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Chemical Prevention and Control of the Green Tide and Fouling Organism *Ulva*: Key Chemicals, Mechanisms, and Applications

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The green algae, *Ulva* spp., have been causing environmental problems worldwide, e.g., green tides and biofoulings. Green tides resulted from bloom floating *Ulva* have caused substantial economic losses. *Ulva* foulings increase the maintenance cost of marine facilities and contribute to the biomass of floating algae. Chemical methods are generally very inexpensive and convenient for suppression of *Ulva* spp. during their early life stages, thus solving the green tide and fouling problem at the source. In this paper, classical chemical methods that have been or are in use and emerging chemical methods under research are systematically reviewed. The advantages, disadvantages, mechanisms, and applications of these methods are also summarized. Highly toxic reagents are used in classical chemical methods, including oxidants, acids, heavy metal compounds, and synthetic biocides directly used or applied in antifouling coatings to kill or inhibit *Ulva* effectively. However, these toxic reagents have a high risk of resulting in secondary environmental problems. In order to minimize other environmental impacts while solving the current problem, emerging, and environmentally friendly chemical methods have been developed, such as the utilization of degradable natural products (mainly allelochemicals) and semi-natural products for *Ulva* inhibition and fouling control, and the use of flocculating agents to prevent microscopic propagules from germinating. All these chemical methods provide a promising direction for the prevention and control of *Ulva*.

Keywords: *Ulva*, microscopic propagule, green tide, antifouling, heavy metal, allelochemical, natural product, modified clay

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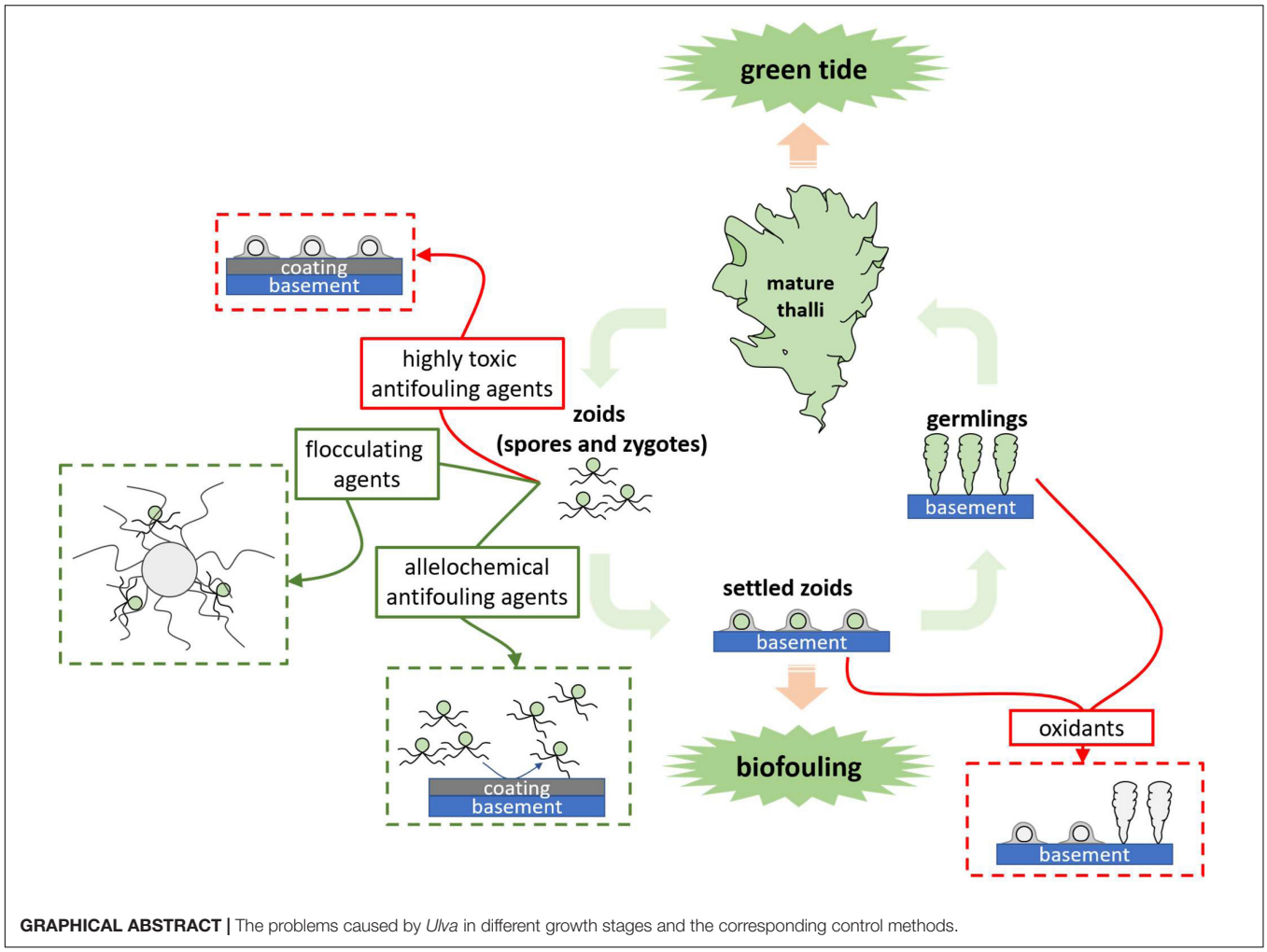
EMERGING ENVIRONMENTAL CHALLENGES RAISED BY *ULVA*

The Global Expanding Green Tides

"Green tide" is a phenomenon of green macroalgae (Chlorophyta) blooming in water bodies such as rivers, lagoons, bays, estuaries, and coastal zones (**Table 1**). Green tides have occurred in a few locations since times immemorial; between 1960 and 1970, green tides have increased in extent and have finally become a global problem (Morand and Merceron, 2005). The most common green tide organisms are various *Ulva* species, which are distributed on almost all the continents



GRAPHICAL ABSTRACT | The problems caused by *Ulva* in different growth stages and the corresponding control methods.

(Fletcher, 1996; Ye et al., 2011; **Table 1**). Although green tide sometimes breaks out in non-eutrophic waters, it is generally believed that human activities contribute immensely to coastal waters' enrichment, thereby exacerbating the outbreaks of green tides. Since 2007, green tides have occurred in the Yellow Sea during spring and summer every year. The largest event appeared in 2008 when it covered the Qingdao Olympic Sailing Center just before the match. The government spent about 2 billion CNY (~300 million USD) to remove more than 100,000 tons of green algae, causing substantial economic losses (Ye et al., 2011). According to molecular biology identification, a kind of Chlorophyte, *Ulva prolifera*, is responsible for the Yellow Sea green tide (Zhao et al., 2013). The ongoing outbreak of *U. prolifera* has resulted from its various reproduction methods, including sexual, asexual, and vegetative reproduction (Hiraoka et al., 2003), as well as its rapid growth rate. It is generally considered that these recalcitrant green algae are mainly from *Pyropia yezoensis* (a kind of laver) aquaculture area. The bamboo poles and the ropes used as laver farming rafts are easily fouled by several green macroalgae (Chlorophyta), including *U. prolifera* (Song et al., 2018). During rafts withdrawing, a massive amount of green algae attached to the cables are scraped off, washed out into the sea, and become the primary source of floating green algae (Zhang et al., 2018). The floating green algae biomass keeps growing and reproducing and finally forms the green tide dominated by *U. prolifera* (Han et al., 2019).

The forms of *Ulva* spp. invisible to the naked eyes, called *Ulva* microscopic propagules (UMPs), include spores, gametes, zygotes, microscopic germlings, and vegetative thalli fragments. There is a tremendous amount of UMPs distribution in the seawater and sediments along the East China Sea coast (Liu et al., 2012; Song et al., 2015, 2018). The nature of UMPs helps these algae survive the winter; in spring, once the environmental factors such as temperature and light are suitable for growth, these "seed bank" of green tide start activities (Liu et al., 2012).

Fouling

Biofouling is when marine organisms get attached to solid surfaces, such as ship hulls. The problem of fouling caused by *Ulva* is quite irritating. *Ulva* is a major ship fouling organism all over the world (Callow, 1986). Fouling on the ship hull increases resistance, causing additional fuel consumption, energy waste and the maintenance costs. Callow et al. (1997)

TABLE 1 | Major species of *Ulva* causing green tide.

