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Reverse osmosis desalination system and algal blooms Part I: harmful algal blooms (HABs) species and toxicity

Mohamed A. Darwish, Hassan K. Abdulrahim, Ashraf S. Hassan, Basem Shomar*

Qatar Environment and Energy Research Institute, HBKU, Qatar Foundation, P.O. Box 5825, Doha, Qatar, Tel. +974 4454 2892; emails: madarwish@qf.org.qa (M.A. Darwish), habdelrehem@qf.org.qa (H.K. Abdulrahim), ahassan@qf.org.qa (A.S. Hassan), bshomar@qf.org.qa (B. Shomar)

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ABSTRACT

Harmful algal blooms (HABs) are a serious concern in the countries surrounding the Arabian Gulf (AG). A recent HAB event (2008–2009) forced partial (or full) shutdown of desalination plants, and reduced their productivity. Strong fouling in filter media occurred, and frequent backwash was not sufficient to maintain their removal. Some plants were shut down for as much as 32–55 d—in places where water storage may only be a few days—when pretreatment processes struggled to remove the increased biomass caused by the HAB species, and were shut down before more irreversible fouling of the reverse osmosis (RO) membranes could occur. HAB challenges are not limited to the algal biomass that may foul membranes, but extend to the toxins that can pass through the membranes and find their way into finished water. Within the AG region, great care is given to the engineering part (operation and maintenance) under normal conditions of the seawater; however, challenges in all levels and scales emerge due to HAB incidents. This review article is the first part of three articles, focusing on the HAB identification and pretreatment technologies to deal with them. This part comprehensively focuses on the types of HAB species reported in AG seawater, physical conditions associated with HAB occurrence, morphology, taxonomy, and their potential impacts on desalination plants. The identification of the HAB species and their toxins is necessary to adopt the best pretreatment strategies to achieve the required feed water quantity and quality. As the AG countries are moving fast toward membrane desalination technologies to secure their municipal water requirements, they will need to adapt and deploy the technologies of HAB removal at very early stages of pretreatment.

Keywords: Harmful algal blooms (HABs); Reverse osmosis plants; Water security; Arabian seas

1. Introduction

Water security in the countries of the Gulf Cooperation Council (GCC) has difficult and complicated meanings. GCC states depend mainly on seawater desalination due to the absence of significant natural water resources, with some limited exceptions in Oman and parts of the Kingdom of Saudi Arabia where some fresh groundwater is available. Challenges of water security were and are still urgent and

*Corresponding author.

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include water strategies, policies, and action plans. The region is growing very fast, and major changes appear in population growth, socioeconomic factors, oil and gas price instability, and construction of mega projects, among others. These changes are not in parallel with water projects aiming at producing more water with good quality.

Components of water security in some of these countries (e.g. Qatar and UAE) include desalination technologies, groundwater recharge, and water reuse. One of the top priorities is desalination, where the water storage capacity is few days only and the existing technologies cannot deal with big threats such as oil spills, radioactive material contamination, and harmful algal blooms. As most of these countries are moving from thermal (mainly MSF) to membrane desalination (mainly RO), special care should be given to the occurrence of algal blooms: their occurrence, toxicity, and treatment. Adding to concerns are the attacks of HABs on desalination plants that have occurred in recent years, which have resulted in significant damage to several plants.

2. Physical conditions of the Arabian seas

The Arabian Seas include the Arabian Gulf (AG), the Gulf of Oman, and the Arabian Sea. The Strait of Hormuz connects the AG with the Gulf of Oman. The AG is a small, semi-enclosed, shallow sea surrounded by arid and semi-arid areas. The AG area is 240,000 km^2 with 8,630 km^3 estimated water volume. The AG varies in width from 75 to 370 km, with an average width of 240 km. The AG extends 900 km from the Shatt Al-Arab in the north to the Strait of Hormuz in the south. Fig. 1a shows the AG's geographical location [1]. The average depth of the AG is 35 m, and it is noticeably shallow (less than 20 m) alongside the United Arab Emirates (UAE), and relatively deep (80 m) in the north along the Iranian coast [2]. A bathymetric map showing the seawater (SW) depth in the AG is shown in Fig. 1b.

The AG is considerably higher in salinity than typical seawater. Fig. 1a shows that the AG has high SW salinity along the UAE coast due to its shallowness, and salinity up to 57 g/L along Qatar west coast due to high evaporation in this enclosed area. The AG receives about 48 km^3/y (or 48,000 $m^3/y/240{,}000\ m^2$) = 0.2 m/y of fresh water inflows from the Tigris, the Euphrates, and the Karun rivers at the delta of the Shatt Al-Arab. The annual evaporation is estimated at 1.5 m/y [2]. Other reports have estimated the combined average discharge of the Tigris and Euphrates rivers at 22.4 km^3/y, while the outflow of the Karun River was given as 23.7 km^3/y [1]. The estimated outflow from the AG is in the range of 14.7×10^9–$34.5 \times 10^9\ m^3/d$, with an annual mean flow of 17.3–$21.6 \times 10^9\ m^3/d$. This estimation was done using acoustic doppler current profiler (ADCP) in the Strait of Hormuz [2]. The AG is used as a heat sink for power plants and desalted seawater (DW) plants (of about 57% of global DW capacity), which are spread along the AG coast. Warm brine (up to 10°C above SW temperature) and high salinity (up to 50% higher than the original SW salinity) are discharged from these DW plants to the AG. The temperature and salinity variations create density variations and thus, induce current movement. The Arabian Sea currents include several eddies and flows formed due to heat fluxes, density differences, and seasonal winds blowing through the region. These currents cause the transport of the formed algal blooms from the Arabian Sea to the AG and Gulf of Oman [3–5]. Fig. 1c shows SW flow currents driven primarily by density gradients. The SW enters the AG through the Strait of Hormuz, and moves northward along the Iranian coast. A major factor in the current pattern within the Arabian Gulf is the Coriolis Effect circulation which causes the current entering from the Arabian Sea to hug the northern boundary of the AG. A secondary coastal current flows to the south along the Iranian coast, against the inflow SW in the Strait of Hormuz, driven by density differences from river runoff in the north. A southward coastal flow moves along the southwestern coastline of the AG at high salinity, due to high evaporation and the shallowness of the Gulf in this area. This higher density water sinks and flows toward the entrance of the Gulf, where it lies beneath the incoming water. Fig. 1d shows the surface and bottom flow due to density gradients in summer.

3. The Arabian Gulf and algal blooms

An algal bloom is a "population explosion" of naturally occurring phytoplankton triggered by seasonal changes in temperature, abundance of sunlight, high concentration of nutrients in water, and water currents. Phytoplankton are photosynthesizing microscopic organisms that exist in sunlit layers of seawater or in fresh waters. The similarity of these algae and heterotrophs often makes it difficult to identify the precise cause of harmful algal blooms (HABs), or to predict their impact on a given ecosystem [8]. The major groups of algae causing severe blooms in marine environments are diatoms and dinoflagellates, haptophytes, raphidophytes, chlorophytes, and cyanobacteria [9].

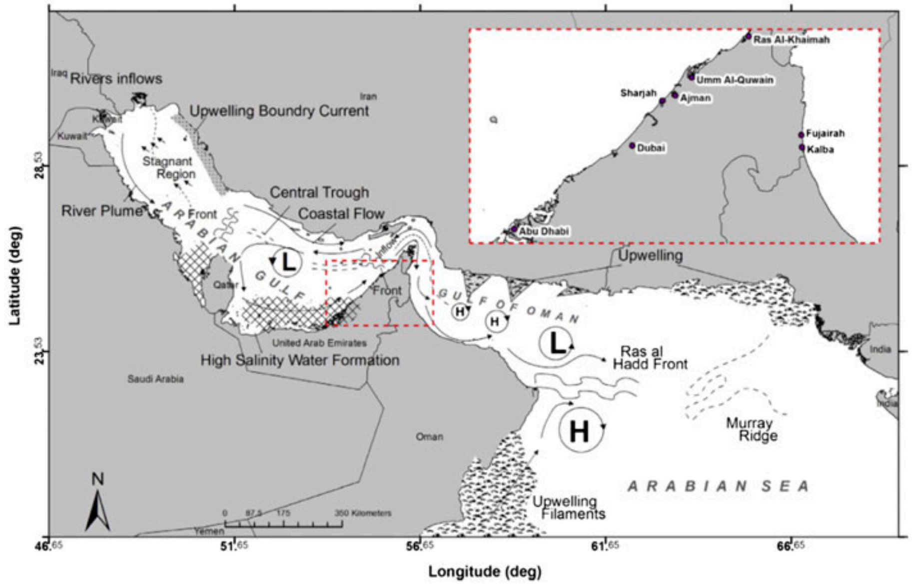

Fig. 1a. Geographical location and water currents of the Arabian Gulf, the Gulf of Oman, and the Arabian Sea [1].

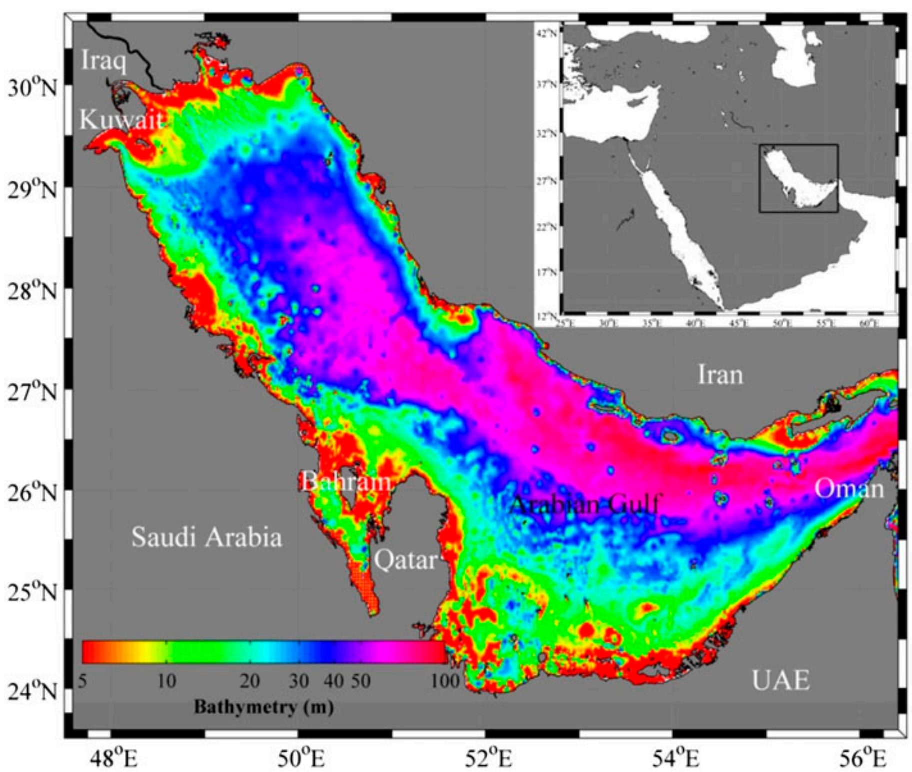

Fig. 1b. The bathymetric map featuring the Arabian Gulf [6].

