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The Role of Phytoplankton in Phycoremediation of Polluted Seawater: Risks, Benefits to Human Health, and a Focus on Diatoms in the Arabian Gulf

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Review

The Role of Phytoplankton in Phycoremediation of Polluted Seawater: Risks, Benefits to Human Health, and a Focus on Diatoms in the Arabian Gulf

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Abstract: Diatoms in the Arabian Gulf region contribute to various biological carbon pumps, playing crucial ecological roles and producing bioactive compounds beneficial to both humans and marine animals. Despite their significance, some diatoms pose risks to human health and the economy; however, research on their roles in Qatar remains limited. This review explores the roles of diatoms in the Arabian Gulf, highlighting their potential for remediating polluted seawater and their applications in pharmacology, biofuel production, and detoxification of chemical waste and hazardous metals. Among the 242 diatom species identified along the coastline of the Gulf and Qatar, several genera represent 50% of the identified species and have demonstrated notable efficiency in phycoremediation and bioactive compounds production. These include antibacterial agents with therapeutic potential, antioxidants to neutralize harmful free radicals, compounds that degrade toxic substances, and agents for remediating heavy metals. Additionally, diatoms contribute to the production of biofuels, nutritional agents, dyes, and extracellular polymeric substances, and some species serve as bioindicators of pollution stress. To fully utilize their potential requires significant efforts and comprehensive research. This review explores the reasons behind the current lack of such initiatives and highlights the importance of conducting targeted studies to address the environmental challenges facing the Arabian Gulf.

Keywords: bioactive agents; cyanobacteria; diatoms; dinoflagellates; phycoremediation; phytoplankton; pollution

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1. Introduction

Diatoms are microscopic, unicellular, photosynthetic organisms found in both freshwater and marine environments. These phytoplankton are the most dominant and diverse group, accounting for approximately 45-50% of oceanic primary productivity. They are also considered key players in the biological carbon pump [1,2]. In the Arabian Gulf, these golden-brown algae are present along the coastline as well as in sabkhas. They play a significant role in the global carbon cycle, fixing approximately 25% of carbon each year. Additionally, diatoms, along with other phytoplankton, such as cyanobacteria and other algae, perform various essential ecological functions [3,4]. Phytoplankton in the seawater of the Arabian Gulf (Figure 1) include diverse groups such as cyanobacteria (Cyanophyta), microscopic green algae (Chlorophyta), diatoms (Gyrista), dinoflagellates (Myzozoa), and other groups like coccolithophores and cryptophytes. Early studies recorded 224 diatom taxa in the Arabian Gulf around the Qatar Peninsula, highlighting diatoms as a prominent group among these phytoplankton [5,6]. Diatoms form a large group of phytoplankton primarily found in oceans, waterways, and soil, constituting a significant portion of the Earth's biomass, and producing a substantial amount of the oxygen generated by photosynthesis.

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Figure 1. Map of the Arabian Gulf region and its bordering countries, adapted from Figure 1 [4].

Most diatom species (about 75%) inhabit shallow or deep waters in seas and oceans. Approximately 50% of the diatom population in the oceans belong to the genera *Amphora*, *Chaetoceros*, *Coscinodiscus*, *Diploneis*, *Navicula*, *Nitzschia*, *Rhizosolenia*, and *Surirella*. Additionally, a notable number of littoral species (25%), which are benthic, are observed among planktonic forms. Fifteen diatom species are perennial, including *Chaetoceros coarctatus*, *Climacodium frauenfeldianum*, *Coscinodiscus radiatus*, *Guinardia flaccida*, *Hemiaulus sinensis*, *H. membranaceus*, *Leptocylindrus danicus*, *Rhizosolenia alata, R. bergonii*, *R. calcar-avis*, *R. clevei*, *R. imbricata*, *R. indica*, *R. stolterfothii*, *Skeletonema costatum*, and *Thalassionema nitzschioides* [5,7,8].

1.1. Roles Played by Diatoms in the Marine Ecosystem

While oil and gas production has significantly enhanced human lifestyles, their negative environmental impacts on human health are equally prominent and have been well-documented over the last two decades. Diatoms, however, offer a sustainable and nature-based solution to several environmental challenges [9,10]. They serve as bioindicators of metal toxicity and have applications in biomineralization, the synthesis of biomaterials, and waste degradation. Recently, B-Béres et al. [11] highlighted the diverse roles diatoms play in promoting human well-being. In addition to their significant contribution to carbon sequestration—by converting carbon dioxide into complex organic molecules through photosynthesis—diatoms play a pivotal role in the degradation, speciation, and detoxification of chemical waste and hazardous metals in polluted environments. These functions are essential for preserving marine ecosystems and provide both direct and indirect benefits to human societies. The following is a brief overview of the roles of diatoms in marine and freshwater environments.

(a) Diatoms possess several photosynthetic pigments, including chlorophylls and carotenoids. Chlorophylls *a* and *c* capture light energy primarily in the blue and red regions of the electromagnetic spectrum. The carotenoids, which include fucoxanthin, β-carotene, xanthophylls, diadinoxanthin,

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diatoxanthin, violaxanthin, and zeaxanthin, complement this process. Fucoxanthin absorbs light in the green region, bridging the gap left by chlorophylls. These pigments play a crucial role in photosynthesis by facilitating oxygen evolution and carbon dioxide uptake, processes essential for maintaining life and ecological balance in aquatic environments. However, pollution in marine and freshwater ecosystems, particularly from oil and gas activities, can significantly disrupt photosynthesis. For example, research on the diatom *Nitzschia palea* has shown that such pollution negatively impacts photosynthetic rates [12]. Subsequent investigations on some species of *Thalassiosira* have explored the proteins associated with the structural and molecular electron transport system of photosynthesis. These studies revealed that pollution-induced disruptions deprive the cells of energy and carbon necessary for growth [13]. Notably, the role of diatoms in converting CO_2 into O_2 has been demonstrated in numerous studies. Additionally, these phytoplankton serve as a primary food source for zooplankton, molluscs, and fish.

