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Review

Microalgal bioremediation of emerging contaminants - Opportunities and challenges

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ABSTRACT

Emerging contaminants (ECs) are primarily synthetic organic chemicals that have a focus of increasing attention due to either increased awareness of their potential risks to humans and aquatic biota, or only recently been detected in the aquatic environment or drinking water supplies, through improved analytical techniques. . Many ECs have no regulatory standards due to the lack of information on the effects of chronic exposure. Pharmaceuticals, personal care products, pesticides and flame retardants are some of the most frequently detected ECs in aquatic environments, with over 200 individual compounds identified, to date. Current wastewater treatment is ineffective at removing ECs and there is a vital need for the development of efficient, cost-effective EC treatment systems that can be applied to a range of scales and wastewater types.

Microalgae have demonstrated potential for detoxifying organic and inorganic pollutants, with a number of large-scale wastewater treatment microalgal technologies already developed. There are three main pathways that microalgae can bioremediate ECs; bioadsorption, bio-uptake and biodegradation. Microalgal bioadsorption occurs when ECs are either adsorbed to cell wall components, or onto organic substances excreted by the cells, while bio-uptake involves the active transport of the contaminant into the cell, where it binds to intracellular proteins and other compounds. Microalgal biodegradation of ECs involves the transformation of complex compounds into simpler breakdown molecules through catalytic metabolic degradation. Biodegradation provides one of the most promising technologies for the remediation of contaminants of concern as it can transform the contaminant to less toxic compounds rather than act as a biofilter. Further research is needed to exploit microalgal species for EC bioremediation properties, such as increased bioadsorption, enhanced biodegrading enzymes and optimised growth conditions. When coupled with nutrient removal, microalgal treatment of EC can be a cost-effective viable option for the reduction of contaminant pollution in waterways.

Contents

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1. Background

Water quality management for the protection of aquatic and human health values has traditionally focused on nutrients, suspended sediment, heavy metals and human pathogens (Pal et al., 2014). However, in recent years, there have been increasing concerns over the presence of emerging contaminants (EC) in aquatic environments and their associated risks and impacts to both aquatic ecosystems and human health. ECs are primarily synthetic organic chemicals that have, while present in the environment for some time, only recently been detected due to either improved analytical techniques or increased awareness of their risks (Escapa et al., 2015; Ahmed et al., 2017; Tran et al., 2018). ECs are described as substances that either have no current, or have emerging and evolving regulatory standards and they could potentially cause deleterious effects to the aquatic environment, or humans, at environmentally relevant concentrations (US-EPA, 2008).

Most ECs enter waterways via human-mediated routes including direct discharge of raw, or treated municipal wastewater streams, landfill leachate, urban and rural surface and groundwater runoff, or from industrial waste discharge (Tran and Gin, 2017; Ali et al., 2018; Tran et al., 2018). Municipal wastewater treatment plants have been shown to contribute the most continual and EC rich discharge into the aquatic environment, with the number of specific ECs reported in wastewater discharge ranging from 25 to 200 compounds (Wang et al., 2016; Tran and Gin, 2017; Villar-Navarro et al., 2018). However, these numbers are likely to increase with improved analytical techniques and industrial application of newly created compounds that will become new ECs.

ECs typically fall into several broad categories including pharmaceuticals, personal care products, illicit drugs, artificial sweeteners, pesticides, plasticisers and flame retardants (Petrie et al., 2015; Norvill et al., 2016; Tran et al., 2018). Pharmaceuticals, pesticides and personal care products are the most frequently detected ECs in aquatic habitats due to both their high use and high solubility (Rykowska and Wasiak, 2015; Manamsa et al., 2016; Bai et al., 2018). However, both the number and concentration of different ECs present in the waterways is dependent on the socio-economic composition of the community contributing to the EC discharges (Tran et al., 2018). While pharmaceuticals and personal care products (PCP) in aquatic environments are often reported at low concentrations, their presence in both aquatic environments and drinking water supplies is of concern for both human and ecosystem health (WHO, 2011; Rodriguez-Narvaez et al., 2017). Types of pharmaceutical and PCP compounds frequently reported in the aquatic environment include human and veterinary antibiotics, antimicrobial agents, neuroactive drugs, hormones, painkiller medication, sunscreens, insect repellents and fragrances (Norvill et al., 2016, Xiong et al., 2018a). Concerns regarding these compounds as ECs include the potential effects of endocrine disruptors and hormones on the life stages of aquatic biota, as well as the development of antibiotic resistance genes from chronic exposure to antibiotic and antimicrobial agents, which can enter food chains and infect humans (Petrie et al., 2015; Tran et al., 2018, Xiong et al., 2018a). Studies have shown that continuous exposure to low, sub-toxic concentrations of certain PCPs has resulted in endocrine, developmental, and epigenetic disruption to aquatic organisms and direct impact on human health (Wilkinson et al., 2016; Ebele et al., 2017).

