and 56.25 mg $g^{-1}$, respectively [85]. Controlled laboratory tests highlighted that a microalgae consortium consisting of *Chlorella variabilis* and *Scenedesmus obliquus* can grows in DWW and removes contaminants [86]. It has also been successfully demonstrated that algae biomass grown in dairy effluents can replace the use of synthetic fertilizers. For example, vegetables were cultivated by using the slow-release of nutrients from the algal biomass generated in DWW [87].

Fifteen microalgae isolated from DWW including *Chlorella* sp. ASK14, *Chlorella* sp. ASK25, *Chlorella* sp. ASK27, *Desmodesmus* sp. ASK01, *Scenedesmus* sp. ASK16, and *Scenedesmus* sp. ASK22, were screened for their ability to grow in WW and accumulate lipids. A biomass yield of 1.22 g $L^{-1}$ with oil content of 30.7% (w/w) could be achieved. The fatty acid composition of the latter oil was as follows: C15:0 (2.02%), C16:0 (29.23%), C18:0 (13.5%), C18:1 (46.2%) and C18.3 (9.59%) which is suitable for producing biodiesel production [84]. Isolation of native microorganisms directly from WW streams that will be treated can improve the biological treatment efficiency due to better adaptation of the organisms to their native environment.

### 3.2.2. Swine wastewater

Meat is an important source to meet protein requirement in human diet. Pork consumption has been increasing steadily during the last 60 years. Between 2010 and 2017, nearly one-billion hogs were raised for food markets worldwide annually [88,89]. Swine farms occupy large land areas, consume energy, and have a significant adverse environmental impact due to the release of greenhouse gases (GHS). WW from swine farms is known to be one of the main causes of water eutrophication as well as water pollution [90]. Swine wastewater (SWW) derives mainly from the cleaning of manure, animals and closed and open animal housing. SWW is rich in N, P and certain metal ions. Typically, it contains 800–2300 mg $L^{-1}$ N and 50–230 mg $L^{-1}$ P with an N:P ratio of 12–17 [91,92]. In addition, SWW contains high levels of suspended solids, organic matters and toxicants such as HMs, antibiotics and hormones. Discharge of raw or improperly treated SWW can cause serious environmental pollution including eutrophication of water streams, soil pollution, odor related concerns, harbor resistant genes/bacteria, presents estrogenic activity risks, and emit GHG potentially risking human health [93,94].

Current SWW treatment methods designed to lower TN, total phosphorus (TP), BOD and COD levels to the specific standard levels proposed by the regulatory agencies, such as US Environmental Protection Agency (EPA) are not sustainable because of the related high energy costs and generation of secondary waste streams during the treatment. The most common technology for SWW treatment is anaerobic digestion, which converts organic matter to biogas [72].

There is a call for new sustainable SWW treatment techniques that will mitigate further exacerbation of the energy crisis and global climate change [95,96]. With this urge in mind microalgae cultivation in WW for contaminant removal and energy-rich microalgal biomass production has been studied extensively in recent years [97].

Development of easy to operate, inexpensive and energy-efficient integrated systems involving algal biomass production using the nutrients naturally present in SWW and then converting it to bioenergy and biochemicals is vital for the sustainability of the swine production industry [98,99]. An untreated SWW sample was used to evaluate the growth capacity of three indigenous microalgal strains isolated from Taiwan, *Chlorella sorokiniana* AK-1, *Chlorella sorokiniana* MS-C1 and *Chlorella sorokiniana* TJ5. *Chlorella sorokiniana* AK-1 attained the maximum biomass concentration of $4.70 \pm 0.20$ g $L^{-1}$ which was significantly greater than the other two species. After two weeks of cultivation, the same strain also showed higher nutrient removal efficiencies than the other strains for COD, TN and TP which were 88.8%, 78.3% and 97.7% respectively, than the other strains [89]. Typically, pre-treatment of SWW is necessary for efficient algal biomass production and reducing high concentration of the nutrients such as ammonia-nitrogen ($NH_3$-N), TP and COD present in WW [94]. Two auto-flocculating microalgae, *Tribonema* sp. and *Synechocystis* sp., were grown in diluted anaerobic digestion SWW, with and without pretreatment to evaluate the effect of pre-treatment. Both strains grew better in titanium dioxide ($TiO_2$) and intense pulsed light (T-IPL) treated SWW as compared to the growth in untreated WW indicating that pre-treatment of WW before algae cultivation enhances WW remediation efficiency [94].

Carbohydrate production in microalga *Chlamydomonas* sp. QWY37 grown in SWW was enhanced by optimizing culture conditions (30 °C, 500 μmol $m^2$ $s^{-1}$) [100]. The highest carbohydrate productivity (944 mg $L^{-1}$ $d^{-1}$) and pollutant removal efficiency (81% of COD, 96% of TN, and 100% of TP) in SWW were achieved by using QWY37 strain in a semi-continuous mode of operation. It is important to emphasize that it is still difficult to remove all the concerned pollutants using a single algae strain or bioprocess [94].

### 3.2.3. Wastewater from agricultural run-off

The rapid world population growth has led to a strong demand for food production requiring increased crop yields. Intensified fertilizer and pesticide applications along with use of advanced management practices improved food production to a certain extent. However, increased N, P, and other mineral inputs, and subsequent transfer of excess nutrients from farmland to water streams intensified the environmental degradation in various ecosystems [101]. Presence of excess nutrients in the environment promotes biological growth whose decomposition leads to eutrophication and hypoxia, resulting in loss of biodiversity [101–104]. Ultimately, oxidized forms of N, nitrate and nitrite return to the atmosphere through microbial denitrification. Wetlands (natural or constructed), buffers (riparian or saturated) and denitrifying bioreactors are among the nutrient mitigation strategies that have been developed to remove the excess of N species at the source

[105,106].

The presence of pesticides in agricultural streams alter the macroinvertebrate community structure as well as ecosystem functions [107]. Bioreactors are designed to enhance remediation of agricultural water run-offs through simple and passive denitrification of nitrate present in WW [108]. Several phytoremediation technologies, such as construction of buffer strip, wetlands or microalgae-based ponds, can be used to overcome the problem [109]. Establishment of wetlands and microalgae cultivation for pesticide reduction in agricultural run-offs are receiving great attention for many reasons. First, algal treatment of agricultural-run-offs cleans up the water while generating biomass that can be used as fertilizer or for production of biofuels [82]. Volatilization, photo-degradation, biodegradation, or microalgae uptake are some of the mechanisms for pollutant reduction in WW [110–112]. An integrated system where agricultural run-off treatment is coupled with the microalgal biomass production at large scale has been recently evaluated, by Bohutskyi et al. [113]. In the latter study two filamentous green microalgae (*Cladophora* sp. and *Rhizoclonium* sp.) were used in an Algal Turf Scrubber (ATS®) with a treatment capacity of 10 million gallons of WW per day [113]. According to the authors, a maximum biomass productivity was 22 g $m^2$ $d^{-1}$ was achieved and the produced algal biomass was suitable for biogas generation via anaerobic digestion [113]. The efficiency of algal nutrient removal from a mixture of agricultural run-off (90%) and pre-treated domestic WW (10%) was demonstrated by García et al. [114]. About 65% N and 95% P removal efficiency could be achieved using three horizontal tubular PBRs each having a volume of 11.7 $m^3$ during one month of operation.