(b) Nutrient cycling is another critical role played by diatoms in marine and freshwater environments [11]. It is worth noting that, through photosynthesis, diatoms produce significant amounts of organic material that sustain marine ecosystems and contribute to the Earth's carbon cycle. Additionally, they play major roles in the biogeochemical cycling of other nutrients, such as nitrogen and silicon [4].

(c) Climate change mitigation is an important role played by diatoms, particularly through their ability to sequester CO_2. Diatoms remove CO_2 from the atmosphere and transfer carbon to the deep sea when they die and sink. However, anthropogenic activities and warming oceans may reduce diatom diversity, exacerbating CO_2 levels in the atmosphere. These negative consequences could potentially be mitigated through industrial carbon sequestration. Furthermore, secondary metabolites produced by diatoms have various valuable applications, including the production of lipids, omega-3 fatty acids, pigments, and antioxidants [1,15]. Recent reports [16] have also suggested that diatoms are a promising feedstock for developing bioactive agents, such as carotenoids, functional foods, bioactive pharmaceutical, cosmetics, and biofuels [4,17].

d. The biogeochemical cycle refers to the movement and transformation of chemical elements and compounds among living organisms, the atmosphere, and the Earth's crust. During the last decade, studies have highlighted the critical role of diatoms as major contributors to biogeochemical cycles involving such elements as carbon, nitrogen, and silicon. Their abundance, diversity, and contributions to these cycles likely enhance the export of these elements to the deep ocean. This process may play a significant role in sustaining fossil fuel reserves [14,18].

(e) Diatoms are among three groups of microalgae, i.e., cyanobacteria, diatoms, and dinoflagellates, which produce sporadic blooms that occur during various seasons [14,19,20] (Figure 2).

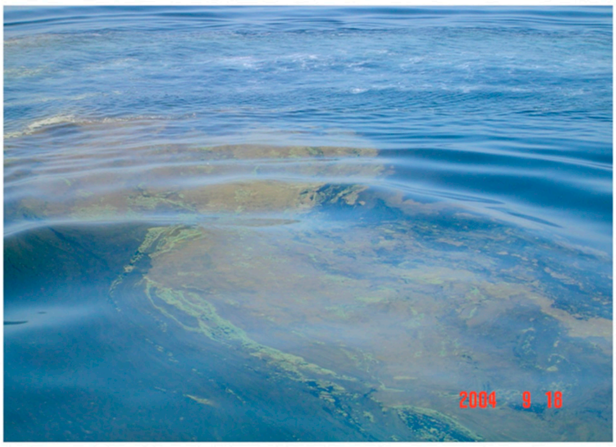

Figure 2. A bloom resulting from a substantial increase in the populations of cyanobacteria, diatoms, and dinoflagellates (Figure S1) [4].

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For example, diatoms are present during both the summer [21] and winter monsoons [22]. Recent investigations [23] have shown that certain diatoms, such as *Coscinodiscus* and *Rhizosolenia*, both found in the Arabian Gulf along the coastline of Qatar, are major contributors to bloom formation and dominate the flux of biogenic silica [24]. The impact of these blooms on marine life was recently examined in detail by Al-Thani and Yasseen [4]. Two negative effects were highlighted: amnesic shellfish poisoning caused by *Pseudo-nitzschia* spp., whose presence in the Arabian Gulf and Sea of Oman requires confirmation, and damage to fish and invertebrates caused by non-toxic species such as *Chaetoceros* spp., which can harm or clog gills. Interestingly, 34 species within the genus *Chaetoceros* have been shown to play diverse roles in phycoremediation, heavy metal remediation, and the production of bioactive agents. Notably, harmful algal blooms (HABs) can produce toxins that pose risks to humans and marine animals, including fish (Figure 3) [25]. These toxins include Beta-N-methylamino-L-alanine (BMAA), a non-protein amino acid that can cause neurotoxicity and is produced by diatoms such as *Achnanthes* sp. and *Thalassiosira* sp. Domoic acid (DA), a heterocyclic amino acid that causes amnesic shellfish poisoning, is produced by species in the *Pseudo-nitzschia* genus. Oxylipins, secondary metabolites produced by various diatom species, are also notable, as are iso-domoic acid D (in multiple forms) and iso-domoic acid C. Moreover, other toxins, such as brevetoxin, azaspiracid, ciguatoxins, and okadaic acid, are found in many diatom species. These toxins can lead to a range of symptoms, including coughing, difficulty breathing, paralysis, rashes, seizures, skin irritation, uncoordinated movements, vomiting, and wheezing. In severe cases, exposure may result in death [26,27].

(f) The formation of mutualistic interactions with bacteria and archaea, and these activities might help both to survive the harsh environments. Many examples of mutualistic interactions between diatoms and bacteria exist, including exchange of metabolites, protection, detoxification, obtaining metals, growth of both diatoms and bacteria, nutrient availability, and cultivation conditions [28–30].

Figure 3. Fish kills: A negative impact of cyanobacteria, diatom, and dinoflagellate blooms on marine life (Figure S1) [4].

2. General Findings on Diatom Research in the Arabian Gulf Region

2.1. Phycoremediation and Its Bioactive Applications

Diatoms are microalgae with diverse abilities, making them suitable for multiple applications, such as the production of various bioactive agents and the remediation of pollutants from industries, including agriculture, oil and gas, and other anthropogenic sources [2]. Considering their roles in phycoremediation and industrial applications, the primary aspects to discuss include wastewater treatment and the production of various bioactive agents, such as biofuels, biofertilizers, nutritional supplements, and pharmaceuticals for disease treatment [31]. These applications involve eicosapentaenoic acid (EPA), docosahexaenoic acid (DHA), and pigments such as fucoxanthin [32]. EPA and DHA can influence various aspects of cardiovascular function, including inflammation, peripheral artery disease, major coronary events, and anticoagulation. Additionally, these compounds have shown promising results in prevention strategies, weight management, and improving cognitive function in individuals with very mild Alzheimer's disease.