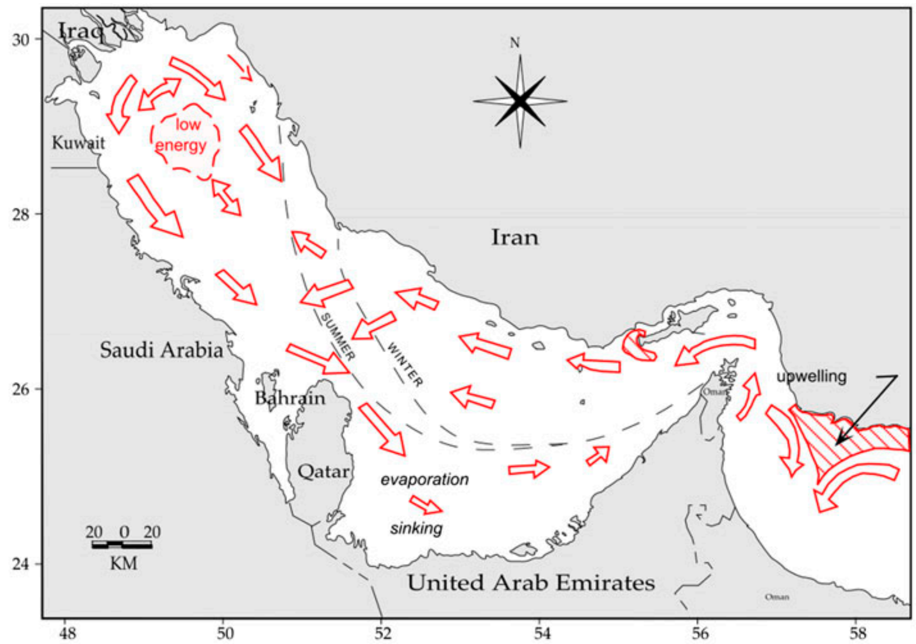

Fig. 1c. Schematic of surface currents and circulation processes [4].

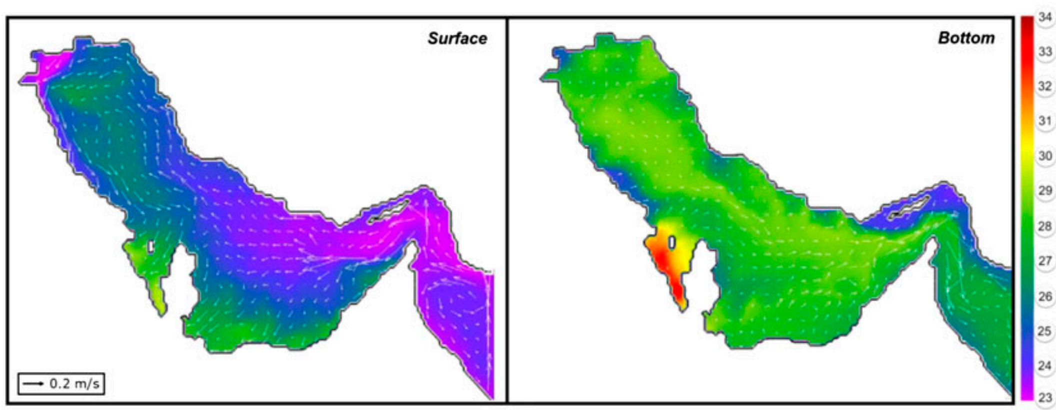

Fig. 1d. Lateral distributions of surface and bottom flow vectors (arrows, m/s) over density (colors, sigma-t units) averaged over summer months (June–August). Flow vectors are averaged over 5 × 5 grid cells for visualization purposes [7].

The source of nutrients that induces major algal blooms is commonly caused by oceanic perturbations of circulation that cause unusual upwelling effects which transport very large concentrations of limiting nutrients to the photic zone.

Chlorophyll pigments in phytoplankton give them a green color and play a major role in photosynthesis. Phytoplankton are considered to be the base of the food chain: they are food to organisms called zooplankton, which are consumed by small fish, and which in turn are food to larger fish and animals like penguins and seals, up to whales and humans. The phytoplankton have different shapes and are classified according to their size as given in Table 1.

Harmful algal blooms produce complex organic compounds (such as carbohydrates, fats, proteins, and extracellular secretions including TEP) from carbon dioxide dissolved in the water using energy from light or inorganic chemical reactions (chemosynthesis) [16,17]. The presence of phytoplankton decreases dissolved oxygen concentrations and light penetration in seawater. The resulting deficiency in dissolved oxygen as well as the toxicity of certain phytoplankton species can result in fish kills. The algal organisms are not

Table 1
Phytoplankton classification according to size [9]

Designation	Comment	Size in micrometers		
		Refs. [10–12]	Ref. [13]	Refs. [14,15]
Macroplankton	Visible to the naked eye	200–2,000		
Netplankton	Older term based on plankton net with 80 micrometer mesh	–		Greater than 22
Microplankton		20–200	50–500	
Nanoplankton		2–20	10–50	5–22
Ultraplankton			0.5–10	0.2–5 or less than 5
Picoplankton		Less than 2 or 0.2–2		Less than 1
Femtoplankton	Viruses and small bacteria	Less than 0.2		

toxic but their secretions are. The Arabian Gulf has historically been susceptible to HABs, and HABs have occurred more frequently in recent years both in the AG and around the world. Table 2 provides a timeline of recorded HABs in the AG.

Oman, Kuwait, and the UAE were affected by algal blooms during 2008 and 2009. A key indicator for algal blooms is an increase in the concentration of chlorophyll in the marine system. Fig. 2a shows the chlorophyll concentration over time during the AG HAB from August 2008 to May 2009. This was monitored by the presence of chlorophyll from NASA MODIS picture [18]. Fig. 2b shows the surface sea temperature (SST) (right) and chlorophyll a (left) of MODIS Aqua on 31 October 2008 [19].

The 2008–2009 AG HAB event was caused mainly by the *Cochlodinium polykrikoides* (*C. polykrikoides*) species, observed for the first time in the region and expected to be a persistent problem for the AG. The bloom, as reported by Richlen et al. [5], caused massive fish kills, damaged coral reefs, restricted fishing activities, and forced the stoppage of seawater reverse osmosis (SWRO) desalination plants in Oman and the UAE due to clogging of intake filters or fouling of reverse osmosis (RO) membranes. The *C. polykrikoides* is an unarmored, marine, planktonic dinoflagellate species with a distinctive spiral-shaped *cingulum*. The majority of cells observed in cultured material were in two-celled chains, Fig. 3(A)–(C); rarely, four-celled chains were observed Fig. 3(D) [5].

In March 2013, HAB patches were found in Fujairah, UAE coastal line along the Gulf of Oman. This transport of HAB from the Arabian Sea to the AG is higher in summer than winter because of the change occurring in the water speed of the Arabian Sea [5]. Part of the Arabian Sea is highly affected by the inflow of seawater from the Indian Ocean, which is rich in phosphorus (nutrient). Its impact on the environment was so high that it caused massive fish mortalities. Around 101 HAB events have been recorded in Indian waters between 1908 and 2009, dominated by *Trichodesmium erythraeum* and *Noctiluca scintillans* species. Table 1 shows that the *T. erythraeum* was observed in India (the Arabian Sea region) in 1908, 1935, 1982, 1998, 1999, and 2005; and in Iran and Kuwait in 1999; and in Oman in 2005. Also, the *N. scintillans* was observed in India in 1908, 1935, 1982, and 1998; Oman in 1976, 1988, 1996, and 2005; Pakistan in 1979; Bahrain and Saudi Arabia in 1976; the UAE in 1996; and in Kuwait in 1988, and 1999.

The *T. erythraeum*, Fig. 4a, bloom was found to persist for a longer period (May up to October) in Qatari's seawater than its typical. *Dinophysis caudata* and *Dinophysis miles*, Fig. 4b, were noticed to form blooms at the offshore stations and sometimes were found to associate with *Trichodesmium* blooms during summer months in Qatar's coastal waters. The phytoplankton species that form blooms in Omani waters cause pale yellow, orange red, brown, and green tides.

Boerlage and Nada [21] reported that the HAB events in the AG and Gulf of Oman appeared for 10 months from August 2008 to May 2009, and affected 1,200 km of coastline. Cell counts reached 11–21 million cells/L for surface waters during the bloom period near Fujairah [21]. These led to the closure of several SWRO desalination plants (DPs) and reductions in output capacity from some thermal DPs [21]. Some of the SWRO plants were shut down for up to 32–55 d in the UAE, and pretreatment processes struggled to remove the increased biomass and to produce correct feed seawater of sufficient quality for RO membrane treatment. Additionally, five DPs have been closed due to the failure of pretreatment processes to eliminate the algal bloom species. Action has

Table 2
Records of the main HAB occurred in the Arabian Seas [1]

Country	Region	Year	Season	Observed species
India	Arabian Sea	1908	–	*Trichodesmium erythraeum*, *Noctiluco scintillans*
India	Arabian Sea	1935	–	–
Oman	Gulf of Oman	1976	August October	*Gonyaulax* species, *Noctiluca* species
Bahrain KSA	Arabian Gulf	1976	–	–
Oman	Gulf of Oman	1978	February	*Gonyoulax* species, *Noctiluca* species
India	Arabian Sea	1979	June September	*Cyanobacteria*, dinoflagellates, diatoms
India	Arabian Sea	1979	October November	*Thalassiothrix longissima*, *Arnphiprora* species, *Thalassiosira* species
India	Arabian Sea	1979	December	*Fragilaria cylindrus*
Pakistan	Arabian Sea	1979	–	*Noctiluca scintillans*
India	Arabian Sea	1982	–	*Noctiluca scintillans*, *Trichodesmium* species
Oman	Gulf of Oman	1988	March September	*Noctiluca scintillons*
Kuwait	Arabian Gulf	1988	–	–
Pakistan	Arabian Sea	1990	–	*Prorocentrum minimum*
Oman	Gulf of Oman	1995	May	*Prorocentrum arabianum*
	Arabian Sea		June	
UAE	Arabian Gulf	1996	February	*Noctiluc scintillons*
Oman	Gulf of Oman		April	
–	Arabian Sea	1996	July August	*Phaeocystis globosa*, *Nitzschia longissima*, *Novafabricia Bilobata*, *Navicula diretta*, *Rhizosolenia hebetate*, *Rhizosolenia stolterfothii*, *Rhizosolenia styliformis*, *Rhizosolenia alata*, *Chaetoceros didymus*
Oman	Gulf of Oman Arabian Sea	1996	November	–
Qatar	Arabian Gulf	1996 1998	–	*Alexandrium* species, *Dinophysis* species, *Pseudo-nitzschia* species, *Gymnodinium breve*
Pakistan	Arabian Sea	1997	–	*Phaeocystis* species
India Iran	Arabian Sea	1998	November	*Trichodesmium erythraeum*, *Noctiluco Scintillans Karenia* species
Kuwait	Arabian Gulf	1999	September	
Kuwait	Arabian Gulf	1999	September	*Gymnodinium* species
India	Arabian Sea	2000	–	–