Matamoros and Rodríguez [111] evaluated the effect of hydraulic retention time (HRT) and the mode of operation (batch or continuous) on the removal efficiency of 11 pesticides in an algal treatment system. Microalgae were able to remove 50% of lindane, alachlor and chlorpyrifos. Continuous mode of operation was more efficient than the batch mode for the removal of pentachlorobenzene, chlorpyrifos and lindane [111].

#### 3.2.4. Eutrophic wetlands

Eutrophication is a phenomenon that affects more than 450 coastal areas globally. The imbalanced nutrient cycles in natural wetlands are due to the contamination from untreated or insufficiently treated municipal, agricultural, animal, and industrial WW. Nutrients rich water discharged to aquatic ecosystems causes deterioration of water quality [115] and compromise biodiversity in ecosystems [116].

In many cases, ecological engineering techniques can be used to reverse quality deterioration and restoration of aquatic ecosystems [115]. Many examples of effective use of wetlands for the treatment of contaminated discharges have been reported [117–120].

The use of constructed wetlands (CWs) built close to the natural ones has been receiving attention for efficient removal of suspended solids and nutrients from polluted water [121,122]. Constructed wetlands improve water quality and enhance biodiversity [116,123].

Recently, Chen et al. [124] isolated *Scenedesmus* sp. strain from a CW, which received municipal and SWW. The latter strain assimilated up to 81% of TN, 64% of TP and 60.7% of COD from SWW under mixotrophic conditions [124]. In another study, a bioreactor integrated into wetlands was used to simulate a full-scale reconstructed wetland to treat SWW. The bioreactor-wetlands integrated system achieved high contaminant removal efficiency of 92%, 98% and 96% for COD, $NH_3$-N and in TN, respectively [125].

Low operating cost and low energy consumption and efficient high pollutant removal efficiency are some of the advantages of wetlands. In a recent review article, SWW treatment in a CW using microalgae and duckweed was described [126]. In another study, microalgae based CWs were deemed as an outstanding alternative for urban, industrial and agricultural pre- and post-treatment [127].

### 3.3. Wastewater from fossil fuel extraction and processing

The term petrochemical refers to many chemicals produced directly or indirectly from petroleum or natural gas. About 5% of the global oil and gas production is converted to petrochemicals every year [128]. About 40% of the global chemical markets is dominated by petrochemicals [129] which are indispensable part of many products that are essential in daily human life, i.e. food packaging, clothing, home furnishings, means of transport (boats, automobiles, buses, trains, aircraft) and many other products.

Production, extraction, transportation and utilization of petrochemicals generate large amount of waste [130]. Petrochemical based contaminants can be found in soil and in water, thus, potentially resulting in long term damages to the environment.

The role of microalgae in biodegradation of petrochemical based contaminants has been scarcely addressed. Most of the catabolic pathways addressed in the degradation of petrochemical based contaminants by algae remain unknown. For instance, the role of algae in petroleum hydrocarbon-polluted sites harboring both algae and bacteria is not well understood [131]. Some of the microalgae strains investigated for their ability to degrade hydrocarbons are reported in Table 2.

A pioneering work on the tolerance of microalgae towards organic pollutants was carried out in 1969 by Palmer [132]. *Chlamydomonas* sp., *Chlorella* sp., *Euglena* sp., *Navicula* sp., *Nitzschia* sp., *Oscillatoria* sp., *Scenedesmus* sp. and *Stigeoclonium* sp. were identified as the most petrochemical tolerant genera amongst green algae, blue-green algae, flagellates and diatoms. In 1975 Walker and coworkers [158] were the first to report that an achlorophyllous microalgae strain, *Prototeca zopfii*, which belong to the family of Chlorellaceae, could degrade petroleum hydrocarbons found in crude oil. The latter strain was able to degrade 38–60% of the aliphatic and 12–41% of the aromatic hydrocarbons in oil. However, hydrocarbons removal efficiency of the same algae strain from motor oil was lower, 10–23% for saturated aliphatic hydrocarbons and 10–26% for the aromatic hydrocarbons [158]. Hydrocarbon degrading capacity of this microalga was also corroborated by other researchers [112,159–161].

Another freshwater microalga belonging to the family of Selenastraceae, the unicellular green algae *Rapidocelis subcapitata*, is known as a good indicator or bioassay organism for detecting petroleum hydrocarbons [152]. The latter strain and some blue-green algae cyanobacteria are capable of degrading compounds such as benzene, toluene, naphthalene, phenanthrene (PHE), and pyrene (PYR) [162]. Chan et al. [153] reported that *S. capricornutum* could degrade up to 96% of PHE, 100% of fluoranthene (FLA) and 100% of PYR when cultivated in a mixture of polycyclic aromatic hydrocarbons (PAHs) for 4 days. In the same study, it was shown that degradation efficiency was positively correlated with cell density. The growth of *S. capricornutum* in the presence of seven different PAHs such as PHE, fluorene, FLA, PYR, benzopyrene, benzofluoranthene, and benzoperylene, was reported by Luo et al. [154]. Degradation efficiency varied depending on the type PAH evaluated. Seven hydrocarbon degrading microalgae strains were isolated from Nile River by Ibrahim and Gamila [145]. *Scenedesmus obliquus* and *Nitzschia linearis* were the most effective strains degrading hydrocarbons and n-alkanes, respectively.