Approximately 70 genera of diatoms, encompassing about 224 species, have been reported in the Arabian Gulf, based on studies of diatoms around the Qatari coastline and other Arabian Gulf States, as shown in Table 1 [5,33,34]. Despite the ecological importance of these diatom species, limited research has been published on their roles in phycoremediation and the production of bioactive agents. These genera have the potential to address various environmental, ecological, economic, and health challenges, warranting thorough investigation into their applications in these areas. Notably, some genera have already demonstrated efficiency in certain domains. For instance, *Amphora* produces antioxidants, while *Bacillaria* plays a role in the degradation, speciation, and detoxification of chemical waste, as well as in the prevention of heavy metal toxicity. *Bacteriastrum* has shown effectiveness in wastewater remediation, and *Bellerochea* produces nutritional agents and bioactive molecules that promote the health and survival of aquatic species, such as fish, bivalves, and shrimp. *Biddulphia* produces bioactive compounds as well as nutritional agents, while *Campylodiscus* reduces the toxicity of heavy metals that might be used in improving water quality. *Cerataulina*, activates defense mechanisms through production of antioxidants and metal chelators. *Chaetoceros* has shown the ability to remediate heavy metals and may synthesize silver nanoparticles (Ag NPs) with therapeutic potential against pathogenic microbes, including bacteria, viruses, and fungi, as well as applications in biosensing. Notably, at least 34 species of this diatom play a multifaceted role in remediating petroleum hydrocarbons and heavy metals while also producing bioactive agents; for example, they may produce enzymes such as oxygenases and lipases, which facilitate the degradation of petroleum hydrocarbons.

Table 1. Diatom species recorded in the Arabian Gulf around the Qatari peninsula and their possible role in phycoremediation of industrial pollution [2,35–37].

Genus	No. of species	Remediation of organic and inorganic components	Remarks and other possible roles	References**
Achnanthes	1	*	Needs testing; some roles have been reported	[38,39]
Actinoptychus	1	*	Needs testing; shows antibacterial activity	[40,41]
Amphiprora	4	*	Needs testing; biofuels and oil production have been reported	[42–44]
Amphora	7	*	Needs testing; produces bioactive compounds such as antioxidants, and	[44–46]

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			against toxicities of some living organisms	
Asterolampra	1	*	Needs testing; might remediate heavy metals	[44,47,48]
Asteromphalus	3	*	Needs testing; might remediate heavy metals	[4,44,49,50]
Auliscus	1	*	Needs testing; might remediate heavy metals	[2,35,51,52]
Bacillaria	1	*	Needs more investigation; degradation, speciation, and detoxification of chemical wastes and hazardous metals	[2,35,53]
Bacteriastrum	6	*	Needs more investigation; possesses sustainable metabolic efficacy to remediate diverse wastewater	[2,35,54]
Bellerochea	1	*	More studies are needed; produces nutritional agents, bioactive molecules lipids, polysaccharides, proteins, pigments, vitamins, bio-pharmacological activities, and nutraceutical applications; promotes the health and survival of aquatic species like fish, bivalves, and shrimp	[2,35,55–57]
Biddulphia	6	*	More studies are needed as many bioactive compounds are produced and nutritional values were reported	[2,35,56,58]
Campylodiscus	3	*	More studies are needed; can reduce the toxicity of heavy metals by enhancing extracellular adsorption; might be used in improving water quality	[2,35,41,59]
Cerataulina	1	*	Needs more investigation; activates defense mechanisms such as the production of antioxidants and metal chelators	[2,35,60]
Chaetoceros	34	*	Variety of applications and silver nanoparticles (Ag NP) that hold immense therapeutic potential against pathogenic microbes; other applications of a least toxicity and biodegradable nature; remediate heavy metals such as Cd, Cu, and Pb	[61–63]
Climacodium	1	*	More investigation needed; reduces heavy metal toxicity, wastewater	[2. 35, 41, 57, 64]

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			treatment, biomass can be turned into biofuels, biofertilizers, nutritional supplements for animal production;used for pharmaceutical applications	
Climacosphenia	1	*	Further investigation is needed, as it might identify various peptides that facilitate the accumulation of heavy metals and contribute to mechanisms that defend against them	[52,65]

Genus	No. of species	Remediation of organic and inorganic components	Remarks and other possible roles	References**
Cocconeis	1	*	Survive polluted seawater and removal of heavy metals; pollution bioindicator; production of some important bioactive agents at various aspects, such as energy, pharmaceuticals, and aquaculture feedstocks	[57,66–68]
Corethron	2	*	More investigation is needed; could remove heavy metals by adsorption and bioaccumulation; bioindicator for heavy metal pollution	[44,59,60]
Coscinodiscus	10	*	Needs testing; possible roles in maintaining marine ecosystems; might have direct and indirect benefits for humans	[11,41]
Coscinosira	1	*	Needs testing; might survive polluted seawater and remediate and remove heavy metals, pollution bioindicators; production of some important bioactive agents for various aspects, such as energy, pharmaceuticals, and aquaculture feedstocks	[41,57,67,69]

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Cyclotella	2	Uptake petroleum hydrocarbons and heavy metals	More research needed; accumulates titanium, detoxication of heavy metals	[70,71]
Cylindrotheca	1	*	Needs more investigation; one species, *C. closterium*, proved suitable for sediment heavy metal toxicity tests	[41,72,73]
Cymbella	1	*	More research needed; can be used to remediate some pollutants in sewage sludge such as triclosan	[44,74,75]
Dactyliosolen	1	*	Needs confirmation; possible removal of heavy metals by adsorption, and bioaccumulation; bioindicator for heavy metal pollution	[59,65]
Diatoma	1	*	Needs confirmation; possible role in heavy metal remediation	[65,68]
Diploneis	9	*	Needs testing; possible remediation candidate for heavy metals	[44]
Ditylum	2	*	Needs testing; possible heavy metal remediation	[41]
Epithemia	1	*	Needs testing and more investigation	[65]
Ethmodiscus	1	*	Needs testing and more investigation	[41, 65]
Eucampia	2	*	Needs testing and more investigation	[41,65]
Fragilaria	4	*	Needs testing; benthic diatoms are sensitive to sediment contamination; can be used to monito, resist, and accumulate Cd and Zn	[68,76,77]

