Harmful Algal Blooms and Their Impact on Various Sectors

Harmful algal blooms (HABs) are associated with an excessive bloom of toxic or high-biomass-producing microalgae that negatively impact aquatic ecosystems, public health, and economic losses. The algal bloom can take place in both freshwater and marine environments. The HABs phenomenon is considered harmful due to the production of massive biomass and toxins and severely depleting oxygen content (Pal et al. 2020). The three major groups of microalgae that causes HAB and may produce toxins are diatoms (e.g., *Pseudo-nitzschia*, *Skeletonema costatum*), dinoflagellates (e.g., *Alexandrium*, *Pyrodinium*, *Karenia*, and *Prorocentrum*), and cyanobacteria (e.g., *Microcystis*, and *Nodularia*) (Lin et al. 2015; Ralston & Moore, 2020). Once the concentration of single-celled algae increases, the pigment from the different types of algae can turn the water bodies cloudy and foamy with patches of different colors such as blue-green, orange, yellowish-brown, and red (Zohdi & Abbaspour, 2019).

The HABs affect humans and animals through consuming seafood or drinking water contaminated with algae toxins, skin contact with the biotoxin-contaminated water, and/or inhaling aerosolized biotoxins. Cooking or processing the biotoxin-contaminated seafood will not mineralize the biotoxins (Berdal et al., 2015), and naked eyes cannot detect the biotoxins because they do not have distinctive odors or taste (Zaias et al. 2010). Hence, making humans and animals more prone to be victims of HABs.

The hemolytic or cytotoxic biotoxins produced by fish-killing HAB species can cause damage to the fish gills leading to suffocation and death. The degradation of the algae cell and utilization of the organic matter by bacteria reduces the oxygen concentration in the water column creating hypoxic or anoxic conditions. The depletion of oxygen can kill fish and other aquatic organisms. The excessive biomass produced can reduce the light penetration and lead to excessive ammonia production and hypothermia in marine birds due to the accumulation of surfactant-like proteins (Berdal et al., 2016).
The impact of HAB can be so devastating that it will cost a huge loss, reaching up to millions of USD (Lim et al., 2014; Bechard, 2019, Berchard, 2020; Imai et al., 2021). In the USA, from 1987 to 2000, the average annual economic impact of HABs was approximately US $75 million (Anderson et al. 2000). In Korea, over the past three decades, the fisheries damage was estimated to be a total of USD 121 million (Park et al. 2013). In contrast, the estimated fisheries damage in Japan from 1972–2012 was over 52.5 billion yen per year (Imai et al., 2021). The data presented in Table 1 indicate that the severity of HABs impacts various sectors. Without proper monitoring and mitigation strategies, combined with increasing numbers of contributing factors, HABs occurrence can worsen soon.

**Factors Contributing to HABs**

Nutrients and minerals such as nitrogen and phosphorus are essential for algae growth. Hence, excessive nutrients and minerals in the water column stimulate algal growth. Massive algal bloom leads to dissolved oxygen depletion, increased turbidity, reduced the water column’s esthetic appearance, and changes the aquatic environment. This condition is known as eutrophication (Seitzinger et al., 2010; the United States Environmental Protection Agency, 2015; Sun et al., 2018). The excess nutrients and minerals in the aquatic environment are widely contributed by anthropogenic activities such as municipal wastewater discharge, industrial wastewater discharge, concentrated animal feeding operations, animal feeding operations, agriculture runoff, urban stormwater runoff, and failing septic systems and fossil fuels (Gatz, 2019). The use of fertilizer has been identified among the top contributor (Seitzinger et al., 2010; Paerl et al., 2018; Sun et al., 2018; Glibert, 2020).

Global warming has been increasingly acknowledged as another factor contributing to increasing HABs occurrences. Based on high-resolution sea-surface temperature records and temperature-dependent growth rates of two algal species, (Gobler et al., 2017) reported that increasing ocean temperature could facilitate the intensification of HABs in North America. Hinder et al., 2012 found that from 1960 to 2009, there was a marked increase in the relative abundance of diatoms vs. dinoflagellates driven by the effects of both increasing sea surface temperature and increasing wind stress conditions in summer. However, the exact effect of global warming on the occurrence of HAB is still uncertain due to the complex interactions among environmental factors (Ralston & Moore, 2020) and the lack of reliable monitoring methods and data (Gobler, 2019; Zhou et al., 2022).

Climate-induced temperature changes are affected by multiple overlapping or sequential changes in the physical structure of the water column, nutrient supply and seasonality, and light availability (Behrenfeld et al., 2006; Johnson et al., 2006). Thermal stratification occurs when warmer surface water comes into contact with colder bottom water. Vertical stratification and mixing (turbulence) of the water column strongly affect phytoplankton dynamics in all aquatic ecosystems. They can modulate HAB dynamics with other physical processes (Timmerman et al., 2014). This condition may restrict the vertical movement of oxygen and nutrients in the water. When blooms are formed, sunlight penetration to the bottom water column will be blocked for other aquatic organisms, preventing them from getting to the surface for air. This environment allows algae to survive with less competition from other aquatic organisms. Most bloom-forming cyanobacteria can form gas vehicles that allow them to swim up and down the water column. In addition, higher temperature will dilute the viscosity of the water, this will also facilitate the algae to move up and down the water column compared to other larger algae or organisms.