It has been established that a consortium of algae strains and other microorganisms, such as bacteria, rather than a monoculture is more effective in pollutant removal from WW due to the enhanced $O_2$ production via photosynthesis. Bacteria produce $CO_2$, which effectively provides a source of carbon for algae growth and consequently promoting $O_2$ production by algae cells. Carpenter and co-workers [163] demonstrated that a diverse community of microorganisms (algae, bacteria, yeasts/fungi) could assimilate phenols in an oily bilge waste discharged from off-loading ships. Algae were able to start the mineralization of phenol after 24 h while bacteria and fungi community showed a lag-phase of 384 h for the same reaction. An algal–bacteria consortium containing the green algae *Chlorococcum* sp. and nine

**Table 2**
A list of the most studied microalgae strains capable of degrading hydrocarbons.

| Algae | Hydrocarbons degraded | Reference |
|---|---|---|
| *Euglena* sp., *Oscillatoria* sp., *Chlamydomonas* sp., *Scenedesmus* sp., *Chlorella* sp., *Nitzschia* sp., *Navicula* sp. and *Stigeoclonium* sp. | organic pollutants | [132] |
| *Agmenellum quadruplicatum* | benzopyrene, naphthalene | [133, 134] |
| *Amphora* sp. | naphthalene | [134] |
| *Anabena* sp. | naphthalene | [133] |
| *Aphanocapsa* sp. | naphthalene | [135] |
| *Cladophora glomerata* | benzopyrene | [136] |
| *Chlamidomonas angulosa* | naphthalene | [133] |
| *Chlamidomonas reinhardtii* | iso-octane-extracted PAHs | [137] |
| *Chlamidomonas* sp. | naphthalene | [138] |
| *Chlorella autotrophica* | naphthalene | [133] |
| *Chlorella kessleri* | benzopyrene | [139] |
| *Chlorella sorokiniana* | naphthalene, fenantrene | [133, 140] |
| *Chlorella vulgaris* | benzopyrene | [141] |
| *Chlorococcum* sp. | polycyclic aromatic hydrocarbons | [142] |
| | diclofop-methyl | [143] |
| *Cocchloris elabens* | naphthalene | [135] |
| *Cylindroteca* sp. | naphthalene | [133] |
| *Dunaliella tertiolecta* | naphthalene | [135] |
| *Enteromorpha* sp. | benzopyrene | [136] |
| *Merismopedia quadruplicata* | naphthalene | [135] |
| *Navicula* sp. | naphthalene | [134] |
| *Nitzschia* sp. | naphthalene, fluoranthene and phenanthrene | [134, 144] |
| *Nitzschia linearis* | hydrocarbon pollutants | [145] |
| *Nostoc* sp. | naphthalene | [133] |
| *Ochramonas danica* | phenol | [146] |
| *Oscillatoria* sp. | naphthalene | [147, 148] |
| *Oscillatoria quadripunctulata* | dissolved solids | [149] |
| *Porphyridium cruentum* | naphthalene | [133] |
| *Scenedesmus obliquus* | naphthalene | [150] |
| *Sphingomonas* sp. | 4,4 P- and 2,4-dihalodiphenyl ethers | [151] |
| *Selenastrum capricornutum* | bioassay organism for petroleum hydrocarbon exposure | [152] |
| | phenanthrene, fluoranthene, pyrene | [153] |
| | phenanthrene, fluorene, fluoranthrene, pyrene and benzopyrene | [154] |
| | chlorobenzene, 1,2-dichloro-benzene, nitrobenzene | [155] |
| | benzopyrene | [156] |
| *Skeletonema costatum* | fluorantrene, penanetrene | [144] |
| *Spirulina platensis* | dissolved solids | [157] |

different bacteria (belonging to the genus *Pseudomonas* sp., *Comamonas* sp., *Enterobacter* sp., *Bacillus* sp., *Xanthomonas* sp., and *Sphingobacyerium* sp.) were isolated from a soil sample containing the herbicide diclofop-methyl as the sole carbon source. The integration of algae to bacterial culture increased the diclofop-methyl removal by 36% during a continuous mode of operation [143]. A consortium of four different oil degrading bacteria (*Sphingomonas* GY2B, *Pseudomonas* GP3A *Pandoraea pnomenusa* GP3B, and *Burkholderia cepacia* GS3C) and oil-tolerant microalgae *Scenedesmus obliquus* was constructed to investigate aliphatic and aromatic hydrocarbons degradation in a crude oil [164]. Although *S. dimorphus* did not exhibit a particular ability for degrading oil, it significantly improved the PAH degrading efficiency of four bacteria. *Chlamydomonas reinhardtii* was shown to remove some of the PAHs, such as iso-octane extracts from the particulate exhaust of diesel fuel after a long lag phase [137]. However, higher concentration of PAHs in the extract caused cell death.