Genus	No. of species	Remediation of organic and inorganic components	Remarks and other possible roles	References**
Glyphodesmis	1	*	Needs testing and more investigation	[41,78]

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Gossleriella	1	*	Requires further testing and investigation; acts as smart nanocontainers capable of adsorbing various trace metals, dyes, polymers, and drugs, some of which are hazardous to human and aquatic life	[57,79,80]
Grammatophora	1	*	Needs testing and more investigation; may play a role in degradation, speciation, and detoxification of chemical waste and hazardous metals	[2,35,65]
Guinardia	1	*	Needs testing and more investigation; *can reduce the toxicity of heavy metals* by enhancing extracellular adsorption	[2,35,65]
Gyrosigma	2	Promising role in phyco-remediation and as a pollution indicator	More investigation is needed; can be used as agent for wastewater treatment and biofuels research	[81–84]
Hemiaulus	3	*	Further investigation is needed into possible role in metal pollution and its impact on essential processes, such as nitrogen fixation, food production, and climate change mitigation through CO_2 utilization	[59,85,86]
Hemidiscus	2	*	Needs more investigation; possible remediation of heavy metals	[2, 35, 74,]
Hydrosilicon	1	* Possible role in industrial effluents	Needs more investigation; phycoremediation proved in some diatoms	[74,80]
Lauderia	1	*	Needs more investigation; phycoremediation of heavy metals is possible	[2,35,65]
Leptocylindrus	1	*	Needs a proof; possible role in heavy metal remediation	[2,35,59,87]

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		Possible candidate for phycoremediation of industrial effluents		
Licmophora	2	Possible candidate for phycoremediation	Needs testing; possible roles in maintaining marine ecosystems	[11,74,88]
Mastogloia	1	*	More investigation is needed; possible detoxification of chemical wastes and hazardous *metals* from polluted sites; might remediate heavy metals	[2,35,65,89]
Melosira	1	*	More investigation is needed; possible role in heavy metal remediation	[68,74]
Navicula	8	Remediates petroleum hydrocarbons	More investigation is needed; proved efficient in removing Cd, Cu, and Zn from polluted sites; production of biofuels is very possible	[42,74,76,90]
Nitzschia	14	Remediates petroleum hydrocarbons	More investigation is needed; could remediate heavy metals and dyes	[2,35,36,74,91]

Genus	No. of species	Remediation of organic and inorganic components	Remarks and other possible roles	References**
Paralia	1	*	Needs testing; indicator of pollution; could be *potent metal bioremediation agent*	[2,35–37]
Pinnularia	1	*	Needs more testing; can remediate various pollutants, such as heavy metals, dyes, and hydrocarbons detected in wastewater	[37,80]
Plagiogramma	1	*	Needs testing; *increases the production of* extracellular polymeric substances *(EPS)#*, which bind to the metal nanoparticles outside the cell	[37,59]

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Planktoniella	1	*	Needs more investigation; might assimilate heavy metals, tolerate heavy metals; biological pollution indicator of water quality; efficient model in assimilation and detoxification of toxic metal ions	[92–95]
Pleurosigma	9	*	Needs more investigation; possible heavy metal remediation	[2,35,41,96]
Podocystis	1	*	Needs more investigation; might survive polluted seawater and remediate heavy metals; produces some bioactive agents in various aspects of energy, pharmaceuticals, and aquaculture feedstocks	[69,97,98]
Podosira	1	*	Needs more investigation; possible role in heavy metal remediation	[2,35,49]
Rhabdonema	2	*	Needs more investigation; possible role in heavy metal remediation	[41,59,97]
Raphoneis	1	*	Needs more investigation; might activate defense mechanisms, such as the production of antioxidants and/or metal chelators; possible metal remediation	[60,96,99]
Rhizosolenia	22	*	Needs further investigation; extracts of these species might have antibacterial activity against human pathogens	[37,68,100]
Rhoicosigma	1	*	Needs more investigation; might remediate heavy metals	[67,101,102]
Schroederella	1	*	Needs testing; can reduce the toxicity of heavy metals; possible biosensing pollution; might be ideal bioindicators	[2,35,41,80]

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Skeletonema	1	*	Needs further investigation; contains some important bioactive compounds, such as vitamins, polyunsaturated fatty acids, polysaccharides, and pigments; biological indicators; can reduce the toxicity of heavy metals	[44,94,103]

Genus	No. of species	Remediation of organic and inorganic components	Remarks and other possible roles	References**
Stauroneis	2	*	Needs more investigation; might remediate heavy metals; could increase the production of EPS# to bind metal nanoparticles outside the cell	[44,49,59]
Streptotheca	1	*	Needs more investigation; can reduce the toxicity of heavy metals by enhancing extracellular adsorption	[2,35,41]
Striatella	2	*	Needs more investigation; might play a role in detoxification of heavy metals	[49,65,67,101]
Surirella.	8	*	Needs more investigation; might remediate heavy metals	[44,80]
Synedra	3	* Remediate hydrophobic hydrocarbons from aquatic systems	More investigation is needed; might produce potent metal bioremediation	[2,35,104]
Thalassionema	1	*	Needs more investigation; might remediate heavy metals	[2,35,44]
Thalassiosira	2	Degrade and remediate petroleum hydrocarbons	More investigation is needed to study the phycoremediation of petroleum hydrocarbons of oil and gas activities; has been used for genetic	[13,105–107]

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			manipulation to study many physiological activities including silica biomineralization; Possible biofuel production	
Thalassiothrix	4	*	Needs further investigation; might help to maintain and stabilize heavy metals, and increase the production of EPS	[44,59,97]
Trachyneis	1	Little work has been done	Needs testing and investigation; might be useful for heavy metal remediation and bioindicators	[98,108]
Triceratium	5	*	Needs more investigation; might offer several advantages as potent metal bioremediation agent	[2,35,44,49]
Tropidoneis	1	*	Further investigation is needed as it might be capable of heavy metal remediation and could increase the production of EPS, boosting resistance against various environmental stresses, including pollution	[41,59,109]

*Possible role in remediation of petroleum hydrocarbons. **Not all the references were related to diatoms, but they provide some comparability between microorganisms and diatoms. #EPS: Extracellular Polymeric Substance refers to a complex mixture of high-molecular-weight compounds secreted by microorganisms, primarily in biofilms, and is described as a glue-like substance produced by microbes, predominantly composed of sugar-based building blocks.