Species	Distribution (data from algaebase.org)	Green tide events
U. lactuca	Arctic, Europe, North America (United States, Mexico), Central America, South America, Africa, Asia, and Oceania	Mactan Island, Philippines, 1999 (Largo et al., 2004)
		Knysna Estuary, South Africa, 2014–2015 (Allanson et al., 2016)
U. prolifera	Arctic, Europe, North America, Central America, South America, Africa, Asia, and Oceania	Yellow Sea, east of China, 2007–2020 (Wang et al., 2015)
U. pertusa	Europe, North America, South America, Africa, Asia, and Oceania	Yatsu tidal flat, Tokyo Bay, Japan, 1996–2007 (Yabe et al., 2009)
		Japan (Yokohama, Mikawa, Miyajima, Kochi and Hakata), 1997–1998 (Hiraoka et al., 2004)
U. reticulata	South America, Africa, Asia, Oceania	Mactan Island, Philippines, 1999 (Largo et al., 2004)
U. linza	Arctic, Europe, North America, Central America, South America, Africa, Asia, Oceania	Yellow Sea, southwest of Korea, 2009 (Kim et al., 2011; Kang et al., 2014)
U. intestinalis	Arctic, Europe, North America, Central America, South America, Africa, Asia, and Oceania	Olkiluodonvesi, west coast of Finland, Baltic Sea, 1992–2000 (Blomster et al., 2002)
U. ohnoi	Europe (Italy, Spain), North America (United States, Mexico), Africa (Tunisia), Asia (Japan, Korea, Iran, India), and Oceania (Australia)	Japan (Kochi, Fukuoka, Okinawa), 1997–2000 (Hiraoka et al., 2004)
		Yatsu tidal flat, Tokyo Bay, Japan, 1996–2007 (Yabe et al., 2009)
U. fenestrata	Europe (Britain, Denmark, Ireland, Norway, Sweden), North America (US), Africa (Somalia), Asia (Japan, India, Pakistan Sri Lanka, Singapore, Vietnam), Oceania (New Zealand)	Blakely Island, Washington, United States, 1998–2000 (Nelson et al., 2003)

described the detailed settlement process of *Ulva* spore by high-resolution video microscopy. After being released, the *Ulva* spores use 2 or 4 flagella to rotate and search for attachments. The spores will first rotate rapidly on the attachment base's surface like a gyro, meanwhile releasing a small amount of glycoprotein binder for pre-settlement. If the place is not suitable for attachment, the spore will leave only a small amount of adhesive and then swim away to try another base. Once a suitable base is found, the spore will release a large amount of adhesive, then retract the flagella quickly. The spore shape will become round, an amoeboid-like "spreading" and space-filling movement within a minute would be achieved. The cell wall formation will then begin, and within a few hours, germination into a germling will commence. Atomic Force Microscopy showed that the freshly released adhesive was very sticky, then became less sticky and more compressible, assuming a consistency similar to natural rubber (Callow and Callow, 2002).

PREVENTION AND CONTROL APPROACHES OF *ULVA*

The intensification of the green tide phenomenon in the past few decades is believed to result from eutrophication. Reducing nutrients input is an effective way to mitigate green tides fundamentally, however, it is often in contradiction with regional economies (Ye et al., 2011) and may take up to several decades to reach the goal. There is an urgent need to develop prevention and control methods for *Ulva*. Presently, various approaches, like physical, biological, and chemical methods, have been developed (**Table 2**). Physical approaches focus on the treatment of green tides or biofoulings that have developed, while biological and chemical approaches are applicable to the control of the initial biomass of *Ulva* whereas mitigating the problems at the source.

Physical Approaches

Physical methods have been used to clean the overwhelming *Ulva* thalli. Removing the floating macroalgae with boats or machines is the most common method (Fletcher, 1996). More recently, offshore intercepting nets have been set up in Qingdao to stop the *Ulva* from landing, according to the situation of floating green algae monitored by satellite remote sensing and unmanned aerial vehicles. The fouling *Ulva* can be cleaned by conventional machineries or hydraulic cleaning devices (Holm et al., 2003). Despite the damage to the ship hull when scraping fouling *Ulva*, these physical methods are natural and harmless. However, it cannot solve the problem from the source, that is, to reduce the settlement of *Ulva* spores on objects.

Biological Approaches

Limited information is available for the biological treatment in *Ulva* prevention, which is still in a relatively primary stage. For instance, the grazing effect of shrimp *Ampithoe valida* was found to reduce the biomass of *U. lactuca* (Zheng, 2008; Zheng et al., 2014). Oyster *Crassostrea gigas* and mussel *Mytilus edulis* could effectively filter out *U. prolifera* spores in both laboratory experiments and wild tests (Gao et al., 2018), both having the potential to be used in the early prevention of green tide.

Chemical Approaches

Classical Chemical Approaches

Classical chemical approaches use highly toxic reagents, such as oxidants, acids, heavy metal compounds and synthetic biocides to kill *Ulva* (**Graphical Abstract** and **Figure 1**). They can be added directly into *Ulva* threatened water bodies, applied on the *Ulva* fouled surfaces, or used as antifoulants in coatings to prevent the settlement of *Ulva* spores. Direct use of highly toxic chemicals can be very cheap and convenient; however, they may have substantial environmental issues. For instance, application of $CuSO_4$ may

TABLE 2 | Current methods developed for *Ulva* control, including the targets, application, technology maturity, ecological impact, and cost of these methods.

Category	Method	Technology or agents	Targets	Application	Maturity*	Ecological impact**	Cost
Physical	Mechanical cleaning	Boat or machine	*Ulva* thalli	Remove green tide algae on or near shore	4	–	*Ulva* removing: range from €120/t wet weight to $4050/t dry weight (Morand and Merceron, 2005; Gladyshev and Gubelit, 2019)
	Blocking	Arresting net	*Ulva* thalli	Block drifting algae from landing	4	–	NA
Biological	Predators	Shrimp *Ampithoe valida*; oyster *Crassostrea gigas*; mussel *Mytilus edulis*	*Ulva* thalli and UMPs	Reduce the biomass of *Ulva*	1	–	NA
Chemical	Oxidants	NaClO, ClO_2	UMPs and germlings	Applied on laver aquaculture rafts to clean fouling *Ulva*	2	NA	ClO_2: ∼1 CNY/mu (∼2.1 USD/ha) (Shao et al., 2019)
	Acids	HCl, H_2SO_4, H_3PO_3, citric acid	UMPs and germlings	Applied on laver aquaculture nursery nets to clean fouling *Ulva*	2	NA	NA
	Heavy metals and relative compounds	Organotins (banned), Cu_2O, Zn, Ag	UMPs	Applied in antifouling coatings	4	+ (others) +++ (organotins)	Cu based coating: range from 13.86 to 53.86 USD/m^2 (Belamarić and Belamarić, 2010)
	Synthetic biocides	Irgarol 1051, Sea-nine 211, etc	UMPs	Applied in antifouling coatings	3	++	NA
	Natural products	Fatty acids, benzenoids, alkaloids, etc	UMPs	Directly added or applied in antifouling coatings	1–2	NA	NA
	Flocculating agents	Modified clay	UMPs	Directly added into seawater	2	+	NA

**Maturity: 1, in lab research or small-scale tested; 2, mesocosm tested; 3, large-scale tested; 4, in application (with patents issued).*
***Ecological impact: –, no harm; +, small impact; ++, a greater impact; +++, severe impact.*

contaminate water bodies with the heavy metal copper. While a classical chemical method is applied, it is necessary to fully consider both the concentration of reagents and the growth state of the target *Ulva* to minimize environmental pollution.

Emerging Chemical Methods

It is necessary to find solutions for balancing *Ulva* control and environmental protection. The use of easily degradable or low-toxic chemicals (**Graphical Abstract** and **Figure 1**) to replace the highly toxic ones for *Ulva* inhibition is a good idea. Natural products are metabolites of various organisms, including fatty acids, terpenoids, and alkaloids, etc (DerMarderosian and Beutler, 2002), and they are degradable in the environment. Some natural products act as allelochemicals and are effective on *Ulva* growth inhibition or fouling control. Another clean approach is using flocculant in precipitating the UMPs and prevent them from germinating (Sun, 2014; Li, 2017; Li et al., 2020).

Fouling-released coatings (FRCs) is a clean and effective antifouling method on vessels. This method utilizes the low surface energy of non-toxic synthetic materials, so that *Ulva* is not firmly attached and is easily washed down under the action of water flow (Youngblood et al., 2003; Ekin et al., 2007; Hu et al., 2009; Dimitriou et al., 2011). These emerging methods help reduce *Ulva* problems while minimizing additional environmental challenges.