#### 3.3.1. Wastewater from oil and gas extraction operations

Hydraulic fracturing (thereafter denoted as fracking) is a technology often used to stimulate production of oil and natural gas. Currently about 90% of the oil and gas wells in U.S. rely on this technology. According to the Energy Information Administration (EIA) the top ten countries with the largest shale oil and gas resources are U.S., Russia, Lybia, China, Argentina, U.A.E., Chad, Australia, Mexico and Venezuela [165]. Briefly, fracking technology involves injection of a pressurized fluid containing water and other ingredients (sand and chemicals additives) into the shale formations to create fractures and fissures and facilitate release of trapped gas and oil thus improving the efficiency and the profitability of an otherwise expensive extraction process. Once the fractures have been generated, fluid injection is ceased and well is depressurized causing the fluids to flow back to the surface. About 10–40% of injected water is recovered from the system during this process. The fluid returning to the surface is called flowback water (FW). Typically FW is stored in open pits or in tanks located at the well site prior to disposal [166]. The water stream that comes to the surface mixed with oil and gas during the production period is designated as produced water (PW). The latter is the most concerning WW due to its larger production volume than FW and its potentially harmful chemical composition. PW may contain minerals and radioactive elements, including sodium (Na), potassium (K), chloride (Cl), bromide (Br), calcium (Ca), barium (Ba), strontium (Sr), radium (Ra), and uranium (U), as well as organic chemicals such as solvents, biocides, and scale inhibitors [166,167]. PW and FW may qualify as hazardous materials and carcinogens. Moreover, they may contaminate groundwater resources adversely affecting humans and wildlife [168]. In a recent paper, Colborn et al. [169] analyzed 632 chemicals commonly used at natural gas operations. Petroleum distillates such as kerosene and diesel fuel containing benzene, ethylbenzene, toluene, xylene, naphthalene and other chemicals, PAHs, methanol, ethanol, isopropanol, formaldehyde, glutaraldehyde, ethylene glycol, glycol ethers, hydrochloric acid, phosphoric acid, ammonium chloride, potassium chloride, potassium hydroxide and sodium hydroxide were some of the compounds identified. Recently, Sun et al. [166] reported organic contents of fracturing WW from typical shale gas wells, as well as their health effects and allowed regulatory limits in water. A comprehensive analysis of the current PW and FW handling and disposal methods has been carried out by Sun et al. [166]. Underground injection into the wells that meet the requirements of geological conditions (such as permeability, thickness, and areal extent to accommodate large volumes of injected waste); pretreatment before disposal or reuse; mixing with fresh water to dilute the pollutants and recycling after treatment at an authorized industrial WW treatment plant near the well are some of the most diffused practices used by the industry. However, the latter WW management option are usually challenging due to their high cost and damaging environmental impacts. In particular, underground injection is not a viable option in fragile geological environments (i.e. Marcellus shale gas basin in the U.S. and the Eastern Sichuan basin in China) [170]. Thus, remediation mediated by microorganisms could represent a potential solution to the frac water problem. Usually, frac water is characterized by its high $O_2$ demand, high salinity in terms of total dissolve solids (TDS) (up to 100.000 mg $L^{-1}$) and the presence of a microbial population that is capable of consuming organic matter in extreme environments under aerobic or anaerobic conditions. Zhuang et al. [170] reported the co-treatment of PW and municipal WW with particular emphasis on the chemical PW pre-treatment to remove a large portion of organic matters. Microbial treatment of the mixed WW removed 90% of the COD and 20% of the acute toxicity in a moving bed biofilm reactor at laboratory-scale. An extensive review article by Liu et al. [171] reviews algal removal of wide range of contaminants from WW. Despite the well-known capacity of microalgae to uptake typical contaminants such as hydrocarbons and HMs present in PW, only a few studies have been presented in the literature about the viability of growing algal biomass in PW for further processing and conversion to valuable products. Algal biomass grown in industrial WW such as PW and FW would only be suitable for development of industrial product, such as renewable fuels and biopolymers [166]. Ranjbar et al. [172] used halophilic microalga, *Dunaliella salina*, for treating PW and using the generated biomass for producing biodiesel rich in unsaturated fatty acid methyl esters. Thirteen strains of microalgae isolated in southern Brazil were shown to be capable of growing in PW and removing pollutants. A cyanobacterium isolated from a WW treatment facility at Logan City, Utah, U.S., was shown to be capable of producing 4.8 $m^2$ $day^{-1}$ ash free dry biomass when cultured in a biofilm reactor containing undiluted PW as the growth medium [173]. Racharaks et al. [174] examined nutrient requirement for the marine microalgae strains *Nannochloropsis salina*, *Dunaliella tertiolecta*, and *Dunaliella salina*. *N. salina* and *D. tertiolecta* had the highest biomass productivity when they were grown in a 6% (v $v^{-1}$) blend of FW and anaerobic digestion effluent. The latter strains could also grow in unsterilized FW [174]. Mixed community cultivation of algae in a coal seam gas (CSG) water sample indicated that algae could grow in CGS. A strong correlation between the water chemistry and the microbial community structure was found via 18S rRNA gene identification analysis [175]. Cultivation of *Dunalliella tertiolecta* in a bicarbonate-rich CSG water supplemented with nutrients (10 g NaCl $L^{-1}$ and 200 mg carbon $L^{-1}$) in a non-aerated batch reactor at a cell growth rate of 49.7 mg $L^{-1}$ $d^{-1}$ produced a biomass containing 22% total lipids [176]. *Scenedesmus* sp. MKB strain isolated in Oman was grown in an open pond on non-arable land in an Oman arid region, using a pre-treated PW sample from an oil extraction operation and enriched with nutrients by adding a commercial fertilizer [177]. An average biomass productivity of 15.7 g $m^2$ $d^{-1}$ was measured during two months long experiments performed in years 2013 and 2014. Over time, the culture photosynthetic activity was negatively affected by the presence of weed algae (cyanobacteria and diatoms) in open ponds. Godfrey [178] examined the growth of eight strains of microalgae in PW to produce neutral lipids that can be converted to biofuels. Cell growth and lipid production were enhanced by adding 150 and 300 mg $L^{-1}$ sodium nitrate (no phosphate) to the PW for the diatom *Amphora coffeiformis* and the green algae *Chaetoceros gracilis* and *Chlorella* sp, respectively. Lipid productivity was remarkably high (up to 63.8 mg $L^{-1}$ $d^{-1}$) for the strains. When five microalgae strains (*Scendesmus* sp., *Neochloris* sp., *Chlorella* sp., *Monoraphidium* sp., *Dictyosphaerium* sp.) were grown in PW collected from a natural gas field in Qatar, 100% Al, zinc (Zn), and iron (Fe) and a very low K (11.3%) removal was accomplished by all the strains examined [179]. Metal removal efficiency and the growth rate of *Dictyosphaerium* sp. were the highest among the strains evaluated.

Recently, Lutzu and Dunford [180,181] reported the effect of Oklahoma native microalgae strains grown in FW and PW on residual water quality. Thirteen microalgae strains were cultivated in FW [180] and eleven in PW [181]. FW and PW quality before and after algae treatment was evaluated. Although microalgae were able to grow both in FW and PW, the biomass production was constrained by the limited nutrients availability in the growth medium. Volatile matter, fixed carbon and ash contents of the algal biomass grown in FW and PW were strain specific. The biomass with the highest fixed carbon content and high heating value (HHV) was produced by the cyanobacteria *Pseudoanabaena* sp. cultivated in PW.

### *3.3.2. Metal removal from wastewater*

The term “heavy metal” (HM) refers to any element that possess metallic properties and has an atomic number higher than 20 and a density greater than 5 g $cm^{-3}$ [182]. HMs category includes micronutrients such as Zn, copper (Cu), nickel (Ni), manganese (Mn), Fe, molybdenum (Mo) and cobalt (Co) that are essential elements for algae growth and cell metabolism [183]. Other elements without no biological function (non-essential elements) such as cadmium (Cd), lead (Pb), chromium (Cr), mercury (Hg), silver (Ag) and arsenic (As) are also considered HM which can be very toxic even at low concentration [184]. It is important to underline that the toxicity of HM on living systems depend on their biological availability to the organisms [23].

HMs can naturally be present in the environment or may originate from anthropogenic activities which are the main source of these compounds. Mineral weathering, erosion, volcanic eruptions, and continental dust are some of the natural phenomena contributing to HMs release in different environmental environments [185,186]. Industrial activities like mining, smelting, electroplating, metallurgical and cement production effluents, use of pesticides and fertilizers for agricultural purposes also release HMs to the environment [185,187,188]. The main characteristics of HMs are their persistence and accumulation in the environment (soil, air, water) and subsequent entry to the food chain lead to their bioaccumulation and/or biomagnification at high trophic levels consequently posing severe health threats not only to animals and plants, but also to human health [185]. HMs can cause oxidative stress by catalyzing formation of reactive oxygen species (ROS), which disrupt the antioxidant defense system leading to cell damage in humans and animals. In extreme cases the damage can be fatal [189]. For all these reasons, the removal of HMs from the contaminated matrices is vital for protecting the environment and human health.