It is well acknowledged that CO₂ emission is one of the main contributors to global temperature rise. Despite economic slowdown due to Covid-19, the global average atmospheric carbon dioxide in 2020 was 412.5 ppm. It is a jump of 2.6 ppm over 2019 levels (Lindsey, 2022). An increase in atmospheric CO₂ will increase the dissolved CO₂ in the water column. This condition is known as ocean acidification. This condition benefits cyanobacteria that can easily float to the surface compared to other algae and directly utilize CO₂. Similar to the effect of temperature, CO₂ on the HABs is challenging to measure.

**Mitigation of HABs**

Mitigation is a term used to describe the actions taken to deal with an existing or ongoing bloom by taking necessary steps to reduce the negative impact of the bloom. Kim, 2006 categorizes HABs mitigation strategies into two; precautionary impact preventions and bloom controls. Precautionary impact prevention strategies include HAB monitoring, forecasting, and emergent actions such as moving fish cages to the non-blooming areas and improving water circulation and aeration to increase oxygen levels in the water. HABs monitoring involves identification of target species (using microscopic or/and molecular observations), determination of toxins, analysis of environmental and meteorological changes, and understanding relationship between algae population dynamics and environmental/oceanographic properties.
<table>
<thead>
<tr>
<th>HAB Species</th>
<th>Location</th>
<th>Year</th>
<th>Losses</th>
<th>Impacted sector</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karenia brevis</td>
<td>Ft. Walton and Destin beaches, USA</td>
<td>2007</td>
<td>Coastal lodging and restaurants lost about 30% of sales in a month during the HAB season.</td>
<td>Tourism, recreation &amp; Public Safety</td>
<td>Larkin &amp; Adams (2007)</td>
</tr>
<tr>
<td>Microcystis</td>
<td>Lake Taihu, China</td>
<td>2007</td>
<td>Drinking water contaminated with Microcystis toxin.</td>
<td>Public Safety</td>
<td>Qin et al. (2010)</td>
</tr>
<tr>
<td>Karenia brevis</td>
<td>Manatee County, USA</td>
<td>2009</td>
<td>The average loss in sales for three restaurants was 14% on a singular day when red tide present.</td>
<td>Tourism, recreation &amp; Public Safety</td>
<td>Morgan et al. (2009)</td>
</tr>
<tr>
<td>A. minutum</td>
<td>Bay of Plenty beaches between Mt Maunganui and Papamoa, New Zealand</td>
<td>2012</td>
<td>At least 20 people were reported to have become ill due to paralytic shellfish poisoning (PSP) from consuming surf clams (Paphies subtriangulata) collected by recreational gatherers.</td>
<td>Public Safety</td>
<td>MacKenzie, (2014); Hallegaer et al. (2021)</td>
</tr>
<tr>
<td>Pyrodinium bahamense var compressum</td>
<td>Sabah, Malaysia</td>
<td>2013</td>
<td>58 cases of paralytic shellfish poisoning (PSP) with four deaths.</td>
<td>Public Safety</td>
<td>Saleiman et al. (2017)</td>
</tr>
<tr>
<td>Karlodinium australi</td>
<td>West Johor Straits, Malaysia</td>
<td>2014</td>
<td>About four tonnes of fish cages (Epinephelus coloides Hamilton, Lates calcarifer Bloch, Lutjanus gibbus Forskål and Eleutheronema tetractylum Shaw) died.</td>
<td>Agriculture</td>
<td>Lim et al. (2014)</td>
</tr>
<tr>
<td>Karenia brevis</td>
<td>Sarasota County, USA</td>
<td>2019</td>
<td>The lodging sector lost about 15% of sales, whereas the restaurant sector lost 2% on average during the HAB season.</td>
<td>Tourism, recreation &amp; Public Safety</td>
<td>Bechard, (2019)</td>
</tr>
<tr>
<td>Karlodinium australi</td>
<td>West Johor Straits, Malaysia</td>
<td>2015</td>
<td>Fish cages (30 tonnes) and wild populations (including some demersal fishes and crustaceans).</td>
<td>Agriculture</td>
<td>Teng et al. (2016)</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td>Sonoma County, USA</td>
<td>2015</td>
<td>3-year-old golden retriever died.</td>
<td>Agriculture</td>
<td>Moore (2015)</td>
</tr>
<tr>
<td>HAB species not specified</td>
<td>Qinhuangdao, China</td>
<td>2016</td>
<td>Poisoning due to PST-contaminated mussels (numbers not stated).</td>
<td>Agriculture</td>
<td>Yu et al. (2018)</td>
</tr>
<tr>
<td>Karenia brevis</td>
<td>West Coast of Florida, USA</td>
<td>2018</td>
<td>Marine animals such as manatees, dolphins, and 300 sea turtles died.</td>
<td>Marine Ecosystem</td>
<td>Resnick (2018)</td>
</tr>
<tr>
<td>Green algae</td>
<td>Morlaix Bay, France</td>
<td>2019</td>
<td>An 18-year oyster farmer and 70-year-old pensioner died after inhaling toxic fume of green algae.</td>
<td>Public health</td>
<td>Manoylov (2020)</td>
</tr>
<tr>
<td>Margalefidinium sp.</td>
<td>Penang and Perak, Malaysia</td>
<td>2020</td>
<td>More than 418 tonnes of fish (groupers, snapper and Asian seabass) were killed, worth around RM 11 million loss.</td>
<td>Aquaculture</td>
<td>Chen (2020); Roziaiati et al. (2020)</td>
</tr>
<tr>
<td>Alexandrium catenellais</td>
<td>The Alaskan Arctic</td>
<td>2021</td>
<td>Possess threats to public and ecosystem health.</td>
<td>Public safety and ecosystem</td>
<td>Anderson et al. (2021)</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td>Sierra National Forest, California</td>
<td>2021</td>
<td>A family of three and their dog died.</td>
<td>Tourism, recreation &amp; Public Safety</td>
<td>Spocchia (2021)</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td>Lake Welch Beach and Picnic Grounds in Harriman Skate Park, Rockland County, New York</td>
<td>2022</td>
<td>The destinations were closed to the public due to the bloom.</td>
<td>Tourism, recreation &amp; Public Safety</td>
<td>Taliaferro (2022)</td>
</tr>
</tbody>
</table>
to make predictions using specific HABs models (Kim, 2006; Imai et al. 2021). Bloom controls can be classified as either indirect or direct. Indirect control includes reducing nutrient input, modifying water circulation, and bio-remediation to prevent HABs from spreading or reducing the expansion of HABs. Implementing nutrient reduction strategies to inhibit certain types of algal blooms or disrupt stratification, thus altering microalgae community composition as demonstrated by legislation or policy measures adopted in the Seto Inland Sea, Japan, and Tolo Harbor, Hong Kong (Anderson, 2004). Direct bloom controls include physical, chemical, and biological approaches to eliminate/reduce/destroy the HABs population.