Additionally, *Chaetoceros* along with others, secrete extracellular polymeric substances (EPS) that enhance the emulsification of hydrocarbons [110]. Moreover, it may exist in symbiosis with hydrocarbonoclastic bacteria like *Pseudomonas* and *Alcanivorax*, significantly improving the efficiency of hydrocarbon biodegradation [111]. In the context of heavy metal remediation, *Chaetoceros* has demonstrated potential in accumulating and biosorbing heavy metals such as cadmium (Cd), lead (Pb), arsenic (As), and mercury (Hg), which are commonly present in oil and gas components [112–114]. Further research is needed to clarify the roles of *Chaetoceros* and other diatom species in seawater around the peninsula of Qatar. *Climacodium*, reduces heavy metal toxicity, and plays numerous roles in treating wastewater; it produces bioactive agents, such as biofuels, biofertilizers, and nutritional supplements. Furthermore, it has pharmaceutical applications and is a good option for wastewater treatment. Biomass can be converted into biofuels, biofertilizers, nutritional supplements for animal

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production, and pharmaceutical products. *Climacophobia* might produce various peptides that help in the remediation of heavy metals and build a defense mechanism against them [51]. *Cocconeis* produces bioactive agents with applications in various fields, including energy, pharmaceuticals, and aquaculture feedstocks. Moreover, this diatom has proven its ability to survive in polluted seawater, remove heavy metals, and serve as a pollution bioindicator. *Corethron*, can remove heavy metals by adsorption, and bioaccumulation, and can be considered as bioindicator. *Coscinosira* produces bioactive agents, survives polluted seawater, remediates heavy metals, and is a pollution bioindicator. *Cyclotella*-accumulates titanium and provides detoxication of heavy metals. *Cylindrotheca*, particularly the species *C. closterium*, can be used to test sediment for heavy metals and toxicity, while *Cymbella*—can be used to remediate certain pollutants in sewage sludge, such as triclosan. Notably, a total of 11 metabolites have been identified in *Cymbella*, with proposed degradation pathways. These pathways include hydroxylation, methylation, dechlorination, amino acid conjugation, and glucuronidation, which contribute to the transformative reactions of triclosan. These reactions produce biologically active products (e.g., methyl triclosan) and conjugation products (e.g., glucuronide or oxaloacetic acid-conjugated triclosan) that may play a role in the detoxification mechanism of triclosan.

Dactyliosolen might remove heavy metals by adsorption and bioaccumulation and can be used as bioindicator for heavy metal pollution. *Gossleriella*, acts as a nanocontainer capable of adsorbing heavy metals, dyes, polymers, and drugs, some of which are hazardous to human and aquatic life. *Gyrosigma*-can be used to treat wastewater and possible biofuel production. *Hemiaulus* may play a role in remediation of heavy metals and other essential processes, such as nitrogen fixation, food production, and mitigation of climate change through CO_2 utilization in photosynthesis. *Mastogloia* might have a role in the detoxification of chemical waste, including hazardous metals. *Navicula* has been proven efficient in removing some heavy metals, such as Cd, Cu, and Zn. *Paralia* has been used as an indicator of pollution and metal bioremediation agents. *Pinnularia* can remediate various pollutants such as heavy metals, and dyes, and acts as a bioindicator for hydrocarbons in the wastewater. The presence of *Plagiogramma* may increase the production of EPS, which binds to the metal nanoparticles outside the cell, while *Planktoniella* might tolerate, assimilate, and detoxify heavy metals and biological pollution. *Podocystis* might survive polluted seawater and remediate heavy metals, and produces some bioactive agents in various aspects of energy, pharmaceuticals, and aquaculture feedstocks. The presence of *Raphoneis* activates defense mechanisms, which include the production of antioxidants and metal chelators and possible metal remediation. Extracts of the diatom *Rhizosolenia* might provide antibacterial activity against human pathogens. *Schroederella* can reduce the toxicity of heavy metals, possible biosensing pollution, and might be an ideal bioindicator. *Thalassiosira* is a genus of centric diatoms with two species identified in Qatar. However, one hundred species have been found in both marine and freshwater environments around the world. This diatom has gained particular significance as the first marine phytoplankton to have its genome sequenced. Moreover, species of *Thalassiosira* have also been pivotal in the development of methods for genetic manipulation of diatoms and the study of silica biomineralization. Its genome revealed novel genes involved in intracellular trafficking and metabolism in diatoms. Consequently, it has become a key model organism for genetic manipulation to study many physiological activities including silica biomineralization, possible biofuel production, degraded petroleum hydrocarbons, and possible remediating petroleum hydrocarbons of oil and gas activities.

Table 2 presents the production and applications of various substances, including activities, such as antioxidant and antibacterial production, biofuel generation, the use of bioindicators, production of dyes and exopolysaccharides (EPS-natural polymers produced by microorganisms), heavy metal remediation (detoxification, remediation, and testing), as well as applications in nutrition, pharmaceuticals, and the phycoremediation of crude oil, gas components, and industrial wastewater (IWW).