Industrial WWs, in particular the effluents from textile, electroplating and other metal processing industries contain HMs, toxic metal ions, organic toxins and surfactants [190]. Physicochemical techniques including chemical precipitation, ion exchange, adsorption, ultrafiltration, reverse osmosis, electrodialysis, coagulation/flocculation and flotation are used for metal remediation of contaminated WW [191]. Unfortunately, some of the latter techniques are not viable due to their high costs and/or technical inefficiencies at metal concentrations less than 100 mg $L^{-1}$ in WW [192]. There is an urgent need for separation techniques that can reduce the metal concentrations in WW to the acceptable range of 1 and 100 mg $L^{-1}$ [23,193]. A potential solution to the problem is bioremediation [194] which exploits the metabolic ability of yeast, fungi or bacteria, to decontaminate soil and water. These microorganisms can use the environmental contaminants as nutrient and energy sources for growth and remove contaminants [195]. During the last decades, algal bioremediation (phycoremediation) has gained a lot of interest, particularly for WW treatment [13]. According to Mehta and Gaur [196], algal treatment of WW for metal removal is efficient even at low concentration of metal ions. Algal treatment can also be useful for recovery precious metals, i.e. Ag, Au, Pt, that are present in the environment at very low concentration [197,198]. Microalgae can decrease toxicity of the metals by several mechanisms [199]: a) binding metals on the cell surface, b) precipitation by forming complexes with insoluble metals, c) excreting metabolites that form complexes with toxic metals, d) using influx pumps that are present on the cells to transport toxic metals from the external environment into the cell cytoplasm, e) converting metals to less toxic forms by modifying their oxidation state, f) converting metals to volatile forms that can easily escape the microalgal cell, g) binding metals to proteins or polysaccharides in the cytoplasm to constrain their toxicity, h) enzymatic methylation of metal ions to prevent their reactions with the -SH groups in the cell.

Phycoremediation process may be carried out using either live or dead cells. Living organisms need some nutrients that can be available in WW. In this case, pollutant removal efficiency is correlated with the cell growth rate and the amount of biomass produced. For a given algae strain, biomass concentration in WW determines the total metal ion biosorption capacity of the process. Using dead or harvested biomass for metal removal via adsorption may be a viable option for some WW treatment operations. Considering that dead biomass require neither nutrient nor $O_2$ [195] pollutant toxicity to the organisms is no longer an issue for the adsorption process [200]. Table 3 summarizes the main advantages and drawbacks in the use of dead or live cells for WW remediation.

The other factors affecting metal ion biosorption by algae are concentration of metal ions, algal biomass type and amount, pH,

**Table 3**
Main advantages and disadvantages of using live or dead microalgal biomass for heavy metal removal.

| | Living Biomass | Dead Biomass |
|---|---|---|
| Advantages | • Metabolic processes positively contribute to HMs remediation<br>• higher uptake of metal ions compared to dead biomass<br>• adsorption of a broader range of metals | • HMs biosorption is greater that in living organisms<br>• Possibility to recycle the dead biomass<br>• Availability of easy physical and chemical treatments for adsorption capacity enhancement<br>• No needs for intensive management<br>• No needs to add growth nutrients<br>• Less expensive |
| Disadvantages | • Low resistance to physical and chemical treatments for recycling<br>• pH changes greatly impact living biomass performances<br>• the management of the culture medium might bring to metal precipitation and bioremediation interference | • The HMs removal might be selective respect to living biomass |

temperature, and the presence or absence of competing ions [190]. Table 4 summarizes the main factors affecting the performance of HM phycoremediation in WW.

Phycoremediation of metals follow two different pathways: a) biosorption which is defined as the binding of metallic species to the cell surfaces, and b) bioaccumulation which is the active intracellular uptake of the metals across the cell membrane by live microorganisms [213]. Biosorption is a passive or physical process because it occurs irrespective of the cell metabolism [192,193,195,214]. Metal binding to cell surface may occur through physical adsorption, ion exchange, complexation or precipitation that may take place simultaneously at different rates [23]. Surface of the algal cell has negatively charged functional groups (carboxyl, hydroxyl, phosphate, amino and sulfhydryl) [24]. These functional groups, along with the polysaccharides, proteins, and lipids forming the external cell layers play a central role in metal biosorption. In addition, microalgae possess many different plasma membrane metal transporters, that are responsible for the translocation of metal ions in the cytoplasm [215]. Bioaccumulation is defined as a biphasic mechanism equivalent to the biosorption of metal ions that are first rapidly bound to the cell surface, and then cations are irreversibly transported across the cell membrane into the cytoplasm at a much slower rate. This process increases biomass generation under suitable growth conditions [216].

During the last decades, many studies have been carried out to decipher the role of microalgae in the removal of HMs from WW, and understand why some microalgal species are more efficient in the removal of different metals than others [190,195,217,218]. Table 5 summarizes the recent studies dealing with the phycoremediation of HMs from industrial and model WW samples formulated to simulate industrial effluents enriched with HMs.

## 4. Production of biopolymers from microalgae

Products made from polymers or plastics play a key role in several aspects of modern life. Most of the commodity products available in the market today are made with plastics derived from petroleum-based chemicals such as polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC). Wide use of these plastics during the years has produced huge adverse environmental impact resulting from $CO_2$ emissions and persistence of non-biodegradable materials in soil and water [232,233].

**Table 4**
Main factors affecting metal removal by microalgae.

| Factor | Effect | Reference |
|---|---|---|
| Temperature | Temperature variation increases/decreases biosorbent capacity of microalgae; some authors observed that the metal adsorption increases with rising temperature, whereas other authors described a lower adsorption at higher temperatures. Temperature variations cause different biosorption behaviors in various algal strains with different metal ions. | [201–204] |
| pH | Higher pH values increase the metal biosorption process, while acidophilic pH decreases it. This can be explained since at low pH, functional groups are associated with the $H^+$, thus preventing the association of positively charged metal ions with the external cell layer. As pH increases, the functional sites are deprotonated, allowing the binding to metal cations in the in the microalgal cell. | [201,205] |
| Salinity | As saline condition increases, $Na^+$ are competitors of the metal binding sites of the cell surface, thus reducing the biosorption rate, analogously to low pH levels. | [205,206] |
| Metal concentration | The initial metal concentration determines the amount of metal removed by microalgae; at the beginning of the process, the sorption level increases with the increase of metal concentration, until it reaches the saturation (i.e. all binding sites are full) and slows down. | [207] |
| Multiple metal presence | Usually, the presence of multiple metal in a solution, common condition in industrial WW, causes a competition for binding sites of the algal cells. It has been observed that all binary solutions show a decrease of metal ion biosorption. | [208] |
| Biomass concentration | Even if with the increase of biomass, the number of binding sites increases as well, in some cases a decrease in biosorption efficiency was observed with an increase of biomass probably due to aggregation phenomena of cells. Biomass concentrations positively increases final bioremoval, but it negatively affects biosorption capacity. | [199,209, 210] |
| Use of living/death biomass | The use of living cells is most efficient for removal of metal ions from large water bodies containing low concentrations of metal ions as they are sensitive to the chemical composition of the WW, to all the operating conditions and to high pollutant concentrations; in some cases, dead biomass is more efficient in metal removal than living biomass. | [199,211] |
| Microalgal specie (s) | The type of microorganism chosen strongly influence the metal remediation performances since different species are characterized by different tolerance levels towards metals, that are presumably due to tolerance mechanisms adopted in presence of the chemical species, to genetic features and to the growth rate. | [212] |
| Contact time | The contact time strongly influences the biosorption rates; this aspect is strongly related to the algal species, and to its metabolics characteristics that determines the rate of metal sorption. | [190] |

Between 1950 and 2015, 8.3 Gt of plastic have been produced worldwide producing 6.3 Gt of waste during the same timeframe [234]. Environmental concerns have increased the demand for biodegradable bio-based polymers. It is estimated that global market share of the biodegradable polymers will be as high as 2.44 $10^6$ tons $year^{-1}$ by year 2022 [235].