(*Continued*)

Table 2 (*Continued*)

Country	Region	Year	Season	Observed species
Oman	Gulf of Oman	2000	–	*Coscinodiscus* species
Kuwait	Arabian Gulf	2001	August September	*Streptococcus agalactiae*, *Gymnodinium impudicus*, *Pyrodinium bahamense*
UAE	Arabian Gulf	2003 2004	October September	*Cyanobacteria*, *Prorocentrum* species
India	Arabian Sea	2004	September	*Noctiluca scitillans*
India	Arabian Sea	2005	May	*Trichodesmium erythraeum*
Oman	Gulf of Oman	2005	October	*Noctiluca scintillans*, *Prorocentrum micans Trichodesmium erythraeum*
UAE	Arabian Gulf	2008 2009	August 2008 May 2009	*Cochlodinium polykrikoides*, *Dinophysis caudate. Dinophysis miles*, *Prorocentrum minimum*, *Pyrodinium bahamense*, *Ceratium lured*, *Pyrodinium bahamense*
Iran	Arabian Gulf	2008 2009	–	*Cochlodinium polykrikoides*

been taken to avoid irreversible biofouling of the RO membranes. Although the major algal bloom species found in the feed water was *C. polykrikoides* which is non-toxic (Fig. 3(A)), the incident called for further studies on HAB and toxicology.

Al Shehhi et al. [1] reported a massive HAB along the Kuwaiti coast in October 1999 and September 2001, and in Qatar and the Southwest of India between 1996 and 1998. These HABs belong to eight different genera of dinoflagellates, diatoms, and cyanobacteria. The HAB events in Qatar and the Southwest of India were due to the high temperature and high nutrient content in seawater. In October 2005 and from fall 2008 to spring 2009, temperature increases were recorded along the coast of Oman (around 27˚C) and the AG (around 28˚C), and caused the outbreak of specific algae species: dinoflagellate *Prorocentrum micans* in the Gulf of Oman and *C. polykrikoides* in the AG.

The common diatoms that cause HABs in the region include *Pseudo-Nitzschia seriata*, Fig. 5a, of width more than 3 μm, and *Thalassiothrix longissima*, Fig. 5b, of 1,000–4,000 μm in length and 3–6 μm in width. The diatoms can be found as single or multi-celled free floating plants. These cells include chlorophyll pigments (a and c) and carotenoids. Pigments are not distributed uniformly in the cell. They are a mixture of green chlorophyll and brownish yellow *carotenoids*, and are placed in small packages called "*chloroplasts*". Some diatom species can be toxic, as in the case of *Pseudo-Nitzschia seriata*, which produces toxic domoic acid and which can be poisonous for amnesic shellfish, marine animals, and humans.

Cyanobacteria are another common species that cause HABs in the Arabian Seas, especially *Trichodesmium* (*T. erythraeum* of 60–70 μm in length, and 7–12 μm in width, and *T. thiebautii*), which were frequently observed during the inter-monsoon periods. Cyanobacteria (cyano = blue-green) are a type of algae found naturally in aquatic and terrestrial environments. A description of the biological features of some of the pre-cited species has been summarized by Al Shehhi et al. [1].

4. Potential risks and consequences of HAB formation in the Arabian seas

While algae benefit the food chain in aquatic environments by recycling nutrients, algae blooms can badly affect the environment and humans due to their high biomass concentrations and the toxins released. The algal blooms can reduce the dissolved oxygen in the water available for fish, submerged aquatic vegetation, and shellfish, and can be detrimental to aquaculture and marine ecosystems. Even if not toxic, blooms can be considered as harmful as they can lead to oxygen depletion as well as light reduction caused by water discoloring. The release of toxins can alter cellular processes and cause mortalities in aquatic organisms and mammals.

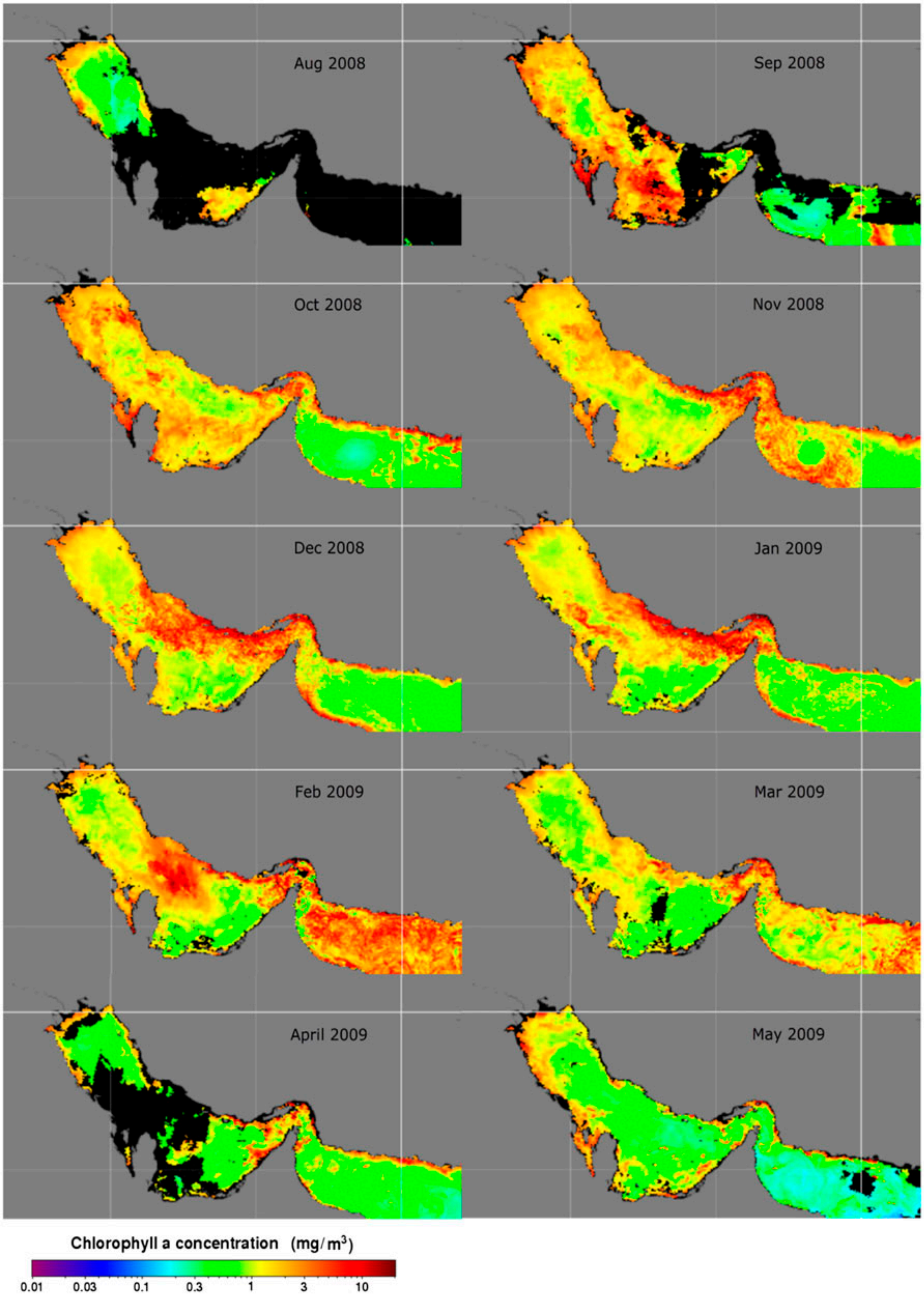

Fig. 2a. Record of chlorophyll concentration in the Arabian Gulf during the 2008–2009 HAB incident in Arabian coast affected many RO plant operations, adopted from [18].

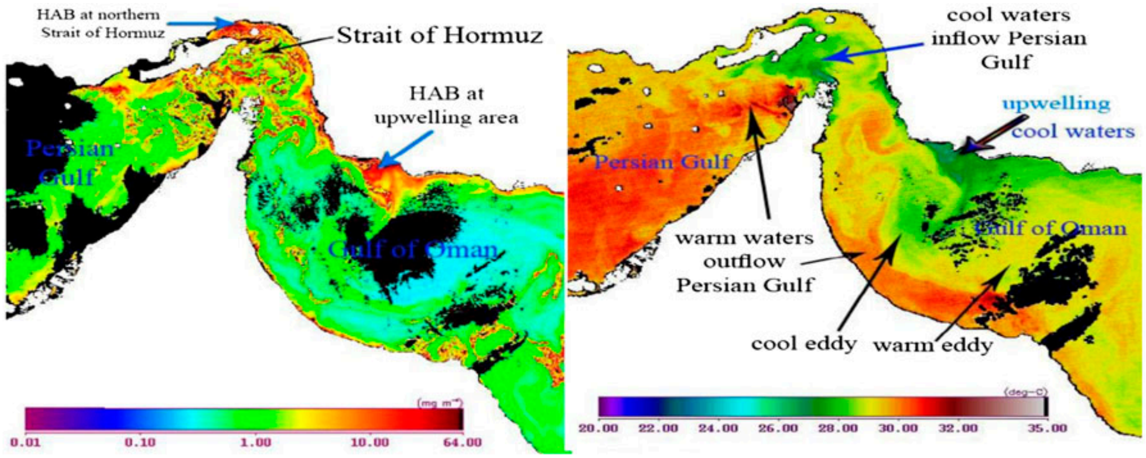

Fig. 2b. SST (right) and chlorophyll a (left) of MODIS Aqua on 31 October 2008 [19].