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2.2. Pathways for Phycoremediation of Petroleum Hydrocarbons Using Diatom

Petroleum hydrocarbons constitute approximately 50-98% of the crude oil and gas volume found in marine habitats, typically introduced through spills and accidents during military exercises and/or transportation. These hydrocarbons are primarily classified into alkanes, cycloalkanes, mono-aromatic hydrocarbons, and polycyclic aromatic hydrocarbons. More details about these components were reported in many studies [3,4,113,115,116]. Eukaryotic microalgae, such as diatoms, are capable of metabolizing petroleum hydrocarbons as sources of carbon and energy. However, diatoms alone may lack the complete enzymatic machinery required to fully degrade petroleum hydrocarbons. Their associated bacteria play crucial roles in addressing various environmental issues [28], including the remediation of heavy metals and the breakdown of the organic components of petroleum hydrocarbons (PHCs). These bacteria, often harbored by diatoms, possess the ability to degrade PHCs, and some strains can even thrive in the presence of crude oil.

Table 2. Potential bioactive applications of diatoms from the Arabian Gulf near Qatar.

Production and applications	Genera	Remarks*
Antibacterial	*Actinoptychus, Chaetoceros, Rhizosolenia*	*Chaetoceros* comprises about 34 species that require modern research to develop antibacterial products
Antioxidants	*Amphora, Cerataulina, Raphoneis*	Some chemicals are produced under extreme stress conditions, such as those caused by pollution from oil and gas activities. These chemicals are unstable and can damage cell membranes and other structures. Diatoms under such conditions may produce antioxidants as a protective response
Aquaculture feedstocks	*Cocconeis, Coscinosira, Podocystis*	Aquaculture feedstocks are raw materials used to feed aquatic organisms in aquaculture, including fish, shellfish, and aquatic plants
Biofuels	*Amphiprora, Climacodium, Cocconeis, Coscinosira, Guinardia, Gyrosigma, Navicula, Podocystis*	Biofuels are fuels made from renewable biological sources. Many types of biofuels are known, including ethanol, biodiesel, biogas, biojet kerosene, and sustainable aviation fuel
Bioindicators	*Cocconeis, Corethron, Coscinosira, Dactyliosolen, Fragilaria, Paralia, Planktoniella, Schroederella, Skeletonema, Trachyneis*	A bioindicator is a living organism that reflects the health of an environment. Bioindicators can exhibit changes in various aspects, such as physiology, chemistry, or behavior. Phytoplankton responds

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		quickly to environmental changes, making it an effective indicator of water pollution
Dyes	*Nitzschia, Pinnularia*	Dyes refer to a variety of pigments and related components, such as carotenoids, chlorophylls, polyphenols, and marennine, a blue-green pigment produced by certain diatoms
EPS production	*Plagiogramma, Stauroneis, Thalassiothrix, Tropidoneis*	EPS, or extracellular polymeric substances, are produced by microorganisms and have potential applications in wastewater sludge treatment
Phycoremediation: phyto-mining (heavy metals), and green liver model (degradation of organic compounds)	*Asterolampra, Asteromphalus, Auliscus, Bacillaria, Bacteriastrum, Campylodiscus, Cerataulina, Climacodium, Climacosphenia, Cocconeis, Corethron, Coscinosira, Cyclotella (HM: Ti), Cylindrotheca, Cymbella, Dactyliosolen, Diatoma, Diploneis, Ditylum, Gossleriella, Grammatophora, Guinardia, Gyrosigm, Hemiaulus, Hemidiscus, Hydrosilicon, Lauderia, Mastogloia, Navicula, Nitzschia, Paralia, Pinnularia, Planktoniella, Podocystis, Raphoneis, Schroederella, Streptotheca, Striatella, Synedra, Thalassionema, Thalassiothrix, Trachyneis, Triceratium, Tropidoneis*	Most diatoms can remediate heavy metals, a topic that requires in-depth research to understand their roles in polluted seawater. The remediation of heavy metals includes detoxification and testing, while organic compounds from oil and gas activities primarily involve petroleum hydrocarbons

Production and applications	**Genera**	**Remarks***
Nutritional	*Bellerochea, Biddulphia, Climacodium*	Diatoms are among the most sustainable sources of nutrients for humans. They are a major source of oxygen, serve as a key food source for higher organisms, and remove significant amounts of CO_2 while synthesizing various metabolites. Diatoms produce a wide range of primary metabolites, including proteins, peptides, fatty acids, sterols, and polysaccharides. Their secondary metabolites include carotenoids, polyphenols, high-value molecules, and silica nanoparticles

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Pharmaceuticals	*Bellerochea, Climacodium, Cocconeis, Coscinosira, Podocystis*	Chrysolaminarin, eicosapentaenoic acid, docosahexaenoic acid, omega fatty acids, fucoxanthin, and biosilica are all substances with potential anticancer properties
Various applications	*Amphora* (against toxicities of other organisms), *Chaetoceros* (various applications), *Climacodium* (biofertilizers), *Cyclotella* (accumulates titanium), *Gossleriella* (smart nanocontainer for various agents), *Hemiaulus* (nitrogen fixation, food production, climate change), *Skeletonema* (production of vitamins, pigments, polyunsaturated fatty acids), *Tropidoneis* (resistant against pollution)	Several roles and applications have been reported

*Table 1 contains all the required references.