According to the IUPAC (International Union of Pure and Applied Chemistry) definition, any polymer derived from biomass is considered

**Table 5**
An overview of the latest (years 2015–2020) literature on microalgal applications of metal bioremediation in industrial WW.

| Organism | Metal (s) | WW type | Biomass type | Reference |
|---|---|---|---|---|
| *Scenedesmus* sp. | Cr, Cu, Pb, Zn | Tannery WW | Living | [219] |
| *Scenedesmus quadricauda* | Cr (iii), Cr (vi) | Laboratory synthetic solution | Dry | [220] |
| *Spirulina platensis* | Pb | Battery manufacturing industry WW | – | [221] |
| *Chlorella vulgaris* | Cr (vi) | Electroplating and galvanizing industry effluents | Dry | [222] |
| *Chlorella minutissima* | Cd, Cu, Mn | Laboratory synthetic solution | Living | [223] |
| *Chlorella vulgaris, Scenedesmus acuminutus* | Tl, Cd | Laboratory synthetic solution | Dry | [224] |
| *Scenedesmus quadricauda* | Cd, Pb | Industrial WW | Dry | [225] |
| *Oscillatoria acuminate, Phormidium irrigum* | Cr (vi) | Tannery WW | Living | [226] |
| *Chlorella vulgaris, Scenedesmus acutus* | Cr (iii) | Tannery WW | Dry | [227] |
| *Navicula subminuscula* | Cr (vi) | Tannery WW | Living | [228] |
| *Chlorella minutissima* | Cr (vi) | Laboratory synthetic solution | Immobilized | [229] |
| *Desmodesmus communis, Monoraphidium pusillum* | Cu, Zn | Laboratory synthetic solution | Living | [230] |
| *Desmodesmus* sp. | Ni, Cu | Synthetic solution simulating industrial WW | Living | [231] |

a bioplastic [236]. Some biopolymers are directly synthetized by microbial cells (e.g. polyhydroxyalkanoates: PHA) or plant cells (e.g. starch) and subsequently extracted from the algal biomass, while others are polymerized starting from suitable building blocks produced by microbial fermentation e.g. lactic acid conversion to polylactic acid (PLA) [234]. Most of the biopolymers, especially the biodegradable ones, have been used in various industrial sectors such as packaging, medical, pharmaceutical and agriculture [237–239].

Considering that most of the biopolymers are currently produced from plants cultivated in agricultural land, their production rises potential threats for competition with the food supply chain. Microalgae can be an alternative feedstock to produce biopolymer because of the following reasons:

- Microalgae can perform photosynthesis in environments that are not in competition with agricultural crops (unfertile lands, marine environment, WWs) [35].
- Microalgae have several different metabolic pathways that can be exploited to produce a large variety of bioplastics [240].

  Three methods have been examined to produce bioplastics from microalgae biomass:
- Utilization of the whole microalgae biomass (whole cells).
- Utilization of biopolymers synthetized by microalgae cells (i.e. starch, PHA, proteins).
- Conversion of microalgae biomass to building blocks suitable for polymerization.

### 4.1. Processing whole microalgae biomass

Microalgal biomass can directly be used to produce bioplastics by extruding the intact biomass obtained after harvesting and drying, and, in some cases, after pre-treatment for cell disruption [241]. This approach has the advantage of minimizing downstream processing and eliminating the cost of extraction and separation operations which may increase the energy consumption, consequently reducing the sustainability of the entire process. Microalgae biomass characterized by high starch content (up to 50%) [242,243] and/or proteins (up to 60%) [244, 245] can be converted into thermoplastic materials by means of extrusion technologies. Small size of many microalgae cells (1–10 μm) makes them particularly suitable for the production of fibers and thin films [245]. The mixtures of *Spirulina*, *Nannochloropsis,* and *Chlorella vulgaris* biomass, 9.5–100%, with PP, PE, polyurethane, corn starch and glycerol have been used to produce bioplastics [245,246]. Glycerol was the best plasticization agent at a 4:1 biomass to glycerol ratio [245]. Bioplastics made with a mixture containing *C. vulgaris* but no *Spirulina* showed better mechanical properties than that made with *Spirulina.* Biomass from *Spirulina* displayed better functionality in blends than its pure form indicating its potential for commercial applications [245]. Both biomass from *Spirulina* and *Chlorella* had properties comparable to other common proteins, such as soy proteins [245]. Tensile strength of the *Chlorella*-PVC composite materials decreased with increasing amount of algal biomass in the mixture, i.e. higher than 30 and 15 MPa for $< 20\%$ and 50% algal biomass in the blend, respectively [247]. A similar trend found in the latter studies [245–247] was that mechanical properties of the bioplastics made with algal biomass and PE or PP blends decreased as the biomass amount increased in the mixture. A common trend was found for the cellulose/*Nannochloropsis* composite films, of which mechanical properties decreased with the increasing algal biomass content in the blend (20–80%) [248].

Extrusion tests carried out using biomass rich in starch (49%) from *Chlamydomonas reinhardtii* in glycerol blends demonstrated desirable morphological plasticization effects of starch [249]. Bioplastic prepared with a 20% blend of *Nannochloropsis* biomass with corn starch, water and glycerol showed that *Nannocloropsis* biomass addition induced 73% and 23% drop in $O_2$ permeability and elastic modulus, respectively, as compared to the control without algal biomass [250]. The negative effects of increasing algal biomass content in the blends on the bioplastic mechanical properties are likely due to the incomplete cell destruction, which is a common issue when whole cells are used [249,250]. When *Nannocloropsis* was replaced with *Spirulina* and *Scenedesmus* biomass, the $O_2$ permeability of the resulting bioplastic increased 60–80% while keeping an elastic module comparable to the one of pure starch. Similar tensile strength and a 54% drop in water vapor permeability as compared to the control (pure starch) were measured for all the plastics made with all three algae species. The differences in permeability were probably due to the lipid presence in the microalgae biomass. Nonpolar lipids contribute to the hydrophobic properties of the bioplastics [241]. When starch blends are used, hydrophobicity of the bioplastics is generally enhanced by adding petroleum derived chemicals.