This review will address the advantages and challenges of these approaches. In addition, the interaction between the mitigating agent and the algae will be discussed as well. Understanding this interaction is vital to overcoming the drawbacks and developing HAB mitigating systems that are more HABs specific and friendly toward other aquatic organisms. To the best of our knowledge, the mitigating agent-algae interactions are rarely focused.

### Biological Approach

The biological approach is the most promising due to its environmental friendliness and high algicidal potential (Backer et al., 2015). Biological control agents regulate HABs through feeding (predators), infecting, or decaying (parasites, bacteria, fungi, viruses) various HABs species. They also help to reduce the density of algal, inhibiting the growth of harmful algal and lysis of harmful alga (Akbar et al. 2008; Pal et al. 2020). Biological control of HABs is primarily still conceptualized due to a lack of scientific research on efficacy and concerns related to undesirable

<table>
<thead>
<tr>
<th>Biological mitigation agent</th>
<th>HABs species</th>
<th>Outcome</th>
<th>Drawback</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endophytic fungus</td>
<td>Chlorella furca</td>
<td>Showing algicidal properties against Chlorella furca in 48 h.</td>
<td>The fungus might affect biodiversity.</td>
<td>Hussain et al. (2014)</td>
</tr>
<tr>
<td>Nile Tilapia</td>
<td>Cyanobacteria</td>
<td>Almost 60% of cyanobacteria was removed.</td>
<td>Increase in water transparency and ammonium concentration</td>
<td>Salazar Torres et al. (2016)</td>
</tr>
<tr>
<td>Zooplankton</td>
<td>Cyanothece sp.</td>
<td>Grazing rate of 200-1000 µm zooplankton size class was high ranging from 0.58 ± 0.093 SE d-1 to 0.18 ± 0.045 SE d-1.</td>
<td>It decreased in grazing impact due to increased salinity level.</td>
<td>du Plooy et al. (2017)</td>
</tr>
<tr>
<td>Notodiaptomus iheringi</td>
<td>-Microcystis aeruginosa</td>
<td>N. iheringi reduced the Cryptomonas to a negative value while increasing the production of Microcystis.</td>
<td>Selective grazing on specific species.</td>
<td>Leïtão et al. (2018)</td>
</tr>
<tr>
<td>Paracoccus sp. Y42</td>
<td>Prorocentrum donghaiense</td>
<td>-5 % Y42 supernatant shows 90 % of algae cell removal in 72 h.</td>
<td>The inhibition of the HAB cell was species-specific.</td>
<td>Zhang et al. (2018)</td>
</tr>
<tr>
<td>Cultivable pelagic bacteria</td>
<td>Pyrodinium bahamense</td>
<td>Cell lysis and decline in total cell abundance were observed.</td>
<td>Formation of Pyrodinium pellicle cyst when exposed to the bacterial cell.</td>
<td>Dungca-Santos et al. (2019)</td>
</tr>
<tr>
<td>Shewanella sp. IRI-160</td>
<td>-Karlodinium veneciferm</td>
<td>The cell growth of K. veneciferm and P. minutum increased by 1.44- and 1.62-fold, respectively, as compared to control within a 6-day exposure.</td>
<td>Also, to increase the growth rate of the cell.</td>
<td>Wang &amp; Coyne (2020)</td>
</tr>
<tr>
<td>Ma-LEP</td>
<td>Microcystis aeruginosa</td>
<td>Ma-LEP has reduced the bloom intensity of Maeruginosa in 14 days.</td>
<td>Longer inhibition time is required, and the Ma-LEP could threaten other organisms.</td>
<td>Jiang et al. (2019)</td>
</tr>
<tr>
<td>HcRNAV</td>
<td>Heterocapsa circularisquama</td>
<td>Virus and sediment treatment was very effective in mitigating. H. circularisquama bloom under field conditions.</td>
<td>- Sedimentation of mitigation agent. - Might affect biodiversity</td>
<td>Nakayama et al. (2020)</td>
</tr>
</tbody>
</table>
Ibrahim, N. H., et al., the dynamics of the remove mechanism and produce an extracellular product to substances (ESPs), resulting in algae cell aggregation. Can also force algae to release extracellular polymeric proteins, and lipids secreted by the bacterial cells can promote accumulation and cause the settling of algae. Polysaccharides, (de Melo et al., 2019). Bacteria usually act as a specific nature, faster reproduction, and high efficiency microorganisms to mitigate HAB due to their host-organisms based on the number of communities (Sun et al., 2018). The HABs deplete oxygen; hence, using zooplankton would only be a short-term solution.