As bioremediation tools, diatoms are particularly well-suited for this role because they are commonly found in marine environments contaminated with PHCs. They can utilize these hydrocarbons as sources of energy and carbon, making them effective agents in polluted ecosystems. Furthermore, diatoms secrete exopolysaccharides (EPS) into their surroundings, which serve as biosurfactants, enhancing the degradation process and aiding in the cleanup of contaminated environments, such as oil spills or polluted water, by aiding the natural degradation of harmful substances [37,117]. Among the diatom species found in the Arabian Gulf, *Navicula* sp., *Nitzschia* sp., *Skeletonema costatum*, *Synedra* sp., and *Thalassiosira* sp. have demonstrated efficiency in metabolizing some of these components, such as oxidizing naphthalene into ethyl acetate-soluble and water-soluble metabolites. Notably, studies by Cerniglia and colleagues and others [37,79,118] revealed that diatoms can produce enzymes that degrade petroleum hydrocarbons into less toxic compounds in seawater. There are numerous enzymes that might be involved in the degradation of these organic components of petroleum hydrocarbons in various microorganisms [119]. These enzymes include:

a. Alkane 1-monooxygenase (EC 1.14.15.3): This enzyme catalyzes chemical reactions such as:

$$\text{Alkane} + \text{Reduced rubredoxin*} + O_2 \overset{E}{\longleftrightarrow} \text{Primary alcohol} + \text{Oxidized rubredoxin} + H_2O$$

Alkane 1-monooxygenase (E) utilizes alkanes as substrates, specifically compounds containing 6 to 22 carbon atoms. Rubredoxins are small iron-containing proteins that function as electron carriers in biological systems; they are involved in reducing superoxide in some anaerobic bacteria and possibly in other microorganisms. While this enzyme might not be present in diatoms, the latter can harbor bacteria that are known to degrade hydrocarbons, and strains of these bacteria can grow in the presence of crude oil. Bioremediation of petroleum hydrocarbons using diatoms and bacteria is an eco-friendly, cost-effective, and non-invasive way to clean up contamination resulting from these compounds, and this method proved faster than using native plants on the land [37,65,89]. Diatoms and bacteria can collaborate to degrade petroleum hydrocarbons, as both groups are commonly found in oil spills. Notably, the degradation of alkane compounds using plants and their associated microorganisms was recently reported [3,113].

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b. Alcohol dehydrogenase (EC 1.1.1.1): The primary alcohols could be further metabolized to end with acetyl Co-A; a metabolite that enters the Krebs cycle and biosynthesis of fatty acids [115,120]. This enzyme catalyzes the oxidation of alcohols to aldehydes or ketones:

$$CH_3CH_2OH \text{ (Alcohol)} + NAD^+ \xrightarrow{E} CH_3CHO \text{ (acetaldehyde)} + NADH + H^+$$ (reversible redox reaction)

This enzyme is found in the bacteria in seawater including those associated with diatoms.

c. Cyclohexanol-dehydrogenase (EC 1.1.1.245): This enzyme catalyzes the chemical reaction:

$$\text{Cyclohexanol} + NAD^+ \xrightarrow{E} \text{Cyclohexanone} + NADH + H^+$$

N.B. (1): Cyclohexanol is an organic compound with the formula $HOCH\ (CH_2)_5$. It is produced industrially from phenol and cyclohexane and can also be derived from petroleum oil and volcanic gases. Cyclohexanol is present in cigarette smoke and serves as a precursor to nylon.

N.B. (2): Cyclohexanone is further metabolized by bacteria, which open the ring through the action of the enzyme cyclohexanone oxygenase (or cyclohexanone monooxygenase). These bacteria might be associated with diatoms. The outcome of this reaction is adipic acid.

Cyclohexanone, a six-membered cyclic ketone, undergoes oxidative metabolism to adipic acid, a six-carbon dicarboxylic acid. These reactions involve enzymatic oxidations catalyzed by enzymes such as monooxygenases or dehydrogenases, producing intermediates such as cyclohexanol or 6-hydroxyhexanoic acid. Further oxidation results in the cleavage of the ring structure and the formation of adipic acid. Once adipic acid is formed, it can be further metabolized in diatoms or other marine organisms through the beta-oxidation pathway. This pathway converts adipic acid into adipoyl-CoA, which is subsequently degraded via β-oxidation to produce acetyl-CoA, a key intermediate in energy production and the biosynthesis of fatty acids [121,122].

d. Methane monooxygenase (EC 1.14.13.25): This enzyme catalyzes the oxidation of methane into methanol and is found in methanotrophic bacteria.

$$CH_4 + O_2 + NAD(P)^+ + H^+ \longrightarrow CH_3OH + NAD\ (P)^+ + H_2O$$

Further metabolism of methanol in these bacteria can be through a variety of reactions. These include anaerobic methylotrophs, aerobes, the Calvin cycle, the dissimilatory hexulose phosphate cycle, the methanol methyltransferase system, and methanogenic methanol conversion. The complete oxidation of primary alcohols produces acids. Notably, the product of methanol metabolism is formic acid, which might cause toxicity, blindness, and even death. Formic acid is further metabolized to CO_2 [123]. More details about the consequences of CO_2 formation after formic acid metabolism in bacteria, and diatoms are discussed in many studies [124–126].

Alkane (C_nH_{2n+2}) in general can be degraded by many microorganisms to produce alcohols that can be further metabolized to produce acetyl-Co. A, which can contribute in metabolic ways to the Krebs cycle and fatty acids [113,127,128].

e. Cyclohexanone 1,2 monooxygenase (EC 1.14.13.22): This is a bacterial flavoenzyme whose main function in the cell is to catalyze the conversion of cyclohexanone into ε-caprolactone, a key step in the pathway for the biodegradation of cyclohexanol (see the enzyme Cyclohexanol-dehydrogenase). This compound is typically found in many products that treat animals for pests, and other products, such as nylon, lacquers, paints, varnishes, and paint removers. Notably, cyclohexane occurs naturally in petroleum crude oil and in volcanic gases [129,130].

f. Cytochrome P450s (E.C. 1.14.-.-): These enzymes belong to the monooxygenase superfamily and are a ubiquitous family of heme-containing proteins. They primarily function as catalysts in the oxidation of organic compounds, including petroleum hydrocarbons and drugs. The common monooxygenation reaction involves the insertion of an oxygen atom into an organic compound:

$$O_2 + RH + NAPDH + H^+ \longrightarrow ROH \text{ (alcohol)} + H_2O + \underline{NADP^+}$$

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The resulting ROH (alcohol) is further metabolized to form acids, which can contribute to various metabolic pathways, producing energy and building molecules [131].