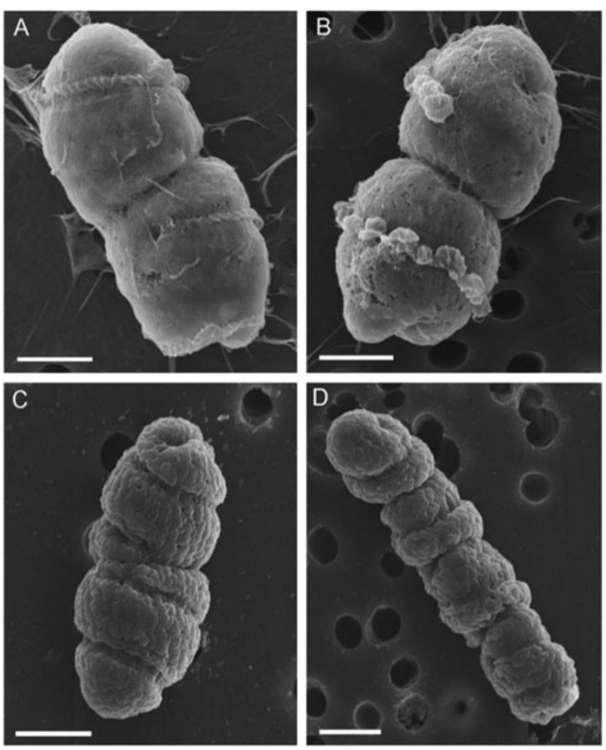

Fig. 3. SEM micrographs of *C. polykrikoides* from the Arabian Gulf. Cells are oriented apically: (A) two-celled chain enmeshed in a mucoid matrix; sulcus can be observed in the top cell, just below the cingulum in the anterior portion of the cell, (B) two-celled chain showing transverse flagellum of each cell; the excavated cingulum of upper cell is clearly visible, (C) two-celled chain following treatment to remove polysaccharide mucilage, revealing excavated cingulum of both cells, and (D) four-celled chain.

Within the comprehensive study of Al-Yamani et al. [22], a total of 62 identified algal taxa have been categorized as potentially harmful species in Kuwait SW. A total of 43 taxa can be classified as potentially toxic to humans and marine biota, and 10 taxa have been described as potentially harmful to fish and invertebrates. Most of the documented algal blooms in Kuwait's marine environment were harmless and were not associated with fish kills, except for one incident of toxic dinoflagellates *K. selliformis* and *P. rhathymum* that occurred in September-October 1999 and caused significant mortality of wild and aqua-cultured fish in Kuwait Bay [23–26]. Marine biotoxins and harmful algae pose a significant and extensive threat to human health and fisheries resources throughout the world [27–29]. Both types of HABs, the toxin producers (e.g. *K. selliformis*) and the high biomass producers occurred in Kuwait's marine environment; however, the latter were prevalent and were supported mainly by the diatoms development.

Microalgal species known to cause all common HAB toxin syndromes were detected in Kuwait's marine environment. The majority of these potentially toxic species were recorded in low concentrations; however, their diversity and common occurrence in the water column and intertidal sediments can be considered as an important finding related to the possible harmful events [30].

The potentially harmful species in Kuwait's marine environment, types of associated poisoning events and known harmful effect toxins, and their abbreviations, are:

(a) Toxic species: PSF—Paralytic Shellfish Poisoning; NT—Neurotoxic; HT—Hepatotoxic; ASP—Amnesic Shellfish Poisoning; DSP—Diarrhetic Shellfish Poisoning; NSP—Neurotoxic Shellfish Poisoning; CFP—Ciguatera Fish Poisoning; OA—okadaic acid; DTX—dinophysistoxin; DA—domoic acid.

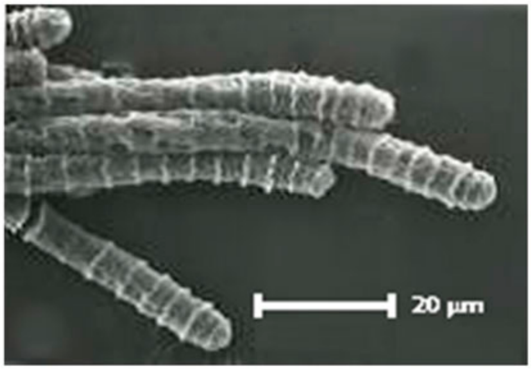

Fig. 4a. The *T. erythraeum* was detected in 2004 [20].

(b) Harmful species: those species that are known to produce blooms associated with fish mortality elsewhere.

(c) Bloom-forming species: bloom or close to bloom abundance (105–106 cells l-1) which was detected in Kuwait are given according to Al-Yamani et al. [25] as follows:

(1) Dinophyceae class including *Akashiwo sanguinea* (surfactant-producing), *Alexandrium catenella* (PSP), *Alexandrium leei* (PSP), *A. minutum* (PSP), *A. pseudogonyaulax* (PSP), *A. tamarense* (PSP), *A. tamiyavanichii* (PSP), *Amphidinium carterae* (Haemolysins), *A. gibbosum* (Cytotoxins), *A. operculatum* (Haemolysins), *Ceratium furca*, *C. fusus*, *Cochlodinium fulvescens* (Ichthyotoxicity), *Dinophysis acuminate* (DSP), *D. acuta* (DSP), *D. caudata* (DSP), *D. miles* (DSP), *Dinophysis norvegica* (DSP), *D. tripos* (DSP), *Gonyaulax polygramma*, *G. spinifera* (Yessotoxin), *Gymnodinium catenatum* (PSP), *Karenia mikimotoi* (Ichthyotoxicity), *Karenia papilionacea* (NSP), *K. selliformis* (NSP), *Lingulodinium polyedrum* (Yessotoxin), *N. scintillans*, *Ostreopsis ovata* (CFP), cf *siamensis* (CFP), *Peridinium quinquecorne*, *Phalacroma mitra* (DSP), *P. rapa* (DSP), *P. rotundatum* (DSP), *Prorocentrum concavum* (OA, DTX-1, CFP), *P. emarginatum* (Haemolytic activity), *Prorocentrum lima* (DSP), *P. micans*, *P. minimum* (NT), *P. rhathymum* (Haemolytic activity), *Protoceratium reticulatum* (Yessotoxin), *Pyrodinium bahamense* var. *compressum* (PSP), *Scrippsiella trochoidea*, *Takayama* cf *pulchella* (Ichthyotoxicity).

(2) Bacillariophyceae class including: *Amphora coffeaeformis*, *Chaetoceros curvisetum*, *C. pseudocurvisetus*, *C. socialis*, *Cyclotella*, *Cylindrotheca closterium*, *Eucampia zodiacus*, *Guinardia flaccida*, *Nitzschia laevis*, *Pseudo-nitzschia pungens*, *Pseudo-nitzschia delicatissima*.

(3) Dictyochophyceae class including: *Dictyocha fibula* and *D. speculum*.

(4) Cryptophyceae class including: *Teleaulax*.

(5) Raphydophyceae class including: *Chattonella marina* var. *antiqua* and *Heterosigma akashiwo*.

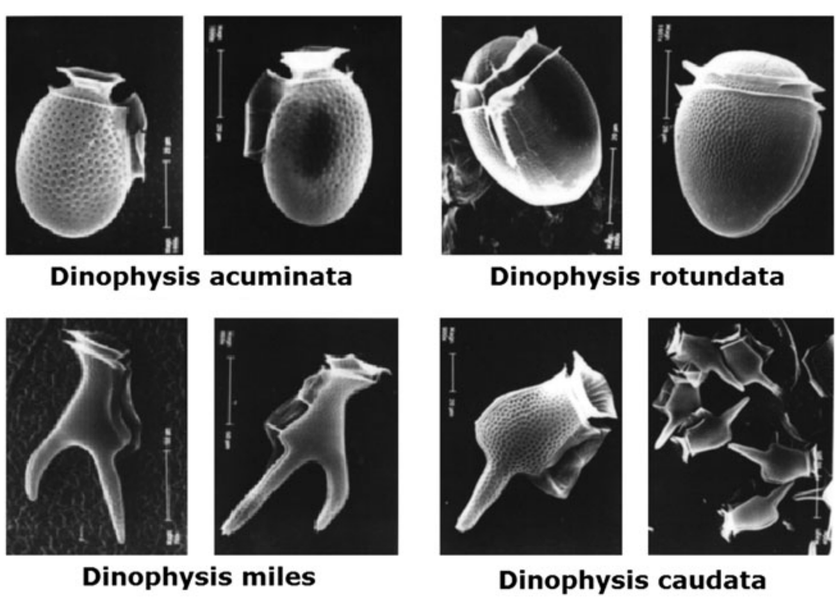

Fig. 4b. Species of Dinoflagellates commonly exist in Qatari waters and also in tropical and subtropical Asian waters [20].

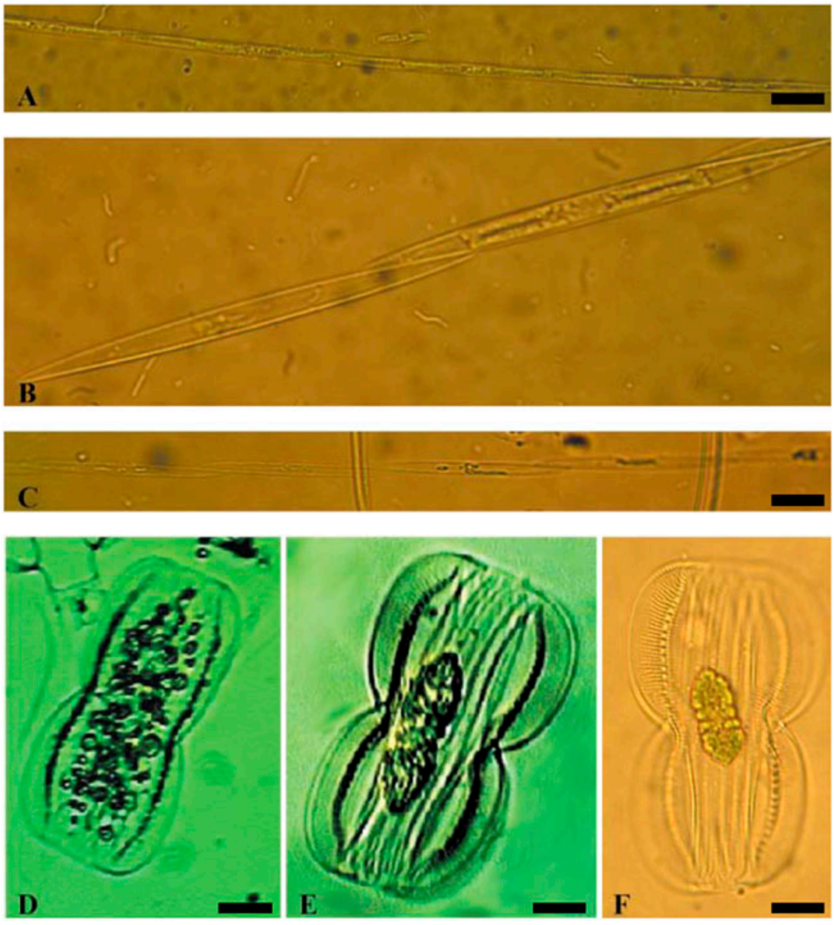

Fig. 5a. Light micrographs of: (A–B), *Pseudo-nitzschia seriata* group: another chains of different cells varied in size; (C), *Pseudo-nitzschia delicatissima* group: chain of thin cells; (D–F), *Entomoneis sulcata*: different cells in valve view: (D–E), from preserved material, (F), from cleaned material. (Scale Bars, (A) = 25.00 μm; (B) = 8.33 μm; (C) = 12.50 μm; (D) = 14.67 μm; (E) = 16.67 μm; (F) = 25.00 μm) [31].