Use of microalgae in bioplastic production can provide environmental advantages when a significant fraction of the fossil-based feedstock can be replaced with biomass while maintaining desirable mechanical properties required for practical applications. Alternatively, other bio-based materials such as PLA and polyvinyl alcohol (PVA) can be used to replace petroleum based feedstock in plastics to reduce their adverse environmental impact [251,252].

### 4.2. Biopolymers synthetized by microalgae

#### 4.2.1. Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are polyesters synthetized by several species of bacteria, including photosynthetic cyanobacteria. The most common PHAs are polyhydroxybuthyrate (PHB) and poly(3-

hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), containing hydroxybutyrate and hydroxyvalerate [253]. PHAs are thermoplastic polymers with tensile strengths and Young's modulus between 18 and 40 MPa and 0.6–3.8 GPa, respectively [254]. They are completely biodegradable in soil, water and compost [234]. PHB has limited application potential because of its low elongation-to-break value (~5%), while PHBV is more elastic [254]. Both PHB and PHBV can be used to replace PP and PE in biomedical, agricultural, and industrial applications [255]. There is a large variability in PHA content found in cyanobacteria with values ranging between 5% and 70% of cell dry weight [253]. The variability is due to differences among strain characteristics and specific cultivation conditions necessary to promote PHA accumulation, e.g. P and N limited growth conditions [253,256].

Current industrial PHA production utilizes monocultures of heterotrophic bacteria and the cost is between 2.5 and 6 € $kg^{-1}$, which is higher than the cost of PP and PE (0.9–1.2 € $kg^{-1}$) [234,257]. The largest contributor to the production cost is the cost of organic substrate used in fermentation (~50%). PHA extraction from biomass is also a major cost of the process. Energy intensive treatments and hazardous organic solvents (e.g. chlorinates) are required to break cells and to achieve high extraction yields [253]. Microalgae have the advantage of producing PHA without organic substrates, however, high energy costs of conventional phototrophic cultivation hinder lowering the cost below 3–5 € $kg^{-1}$ [35]. Thus, the production of PHA from phototrophic microalgae currently does not appear to be economically competitive with the conventional fermentation processes. However, integration of the production of algal biomass with WWs treatment may reduce the associated costs. Exploitation of heterotrophic metabolism (organic substrates), by selecting productive strains [258] and addition of nutrients in the fermentation medium could help lower the cost of production [259], as it has been done for PHA production using activated sludge [260]. Selecting microalgae strains with high PHA accumulation ability and using a cultivation system with repeated cycles of alternating feast and famine phases controlled by substrate rich and poor medium could improve production efficiency [259,261]. In such a growth environment, microalgae that accumulate PHA can grow better than many other unproductive contaminant microbial species thus increasing the plastic yield.

#### 4.2.2. Polysaccharides

Microalgae can synthetize various polysaccharides, depending on the species and the cultivation conditions. Starch, cellulose and hemicellulose are the predominant polysaccharides in eukaryotic green algae [262]. Starch is accumulated as a response to nutrient starvation and day/night cycles [263] at content up to 50% [249,264]. Cellulose and hemicellulose have structural functions in the cell wall. Although starch from terrestrial plants has been widely used to produce bioplastics, only a few studies tested starch produced by microalgae. Microalgae starch productivity under phototrophic conditions might be up to 58 t $ha^{-1}$ $y^{-1}$, which is 10 folds higher than that from conventional sources, such as corn [242]. The use of organic substrates could even increase this value is value [265]. Amylose content of starch from microalgae range from 3% to 39% [242,266,267]. Microalgae based starch has a molecular weight of 6.35 $10^8$ kDa, and a crystalline structure classified as A-type [242], comparable to cereals. A notable feature of algae-based starch is its very small particle size. For example, starch from *C. sorokiniana* has an average particle size of 1.5 μm (0.8–5.3 μm) [242], which is among the smallest size reported in the literature. The size of the starch from terrestrial plants is typically 20–30 μm [268]. Starch with small particle size is particularly suitable for applications such as thin films and flavor carriers widely used in food industry [268,269]. A major issue in starch production from microalgae is that it is hard to extract. In its native form starch is insoluble in conventional solvent such as alcohols and alkanes and easily degrade at high temperatures. Thus, a mild disruption of algal cell is needed to break up the biomass to release starch. A liquid-liquid (polyethylene glycol 400/water-choline dihydrogen phosphate) extraction method for recovering starch from algal biomass has been developed by Ruiz et al. [270].

Cyanobacteria produce internal storage polysaccharides such as glycogen and amylopectin-like glucans [271,272], cell wall polysaccharides (used for sheath and capsule production) [271] and extracellular polysaccharides (EPS) [271,273–275] which are characterized by their complex and heterogeneous structures [271,273,275]. They can have molecular weight between 80 and 1900 kDa [275]. EPS are usually harvested from the cell free culture media by means of ethanol precipitation. However, so far, not any report was found about bioplastic production by using exopolysaccharides from cyanobacteria in the literature.

#### 4.2.3. Proteins

Proteins that can be used to produce thermoplastic biopolymers are present in every microalgal cell at concentrations ranging from about 10% to over 60% [244]. They can be processed by injection-molding or electrospinning, have good film forming properties and biocompatibility, and can adhere to various substrates, e.g. human tissues and wood [276–278]. Furthermore, the structural properties of proteins vary significantly depending on the algal strain they are isolated from. Their structural properties can be improved by DNA modification [279]. Plastics have been produced mainly from collagen, gluten, casein, soy proteins and other minor vegetable sources [276,277,280]. Protein-based bioplastics can be applied to the production of biodegradable films, in biomedical applications, food packaging, and to replace various petroleum-based plastic products [234,280].

Although several methods for purification of proteins from microalgae biomass have been recently developed [270,281,282], currently whole microalgae cell rather than purified proteins are being explored for bioplastic production. In this light, proteins rich microalgae biomass was tested for bioplastic production to exploit thermoplastic effects of proteins.

Bioplastic fibers have been produced by electrospinning of a blend of polyethylene oxide and protein concentrate (72% proteins) obtained by alkaline extraction from defatted *Botryococcus braunii.* The final product consisted of 93% protein concentrate by weight [283].

A biomass residue rich in proteins (42%) and ash (37%) obtained after biodiesel production from *Nannochloropsis gaditana* was tested for bioplastic production by blending with polybutylene adipate-co-terephthalate (PBAT) [284]. Biomass addition to PBAT increased tensile modules and reduced tensile strength and elongation at break point. The best results were obtained with 20% of biomass.