g. Flavin-binding monooxygenase (EC 1.14.13): It is a subfamily of class B external flavoprotein monooxygenases, which belong to the family of monooxygenase oxidoreductases. These are found in many living organisms, such as fungi, yeast, plants, mammals, and bacteria. Flavin-binding monooxygenases (FMOs) catalyze a variety of reactions, including hydroxylation, epoxidation, Baeyer-Villiger oxidation, oxidative decarboxylation, halogenation, and sulfur oxidation [132,133].

h. Catechol dioxygenase (catechol 1,2-dioxygenase: EC 1.13.11.1) and (catechol 2,3-dioxygenase: EC 1.13.11.2): This enzyme catalyzes the catechol to form *cis,cis*-muconic acid from catechol as shown in the reaction:

$$\text{Catechol} \xrightarrow{\quad E \quad} \textit{cis,cis}\text{-muconic acid}$$

Then, **cis, cis-muconic acid** can be converted to **trans, trans-muconic acid** through isomerization, and the latter can be further converted to **fumaric acid** via electrocatalysis. Fumaric acid serves as a precursor for various organic acids and amino acids. Organic acids derived from fumaric acid include **malate** and **oxaloacetate**, while amino acids such as **aspartate, phenylalanine,** and **tyrosine** can be synthesized through amino acid interconversions. Therefore, some organic components of petroleum hydrocarbons can be converted to useful metabolites such as acetyl Co. A and fumaric acid that can contribute to the metabolic activities of living organisms such as diatoms [113,128,134,135].

3. Challenges and Future Work

A review of published studies from the Arabian Gulf countries, including Iran and Iraq, reveals that few studies have focused on the role of diatoms in remediating polluted seawater and freshwater ecosystems, particularly concerning organic components [37]. The limited progress in utilizing diatoms for the phycoremediation of petroleum hydrocarbons can be attributed to several challenges and constraints, including: (a) Complexity and toxicity: The complex composition of petroleum hydrocarbons and the toxicity of certain components adversely affect diatoms, as well as other phytoplankton and microorganisms [88]. (b) A focus on other microalgae: Research efforts have predominantly concentrated on green algae, such as *Chlorella*, and cyanobacteria [4] due to their robust growth, ease of cultivation, and demonstrated efficacy in hydrocarbon degradation. Diatoms, by contrast, have received limited attention, and their metabolic pathways for degrading petroleum hydrocarbons remain underexplored. (c) Cultivation challenges: The effective cultivation of diatoms poses significant challenges, including their unique requirement for silica to form frustules (cell walls), which complicates large-scale production. Additionally, diatoms are highly sensitive to environmental factors, such as pH, salinity, light, and specific nutrient needs. The involvement of microorganisms, such as bacteria, is also crucial for facilitating the biodegradation of organic compounds, further increasing the complexity of their application [2,66,136]. (d) Limited genetic characterization: There has been little progress in leveraging genetic tools to enhance the ability of diatoms to degrade petroleum hydrocarbons. Diatoms alone demonstrate limited capabilities in fully degrading organic compounds and rely on associated microorganisms, such as bacteria, to complete the process [37,137]. (e) Economic and technical constraints: The cultivation of diatoms is expensive and subject to challenges, such as competition from other organisms and the effects of fluctuating environmental conditions. Toxic heavy metals and organic pollutants can inhibit diatom growth, and some compounds may be inaccessible to diatoms due to adsorption onto surfaces. Additionally, technical issues, along with the need for more research attention and standardized protocols for measuring remediation efficiency, further complicate the application of diatoms in phycoremediation projects.

On the contrary, some genera of diatoms have proven to be promising in the remediation of petroleum hydrocarbons. These include *Cyclotella*, *Gyrosigma*, *Hydrosilicon*, *Leptocylindrus*, *Licmophora*, *Navicula*, *Nitzschia*, *Synedra*, and *Thalassiosira*. Species from these genera are worth testing for their

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potential in remediating industrial wastewater. Furthermore, adopting modern biotechnology could help develop and enhance phycoremediation techniques. These factors highlight the need for increased research efforts to overcome the challenges of utilizing diatoms for the remediation of polluted seawater and freshwater ecosystems. One promising area of study is horizontal gene transfer (HGT), which may play a significant role in the evolution of diatoms [138–141]. HGT from bacteria to diatoms could enable the development of metabolic pathways for degrading petroleum hydrocarbons [37,142,143]. Advancing modern molecular research in this area is essential to enhance the ability of diatoms to remediate petroleum hydrocarbons and heavy metals effectively.

4. Concluding Remarks

Diatoms are major contributors to the productivity of phytoplankton in seawater, accounting for approximately 50% of global carbon pumps and bioactive agents. They play a crucial role in various applications, including antibacterial and antioxidant activities, aquaculture feedstocks, biofuels, bioindicators, nutrition, pharmaceuticals, and the phycoremediation of heavy metals and organic petroleum hydrocarbons, along with the production of many other valuable products. However, some negative impacts of this group have been reported, such as harmful algal blooms that cause fish kills. Given their ecological and industrial significance, this group of marine phytoplankton warrants considerable attention for addressing pollution caused by oil and gas activities in the Arabian Gulf. While diatoms alone may not be capable of fully degrading petroleum hydrocarbons, their associated bacteria can cooperate with them to initiate the degradation process. The final stages of degradation are completed by diatoms, resulting in the production of useful metabolites that contribute to essential metabolic pathways such as the Krebs cycle, fatty acid biosynthesis, and amino acid interconversions. Identifying the microorganisms associated with diatoms is a crucial step in understanding the roles these associations play in the bioremediation and phycoremediation of organic pollutants and trace elements in seawater. Among the diatom genera known for their ability to remediate crude oil and gas components, *Thalassiosira* has emerged as a promising model for physiological and molecular studies. Comprehensive investigations of these phytoplankton and their associated microorganisms are essential to ensure the safety and sustainability of the marine ecosystem in the Arabian Gulf region. Future research should explore the possibility of enhancing diatoms, either through natural development or modern biotechnological approaches, by incorporating genes with remediation capabilities from microorganisms such as bacteria.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org.

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