Pesticides and other agri-chemicals are used widely in both urban and rural environments. Their high application rate, high mobility and persistence in soils results in the transport of these ECs into waterways via runoff and percolation (Loague et al., 1990; Pal et al., 2014). Pesticides have been known to negatively impact ecosystem function and biodiversity values as well as bio-accumulation into aquatic organisms, disrupting the food chain and posing a potential risk to human health (Rodriguez-Narvaez et al., 2017; Knillmann et al., 2018; Machado and Soares, 2018). However, for many of the ECs detected in the aquatic environment, the lack of ecotoxic and ecological data means that their potential ecological risks are not understood (Bai et al., 2018).

Many reports cite EC concentrations typically in the nanogram to low micrograms per litre range in wastewater, surface water, groundwater and drinking water, but some contaminants, such as the antibiotic ciprofloxacin and per- and polyfluoroalkyl substances (PFAS) have been reported as high as milligrams and grams per litre range, respectively (Nakayama et al., 2019; Kelly and Brooks, 2018). While ECs are not currently regulated, public concern regarding their presence in the environment has led to the development of interim aquatic guidelines for a number of ECs, including, but not limited to, nitrophenols, PFAS, carbamazepine and ibuprofen (SCHER, 2011; Petrie et al., 2015; ANZECC, 2018; CCME, 2018) and priority pollutant lists have been developed by the European Union Water Framework Directive and the United States Environment Protection Agency. However, one of the challenges that regulators, waterbody managers and other stakeholders face when considering the impacts of ECs is a scarcity of published information on the effects of long-term exposure to these compounds and their metabolites on aquatic biota and human health.

Conventional wastewater treatment plants (WWTP) are not currently designed to sufficiently treat and remove ECs from the influent. While partial removal of some ECs from the wastewater occurs through adsorption onto activated sludge (Guerra et al., 2014) relatively high concentrations of ECs still remain in the effluent leaving the WWTP (Tran and Gin, 2017; Ali et al., 2018). Furthermore, disposal of the EC-laden sludge onto land, such is common practice for many WWTPs, may result in ECs percolating into groundwater or surface runoff as the sludge degrades, thus resulting in further contamination of new environments. A number technologies, such as chemical precipitation, solvent extraction, constructed treatment wetlands, electrocoagulation and anaerobic bed reactors have been trialled for the treatment and removal of ECs in wastewater (Lee et al., 2012; Lladó et al., 2016). However, these methods are often ineffective, particularly at dilute concentrations, or the construction and operation costs make implementation of some of these options cost prohibitive (Marchal et al., 2013; Ali et al., 2018).

Due to the rising number of ECs, their persistence in the

environment, and bioaccumulation in the food web, as well as potential adverse ecological and human health effects, there is a growing need for cost-effective mitigation technologies that can be applied to a range of ECs, across a range of industrial scales. Using microalgae to treat emerging contaminants provides an opportunity to meet the needs of enhanced wastewater treatment. Here we review the opportunities and challenges for the use of microalgal-based technologies for the bioremediation of ECs.

2. Microalgal bioremediation mechanisms

Over the last several decades, the use of microalgae for the bioremediation of nutrients, such as nitrogen, phosphorus and carbon, from various wastewater streams has been successfully demonstrated at a range of scales (Sutherland et al., 2018). Microalgal-based wastewater treatment systems were shown to have lower capital and operational costs, provide natural disinfection and be more efficient for remediating nutrient pollution compared to traditional wastewater treatment systems (Benemann, 2008; Craggs et al., 2012). When coupled with wastewater treatment, microalgae have the potential to provide cost-effective remediation of ECs. Another advantage of using microalgae for bioremediation is the ability to recover resources for beneficial re-use through biorefinery of the microalgal/bacterial biomass for a range of both high-value and low-value products, such as fertiliser, algal plastics and fibres, or protein-rich feed (Sutherland et al., 2018). While the potential for microalgae to detoxify organic and inorganic pollutants has been well documented over the last 30 years, only recently has attention been paid to the use of microalgae for bioremediation of the current ECs. Coupling nutrient removal with EC bioremediation further improves the cost-efficiency of microalgal-based for wastewater treatment, while further protecting the environment through the removal of ECs. The potential mechanisms for microalgal bioremediation of ECs by are discussed below.