Filter-feeding fish and bivalves are always an option to remove HAB since some fish and bivalves can ingest and digest the toxin by themselves and balance the ecosystem. Tilapia, bighead carp, silver carp, and mussels are used in many countries to control cyanobacteria bloom. Despite its advantages, many cases related to seafood poisoning involving certain filter-feeding fish and bivalves have been reported (Aljerf, 2018). Consumption of contaminated seafood is due to the lack of knowledge among the general population about HABs and seafood poisoning caused by HABs. The general public should be educated on the identifying blooming season and which filter-feeding fish and bivalves to avoid during the season. If this approach is adopted, frequent monitoring and stricter regulation must be imposed. Regular and appropriate HABs monitoring programs such as in-situ survey/sampling samples on-site or real-time water analysis, satellite remote sensing, and toxin analysis are required to detect algal blooms, provide early warning to the public, and mitigation actions.

Microorganism-based methods can be classified into single-species microorganisms and multi-species organisms based on the number of communities (Sun et al., 2018). Bacteria are among the most promising microorganisms to mitigate HAB due to their host-specific nature, faster reproduction, and high efficiency (de Melo et al., 2019). Bacteria usually act as a bioflocculant in controlling HABs. The polysaccharides, proteins, and lipids secreted by the bacterial cells can promote accumulation and cause the settling of algae cells in the water column (Sun et al., 2018). Bacteria can also force algae to release extracellular polymeric substances (ESPs), resulting in algae cell aggregation. For instance, some Bacillus sp. use a cell-to-cell contact mechanism and produce an extracellular product to remove M. aeruginosa (Zhang et al., 2019).

Viruses have been mainly responsible for controlling the dynamics of the most abundant aquatic prime producers. Viral treatment involves species-specific interaction and the virus lytic cycle (Mankiewicz-Boczek et al., 2016). Species-specific interaction happens when the virus directly attacks the algae and inhibits the cell’s reproduction pathway. The virus lytic cycle involves the reproduction of viruses using a host cell for manufacturing more viruses, followed by eventual release from the cell. The first stage of the virus lytic cycle is the attachment of the phage onto the host cell, followed by the DNA penetration from the phage into the host cell. The third stage is biosynthesis, where the phage DNA replicates, and phage proteins are made. The fourth stage is the maturation of the new phage; finally, the cell undergoes lysis, releasing the new phage. The advantage of this process is that the algae cells could be permanently killed (Ryu, 2017; Weynberg, 2018). However, the new phage can attack other marine organisms and continue to produce more phages. In the long run, releasing the produced phages can disrupt the balance of the microorganism community in the environment and might cause a new environmental concern or outbreak.

Fungal flocculants have been well studied in reducing microalgal biomass. Fungi act as natural flocculants by interacting with algal cells, leading to microbial aggregation (Sun et al., 2018). Formation and precipitation of fungus–alga pellets result in algae removal from water columns through the pelletization process. The pelletization process is influenced by the cultivation parameters, such as pH values, salinity, and rheological behavior (Espinoza-Ortiz et al., 2016). Despite many successful laboratory-scale reports, field management’s success rate appears relatively low.

Microorganism growth is affected by various conditions such as nutrients, pH, and temperature. These conditions can be well controlled on a laboratory scale compared to the field. Hence, a better outcome is often obtained on a laboratory scale. Even though effective, considering the long-term effect of using microorganisms on other aquatic organisms and humans, this method might not be feasible in the field.

As shown in Table 3, seaweeds have also been identified as a potential mitigating agent regardless of their limitations. The presence of seaweed inhibits the HAB’s growth through allelopathy effects and by competing for nutrients, such as nitrogen. The allelochemicals produced by the seaweeds will act as either growth stimulators or inhibitors. Several allelochemicals extracted from seaweed showed an inhibitory effect on the algae cell growth: dithiolane, trithiane (Tang & Gobler, 2011), loliolide, N-phenethylacetamide, squamoline and 2-ethylidene-4-methylsuccinimide (Lu et al.2011). These chemical compounds produced by the seaweeds did not harm other marine organisms. However, much seaweed is
required to achieve the inhibitory effect. Therefore extensive research on 1) determining the optimum amount of bioactive compound to inhibit HABs, 2) culturing the potential seaweed to prevent ecosystem deterioration due to collecting a large amount of seaweed from the field, 3) using seaweed that has an established culture system to save cost and decrease the impact to ecosystem and 4) production of the bioactive compounds synthetically are needed.

**Chemical and Chemical-physical Approaches**

Herbicides, photosensitizers (hydrogen peroxide), metals (Al, Fe, Cu, Ca), and other chemicals are commonly used to reduce bloom under chemical-based approaches. Some examples of reported chemical and chemical-physical approaches are listed in Table 4. Using chemical controls may risk releasing certain toxic chemicals that may cause the death of non-target microalgae or harm benthic communities and long-term effects on the aquatic environment. It is hard to find an environmentally acceptable chemical treatment to control particular harmful algae/species-specific which does not have a potential negative impact on ecological balance (Fentie, 2020). Due to their possible environmental effects, more research is needed to implement chemicals in the field entirely. In addition, these control activities can be an issue or controversial due to concerns about the unwanted ecosystem effects of these controls.