CLASSICAL CHEMICAL PREVENTION USING OXIDANTS, ACIDS, HEAVY METALS AND SYNTHETIC BIOCIDE

Using compounds with high toxicity to directly kill *Ulva* has the advantages of high efficiency, thorough removal effect, and are considered as a mature technique with low cost. However, highly toxic compounds tend to non-selectively impact all the organisms including keystone species, causing an imbalance in the ecosystem. Some compounds are difficult to be degraded and may cause continuous pollution in the water body. Commonly

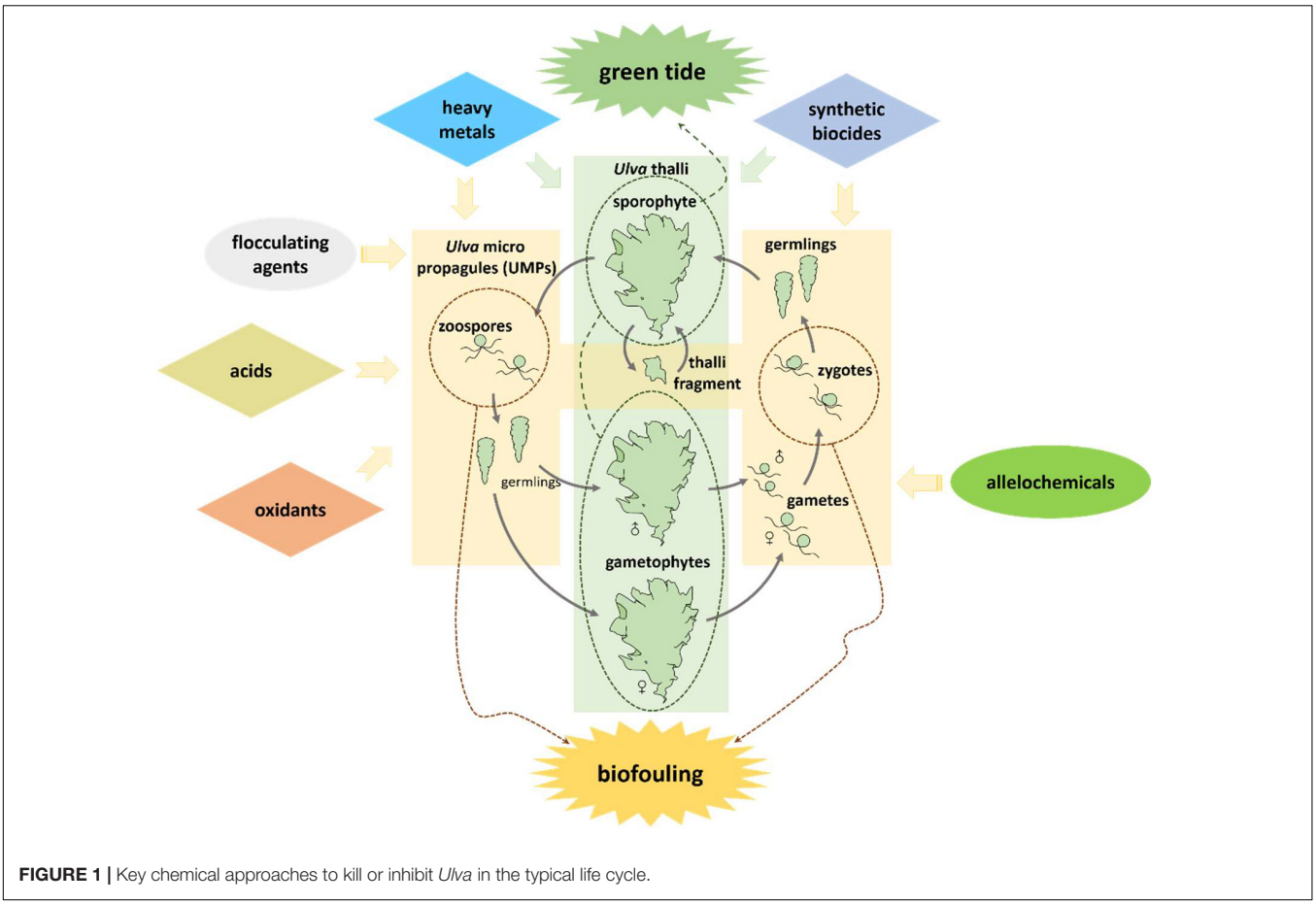


FIGURE 1 | Key chemical approaches to kill or inhibit *Ulva* in the typical life cycle.

used chemicals include oxidants, acids, heavy metals and synthetic biocides (**Table 3**). Unless field tests are specifically mentioned, the experiments cited in the text were conducted under laboratory; the substrates on which spores settled were mostly glass and plastic.

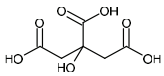
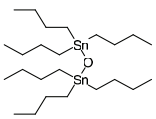
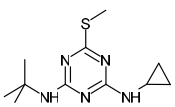
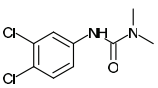
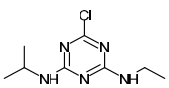
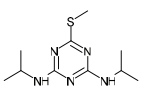
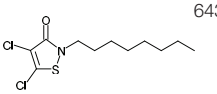
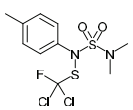
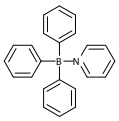
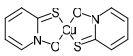
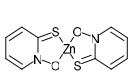
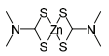
Oxidants

Oxidants can disturb the normal redox state of cells, damage vital biomolecules including proteins, enzymes, lipids and DNA, destroy the physiological functions of cells, and cause cell damage or death (Drábková et al., 2007; Rezayian et al., 2019). Chlorine-based oxidants such as sodium hypochlorite (NaClO) (**1**) and chlorine dioxide (ClO_2) (**2**), along with hydrogen peroxide (H_2O_2) (**3**) are commonly used as disinfectants due to their strong oxidation activity and broad-spectrum killing or inhibitory effect. They are widely used in sterilization and disinfection of hospitals, pools and homes, and their algicidal effects on *Ulva* have been tested.

Sodium hypochlorite was reported to kill *U. compressa* effectively at 4 mM, and suggested to be an ideal reagent for *Ulva* removal in laver aquaculture area (Zhu et al., 2014). However, a soybean-sized core of *U. prolifera* was found to remain green in high concentration NaClO solution, while the rest of thalli was bleached out and killed; this inferred a protection mechanism that sacrifices the periphery and preserves the core (Sun et al., 2008). A patent described the method of applying NaClO solution (acidified with citric acid just before use) to the laver culture rafts and ropes at low tide, to kill all fouling green algae including *Ulva* (Yu et al., 2012). Ministry of Natural Resources of the People's Republic of China has incorporated the NaClO method into the green tide prevention work plan[1]. Another patent pointed out that the attached UMPs of *U. prolifera* on the cables of the laver culture rafts can be effectively killed, by smearing or spraying the solution of commercially available ClO_2 effervescent tablets; the cost of ClO_2 in this patent is as low as ∼2.1 USD/ha (Shao et al., 2019). H_2O_2 at 1 mM is enough to reduce the photosynthetic activity of *U. rigida* significantly (Collén and Pedersén, 1996). However, most of the studies on the effect of H_2O_2 on *Ulva* spp. are to investigate the oxidative stress response mechanism of algae (Collén and Pedersén, 1996; Lu et al., 2006), and application research report for *Ulva* control in field is lacking. All these three oxidants decompose rapidly and do not accumulate in the environment. Disinfection by-products (DBPs) of chlorine-based oxidants have attracted attention. The application of ClO_2 in water bodies is more recommended, since the DBPs of NaClO contains carcinogen chloroform. H_2O_2 is generally considered as a very clean oxidant, as it only decomposes into water and oxygen without DBPs, but it is more expensive than chlorine-based oxidants.

[1]http://aoc.ouc.edu.cn/2019/1107/c9828a275333/page.htm

TABLE 3 | Key agents in classical chemical methods and their anti-algal abilities against *Ulva*.