3. Microalgal bioadsorption of emerging contaminants

Bioadsorption by microalgal cells occurs when compounds are either adsorbed to cell wall components, or onto organic substances (such as extracellular polysaccharides (EPS)) that are excreted by the cell into the surrounding environment (Kaplan, 2013; Saavedra et al., 2018). This passive process is a non-metabolic interaction between the contaminant and the negatively charged microalgal cell wall, or secretions (both collectively termed cell surfaces), exhibits some chemical affinity for the positively charged contaminant. The ability of an EC to adsorb onto microalgal cell surfaces is dependent on the chemical structure of the EC. Hydrophobic, cationic ECs are actively attracted toward the microalgal cell surface through electrostatic interactions, whereas hydrophilic ECs are repelled (Xiong et al., 2017a). Once at the cell surface, the amount of EC that can be adsorbed is determined by the area and chemistry of the cell surface (Norvill et al., 2016). The microalgal cell surfaces contain a range of functional groups such as carboxyl, hydroxyl, sulphate and other charged groups which differ in affinity and specificity for various organic and inorganic compounds (Campbell et al., 1997; Dönmez et al., 1999; Hansda & Kumar 2016). Bioadsorption includes a number of chemical processes at the cell surface that may include adsorption reactions, ion exchange reactions with functional groups on the microalgal surface, surface complexation reactions, chelation and micro-precipitation (Dönmez et al., 1999; Schmitt et al., 2001). The rate, or thermodynamics, of the adsorption process is determined by the physico-chemical properties of the immediate environment, including temperature, redox and pH.

Microalgal bioadsorption technologies have been well document in scientific literature over the last decade, with the main focus being on heavy metal removal (e.g Ibuot et al., 2019). However, with an increasing awareness of ECs, there has been an increase in the number of published studies on bioadsorption of ECs by microalgae, with 27% of studies featured in Table 1 showing adsorption to be at least partially involved in the treatment of 16 ECs, where removal mechanisms had been identified. However, reported rates for adsorption of ECs have been variable, with adsorption rates reported to be from 0 to 100%. For example, de Wilt et al. (2016) found that adsorption rates for six pharmaceutical drugs onto the cell surface of the green microalga *Chlorella sorokiniana*, were <20%. Similarly, Peng et al. (2014a) reported approximately 10% adsorption rate of the hormones progesterone and norgestrel by *Scenedesmus obliquus* and *Chlorella pyrenoidosa*. In contrast, Ali et al. (2018) reported microalgal bioadsorption rate of 91% (*Scenedesmus obliquus*) for tramadol, while Guo et al. (2016) microalgal bioadsorption rates of 100% (*Chlorella* sp., *Chlamydomonas* sp., *Mychonastes* sp.) for 7-amino cephalosporanie acid (Table 1). One explanation for the reported low adsorption rates for those pharmaceuticals studied by Peng et al. (2014a) and de Wilt et al. (2016) were that the compounds were water soluble, or hydrophilic. Hydrophilic compounds are anionic (negatively charged) and have low bioadsorption affinity values with microalgal cells due to the cells also being negatively charged. In contrast, lipophilic pharmaceuticals, which are cationic, have high bioadsorption affinity values with microalgae. For example, Gojkovic et al. (2019) found average microalgal bioadsorption rates >70% for the lipophilic pharmaceuticals, Biperiden, Trihexyphenidyl, Clomipramine and Amitriptyline, whereas the hydrophilic pharmaceuticals, Fluconazole, Trimetoprim, Codeine, Carbamazepine, Oxazepam and Tramadol, had low (0–20%) bioadsorption rates.

One of the challenges with microalgal bioadsorption is that the process is non-selective, meaning that, in the case where multiple contaminants are present, binding sites may become saturated with non-target contaminants that may also present in the wastewater. The presence of other contaminants may also interfere with the adsorption rate of the contaminant of concern, regardless of the availability of binding sites on the cell wall.

As bioadsorption is a non-metabolic process, binding of ECs onto the microalgal surface occurs on both living and non-living microalgal cell surfaces, because most of the cell receptors for the contaminant remain viable even after the cell has died (Choi and Lee, 2015). The use of non-living microalgal biomass as a bioadsorption agent has several advantages over living microalgae including: the non-living microalgae is not subject to any contaminant toxicity limitations; with the aid of a suitable desorbing agent, the bioadsorbed EC can be desorbed and microalgal biomass can be reused; operational costs, including the need for growth media, are substantially reduced as there is no requirement to maintain viable microalgal cultures (Mane et al., 2011, Dixit and Singh, 2014). Regardless of whether living or non-living microalgae are used, bioadsorption provides a potential treatment option for some hydrophobic, cationic ECs. However, further research is needed to not only identify which ECs would be most suitable for microalgal bioadsorption treatment technologies but also in optimising the bioadsorption process for the contaminant of concern in order to industrialise the process.