Biological-chemicals control is less harmful to other marine organisms. Still, their algicidal effects are lower than synthetic chemicals and thus require more volume. A constant supply system must be established because it is derived from natural marine organisms (United Nations Environmental Programme, 2007). More research is needed to find environmentally acceptable

Table 3. Summary of previous studies on the effect of seaweeds on HAB species

<table>
<thead>
<tr>
<th>Macroalga (Seaweed)</th>
<th>HABs species</th>
<th>Outcome</th>
<th>Drawback</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Gracilaria tenuistipitata</em> (Rhodophyta)</td>
<td><em>Prorocentrum micans</em></td>
<td><em>G. tenuistipitata</em> is effectively inhibited by the higher content of <em>G. tenuistipitata</em>.</td>
<td>Lower content of <em>G. tenuistipitata</em> enhanced the <em>P. micans</em>.</td>
<td>Ye &amp; Zhang (2013)</td>
</tr>
<tr>
<td><em>Dictyota dichotoma</em> (Ochrophyta)</td>
<td><em>Ostreopsis cf. ovata</em></td>
<td>The growth of <em>O. ovata</em> was inhibited by <em>Ulva rigida</em> and induced cyst formation by all seaweed species.</td>
<td><em>R. pseudopalmata</em> only shows effect at higher concentrations of dry thallus powder.</td>
<td>Accoroni et al. (2015)</td>
</tr>
<tr>
<td><em>Rhodymenia pseudopalmata</em> (Rhodophyta)</td>
<td><em>Ulva rigida</em> (Chlorophyta)</td>
<td><em>G. tenuistipitata</em> is effectively inhibited by the higher content of <em>G. tenuistipitata</em>.</td>
<td>Lower content of <em>G. tenuistipitata</em> enhanced the <em>P. micans</em>.</td>
<td>Ye &amp; Zhang (2013)</td>
</tr>
<tr>
<td><em>Ulva rigida</em> (Chlorophyta)</td>
<td><em>Ostreopsis cf. ovata</em></td>
<td>The growth of <em>O. ovata</em> was inhibited by <em>Ulva rigida</em> and induced cyst formation by all seaweed species.</td>
<td><em>R. pseudopalmata</em> only shows effect at higher concentrations of dry thallus powder.</td>
<td>Accoroni et al. (2015)</td>
</tr>
<tr>
<td><em>Ulva fasciata</em> (Chlorophyta)</td>
<td><em>Skeletonema costatum</em></td>
<td><em>G. tenuistipitata</em> is effectively inhibited by the higher content of <em>G. tenuistipitata</em>.</td>
<td>Lower content of <em>G. tenuistipitata</em> enhanced the <em>P. micans</em>.</td>
<td>Ye &amp; Zhang (2013)</td>
</tr>
<tr>
<td><em>Pyropia haitanensis</em> (Rhodophyta)</td>
<td><em>Skeletonema costatum</em></td>
<td><em>G. tenuistipitata</em> is effectively inhibited by the higher content of <em>G. tenuistipitata</em>.</td>
<td>Lower content of <em>G. tenuistipitata</em> enhanced the <em>P. micans</em>.</td>
<td>Ye &amp; Zhang (2013)</td>
</tr>
</tbody>
</table>
and effective chemicals that only target HAB species with minimal environmental effects and harmless human health (Balaji-Prasath et al., 2022).

Photocatalysis is a branch of Advanced Oxidation Processes (AOPs) that utilizes light to generate electron-hole pairs (e\(^{-}\)/h\(^{+}\)) via semiconductor nanoparticles (SN) as photocatalysts to photodegrade pollutants, including algae. The SN, such as pristine TiO\(_2\) or metal-doped TiO\(_2\), has been reported to be able to deactivate algal cells through flocculation or catalytic degradation method. When exposed to sunlight, the electrons (e\(^{-}\)) in the valence band (VB) of the SN will be excited to the conduction band (CB), leaving behind the holes (h\(^{+}\)). These photogenerated e\(^{-}/h^{+}\) pairs can produce reactive oxygen species (ROS) such as hydroxyl radicals in the presence of moisture (Zhu & Wang, 2017). These radicals in return can deactivate the algal cells by causing damage to their DNA and algae membrane (Mahaseth & Kuzminov, 2017). The general mechanism of ROS generation and the deactivation of algal cells through the photocatalytic degradation method are shown in Figure 1. Various photocatalysts have recently been engineered and investigated as HABs mitigating agents. A summary of the engineered photocatalysts is given in Table 5. The photocatalytic degradation of HABs using photocatalysts seems safer than chemicals such as metal salts or H\(_2\)O\(_2\). The generation of ROS depends highly on the intensity of the sunlight; hence its effectiveness is highly unpredictable since the sunlight intensity changes from time to time.