Category	No.	Name	Formula or structure	CAS No.	Species	Inhibition stages and effective concentration	References
Oxidants	**1**	Sodium hypochlorite	NaClO	7681-52-9	*U. compressa*	Mature thalli killed at 4 mM	Zhu et al., 2014
	2	Chlorine dioxide	ClO_2	10049-04-4	*U. prolifera*	UMPs killed at 40 mg/L (0.6 mM)	Shao et al., 2019
	3	Hydrogen peroxide	H_2O_2	7722-84-1	*U. rigida*	Photosynthesis inhibited at 1 mM	Collén and Pedersén, 1996
Acids	**4**	Hydrochloric acid	HCl	7647-01-0	*U. prolifera*	Germlings killed at pH 2.3 for 1 min Mature thalli killed below pH 3.0 for 20 min	Yan et al., 2011; Wang et al., 2017
	5	Sulfuric acid	H_2SO_4	7664-93-9	*U. prolifera*	Mature thalli killed below pH 2.0 for 3 min	Wang et al., 2017
	6	Phosphoric acid	H_3PO_4	7664-38-2	*U. prolifera*	Mature thalli killed below pH 2.0 for 3 min	Wang et al., 2017
	7	Citric acid		77-92-9	*U. prolifera*	Germlings killed at pH 2.0	Yan et al., 2011
Heavy metals and relative compounds	**8**	Copper ion	Cu^{2+}	15158-11-9	*U. linza U. pertusa*	Mature thalli killed at 7.9 μM (*U. linza*) Photosynthesis inhibited at 16 μM (*U. pertusa*)	Yu et al., 1994b; Liu et al., 2018
	9	Silver ion	Ag^{+}	14701-21-4	*Ulva* sp.	Photosynthesis inhibited at 23 nM (total Ag)	Turner et al., 2012
	10	Tributyltin oxide (TBTO)		56-35-9	*U. conglobata*	Spores settlement completely inhibited at 0.2 mg/L (3 μM)	Hattori and Shizuri, 1996
Synthetic biocides	**11**	Irgarol 1051		28159-98-0	*U. intestinalis*	Spore germination inhibited at 0.4 nM Spores completely killed at 0.2 μM Thalli photosynthesis inhibition: EC_{50} 9.8 nM	Scarlett et al., 1997
	12	Diuron		330-54-1	*U. pertusa*	Spores settlement: EC_{50} 21 μM	Shin et al., 2015
	13	Atrazine		1912-24-9	*U. pertusa*	Photosynthesis inhibited at 5 μg/L (23 nM)	Gao et al., 2017
	14	Prometryn		7287-19-6	*U. pertusa*	photosynthesis inhibited at 1 μg/L (4.1 nM)	Gao et al., 2017
	15	DCOIT		64359-81-5	*U. lactuca U. intestinalis*	Germination: EC_{50} 83 nM (*U. lactuca*) spores settlement: EC_{50} 7 nM (*U. intestinalis*)	Willingham and Jacobson, 1993; Wendt, 2013; Wendt et al., 2013a
	16	Tolylfluanid		731-27-1	*U. lactuca*	Germination: EC_{50} 80 nM	Wendt, 2013; Wendt et al., 2013a
	17	TPBP		971-66-4	*U. lactuca*	Germination: EC_{50} 0.4 μM	Wendt, 2013; Wendt et al., 2013a
	18	CuPT		14915-37-8	*U. lactuca U. pertusa*	Germination: EC_{50} 38 nM (*U. lactuca*); 3.2 μM (*U. pertusa*)	Wendt, 2013; Shin et al., 2015
	19	ZnPT		13463-41-7	*U. lactuca U. pertusa*	Germination: EC_{50} 40 nM (*U. lactuca*); 16 μM (*U. pertusa*)	Wendt, 2013; Shin et al., 2015
	20	Ziram		137-30-4	*U. pertusa*	Germination: EC_{50} 16 μM	Shin et al., 2015

Acids

Acids with a low pH value and a high concentration of hydrogen ions (H^+) can damage various cells, such as destroying the structure of cell membranes or denaturing proteins. Therefore, a proper application of these acids can effectively kill UMPs and achieve the purpose of early prevention of *Ulva* that causes green tide or biofouling.

Hydrochloric acid (HCl) (**4**) is a strong acid widely used in industries and households. It has been reported that after treatment with dilute HCl with a pH of 2.3 for 1 min, all germlings of *U. prolifera* died after a period of time, while most germlings of laver *Porphyra haitanensis* was not affected (Yan et al., 2011). Another common organic acid, citric acid, showed the same algicidal effect against *U. prolifera* at pH 2.0 for 1 min, without impairing *P. haitanensis* (Yan et al., 2011). This method to remove the fouling green algae on laver aquaculture nursery nets has been patented (Luo et al., 2010; Wang et al., 2017). Nevertheless, the acids cannot be directly applied to seawater (otherwise it will greatly damage the environment), so the nets need to be collected on the shore or a dedicated boat (Luo et al., 2010) for acid treatment, consuming plenty of labor and resources. Besides, this method cannot prevent the nets from subsequent fouling in seawater. The high volatility of HCl is also easy to impair the health of workers. According to the published patents (Luo et al., 2010; Wang et al., 2017), non-volatile acids such as sulfuric acid (H_2SO_4) (**5**), phosphoric acid (H_3PO_4) (**6**) and citric acid (**7**) can also be applied in the same way. These non-volatile acids are more convenient in application than HCl.

Heavy Metals and Relative Compounds

Ulva Control by Direct Toxic Effects of Heavy Metal Ions

Many heavy metal ions can cause protein denaturation or cause cellular oxidative stress (Pinto et al., 2003; Kumar et al., 2010) and are therefore toxic to most organisms, and some of them are commonly used as effective algaecides or antifouling agents.

Copper (Cu) is the most widely used heavy metal in marine antifouling applications. At present, about 80% of antifouling coatings use cuprous oxide (Cu_2O) as the main antifouling agent (Wu et al., 2014). Copper ions (Cu^{2+}) (**8**) can combine with sulfur-containing biomolecules such as proteins in cells, destroy their physiological activity, and poison fouling organisms. Cu^{2+} can also replace Mg^{2+} in chlorophyll, thereby inhibiting the photosynthesis of algae (Küpper et al., 2003). It has been reported that Cu^{2+} could inhibit phosphorus uptake of *U. lactuca* (Huang et al., 2002) and could subject cells to oxidative stress (Wu, 2009). Copper salts, represented by copper sulfate ($CuSO_4$), are often used as algaecides in various water bodies. Although copper at high concentrations is toxic to most organisms, it is one of the essential trace elements of organisms with a background concentration of about 0.25 μg/L (3.9 nM) in seawater (Blossom, 2007). The copper released by the antifouling agent of ocean-going ships will be quickly diluted in seawater, and the environmental impact can be ignored. However, when the ship is sailing near the coast or staying in the harbor, the released copper is likely to accumulate in these areas, causing some ecological issues (Schiff et al., 2004). Copper-based antifouling agents may not be very effective on *Ulva*. A report focusing on traditional antifouling agents pointed out that *U. linza* was commonly found attached on some vessels using Cu_2O-based antifouling paints (Callow, 1986). The tolerance of different species and growth states of *Ulva* to copper ions varied greatly. Yu et al. (1994a) exposed the mature *U. linza* thalli to $CuSO_4$ solution to obtain its toxic effect; the threshold of Cu^{2+} was 1.6 μM, and the thalli died soon at 7.9 μM. But according to Sun et al. (2008), mature *U. prolifera* thalli partially survived even though $CuSO_4$ reached a supersaturated concentration (640 μM). Liu et al. (2018) found that Cu^{2+} significantly inhibited the photosynthesis of mature *U. pertusa* thalli at 16 μM.

Silver ion (Ag^+) (**9**) is quite toxic to most biofoulers including *Ulva*. Ag^+ or nanosilver powder has been applied in some laboratory and field antifouling researches (Li et al., 2013; Wu et al., 2014). Total Ag concentration above 23 nM can reduce the photosynthetic efficiency of *Ulva* thalli (Turner et al., 2012), but Ag^+ will combine with Cl^- to form a variety of complexes, resulting in free Ag^+ accounting for only 0.002% of total Ag (Turner et al., 2012). Silver itself is also a precious metal, therefore it may not be economical to be used on marine algal control. The toxicity of nanosilver powder to marine algae is also due to the released free Ag^+, thus nanosilver particles fixed on coatings will also be consumed.

Ulva Control by Self-Polishing Property of Heavy Metal Compounds

Organotins (organic compounds containing Sn) had been used as effective antifouling agents, especially tributyltin (TBT) series compounds represented by tributyltin oxide (TBTO) (**10**). Polyacrylic resin coatings containing TBT continuously hydrolyze in seawater, revealing a new smooth surface and maintaining a low navigation resistance while releasing TBT. This kind of coatings are named self-polishing coatings (SPCs). TBT does not only enhance the hydrolysis of resin, and it is a highly toxic and highly effective antifoulant killing almost all fouling organisms after release. TBTO has a strong inhibition effect both on settlement and germination of *Ulva* spores. At a concentration as low as 3 μM, the settlement of *U. conglobata* spores were completely inhibited (Hattori and Shizuri, 1996). However, TBT is too toxic to non-target organisms, causing sexual aberrations in some shellfish (Jha et al., 2000; Li et al., 2001) and vertebrate immunosuppression (De Vries et al., 1991; Kannan et al., 1998). The International Maritime Organization (IMO) prohibited organotins antifouling paints before 2008 (Bray and Langston, 2006).