(6) Prymnesiophyceae class including: *Phaeocystis globosa*.
(7) Cyanophyceae class including: *T. erythraeum*, Phylum Ciliophora, and *Myrionecta rubra*.

The first known toxic algal blooms in Kuwait's waters were of *Karenia selliformis*, Fig. 6a, as well as of *Prorocentrum rathymum*, which occurred in Kuwait Bay and were implicated with the massive mortality of wild mullets during September–October 1999 [26]. Al-Kandari et al. [31], published an Atlas of marine phytoplankton in Kuwaiti waters and gave examples of toxic micro-algal species that bloomed in Kuwait's waters. These include the dinoflagellates *K. selliformis*, Fig. 6a, *Prorocentrum rhathymum* (*Prorocentrum mexicanum*), *P. bahamense var. compressum*, as well as, the diatom *Pseudo-nitzschia* spp., Fig. 5a, the marine filamentous cyanobacteria *T. erythraeum*, and the *raphidophyte H. akashiwo*.

Furthermore, there are other common toxic species that were found also during certain months of the year (mostly in summer in Kuwait Bay and around) such as *Alexandrium* spp. (*Alexandrium minutum* and *Alexandrium tamarense*), Fig. 6b, *Dinophysis caudata*, *D. miles*, and *Dinophysis mitra*, and Fig. 6c, *Dinophysis norvegica* and *Dinophysis rotundata*, *G. polygramma*, and *L. polyedrum*.

5. Toxins of algae

The HAB release potent toxins causing illness or mortality in humans, fish, marine mammals, and other marine life through direct exposure or ingestion. Within the anoxic conditions and due to the high algal biomass, hydrogen sulfide is produced by bacteria. The HAB have caused death of large quantities of fish, Fig. 7 [32] as happened in Kuwait (2001), Oman

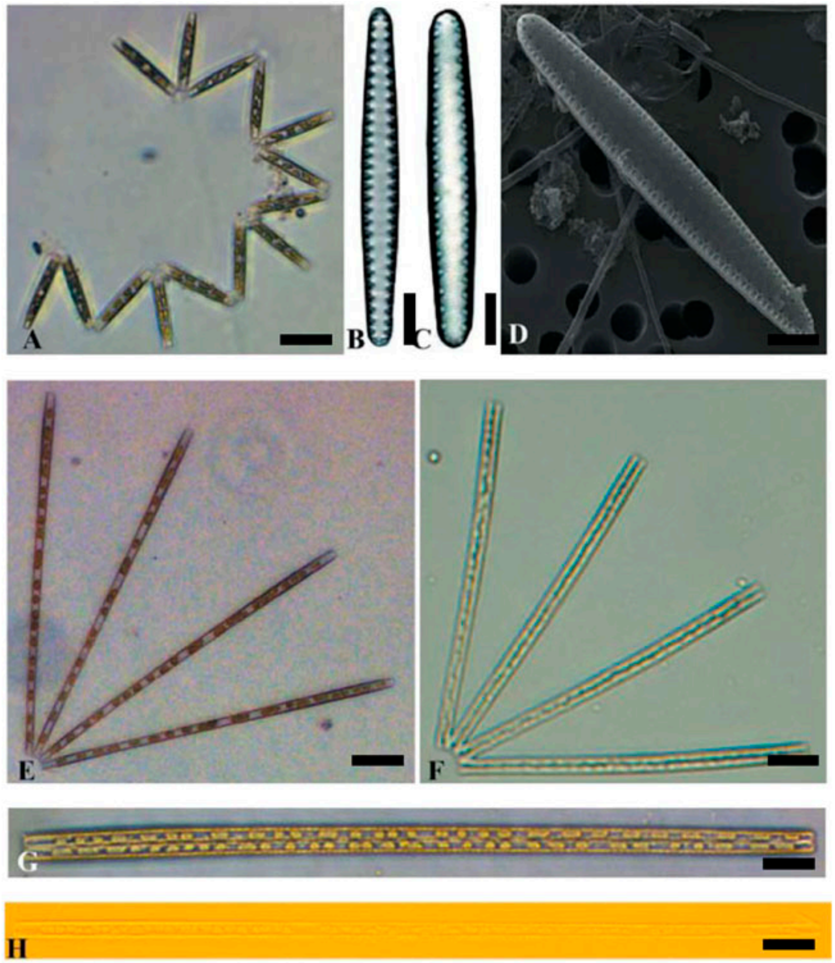

Fig. 5b. Light micrographs of (A–C) *Thalassionema nitzschioides*: (A) chain in girdle view, (B–C) cells in valve view, (D) Scanning electron micrographs of the cell in valve view; Light micrographs of (E–G) *Thalassionema frauenfeldii*: (E–F) colony of four cells, girdle view, (G) one divided cell; (H) *Thalassiothrix* cf. *longissima*: one long cell. (Scale Bars, (A) = 26.88 μm; (B) = 7.27 μm; (C) = 6.92 μm; (D) = 5.58 μm; (E) = 16.90 μm; (F) = 16.52 μm; (G) = 7.59 μm; (H) = 10.00 μm) [31].

(2005), and UAE (2008). Massive marine mortality occurred in Kuwait in 2002 (Fig. 7). These deaths were due to harmful blooms of two HAB species; namely, *K. selliformis* and *P. rhathymum* [32]. These are not toxic but still can be very harmful.

The known kinds of toxic shellfish poisoning are caused by toxic chemicals produced by certain species of toxic algae and released into the shellfish when they consume the algae [33–35]. These poisonings are:

(1) PSP is caused by a group of chemicals called the *saxitoxins* and *gonyautoxins*. Examples of species which cause these types of poisoning are dinoflagellates *A. catenella*, Fig. 8(a), *Alexandrium cohorticula*, *Alexandrium fundyense*, *Alexandrium fraterculus*, *A. leei*, *A. minutum*, *A. tamarense*, *G. catenatum*, Fig. 8(b), *P. bahamense* var. *compressum*). Symptoms include both gastrointestinal and neurologic effects. Toxins may cause difficulty in swallowing, a sense of throat constriction, speech incoherence, or complete loss of speech, as well as brain stem dysfunction. In very severe cases, there is complete paralysis and death from respiratory failure. Other symptoms include headache, dizziness, nausea, vomiting, rapid pain, and anuria.

(2) ASP is caused by domoic acid in shellfish. Symptoms are mainly gastrointestinal. Examples of causative species are the diatoms *Pseudo-nitzschia australis*, Fig. 8(c). *Pseudo delicatissima*, *Pseudo multiseries*, *Pseudo pseudodelicatissima*, *Pseudo pungens* (some strains), and *Pseudo seriata*.

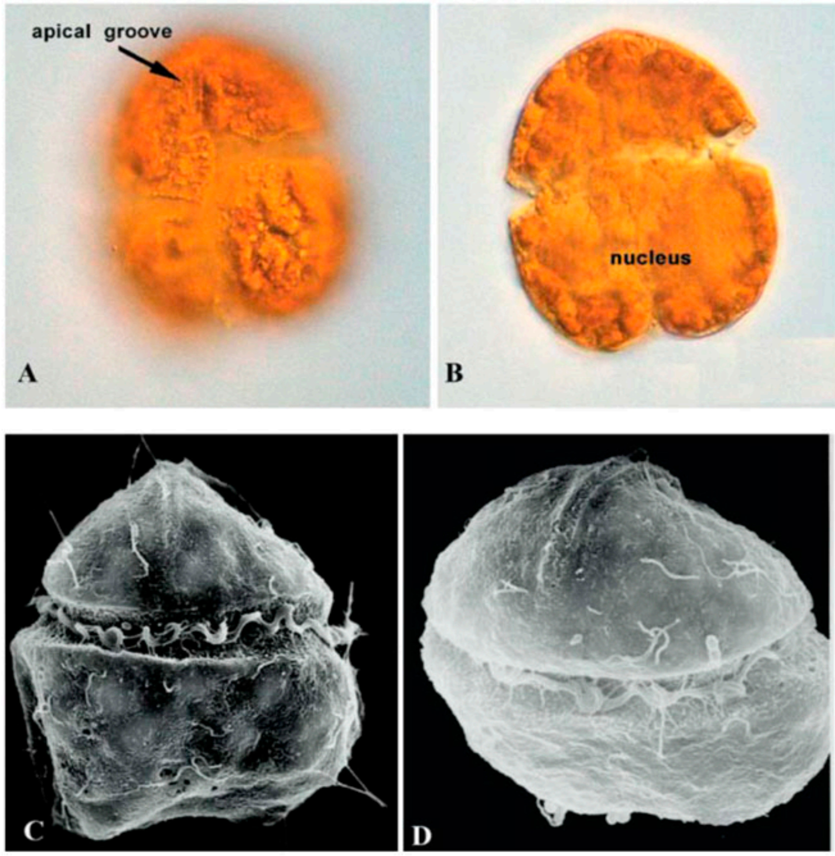

Fig. 6a. Light micrographs of (A–B) *K. selliformis*: (A) ventral view indicates the straight apical groove; (B) dorsal view shows the nucleus in the center; (C–D) Scanning electron micrographs selliformis: dorsal view with clearly visible apical groove, cingulum and transverse flagellum. (Scale Bars, (A) = 4.59 μm; (B) = 4.31 μm; (C) = 3.68 μm; (D) = 3.84 μm) [31].

(3) NSP attacks the nervous system. Symptoms include difficulty in swallowing, double vision, unsteadiness and tremor, nausea, diarrhea, vomiting, numbness, and tingling of the mouth, lips and extremities. NSP is sometimes produced by an algal species known as *K. mikimotoi*, and by the dinoflagellate *Gymnodinium breve*, Fig. 8(d).

(4) DSP is caused by okadaic acid and related compounds. Symptoms are diarrhea, nausea, and vomiting. DSP group toxins are produced by a variety of phytoplankton species. Examples are dinoflagellates *Dinophysis acuta*, *Dinophysis acuminata*, *D. caudata*, *Dinophysis fortii*, *D. norvegica*, *D. mitra*, *D. rotundata*, *Dinophysis sacculus*, Fig. 6(c), P. *lima*, Fig. 8(e).

(5) CFP caused the dinoflagellates *Gambierdiscus toxicus*, *Ostreopsis* spp., and *Prorocentrum*, Fig. 8(f). Cyanobacterial toxin poisoning may be caused by, for example, *Nodularia spumigena*. The toxins produced can cause nausea, pain, cardiac, and neurological symptoms.

Boerlage and Nada [21], and Seubert et al. [36] reported four of the most potent and well-characterized groups of marine toxins such as: *saxitoxin*, *domoic acid*, *okadaic acid*, and *brevetoxin* which could appear at desalination plant intakes. The molecular structures of these toxins are shown in Fig. 9 [37].