It is surprising to know that *Alexandrium tamarense* can reverse the damages caused by ROS. Li et al. 2019 reported that the EC\(_{50}\) value increased from 85.1 mg L\(^{-1}\) on day 4 to 140.9 mg L\(^{-1}\) on day 13. The physiological recovery of *Alexandrium tamarense* is attributed to the algal antioxidant defense mechanisms and increased nanoparticle aggregation. To the best of our effort, we could not find other reports in this regard. Another drawback of ROS is its non-specific nature. In addition to causing damage to the algal cells, the ROS can also interrupt the physiological process of other marine organisms through a similar mechanism. Even though TiO\(_2\) is considered non-toxic, long-term exposure and accumulation in marine organisms can cause adverse effects. TiO\(_2\) has been reported to accumulate in the guts of Artemia and leads to oxidative stress. Renzi and Blaškovič (2019) observed a similar observation. The duo observed the accumulation of

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**Table 4. Chemical and chemical-physical approaches to controlling HAB**

<table>
<thead>
<tr>
<th>Mitigation agent</th>
<th>HABs species</th>
<th>Outcome</th>
<th>Drawback</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan fiber</td>
<td><em>Microcystis aeruginosa</em></td>
<td>Almost 89% of cyanobacterial cells were eliminated in 24 h.</td>
<td>The coloration of fiber.</td>
<td>Park et al. (2013)</td>
</tr>
<tr>
<td>Flumioxazin</td>
<td><em>Prymnesium parvum</em></td>
<td>Flumioxazin has the potential to inhibit <em>P. parvum</em> during the winter season and not in the fall season.</td>
<td>Temperature dependant. Work best at a cooler temperature.</td>
<td>Bloomer (2017)</td>
</tr>
<tr>
<td>CuSO(_4) and CuO NP</td>
<td><em>Chlorella sp.</em></td>
<td>CuSO(_4) decreased the cellular contents of chl-a, chl-b, and carotenoids, ROS production, and lipid peroxidation after exposure for 96 h.</td>
<td>CuO NP is not suitable as it promotes toxicity.</td>
<td>Wan et al. (2018)</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td><em>Microcystis aeruginosa</em></td>
<td>Successfully mitigate all the <em>M. aeruginosa</em> cells within 2 h.</td>
<td>Increased the nutrient content in the water (nitrogen, phosphorus and carbon) and promote the growth of chlorophytes.</td>
<td>Wang et al. (2019)</td>
</tr>
<tr>
<td>Silica-quaternary ammonium “Fixed-Quat” nanofilm coated fiberglass mesh</td>
<td><em>Microcystis aeruginosa</em></td>
<td>Successful control of <em>M. aeruginosa</em> with more than 99% inactivation and E. coli. inactivation rate of 1.3 × 10^{-3} log reduction/cm/min after 10 h of exposure.</td>
<td>High cost.</td>
<td>Diaz et al. (2019)</td>
</tr>
</tbody>
</table>

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![Figure 1. The general mechanism of ROS generation and the deactivation of algal cells through the photocatalytic degradation method.](image-url)
TiO₂ in the digestive system of Daphnia magna, leading to gas bubble disease and mortality.

Under the chemical-physical approach, ballast (sand or clay particles) is modified with organic and inorganic modifiers to improve flocculation and sedimentation properties and to increase ROS generation (Gallardo-Rodríguez et al. 2019). The organic modifier is mostly positively charged compounds with strong charge neutralization and bridging effects that allow HABs mitigation. Synthetic and natural materials such as chitosan and starch are commonly used organic modifiers (Mucci et al., 2017). Polyaluminium chloride (PAC), aluminum chloride, and mixed-metal hydroxide are commonly used inorganic modifiers (Yu et al., 2017). Positively charged inorganic modifiers will change the negatively charged clay surface to positive and promote charge neutralization between the clay and HAB cells. The charge neutralization will enable more HAB cells to adhere to the clay surface for sedimentation and cell lysis. At present, chemical-physical flocculation using clay/sand/soil or modified clay is one of the possible approaches to control HABs in the fields because most effective measure since they are natural, nontoxic, inexpensive, and easy to use in field operations and high ability in mitigating HABs (Park et al., 2013). Over the past 30 years, different clays have been tested and applied to different types of HABs species in several countries such as Japan, Australia, and South Korea to control HABs in the field. In China, clays dispersal has been employed as a standard method to control HABs since 2014 (Yu et al., 2017). However, this approach has not been widely applied in other countries due to concerns associated with its adverse effects on the ecosystem. Even though environmental