Nowadays, zinc (Zn) is also commonly used in the production of SPCs, like zinc acrylate, a replacement of banned organotin SPC (Yonehara et al., 2001). In this kind of coatings, the antifouling agent is not zinc ion itself, but Cu_2O or other low-toxic chemicals released in the control of its self-polishing property. To the best of our knowledge, the antifouling effect of zinc itself on *Ulva* is not clear. A study reported that there are still quite a few *Ulva* attached to a paint containing zinc powder (Jelic-Mrcelic et al., 2006).

Synthetic Biocides

Since the ban of organotin paints on small boats (<25 m) in the 1980s (Voulvoulis et al., 1999; Tolhurst et al., 2007), compromised alternative antifouling methods have been developed. Synthetic herbicides and algaecides with photosystem II inhibition capability were introduced into copper-based antifouling paints as "booster biocides," to enhance the toxic effect on fouling macroalgae (especially the copper-tolerant *Ulva*). Irgarol 1051 (**11**) and diuron (**12**) are two of the most important synthetic booster biocides in antifouling applications (Chambers et al., 2006; Konstantinou, 2006; **Table 3**). The triazine biocide, Irgarol 1051, has a powerful inhibitory effect on *Ulva* spores. It was reported that Irgarol 1051 killed all *U. intestinalis* spores at 0.2 μM and significantly inhibited photosynthesis of mature thalli at 0.02 μM (Scarlett et al., 1997). Two other triazine herbicides with similar structures (not registered as booster biocides yet), atrazine (**13**), and prometryn (**14**), significantly depressed the photosynthesis efficiency of *U. pertusa* (Gao et al., 2017). Diuron was proven effective on settlement inhibition on *U. pertusa* spores, with EC_{50} of 21 μM (Shin et al., 2015). Triazine herbicides and diuron are difficult to degrade in seawater and sediment (Voulvoulis et al., 1999; Thomas and Brooks, 2010), thus they can be accumulated by marine organisms such as sea cucumbers (Tian et al., 2013; Ren et al., 2014), and eventually threaten human health. Sediments contaminated with antifouling paint particles containing Irgarol 1051 can also inhibit the growth of *Ulva* when resuspended (Tolhurst et al., 2007). The long-term use of Irgarol 1051 has caused selection pressure on *Ulva* in some areas, leading to the emergence of Irgarol-resistant *Ulva*. It was reported that spores of *U. lactuca* on the west coast of Sweden were not affected by Irgarol 1051 up to 2 μM (Wendt et al., 2013b).

With the awareness of the environmental problems caused by persistent organic pollutants (POPs), the use of these refractory biocides has gradually been reduced in various regions. All triazine herbicides have been banned in the EU, and Irgarol 1051 and diuron have also been banned on small boats in the United Kingdom (Cresswell et al., 2006; Konstantinou, 2006; Tolhurst et al., 2007). A few kinds of easily degradable booster biocides have been introduced (**Table 3**) as compromises of biofouling control and pollution reduction, before the large-scale applications of "zero-pollution" methods are developed.

DCOIT (4,5-dichloro-2-n-octyl-3(2H)-isothiazolinone, trade name Sea-Nine 211 or Kathon 930) (**15**), is an isothiazolinone broad-spectrum biocide, which strongly inhibits and kills bacteria, fungi, and algae. Tolylfluanid (**16**) was initially used as an agricultural fungicide, but can also be used as a booster biocide in antifouling coatings (Thomas and Brooks, 2010). DCOIT and tolylfluanid have more significant germination inhibition effects on *U. lactuca* spores (EC_{50} 83 and 80 nM, respectively) than Cu^{2+} (EC_{50} 2 μM) (Wendt, 2013; Wendt et al., 2013a). Another research indicated that DCOIT inhibited *U. intestinalis* spore settlement with a very low EC_{50} value of 7 nM (Willingham and Jacobson, 1993). DCOIT has a short half-life between < 1 d and 13 d in the marine environment (Chen and Lam, 2017) and tolylfluanid degrade within 2 weeks in seawater (Lee et al., 2020), but they are highly toxic to most non-target organisms. Therefore, it is necessary to limit their concentration in seawater.

Another booster biocide, triphenylborane pyridine (TPBP) (**17**), can be photolyzed or hydrolyzed in the environment (Thomas and Brooks, 2010). However, as an antifouling agent to *Ulva*, a higher concentration is needed (EC_{50} 400 nM, *U. lactuca* germination inhibition); otherwise the germination will be stimulated in low concentration (∼100 nM) (Wendt, 2013; Wendt et al., 2013a). Therefore, TPBP may not be a good choice for *Ulva* control.

Two metal complexes, copper pyrithione (CuPT) (**18**) and zinc pyrithione (ZnPT) (**19**), are both easily-degradable booster biocides, with a half-life of a few hours in seawater by photodegradation (Konstantinou, 2006). According to the thesis of Wendt (2013), the EC_{50} values to *U. lactuca* germination inhibition were 38 and 47 nM, respectively, which were both more effective than DCOIT, tolylfluanid and TPBP mentioned above. Shin et al. (2015) reported the inhibition effects of CuPT and ZnPT on the spore motility and germination of *U. pertusa*. Another zinc complex fungicide, zinc dimethyldithiocarbamate (ziram) (**20**), has an inhibitory effect on the germination of *U. pertusa* spores (Shin et al., 2015), with the half-life less than 1 day (Konstantinou, 2006). It should be noted that the abuse of these heavy metal-containing compounds may exacerbate heavy metal pollution in the estuary and coastal zone.

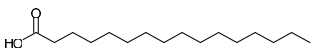
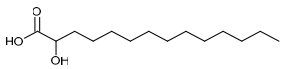
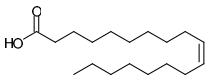
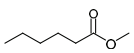
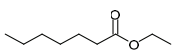
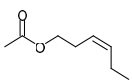
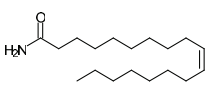
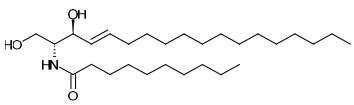
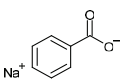
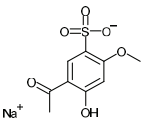
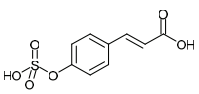
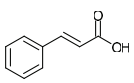
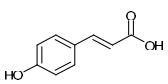
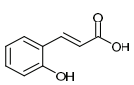
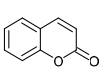
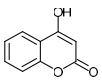
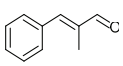
ULVA CONTROL BY NATURAL PRODUCTS (ALLELOCHEMICALS) AND DERIVATIVES

Many organisms, including plants, animals, algae and microbes, can produce various compounds to resist biological stress from other species, or help them in niche occupation. These compounds are often called allelochemicals. Marine macroalgae such as *Ishige okamurae* (Sidharthan et al., 2004) or bacteria like *Pseudomonas* sp. (Burgess et al., 2003) have been shown to produce antifouling allelochemicals to prevent the settlement of *Ulva* spores.

Compared with the highly toxic reagents used in traditional chemical methods, allelochemicals are more easily degraded in the environment and have better biological selectivity. However, many allelochemicals have acute toxicity to target or non-target organisms. Qian et al. (2009) suggested that a safe natural antifouling agent should have a therapeutic index [the ratio of 50% lethal concentration (LC_{50}) to 50% effective concentration (EC_{50})] greater than 50 and an EC_{50} less than 5 mg/L, but one with relatively high therapeutic index (means relatively more toxic) could also be considered if it is highly degradable in the environment.