Table 3 describes the types of toxins associated with HAB and found in the water of southern California. The physical properties as well as the chemical formula, molecular weight, and mechanism of toxification are given.

The main toxin responsible for PSP, *Saxitoxin*, is bio-synthesized by dinoflagellates such as *Alexandrium* spp., *Gymnodinium* spp., and *Pyrodinium* spp., in marine ecosystems. The size range of *Alexandrium* spp., is in the range of 15–48 μm, as shown in Fig. 10(A) for *A. catenella*, an armoured dinoflagellate with two flagella, which typically clumps together in chains of 2–8 cells. *Dinophysis* spp. and *Prorocentrum* cause diarrhoetic shellfish poisoning (DSP), the second most reported after PSP. *Dinophysis* spp. range in size from 54 to 94 μm in length and 43 to 60 μm in diameter as

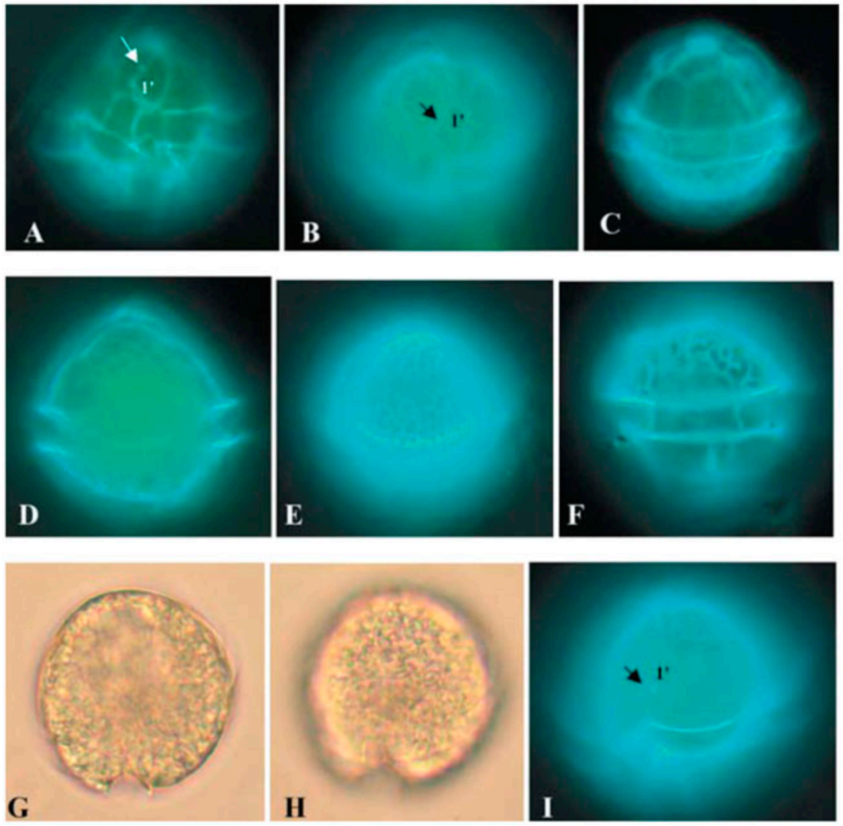

Fig. 6b. Light micrographs of (A–F). *Alexandrium insuetum*: (A–B) ventral view showing small ventral pore on the first apical plate at the middle of the right margin adjoining the 4´ plate (arrows), (C–F) showing the pronounced reticulation of the thecal plates at different sides of the cell; (G–I) *A. leei*: (G–H) ventral view showing the cell shape, (I) ventral view showing the position of ventral pore inside the 1´ plate with an arrow (Figs. (G–H), (LM), bright field; (A–F) and (I), (LM), epifluorescence). (Scale Bars, (A) and (C) = 6.76 μm; (B), (D)–(F) = 6.25 μm; (G) = 10.26 μm; (H) and (I) = 10.00 μm) [31].

shown in Fig. 10(B). They are found as solitary cells not connected to others, such as *A. catenella*.

Brevetoxins are produced by dinoflagellate and raphidophyte algae, for example, *Chattonella* spp. The most commonly studied dinoflagellate that produces *brevetoxins* is *Karenia brevis* (known as the "Florida Red Tide"). Others are *K. mikimotoi*, *Karenia brevisulcata*, and *K. papilionacea* [21]. The *K. brevis* are approximately 10–15 μm in size at the smallest dimension, Fig. 10(C).

Domoic acid production is the cause of amnesic poisoning syndrome (ASP), and the formation of its isomers are confined to a dozen chain forming pennate diatom species within the genus *Pseudo-nitzschia* which are ubiquitous in seawater. An example from this genus, *Pseudo-nitzschia pungens/australis*, shown in Fig. 10(D), has long needle-like algal cells (25–160 μm in length and 0.5–8 μm in width), which forms chains by overlapping the tips of their cells [21].

Saxitoxin, for example, is 1,000 times more potent than cyanide, and 50 times stronger than curare [21]. Humans are exposed to algal toxins principally by consumption of contaminated seafood products, although several types of toxin (*brevetoxin* and palytoxin) also cause respiratory asthma-like symptoms because of aerosol formation due to wave action [21]. A real concern is the potential for HAB toxins to be retained in product of desalted water, though several studies indicate that 99% removal can be achieved through pretreatment, or through direct thermal or RO operations [38].

6. Desalination and HABs

Algal blooms are an emerging environmental threat to SWRO desalination facilities. First, the conventional pretreatment processes that have been used to treat the feed SW before entering the RO

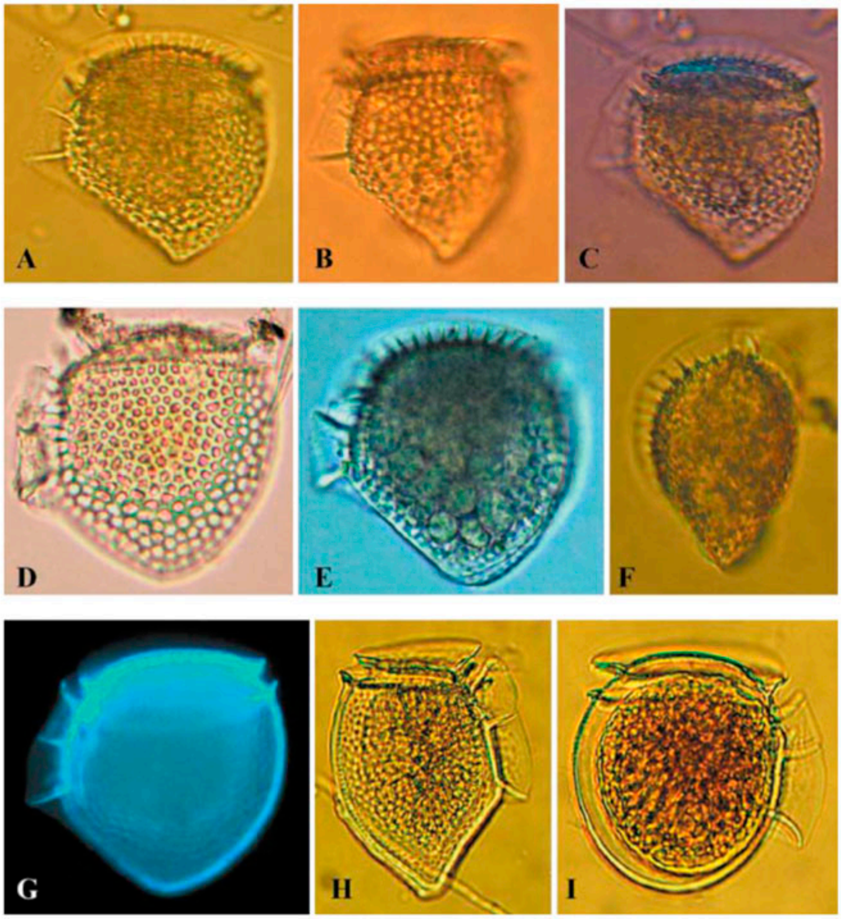

Fig. 6c. Light micrographs of (A–G). *D. mitra*: different cells in different views showing the broad wedge-shaped form, (A–D). Note the course reticulation of the thecal plates and the epicone which is visible above the cingulum; (A–G). Seen in left value view, except (F) which shows the cell in the lateral view, (E) the cell contents often give a dark brown appearance to this species; (H) *D. norvegica*: right valve view which are clearly pointed at the posterior part; (I) *D. rotundata*: right valve view which are rounded at the posterior part. (Figs. (A–F) and (H–I), (LM), bright field; (G), (LM), epifluorescence). (Scale bars, (A) = 12.00 μm; (B) = 11.93 μm; (C) = 12.50 μm; (D) = 12.80 μm; (E) = 12.28 μm; (F) = 14.63 μm; (G) = 13.19 μm; (H) = 12.00 μm; (I) = 9.90 μm) [31].

Fig. 7. Massive marine mortality occurred in Kuwait in 2002 [32].

membranes are not suitable. Second, questions have risen concerning the ability of the membranes to fully remove (100%) the toxins generated by the HAB. The negative effects of the AB on the SWRO pretreatment system are a serious problem that forced SWRO plants to cease operations during the AB in 2008–2009 events. However, an SWRO plant built recently in Kuwait, Fig. 11, was able to remove the HAB species in the pretreatment processes. These processes include coagulation, flocculation, sedimentation, and clarification by dissolved air flotation (DAF), followed by ultrafiltration (UF) membrane process. The UF here substitute the conventional granular media filtration (GMF), which was commonly used. The domain of separation for GMF and membrane filtration processes is shown