### 4.3. Conversion of microalgae to building blocks suitable for polymerization

Besides the direct utilization of polymers synthesized by the microalgae (proteins, starch, PHA), an alternative approach is to produce low molecular weight chemical molecules from microalgae biomass, which can be used as building blocks and polymerized to produce bioplastics [285]. For instance, microalgae polysaccharides can be hydrolyzed to simple sugars and then converted to building blocks such as ethanol, [286] and lactic acid [287,288] via fermentation. An engineered cyanobacteria strain was reported to produce up to 26.6 g $L^{-1}$ of extracellular D-lactate via dark fermentation of intracellular glycogen [272]. Lactic acid can be used to synthesize PLA [234]. Fermentation of microalgae biomass can also be used to produce ethanol, which can be converted to PE, PVC and polyurethanes [234].

Microalgae proteins can be hydrolyzed to single amino acids and then reacted with ethylene diamine and ethylene carbonate to synthesize polyols [289]. Polyols have been used to synthesize polyurethane foams with physical properties comparable to a reference foam prepared with commercial polyols (60–360 mg KOH $g^{-1}$).

Fatty acids in algae oil, i.e. oil extracted from *Phaeodactylum* sp., can be converted to diesters, which can be further reduced to diols. A stoichiometric mixture of diesters and diols can be used to produce bioplastics via a polycondensation reaction in the presence of titanium (IV) tetrabutoxide catalyst at 200 °C [290].

### 4.4. Commercial application of algal bioplastics

The growing demand for more biodegradable and sustainable materials to replace petroleum-based plastics lead many companies to develop microalgae-based bioplastics. The company Algix (MS, U.S.) is producing flexible footwear foams called Solaplast, which contain an algae-ethylene vinyl acetate (EVA) blend, as well as other blends containing 40% algae and 60% PP, PBAT and PLA. The company Algenesis Materials (CA, U.S.) converts algal oil to polyols that are used to formulate polyurethane foams for use in surfboard blanks and flip-flops. In collaboration with Algamoil (FL, U.S.) company Teregroup (Italy) replaced up to 35% of their petroleum-based chemicals with algae biomass to produce foams, bags and other products.

### 4.5. Perspective on the production of biopolymers integrated with wastewater treatment

The production of microalgae biopolymers and bioplastics from algal biomass grown in WW can supplement WW treatment costs and enhance the economic and environmental sustainability of the entire process as compared to the conventional WW treatment methods (i.e. active sludges) [291]. So far, most of the studies on utilization of microalgal biomass has been focused on the production of biofuels and/or high-added value products, as carotenoids and fatty acids. However, biofuels production from dedicated microalgae cultivations is currently economically unsustainable [292], while high-added value products utilize only a fraction of the available biomass. Residual biomass can be further processed for value-added product development, i.e. defatted residual algal biomass after biodiesel production from lipids and remaining biomass after extraction of carotenoids.

Furthermore, almost all the studies dealing with the production of biopolymers and bioplastics from microalgae have been carried out by using biomass produced by cultivation in synthetic culture media. There is a need for further research on biopolymers production from an integrated system that treats WW and produces biomass using biopolymer accumulating algae strains. It is expected that a WW based algae cultivation system properly designed and optimized for biopolymer production can produce and accumulate comparable amount of biopolymers to those based on synthetic media [265]. However, pollutants in WW may adversely affect technical and economic viability of the system. Even though many pollutants are biodegradable during microalgae cultivation, many others are removed by adsorption (i.e. HMs), which means that they accumulated in the biomass potentially lowering quality of the final product. This issue is particularly important when bioplastics are produced from the raw whole biomass. In such a case, a simple desorption/pre-treatment may be necessary to be carried prior to final product recovery from biomass. For instance, desorption of metal ions from algal biomass can be performed by using an acid solution, similar to the process used for regeneration of adsorption columns [293]. An other alternative would be to extract biopolymers from contaminated biomass by means of specific biorefinery processes. With this approach, the different separation phases developed to increase the purity of the biopolymers can work well even for removing large part of the pollutants previously accumulated. However, in the latter case, the fate of the pollutants throughout biomass processing will be a relevant aspect that must be considered for the optimization of the purification process.

Algal biomass grown in WW can be contaminated with other microorganisms such as heterotrophic bacteria, yeast, foreign algae, and rotifers. The latter issue is generally neglected by researches because most studies focus on pollutant removal. However, biomass composition is affected by both inorganic and biological contaminants, potentially reducing the yield of target biopolymers. For instance, a microalgae designed to produce starch can be contaminated by heterotrophic bacteria that do not accumulate starch, thus reducing starch yield. In other cases, biotic contaminants can produce toxins that carryover into the final products, as is the case for certain cyanobacteria. The development of cultivation processes specifically designed to select microalgae strains for their ability to accumulate biopolymers (i.e. starch and PHA) is a promising way to control such contaminants. These selections can be achieved by applying cultivation conditions that give a selective advantage to the cells containing high amount of stored biopolymers, for instance by using uncoupled feeding of substrate and nitrate, which induces a feast and famine condition to the culture environment [259, 294,295].

## 5. Conclusions

In this work, the latest literature developments relating to algal technologies for environmental remediation and bioplastic production were extensively reviewed, with a specific focus on novel applications in the petrochemical and bioplastic production sectors. Most of the technologies discussed herein, albeit producing promising results, are in the early stages of development and are still being carried out at laboratory scale, especially for applications related to the treatment of petrochemical wastewaters. However, in recent years, a growing number of large-scale applications have been coming online, demonstrating the technical and -economical viability of algal technologies.

It is clear that algal technologies have difficulty competing with more conventional approaches due to their higher cost. Biorefinery and/or integrated systems approaches, where several products are produced from the same feedstock within the same system, have been gaining attraction. The latter approach can easily be adapted for manufacturing algae-based products and lowering the overall cost of operations for high value products; this could compensate for some of the manufacturing cost associated with lower value-products, providing ecosystem-friendly methods and ultimately supporting a circular and zero waste economy. An integrated system designed for growing algal biomass in WW and then converting the produced biomass to various high and/or lower value bio-products is a good example of achieving multiple goals while supporting the environmental, business and social aspects of sustainability initiatives, conserving natural resources, and ultimately enhancing the daily lives of the growing world population.

## CRediT authorship contribution statement

**Giovanni Antonio Lutzu:** Writing - original draft preparation, review & editing, Supervision, **Adriana Ciurli**: Writing - original draft and Graphical abstract preparation, **Carolina Chiellini**: Writing - original draft preparation. **Fabrizio Di Caprio:** Writing - original draft preparation, **Alessandro Concas**: Writing - original draft preparation, **Nurhan Turgut Dunford**: Writing - original draft preparation, review & editing, Supervision. All the authors take responsability for the integrity of the whole work and approve its final version to be submitted.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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