<p>| Table 5. Different types of semiconductors in the catalytic degradation method for HAB mitigation |</p>
<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>HABs species</th>
<th>Outcome</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver-TiO₂ nanocomposites</td>
<td>Amphidinium carterae (red tide) or noxious Tetraselmis suecica (green tide)</td>
<td>The algal cells were deactivated within 1 h of exposure to UV light.</td>
<td>Rodríguez-González et al. (2010)</td>
</tr>
<tr>
<td>Nano-TiO₂</td>
<td>Karenia brevis</td>
<td>Algae cells were damaged by ROS accumulation, resulting in lipid oxidation and inhibited algae growth.</td>
<td>Li et al. (2015)</td>
</tr>
<tr>
<td>CeO₂/TiO₂-Fₓ nanostructures</td>
<td>Microcystis aeruginosa</td>
<td>100% removal was achieved within 4 h irradiation. The photosynthetic efficiency of algae cells reduces in the inactivation process, and the electron transport process in the photosynthetic system is inhibited.</td>
<td>Wang et al. (2018)</td>
</tr>
<tr>
<td>0.2PDDEA@NPT-EGC</td>
<td>Microcystin-LR</td>
<td>The highest removal efficiency of 96.55% was achieved for photocatalytic degradation of MC-LR after visible light irradiation for 3 h.</td>
<td>Wang et al. (2018)</td>
</tr>
<tr>
<td>TiO₂–Fe₂O₃ nanoparticles</td>
<td>Chlorella vulgaris</td>
<td>High removal rate of algal cells (99.8%) was achieved within 24 h exposure.</td>
<td>Baniamerian et al. (2020)</td>
</tr>
<tr>
<td>0.6 Nb-N-TiO₃/C</td>
<td>Microcystis aeruginosa</td>
<td>The highest photocatalytic activity under visible light degrades chlorophyll-a in algae cells in 8 h (92.7 %).</td>
<td>Zhang et al. (2020)</td>
</tr>
<tr>
<td>TiO₂-coated expanded polystyrene ball</td>
<td>Cyanobacteria</td>
<td>The concentrations of both Chl-α and phycocyanin decreased.</td>
<td>Lee et al. (2020)</td>
</tr>
<tr>
<td>γFe₂O₃/TiO₂</td>
<td>Microcystin/nodularin-, cylindrospermopsin-, and saxitoxin-producing cyanobacteria</td>
<td>Able to inactivate toxic cyanobacteria from the lake water both in the dark and under visible light conditions.</td>
<td>Madany et al. (2021)</td>
</tr>
<tr>
<td>G-C₃N₄/TiO₂ floating</td>
<td>Microcystis aeruginosa, Microcystin-LR</td>
<td>-75.9% and 83.7% of M.aeruginosa and Microcystin-LR were removed within 6 h irradiation under visible light.</td>
<td>Song et al. (2021)</td>
</tr>
<tr>
<td>F-TiO₂ nanostructure</td>
<td>Microcystis aeruginosa</td>
<td>The removal rate of algae cells is above 97.5% under solar irradiation for 8 h.</td>
<td>Wei et al. (2021)</td>
</tr>
<tr>
<td>Biotemplate-based Bi₂WO₆/TiO₂ composite</td>
<td>Microcystin-LR</td>
<td>85.3% of MC-LR was removed within 3 h exposure.</td>
<td>Lin et al. (2021)</td>
</tr>
<tr>
<td>SNP-TiO₂</td>
<td>Karenia mikimotoi</td>
<td>The growth inhibition rate was 81.8% within 96 h of exposure.</td>
<td>Hu et al. (2022)</td>
</tr>
<tr>
<td>Hybrid chitosan-modified TiO₂ Film</td>
<td>Alexandrium minutum</td>
<td>76.1% of A.minutum was removed within 72 h.</td>
<td>Ibrahim et al. (2022)</td>
</tr>
</tbody>
</table>
studies conducted in South Korea showed no significant negative impacts on using clay dispersal as a routine element of HAB management (Lu et al., 2016), this method might release toxins by lysis action of the toxic algal cells. In addition, smothering or sunken clay into the water column can harm other organisms, especially benthic communities (Anderson et al., 2017). Therefore, selecting a more productive clay that produces less secondary pollution is important.

Figure 2 shows the effects of organic and inorganic modifiers on the algae cell’s flocculation and sedimentation.

**Physical Approach**

Physical approaches generally involve removing the algal cells from the water column, limiting the spatial extent of bloom by a physical barrier, and killing the algal cells (Kidwell, 2015). The physical approach is more sustainable since it has minimal chemical inputs and can be carried out over multiple treatment cycles, unlike biological, chemical, or chemical-physical approaches. Mitigation strategies that use physical approaches such as aeration, ultrasound, skimming, and membrane filtration have been demonstrated in the laboratory or at the mesocosm scale. The application of these devices is widely used in freshwater but limited in coastal systems as it gives little impact on a low-density of benthic HABs organisms and is often expensive when applied in a large volume of water. Table 6 shows the reported physical approaches to removing HAB.

Aeration is supplied by pumping water and air or using surface agitators. Vertical aeration mixing prevents thermal stratification of the water column and warming surface waters that promotes algae growth. Horizontal aeration mixing impairs the algal buoyancy and inhibits the ability of the algae to move independently. Hence, removing the algae from the photic zone prevents photosynthesis (Gallardo-Rodríguez et al., 2019). The physical approach using filtration, skimming, ultrasound, or other related techniques is one of the most applicable techniques in freshwater to remove or prevent HAB cells from impacted areas. Nevertheless, most physical methods are expensive, labor-intensive, and challenging for large blooms areas, especially in coastal areas or oceans, and applied only for short-term management but with minimal environmental aquatic impact.

Three basic steps are mainly implemented in the drinking water treatment: pre-treatment, clarification, and disinfection. The first step involves coarse filtration, where the supplied raw water will undergo a pre-oxidation process followed by the clarification step to remove natural organic matter (NOM). There are specific techniques involved in this step. The first technique is based on the retention of contaminants (coagulation, flocculation, sand/membrane filtration, and adsorption), and the second technique is based on the degradation of contaminants (biodegradation and advanced oxidation) (Merel et al. 2013). The coagulation-flocculation process involves mixing the organic or inorganic modifiers to neutralize the negatively charged cells. The combined flocculant and algal cell will be sedimented at the bottom, and cell lysis occurs. The sludge will be discarded. The skimming technique is often coupled with implementing some coagulant or flocculant. For example, oil-spill skimmers have removed cyanobacteria from these surface scums. An ultrasound device emits ultrasonic waves at a particular frequency to destroy algae’s cellular structure by rupturing internal gas vesicles used for buoyancy control. However, it is difficult to eliminate some cyanobacteria due to the positive buoyancy, low specific density, motility, and variable morphologies (Pham & Dang, 2019). Therefore, filtration will take place to remove the remaining algal cells. The direct filtration method could not potentially remove all the algal cells.