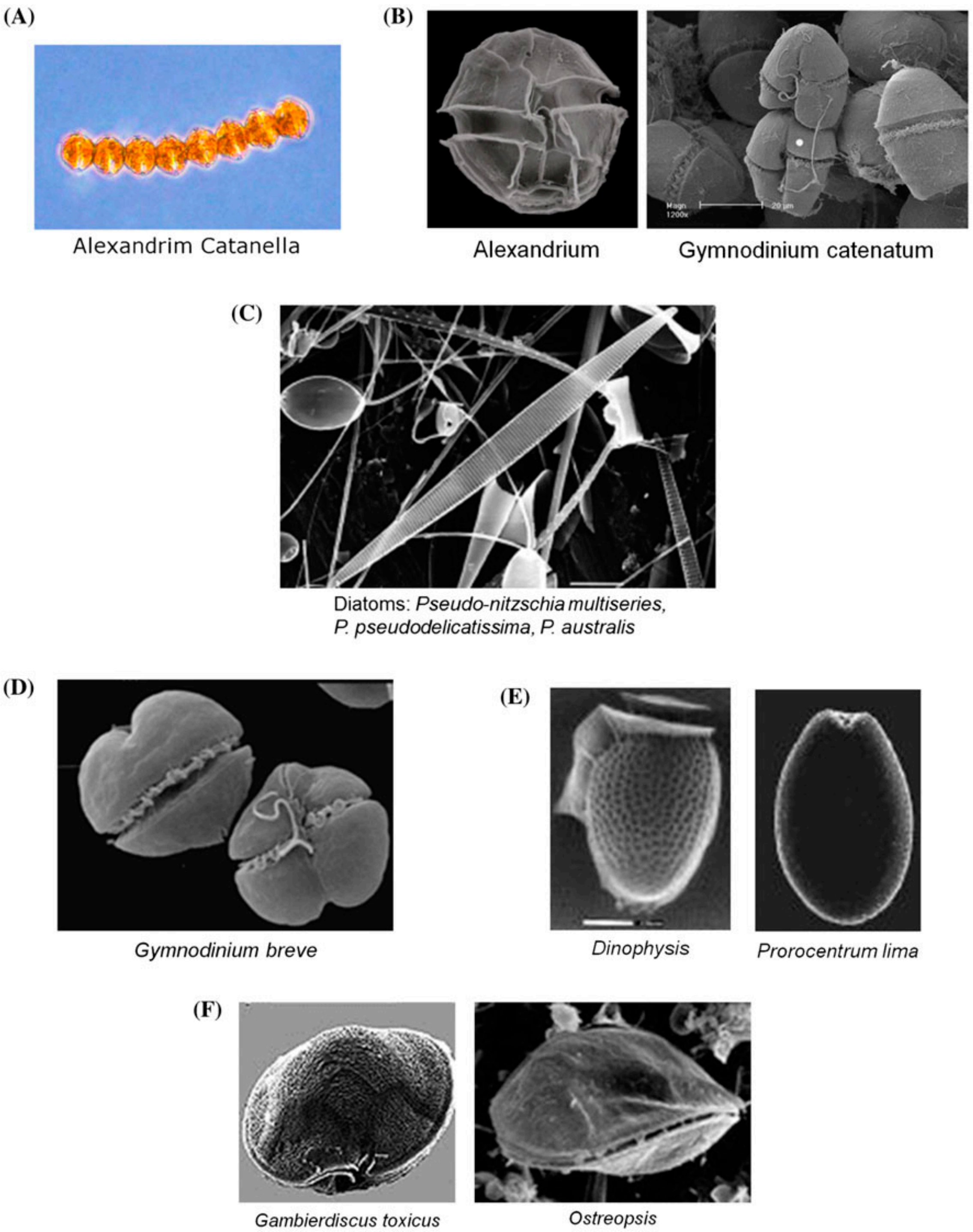

Fig. 8. Electron microscopic of the species cause shellfish poisoning [33].

in Fig. 12 [39]. However, the algal-derived organic matter (AOM) such as transparent exopolymer particles (TEP) can be formed and reach the RO membranes. The TEP initiates or enhances biofilm development on the surface of SWRO membranes.

Research done by the City of Santa Cruz (California, USA) has demonstrated that slow sand filtration of seawater tends to remove a considerable amount of algal toxic. Their research used domoic acid as a proxy [40,41].

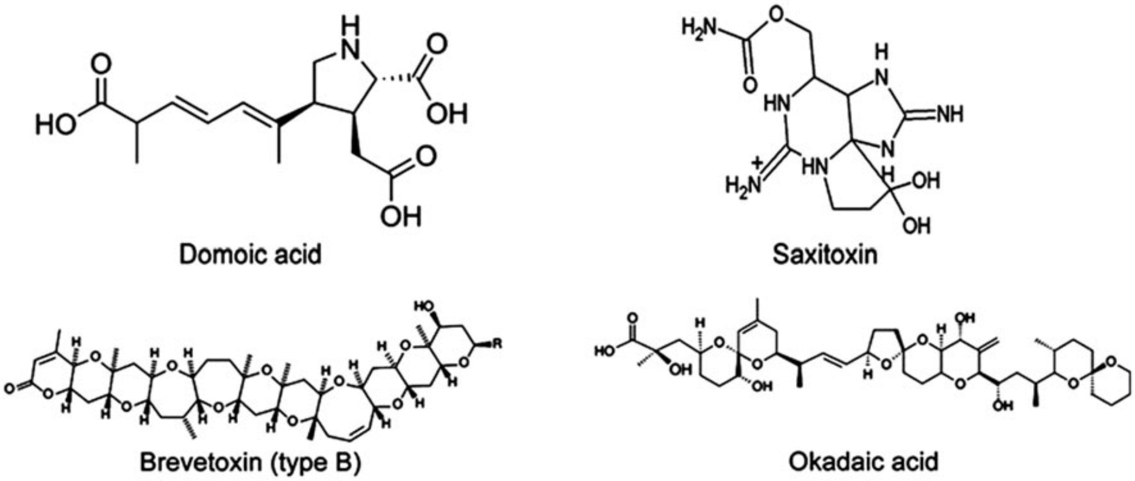

Fig. 9. Chemical structure of major classes of HAB toxins [37].

Table 3
HAB toxins present in water of Southern California

Toxin	Properties	Formula	MW	Mode of action
Domoic acid (DA)	Hydrosoluble at pH 7: DA^{3-}	$C_{15}H_{21}NO_6$	311.14	Binds to glutamate receptors in the brain disrupting normal neurochemical transmission
Saxitoxins (STXs)	Hydrosoluble pH ≤ 7: Stable	$C_{10}H_{17}N_7O_4$	299.3	Bind to site 1 of voltage-sensitive sodium channels and block sodium conductance; Bind to calcium and potassium channels
Brevetoxins (PbTxs)	Liposoluble			Bind to site 5 of voltage-sensitive sodium channels. Shifting activation to more negative membrane potentials and block channel activation
Brevetoxin 2 (PbTx 2)		$C_{50}H_{70}O_{14}$	895.1	
Brevetoxin 3 (PbTx 3)		$C_{50}H_{72}O_{15}$	897.1	
Brevetoxin 9 (PbTx 9)		$C_{50}H_{74}O_{14}$	899.1	
Diarrhetic shellfish toxins				Inhibits protein phosphatases, inhibits dephosphorylation of proteins
Okadaic acid (OA)				
Dinophysistoxins (DTXs)				
Pectenotoxins (PTXs)	Liposoluble			High actin-depolarizing action

According to Tabatabai [42], several forms of AOM produced by the AB including, at varying concentrations [42]:

(1) Intracellular organic matter (IOM) formed due to autolysis consisting of proteins, nucleic acids, lipids, and small molecules.
(2) Extracellular organic matter (EOM) formed via metabolic excretion and composed mainly of acidic polysaccharides [1].

Polysaccharides are complex carbohydrate polymers consisting of more than two monosaccharides that are linked together covalently by glycosidic linkages in a condensation reaction. Being comparatively large macromolecules, polysaccharides are most often insoluble in water. Polysaccharides are extremely important in organisms for the purposes of energy storage and structural integrity. A significant fraction of these exopolysaccharides, known as TEP, are highly surface-active and sticky, and play an important role

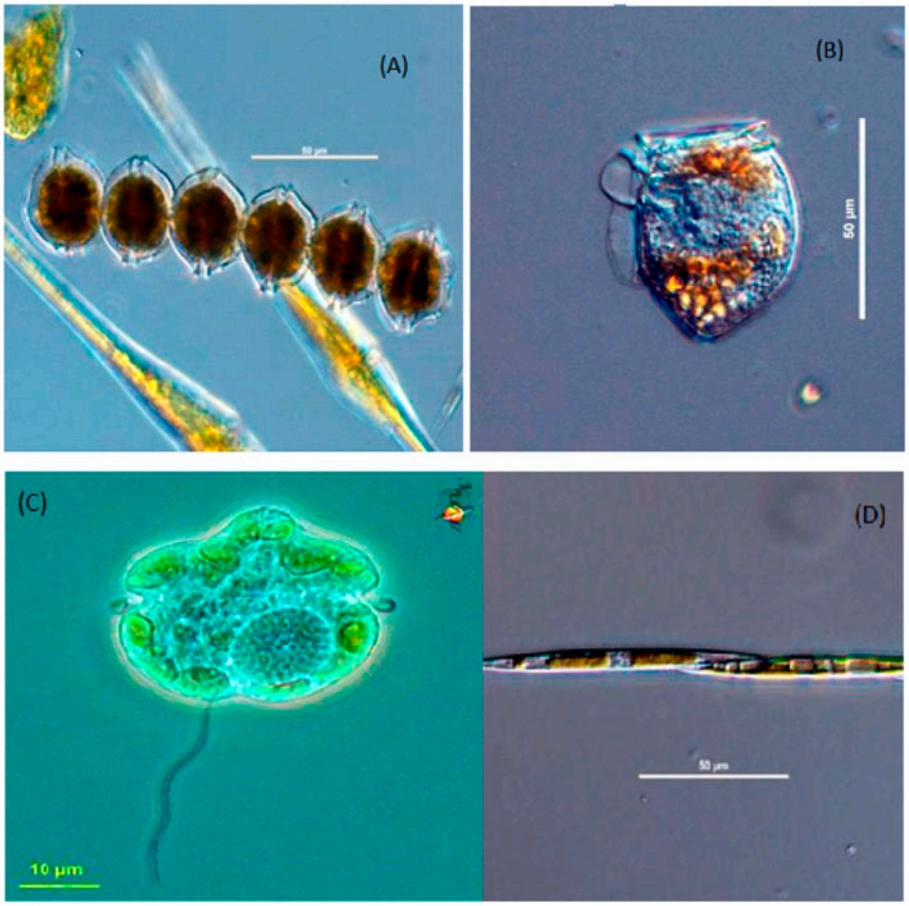

Fig. 10. Toxin producers *A. catenella* (A), *D. acuta* (B), *K. brevis* (C), and *Pseudo-nitzschia pungens/australis* (D) [21].

in the aggregation dynamics of algae during bloom events [1].

Seubert et al. [36] conducted bench-scale RO experiments to explore the potential of extracellular algal toxins contaminating the RO product. Concentrations exceeding maximal values previously reported during natural blooms were used in the laboratory experiments, with treatments comprised of 50 mg/L of domoic acid (DA), 2 mg/L of *saxitoxin* (STX), and 20 mg/L of *brevetoxin* (PbTx). None of the algal toxins used in the bench-scale experiments were detectable in the desalinated product water, although DA and STX were detected sporadically in the intake.

The TEPs are commonly derived from AB species and are described as a class of particulate acidic polysaccharides that are large, transparent organic particles, and can be stained with Alcian blue [44] (Fig. 13).

As reported by Berman [45], TEPs, and planktonic organic microgels play an active role in the process of biofilm formation on surface of membranes. The TEPs, intensely colonized by bacteria and other microorganisms, serve as hot spots of intense microbial activity. The TEPs can potentially initiate and exacerbate biofouling in RO systems [45]. Villacorte [9] investigated the effect of AOM, including TEP, in relation to UF fouling propensity. The effect of algal blooms (AB) on the operation of SWRO will be presented in the forthcoming paper by the current authors.