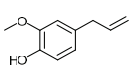
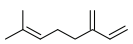
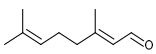
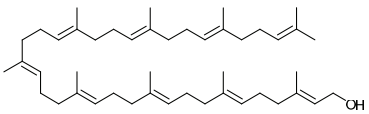
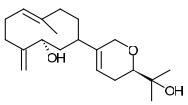
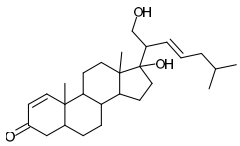
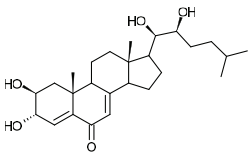
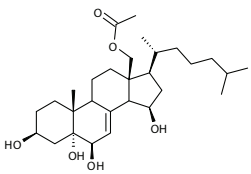
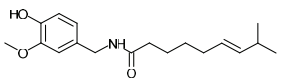
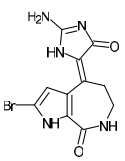
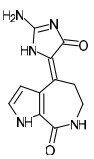
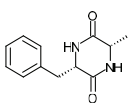
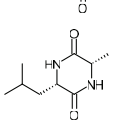
Here, natural allelochemicals and some artificial derivatives with *Ulva*-inhibiting activity with literature records are summarized in **Table 4**. It should be noted that different species or strains of *Ulva* have different stress resistance, therefore the EC_{50} value of these natural products obtained from different laboratories cannot be compared.

TABLE 4 | Natural allelochemicals and derivatives with *Ulva*-inhibiting activity.

Category	No.	Name	Structure	Species	Inhibition stages and effective concentrations	References
fatty acids and relative compounds	**21**	Palmitic acid		*U. lactuca*	Germination: EC_{50} less than 3.0 mg/L (12 μM)	Bazes et al., 2009
	22	2-hydroxymyristic acid		*U. pertusa*	Germination: EC_{50} 10 mg/L (41 μM)	Bhattarai et al., 2007a
	23	Oleic acid		*U. pertusa*	Germination: EC_{50} 100 mg/L (354 μM)	Bhattarai et al., 2007a
	24	Methyl hexanoate		*U. pertusa*	Spores settlement inhibited at 1 mg/L (7.7 μM) Spores motility affected at 100 mg/L (770 μM)	Bhattarai et al., 2007b
	25	Ethyl heptanoate		*U. pertusa*	Spores settlement inhibited at 1 mg/L (6.3 μM) Spores motility affected at 100 mg/L (630 μM)	Bhattarai et al., 2007b
	26	*cis*-3-hexenyl acetate		*U. pertusa*	Spores settlement inhibited at 1 mg/L (7.0 μM) Spores motility affected at 100 mg/L (700 μM)	Bhattarai et al., 2007b
	27	Oleamide		*U. pertusa*	Spores settlement: EC_{50} 0.01 mg/L (0.04 μM) Germination: EC_{50} 0.09 mg/L (0.32 μM)	Cho, 2012a
	28	C10-ceramide		*U. pertusa*	Spores settlement completely inhibited at 0.8 g/L (1.8 mM)	Zhang, 2012
Benzenoids	**29**	Sodium benzoate		*U. prolifera*	1% wt in PDMS coating: antifouling efficiency was 7.2 times vs. blank PDMS coating	Li et al., 2017b
	30	Sodium paeonolsilate		*Ulva* sp.	Showed *Ulva* spores resistance in coatings	Sun et al., 2016
Phenylpropanoids	**31**	Zosteric acid		*U. compressa*	Spores settlement inhibited from 75 μM; EC_{50} 250 μM germination inhibited at 500 μM	Callow and Callow, 1998
	32	Cinnamic acid		*U. compressa*	Spores settlement inhibited at 250 μM Germination inhibited at 500 μM	Callow and Callow, 1998
	33	4-coumaric acid		*U. compressa*	Spores settlement inhibited at 250 μM Germination inhibited at 500 μM	Callow and Callow, 1998
	34	2-coumaric acid		*U. pertusa*	Spores settlement: EC_{50} 0.25 mg/L (1.5 μM)	Kim et al., 2013
	35	Coumarin		*U. pertusa*	Spores settlement: EC_{50} 0.18 mg/L (1.2 μM)	Kim et al., 2013
	36	4-hydroxycoumarin		*U. pertusa*	Spores settlement: EC_{50} 0.13 mg/L (0.8 μM)	Kim et al., 2013
	37	α-methylcinnamaldehyde		*U. pertusa*	Spores settlement: EC_{50} 0.24 mg/L (1.6 μM)	Kim et al., 2013

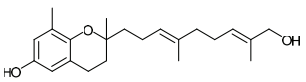
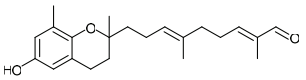
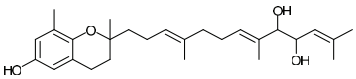
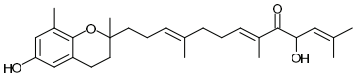
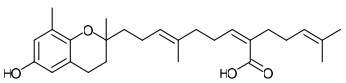
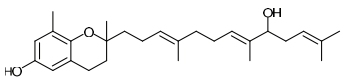
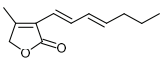
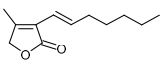
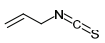
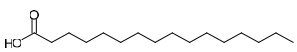
(Continued)

TABLE 4 | Continued

Category	No.	Name	Structure	Species	Inhibition stages and effective concentrations	References
	38	Eugenol		*U. pertusa*	Spores settlement and germination inhibited at 1 mg/L (6.0 μM)	Bhattarai et al., 2007b
Terpenoids and steroids	**39**	β-myrcene		*U. pertusa*	Spores settlement and germination inhibited at 1 mg/L (7.3 μM) Spores motility affected at 100 mg/L (730 μM)	Bhattarai et al., 2007b
	40	Citral		*U. pertusa*	Spores settlement and germination inhibited at 1 mg/L (6.6 μM) Spores motility affected at 100 mg/L (660 μM)	Bhattarai et al., 2007b
	41	Solanesol		*U. pertusa*	Spores settlement and germination inhibited at 1 μg/cm^2 (1.6 nmol/cm^2)	Sidharthan and Shin, 2007
	42	Lobocompactol		*U. pertusa*	Spores settlement: EC_{50} 0.18 mg/L (0.56 μM)	Cho and Kim, 2012
	43	Giffinisterone B		*U. pertusa*	Spores settlement: EC_{50} 0.15 mg/L (0.36 μM) Germination: EC_{50} 1.0 mg/L (2.4 μM)	Cho, 2012a
	44			*U. pertusa*	Spores settlement: EC_{50} 1.2 mg/L (2.8 μM)	Cho, 2012b
	45			*U. pertusa*	Spores settlement: EC_{50} 2.1 mg/L (4.3 μM)	Cho, 2012b
Alkaloids	**46**	Capsaicin		*U. compressa*.	TRPV1 activated and intracellular Ca^{2+} increased	Gómez et al., 2015
	47	Hymenialdisine		*U. prolifera*	Spore settlement: EC_{50} 8.31 mg/L (25.6 μM)	Feng et al., 2013
	48	Debromohymenialdisine		*U. prolifera*	Spore settlement: EC_{50} 0.67 mg/L (2.73 μM)	Feng et al., 2013
	49			*U. pertusa*	Spore settlement: EC_{50} 2.2 mg/L (10 μM)	Cho et al., 2012
	50			*U. pertusa*	Spore settlement: EC_{50} 3.1 mg/L (17 μM)	Cho et al., 2012

(Continued)

TABLE 4 | Continued

Category	No.	Name	Structure	Species	Inhibition stages and effective concentrations	References
Other natural products	**51**			*U. pertusa*	Spore settlement: EC_{50} 0.03 mg/L (0.09 μM)	Cho, 2013
	52			*U. pertusa*	Spore settlement: EC_{50} 0.03 mg/L (0.09 μM)	Cho, 2013
	53			*U. pertusa*	Spore settlement: EC_{50} 0.01 mg/L (0.02 μM)	Cho, 2013
	54			*U. pertusa*	Spore settlement: EC_{50} 0.09 mg/L (0.21 μM)	Cho, 2013
	55			*U. pertusa*	Spore settlement: EC_{50} 0.43 mg/L (1.0 μM)	Cho, 2013
	56			*U. pertusa*	Spore settlement: EC_{50} 0.23 mg/L (0.56 μM)	Cho, 2013
	57			*U. pertusa*	Spore settlement: EC_{50} 0.05 mg/L (0.28 μM)	Hong and Cho, 2013
	58			*U. pertusa*	Spore settlement: EC_{50} 0.03 mg/L (0.17 μM)	Hong and Cho, 2013
	59	Allyl isothiocyanate		*U. pertusa*	Spore settlement and germination inhibited at 1 mg/L (10 μM) Spores motility affected at 10 mg/L (100 μM)	Bhattarai et al., 2007b
	60	Octanol		*U. pertusa*	Spore settlement and germination inhibited at 1 mg/L (7.7 μM)	Bhattarai et al., 2007b

Fatty Acids and Relative Compounds

Fatty acids (FAs) are important primary metabolites of organisms and are generally considered as energy storage substances in cells. Palmitic acid, or hexadecanoic acid (**21**), is the most common saturated FA found in animals, plants and microorganisms. It has a relatively strong inhibition capacity on the germination of *U. lactuca* spores, with a low EC_{50} of less than 12 μM (Bazes et al., 2009). Two long-chain fatty acids isolated from the marine bacterium *Shewanella oneidensis*, 2-hydroxymyristic acid (**22**), and oleic acid (**23**), completely inhibited the germination of *U. pertusa* spores at 41 and 354 μM, respectively (Bhattarai et al., 2007a). The treated plastic plates with coatings containing each of the two FAs (10% wt in dry weight) exhibited excellent antifouling performances in the field test, free from biofouling in 1.5 years, while the untreated controls were covered by various fouling organisms including *U. pertusa* (Bhattarai et al., 2007a).