The membrane filtration method analyses water quality using a special filter to trap the microorganisms that have not been trapped during coarse filtration. It is a very effective method for isolating microorganisms in the water sample. The membrane filtration efficiency depends on membrane pore size. Pores that are too large cannot retain all algae cells but pores too small reduce the permeate flux (Zhao et al., 2017). Membrane separation processes can recover microorganisms, producing stable yield and clean effluent water. Besides, membrane technology can result in removing viruses.
Adsorption-based processes are a technology that has often been reported for achieving low concentrations of o-phosphate, low footprint, and minimal waste generation. One of the limitations of adsorption is its ability only to remove dissolved phosphate. Pre-treatment by advanced oxidation processes can also promote converting the organic forms of phosphorus into phosphate, which can be targeted by adsorption (Mayer et al., 2013). Moreover, the flocculation and filtration method could also reduce the limitation of adsorption-based processes by targeting the particulate phosphorus (Langer et al., 2017).

Manufactured from wood, coal, peat, and coconut shell, activated carbon (AC) has high porosity and a large surface area. In both powdered activated carbon (PAC) and granular activated carbon (GAC) forms, activated carbon has been extensively used for decades to remove pollutants in drinking water and wastewaters. (Roegner et al., 2014) Almost 99% of dissolved microcystins were removed using activated carbon. Although practical, activated carbon filtration displays a limited lifetime for all contaminants, including microcystins (Panteliæ et al., 2013). The filtration needs to be changed frequently, varying between 2 months to 1 year, depending on the type of toxin and the water quality. If it is not monitored, the removal efficiency will decrease.

### Table 6. List of physical approaches to removing HAB

<table>
<thead>
<tr>
<th>Mitigation agent</th>
<th>Algae species</th>
<th>Outcome</th>
<th>Drawback</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1-μm membrane filter</td>
<td><em>Chlorella pyrenoidosa</em></td>
<td>The 0.1-μm membrane was suitable for harvesting <em>C. pyrenoidosa</em> compared to 0.03- and 0.05-μm membranes.</td>
<td>-0.1-μm membrane had the highest flux decline rate. -Fewer algae cell adsorption as the pore size increases.</td>
<td>Zhao et al. (2017)</td>
</tr>
<tr>
<td>Peptide HPA3NT3-A2</td>
<td><em>Microcystis aeruginosa</em></td>
<td>-Have an algicidal effect on <em>M. aeruginosa</em>, which is 79.2 % in 48 h. -No algicidal effect on <em>H. pluvialis</em> and <em>C. vulgaris</em>. -Non-toxic to <em>D. magna</em>.</td>
<td>- Promotes sedimentation - Might affect other organisms.</td>
<td>Han et al. (2019)</td>
</tr>
<tr>
<td>Ultrasonic technology</td>
<td><em>Microcystis aeruginosa</em></td>
<td>The removal rate of <em>Microcystis</em> reaches 99% after 15 min of ultrasound treatment (1200 W).</td>
<td>Removal depends on the species.</td>
<td>Chen et al. 2020</td>
</tr>
<tr>
<td>Water-lifting aerator (WLA)</td>
<td><em>Microcystis aeruginosa</em></td>
<td>Vertical mixing of WLA weakened the photosynthetic ability and reduced the biological activity of algae in situ.</td>
<td>This device can be used in a limited range.</td>
<td>Zhang et al. (2020)</td>
</tr>
<tr>
<td>UV-radiation enhanced alumnum (Al)-based coagulation</td>
<td><em>Microcystis aeruginosa</em></td>
<td>Approximately 93.5% of <em>M. aeruginosa</em> cells and 91.4% of <em>Cyclotella</em> sp. cells were removed after 240 s of UV irradiation with 0.4 mmol/L Al.</td>
<td>- Rapid sedimentation can lead to disturbance of the aquatic system.</td>
<td>Dai et al. (2020)</td>
</tr>
</tbody>
</table>

Conclusions

Technology advancements have allowed researchers to develop various biological, chemical, and physical approaches to mitigate HAB in recent years. Nevertheless, each of these methods has its advantages and disadvantages. Among the approaches, clays are more practical, considering their applicability in the field and fewer threats to other aquatic organisms. However, future development or modification should focus on overcoming sedimentation and reducing the number of clays required. Another aspect that needs to be focused on is increasing the strength of the interaction between the clay particles and the algal cells. Strong interaction will prevent the trapped algal cells from escaping and continuing to grow.

Anthropogenic activities and various environmental changes induced by climate change, such as warming/rising temperature, hydrologic modifications, extremes in rainfall, low dissolved oxygen and low pH (Nwankwegu et al. 2019), can be identified as the root causes of HABs. Hence, impacted countries must formulate tighter regulations to monitor the use and release of chemicals from anthropogenic activities that can contribute to HABs.

Routine HABs monitoring is crucial to serve as early warning systems and forecasts and to be ready to implement appropriate mitigation actions to minimize the impacts of HABs. Comprehensive monitoring data is needed to understand the mechanism of HABs occurrence better and make an accurate prediction,
homing to assist in developing mitigation strategies for HABs (Imai et al., 2021). The mitigation measures should be based on monitoring data and a basic understanding of the unique physiological, ecological, and life cycle traits of the causative species and the aquatic local environment traits. Meanwhile, implementing nutrient reduction strategies through improved wastewater treatment and regulation of point and non-point sources only offers a short-term solution to prevent secure HAB. Nwankwegu et al. 2019 proposed Integrated Management Interventions that combine two or more mitigation measures as a prudent management solution, emphasizing the simultaneous use of management options with preventive and curative measures as key to sustainable HAB management. More research and testing also need to be done to find cost-effective, easy to apply in the field and environmentally friendly HAB control methods while remaining harmless to the environment.

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References


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