Fig. 11 provides a schematic of the configuration of the Shuwaikh SWRO in Kuwait, where the AB issues were considered when designing the plant's pretreatment system, and the use of DAF and UF was adopted. Both DAF and UF treat the difficult SW condition of high total suspended solids occurring during AB. The DAF clarification process has proven effective in removing color, organics, soluble metals, and colloidal solids before feeding the UF membrane system. Aluminum or iron hydroxide is added in the DAF to give low-density flocs. It is known that, in general, solids that are hundreds of microns in size can settle naturally if sufficient retention time is provided, while particles of tens of microns in size will float naturally. The algae in SW can be robustly removed by taking

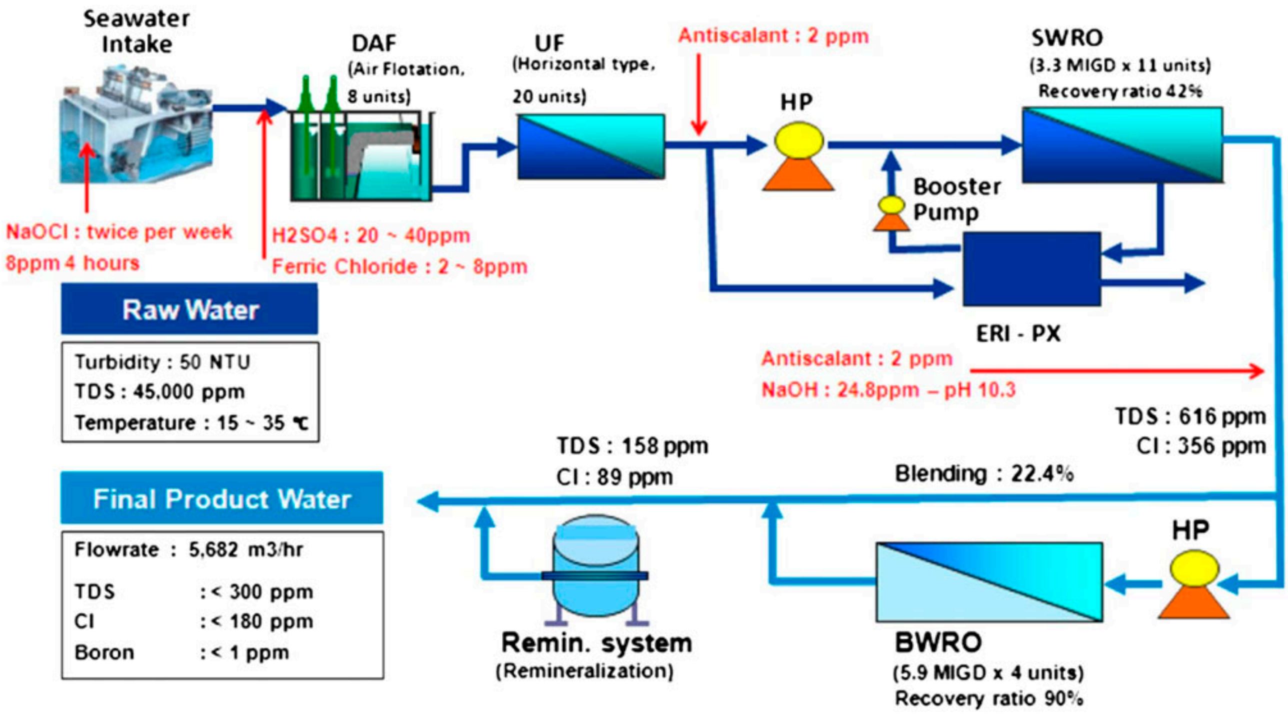

Fig. 11. General configuration of recently built Shuwaikh SWRO plant in Kuwait [43].

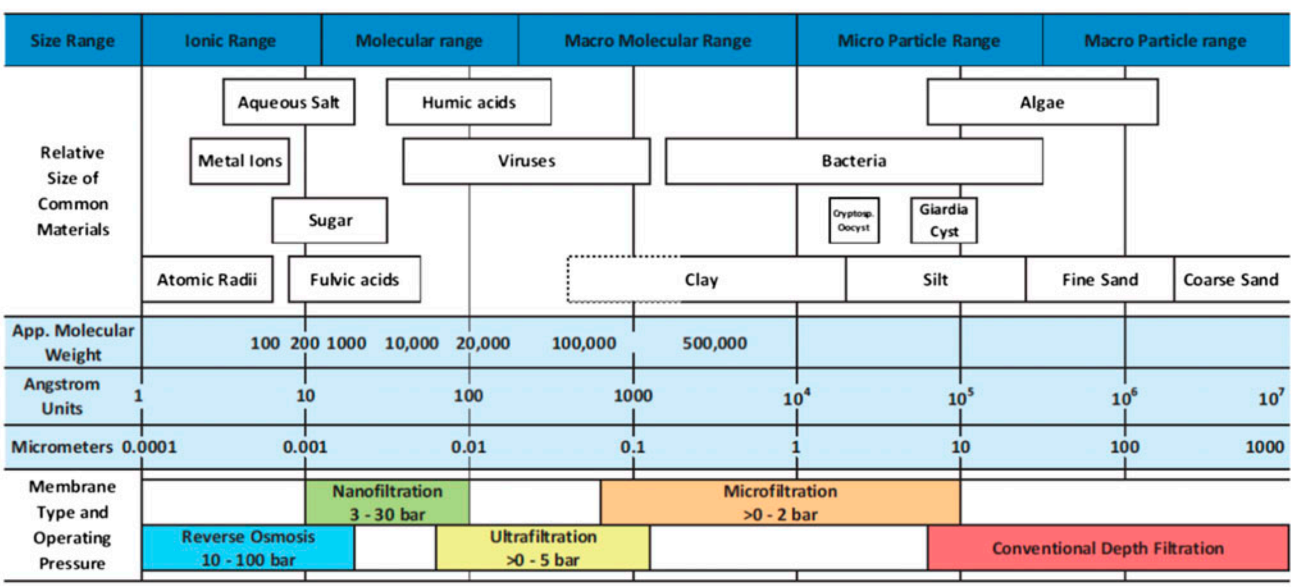

Fig. 12. Domain of separation for conventional and membrane filtration processes [39].

advantage of algae buoyancy and flotation technology that are used in DAF. Air bubbles at the micron size are introduced through diffusers to allow particles to flocculate and separate out of the water by floating them to the surface, rather than settling them to the DAF bottom basin. The UF and microfiltration (MF) systems depend on effective online integrity monitoring method for MF and UF membrane systems, and it is essential to guarantee that the total suspended solids are completely removed. When MF was used upstream of the RO membranes, before the introduction of the UF membranes in SWRO pretreatment, the

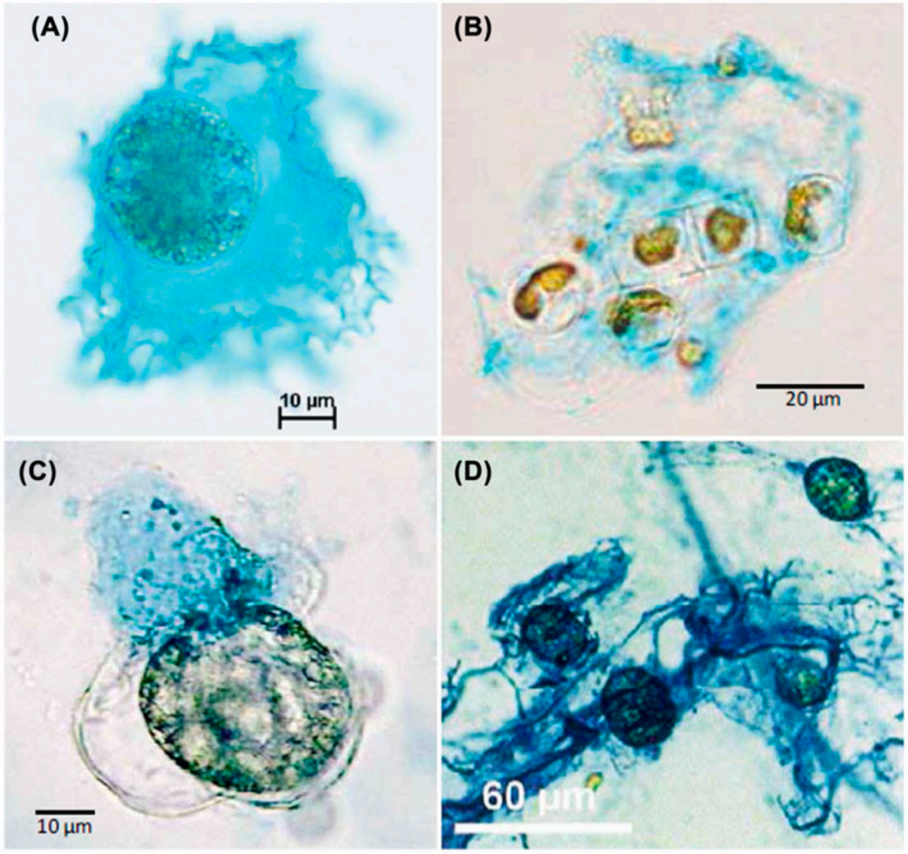

Fig. 13. Alcian blue stained transparent exopolymers particles (TEP) released by bloom-forming algae: (A) excretions by *Lepidodinium chlorophorum*; (B) excretions by *Chaetoceros affinis*; (C) release from a broken *Gonyaulax fragilis* cell; (D) excretions by *Gonyaulax hyalina* [9].

algal related constituents were transferred through the MF unit, providing one of the reasons for introducing the UF. The implementation of DAF in the pretreatment improved the removal of suspended plankton, algae, oil, colloids, fine particles, and organics. It is successfully applied in many plants in the GCC including in Sur, Fujairah, and Shuwaikh. The DAF system consistently produces suitable water for SWRO treatment during algal blooms.

7. Conclusion

The Arabian Gulf characteristics in terms of size, depth, salinity and temperature variations, inflow and outflow, and water movements have been illustrated. These factors affect the creation of algal blooms which have frequently occurred in the last few years.

The species of the most observed recent HAB were mainly *C. polykrikoides*. The reported micrographs of these species as well as the record temperature and chlorophyll in the Arabian Gulf during this event (August 2008–May 2009) were given. The phytoplankton (diatoms, dinoflagellates, cyanobacterias) causing HAB were described in terms of their sizes, shapes, and toxicity. The major groups and species of HAB occurred especially in the Arabian Seas including diatoms, dinoflagellates, haptophytes, raphidophytes, chlorophytes, and cyanobacteria are given with their micrographs collected from different sources.

Technical and management actions on HAB monitoring, toxicity, and pretreatment should be placed on the highest level of priority for water security in the Gulf region, as most of the countries are moving to membrane desalination technologies.

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