Three FA esters, methyl hexanoate (**24**), ethyl heptanoate (**25**), and *cis*-3-hexenyl acetate (**26**) all inhibited *U. pertusa* spores according to Bhattarai et al. (2007b), and they all exhibited good antifouling performances in the field test, without any visible fouling organisms attached during 1 year. The long-chain, colorless waxy solid amide, oleamide (**27**), was also found to be an *Ulva* inhibition agent, which inhibited *U. pertusa* spores settlement (EC_{50} 0.01 mg/L, 0.04 μM) and germination (EC_{50} 0.09 mg/L, 0.32 μM) (Cho, 2012a).

Ceramides are a family of waxy lipid molecules commonly found in eukaryotic cell membrane, making up sphingomyelins. Apart from supporting structural molecules, ceramides participate in various cellular signaling pathways, including regulating differentiation, proliferation, and programmed cell death. C10-ceramide (**28**), extracted from konjac (*Amorphophallus konjac*), completely inhibited the settlement of *U. pertusa* at 1.8 mM (Zhang, 2012).

Benzenoids

Benzoic acid, naturally found in gum benzoin from *Styrax*, is one of the most widely used food preservatives as sodium benzoate (**29**) form, although industrially used benzoic acid comes from artificial synthesis. Li et al. (2017b) applied polydimethylsiloxane (PDMS) coating with sodium benzoate to nylon ropes; after 24 h, only 3.1% of *U. prolifera* spores settled and germinated, showing an antifouling efficiency of 7.2 times vs. blank PDMS control.

Paeonol is mainly derived from the root bark of paeony (*Paeonia suffruticosa*). The artificial sulfonated derivative,

sodium paeonolsilate (**30**), is a semi-natural product and mainly used in medicine. In a study, sodium paeonolsilate was embedded in Zn_2Al layered double hydroxides, then dispersed in resin to form controlled release antifouling coating, which effectively reduced the density of attached *Ulva* spores (Sun et al., 2016).

Phenylpropanoids

The phenylpropanoids are a diverse family of organic compounds synthesized by plants from phenylalanine and tyrosine, with a basic structure of an aromatic phenyl group and a C3 side chain. The phenylpropanoids that have been documented in the literature and have a clear inhibitory effect on *Ulva* are shown below.

Zosteric acid (**31**), extracted from the seagrass eelgrass (*Zostera marina*), is the sulfate ester of 4-coumaric acid. According to Callow and Callow (1998), zosteric acid inhibited the settlement of *U. compressa* spores from a concentration of 75 μM, surpassing cinnamic acid (**32**) and 4-coumaric acid (**33**), which are very similar in structures. Interestingly, zosteric acid did not affect the motility of spores under 250 μM, which indicates that the antifouling activity of zosteric acid at low concentrations is not due to the toxicity to the spores. The authors speculated that the antifouling effect of zosteric acid was due to the combination with the adhesive secreted by the spores, or the attachment to the surface of the glass substrate. The strong hydrophilicity of the sulfuric acid group prevented or reduced the exclusion of the water between the adhesive and the substratum, making it difficult to form the adhesive-substratum interface (Callow and Callow, 1998). In the same year, Shin (1998) reported the antifouling effect of zosteric acid on *U. lactuca* (formerly known as *U. fasciata*) spores, which surpassed that of Cu^{2+} at the same molar concentration. Zosteric acid can be obtained by microbial fermentation (Jendresen and Nielsen, 2019), and this technology will significantly reduce the acquisition cost of zosteric acid.

Besides, 2-coumaric acid (**34**), coumarin (**35**), 4-hydroxycoumarin (**36**), and α-methylcinnamaldehyde (**37**) from the cinnamon tree (*Cinnamomum loureiroi*) have an excellent antifouling activity against *Ulva*, with fairly low EC_{50} values of 0.8–1.6 μM on *U. pertusa* spore settlement inhibition (Kim et al., 2013). Eugenol (**38**), a kind of fragrance substances in many plants, was also found as an antifouling agent against *Ulva*, inhibited both the settlement and germination of *U. pertusa* spores (Bhattarai et al., 2007b; Sidharthan and Shin, 2007).

Terpenoids and Steroids

Terpenoids (including terpenes) are biosynthesized by various organisms, especially plants, via mevalonate pathway. Terpenoids have multiple biochemical functions. Some of them have a broad-spectrum antibacterial effect, and some terpenoids act as allelochemicals against other plants (Peng et al., 2002). Studies have found that several terpenoids can significantly inhibit the settlement and germination of *Ulva* spores, indicating an excellent antifouling effect against *Ulva*. For instances, the common monoterpene β-myrcene (**39**) from bay leaf (*Laurus nobilis*), the monoterpenoid aldehyde citral (lemonal) (**40**) from lemon (*Citrus limon*), and the long-chain terpenoid alcohol solanesol (**41**) from solanaceous plants such as tobacco, potato, and tomato are all antifouling to *U. pertusa* (Bhattarai et al., 2007b; Sidharthan and Shin, 2007). A novel diterpenoid alcohol produced by a marine actinomycete *Streptomyces cinnabarinus*, lobocompactol (**42**), effectively inhibited the germination of *U. pertusa* spores with a very low EC_{50} of 0.56 μM (Cho and Kim, 2012).

Steroids are produced by the cyclization of a special triterpene, squalene, followed by a series of biochemical reactions. Three steroids, giffinisterone B (**43**) and two unnamed compounds (**44**, **45**) extracted from an epiphyte bacterium *Leucothrix mucor* on red alga, exhibited antifouling effects against *U. pertusa* spores (Cho, 2012a; b). Giffinisterone B also inhibited germination with an EC_{50} of 2.4 μM, but the germination inhibition capacity of the two unnamed compounds 44 and 45 were not tested.

Alkaloids

Capsaicin (**46**) is the main pungent chemical in chili that feels hot and spicy. Capsaicin can repel most fouling organisms and is a broad-spectrum natural antifouling agent (Shi and Wang, 2006). A patent of antifouling coating containing capsaicin was proposed by Watts Water Technologies Inc (Watts, 1995). Capsaicin is degradable in the environment and has low ecological risk (Wang et al., 2014). As to *U. compressa*, the intracellular calcium level significantly increased while the thalli were exposed to capsaicin (Gómez et al., 2015). According to Thompson et al. (2007), during the settling process of *Ulva* spores, the cytosolic Ca^{2+} increased to twice the initial value over a period of time, and then recovered to the initial value. This explains the process of *Ulva* spore settlement related to cytosolic Ca^{2+}. Besides, the increase of intracellular Ca^{2+} caused the unicellular green alga *Chlamydomonas reinhardtii* to lose flagella (deflagellation), loss of exercise ability and other cell function disorders, and the same inhibition effect was confirmed among five species in Chlorophyta (Aiyar et al., 2017). We speculate that the antifouling mechanism of capsaicin on *Ulva* may be due to the rapid increase of intracellular Ca^{2+} as the result of the activation of TRPV1 by capsaicin, making the spores hard to settle, or other functional disorders. However, there is no quantitative antifouling research report on capsaicin for *Ulva*. Natural capsaicin is very expensive, but at present artificial capsaicin and its homologs (capsaicinoids) have become a reality (Peng et al., 2011), which will significantly reduce the cost of using capsaicin as an *Ulva* inhibitor.

Hymenialdisine (**47**) and its debrominated derivative debromohymenialdisine (**48**), two alkaloids extracted from sponges *Axinella* sp., were confirmed antifouling against *U. prolifera* spore settlement with EC_{50} values of 25.6 and 2.73 μM, respectively (Feng et al., 2013), and they are synthesizable (Xu et al., 1997). Two diketopiperazines (DKPs) (**49**, **50**) from a marine bacterium *Streptomyces praecox* were quite effective in inhibiting the settlement of *U. pertusa* spores, with EC_{50} values of 10 and 17 μM, and therapeutic indexes of 18 and 21, respectively (Cho et al., 2012).

Other Natural Products

Six chromanols (**51–56**) with long side-chain were extracted from the brown alga *Sargassum horneri*, and they were very effective on the inhibition of *U. pertusa* spore settlement, with astonishing low EC_{50} values of 0.02–1.0 μM; the chromanol 53 was the most effective among them (Cho, 2013). Two furanone derivatives (**57**, **58**) were isolated from a seaweed epibiotic bacterium *Streptomyces violaceoruber* (Hong and Cho, 2013). They both exhibited a strong antifouling performance against *U. pertusa* spores settlement, with supremely low EC_{50} values of 0.28 and 0.17 μM, and very high therapeutic indexes of 94 and 140, respectively (Hong and Cho, 2013). Allyl isothiocyanate (**59**) is the source of the irritating odor of mustard, radish, horseradish and other plants. At a concentration of 1 mM, allyl isothiocyanate affected the motility of *U. pertusa* spores, and showed a fair antifouling capacity (Bhattarai et al., 2007b) against the spores settlement; it also showed antifouling activity at 10 μM. It was reported that octanol (**60**) could inhibit *U. pertusa* spores settlement and germination with a considerable performance at 7.7 μM (Bhattarai et al., 2007b).

Some biomacromolecules such as peptides, proteins, and enzymes have definite antifouling potential against *Ulva*. However, due to their large molecular weight, their chemical compositions are still not clear. The germination of *U. lactuca* was reported to be inhibited by an extracellular component of a marine bacterium, *Pseudoalteromonas tunicata*; the anti-algal component was heat-sensitive, polar and had a molar mass between 3 and 10 kDa, remaining unknown in composition (Egan et al., 2001). Similarly, the extracellular component of another marine bacterium, *Alteromonas* sp., inhibited the settlement and germination of *U. lactuca* spores; the active component was filtered to be protein or peptide, with a molecular size $\geq$ 3500 kDa (Silva-Aciares and Riquelme, 2008).

The adhesive that *Ulva* spores secrete is a kind of glycoprotein, which can be hydrolyzed by enzymes, such as serine protease, to reduce the adhesion of the spores (Christie et al., 1970; Pettitt et al., 2004). Since enzymes are very expensive and could be easily inactivated in seawater, this method is limited to laboratory research by now, and the application needs to be further optimized.

CHEMICAL MODIFIED FLOCCULATING AGENTS

Flocculating agents, such as clays have been used for decades to control harmful microalgae (Kojima, 1961). Natural clays (kaolin, montmorillonite, etc.), are mainly composed of various aluminosilicates. Due to their physical and chemical properties, they form colloidal particles after being sprinkled in water bodies, adsorb microalgal cells and then sink to the bottom, enabling the algal blooms to be quickly cleaned. However, the surface of natural clay colloidal particles and microalgae cells are generally negatively charged, which causes electrostatic repulsion resulting in low adsorption efficiency of natural clay to algal cells; if a chemical modifier is added to the clay to make the surface of the colloidal particles positively charged, the electrostatic effect between the colloidal particles and the cells can be changed from repulsion to attraction, which can greatly improve the adsorption efficiency (Yu et al., 1994b). There have been several successful applications in harmful microalgal bloom control using modified clay (Li, 2017). The zoids (spores and zygotes) of *Ulva* have a similar size to common microalgae in the range of a few to dozen micrometers (Callow et al., 1997), and also negatively charged, therefore can also be effectively adsorbed and cleaned with modified clay (Li et al., 2015).

Polyaluminum chloride (PAC), with a general formula $Al_nCl_{(3n-m)}(OH)_m$, is a commonly used clay modifier. In addition to reversing the surface charge of the clay to positive, its long-chain structure can improve the van der Waals interactions to *Ulva* zoids (Sun, 2014; Li et al., 2015; Li, 2017). Only 0.5 g/L of PAC modified kaolinite can inactivate almost all UMPs in seawater, indicated by a shipboard experiment using the seawater from *U. prolifera* affected sea area (Li, 2017; Li et al., 2017a). Kaolinite modified with aluminum sulfate [$Al_2(SO_4)_3$] has a higher effect on UMPs cleaning, and this may be due to the hydrolysis of aluminum ions to form a large amount of amorphous aluminum hydroxide, encasing the UMPs to flocs, removing them from the water body with the precipitation of clay particles (Zhang et al., 2016).

After precipitation with modified clay particles, the growth of UMPs was halted even when they were resuspended (Li et al., 2015, 2017a). The mechanisms of the inhibition effect are not yet fully understood. The possible mechanisms are as follows: (1) The "shading" effect of clay reduces the light intensity received by algal cells (Li et al., 2017a), though, even at a lower light intensity of 32 μmol m^{-2} s^{-1}, UMPs could still slowly grow (Liu et al., 2012). (2) Damages inside the cells of UMPs. A single-cell model species of Chlorophyta, *Chlorella vulgaris*, showed oxidative stress response as the up-regulation of relative enzymes when exposed to natural or PAC modified kaolinite; it might indicate disruption to the metabolic balance of the algae, resulting in an accumulation of superoxide free radicals ($O_2^-\cdot$) (Liu et al., 2016). Whether UMPs have similar cell damage remains to be further studied. (3) Modified clay colloids have a strong adsorption effect on phosphate, which may cause the phosphate in seawater to diffuse into the flocculated UMPs, which deprives it of nutrition and halts germination.

At present, the method of using modified clay to control green tide algae is still in the stage of mesocosm experiments (Li et al., 2020). If this method is to be applied in the prevention and control of green tides, the following issues need to be fully considered: (1) The negative effects of clay minerals on non-target organisms. It was reported that modified clays could affect the filter-feeding behavior of some shellfish even under an *Ulva*-suppression dosage (Zhang, 2018). (2) Safety issues of modifiers. Aluminum, a metal element that can cause dementia, can be accumulated in some marine organisms, such as shrimps (Sun et al., 2000). (3) The proactive treatment of green tides. For the treatment of microalgae blooms, the modified clay is usually sprayed into the water body to quickly eliminate them after the blooming (Li, 2017). Whereas modified clay application can only be useful before green tides occur, otherwise it will be ineffective to the mature *Ulva* when green tides have formed.

Nevertheless, this method is still a promising method for the early prevention of green tides.

FUTURE RESEARCH PERSPECTIVES

The green algae, *Ulva*, multiplies rapidly and has a strong resistance, bringing the problems of green tides and biofouling. Reducing nutrient inputs is indeed an effective solution for macroalgal blooms, however, it may conflict with policies for local economic development (especially in developing countries and regions) and be difficult to achieve. Due to the urgent need for solutions to these *Ulva* problems, many chemicals have been put into research and application. Classical chemical methods include applying highly toxic compounds such as strong oxidants, heavy metals, and synthetic biocides. The purpose is to quickly kill *Ulva* when they are in the spore or germling state. Classical chemical methods have the advantages of simple implementation and high efficiency. However, they inevitably bring problems such as environmental pollution and ecological damage. With the gradual attention to environmental and ecological issues, utilization of environmentally friendly methods is the future development direction of *Ulva* control, including using natural products with better ecological safety to inhibit the settlement and germination of *Ulva* spores, and using modified clay to inactivate UMPs. These emerging methods have great application prospects, and further research and optimization are needed to promote the progress of application in practical *Ulva* control.

In suggestion, under the premise of fully evaluating the *Ulva* removal effect, the application cost and the ecological risks, classical chemical methods can still be applied. For the early control of green tides, it is highly recommended to use easily decomposable oxidants (like NaClO and ClO_2) to directly eliminate fouling UMPs on aquaculture rafts. This method has the advantages of high efficiency, low cost, and reliability in practical and ecological safety, as long as properly applied. For the fouling problems of ships and marine facilities, we propose to increase the support for the development of degradable booster biocides and natural antifoulants, and gradually phase out the application of highly polluting and toxic ones. We also encourage in-depth application research and feasibility analysis of emerging environmentally friendly chemical methods for *Ulva* elimination, and exploration of comprehensive application of emerging methods, for example, the combination of natural antifoulants with non-toxic antifouling coatings.

AUTHOR CONTRIBUTIONS

XX conceived this review. TT and CL collected data from literatures. JH provided information about physcological physiology. TT, KE, and XX wrote the manuscript, with edits and contributions from all other authors. All authors contributed to the article and approved the submitted version.

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