3.1. Microalgal bioadsorption research opportunities

Opportunities for improving microalgal adsorption technologies for EC bioremediation include bioprospecting for species that have a high affinity for the target EC, preferentially adsorbing it onto the cell surface, essentially acting as ‘hyper-adsorbents’ or ‘hyper-

Table 1
Removal efficiency of a range of emerging contaminants by microalgae.

Emerging contaminant	Microalgal species (percentage removal efficiency)	Pathways
17 α-Boldenone	Mixed consortia (82)[1]	Not determined
17 β-Boldenone	Mixed consortia (75-86)[1]	Not determined
17 α -Estradiol	*Scenedesmus dimorphus* (85)[2]	Biodegradation
17 β-Estadiol	*Chlamydomonas reinhardtii* (100)[3], *Desmodesmus subspicatus* (95)[3], *Nannochloris* sp. (60)[4], *Selenastrum capricornutum* (88)[3]	Bioadsorption, bio-uptake and biodegradation
17 α-Ethynylestradiol	*Chlamydomonas reinhardtii* (100)[3], *Desmodesmus subspicatus* (68)[31], *Nannochloris* sp. (60)[4], *Selenastrum capricornutum* (60-95)[3]	Bioadsorption, bio-uptake and biodegradation
7-amino cephalosporanie acid	*Chlorella* sp. (100)[5], *Chlamydomonas* sp. (100)[5], *Mychonastes* sp. (100)[5]	Photodegradation and bioadsorption
Acetaminophen	Mixed consortia (99)[6]	Not determined
Alprazolam	Mixed consortia (87)[7]	Not determined
Amitriptyline	*Chlorella sorokiniana* (68)[30], *Chlorella vulgaris* (42)[30], *Chlorella saccharophila* (92)[30], *Coelastrella* sp. (60)[30], *Coelastrum astroideum* (68)[30], *Desmodesmus* sp. (37-47)[30], *Scenedesmus sp.* (85)[30], *Scenedesmus obliquus* (69)[30]	Bioadsorption
Amoxicillin	*Chlorella pyrenoidosa* (77)[8], *Microcystis aeruginosa* (18-31)[9]	Not determined
Atenolol	Mixed consortia (85-98)[7]	Not determined
Azithromycin	Mixed consortia (89)[7]	Not determined
Bisphenol A	*Chlamydomonas mexicana* (24)[10], *Chlorella vulgaris* (24)[10]	Bio-uptake and biodegradation
Biperiden	*Chlorella sorokiniana* (35)[30], *Chlorella vulgaris* (93)[30], *Chlorella saccharophila* (89)[30], *Coelastrum astroideum* (9)[30], *Desmodesmus* sp. (41-71)[30], *Scenedesmus sp.* (53)[30], *Scenedesmus obliquus* (48)[30]	Bioadsorption
Bupropion	*Chlorella sorokiniana* (60)[30], *Chlorella vulgaris* (82)[30], *Chlorella saccharophila* (88)[30], *Coelastrella* sp. (89)[30], *Coelastrum astroideum* (94)[30], *Desmodesmus* sp. (86-90)[30], *Scenedesmus sp.* (70)[30], *Scenedesmus obliquus* (95)[30]	Bioadsorption
Caffeine	Mixed consortia (99)[6], (26-81)[30]	Biodegradation
Carbamazepine	*Chlamydomonas mexicana* (35)[11], *Chlorella sorokiniana* (10-30)[12], *Desmodesmus* sp. (71)[30], *Nannochloris* sp. (20)[13], Mixed consortia (4-15)[1], (20)[6], *Scenedesmus obliquus* (35)[11]	Bioadsorption and Biodegradation
Carbendazim	Mixed consortia (14-30)[1]	Not determined
Cefradine	*Chlorella pyrenoidosa* (76)[14], (23)[8]	Not determined
Ciprofloxacin	*Chlamydomonas mexicana* (13-56)[11], *Dictyosphaerium* sp. (11)[15], *Nannochloris* sp. (100)[13], Mixed consortia (20-30)[7], (74-79)[1]	Photodegradation, biodegradation
Clarithromycin	Mixed consortia (100)[1]	Not determined
Climbazole	Mixed consortia (30-70)[1], *Scenedesmus obliquus* (88)[16]	Biodegradation
Clofibric acid	Mixed consortia (0-30)[1]	Not determined
Clomipramine	*Chlorella sorokiniana* (96)[30], *Chlorella vulgaris* (100)[30], *Chlorella saccharophila* (100)[30], *Coelastrella* sp. (34)[30], *Desmodesmus* sp. (29-42)[30], *Scenedesmus sp.* (73)[30], *Scenedesmus obliquus* (78)[30]	Bioadsorption
Codeine	*Chlorella sorokiniana* (50)[30], *Chlorella vulgaris* (57)[30], *Chlorella saccharophila* (42)[30], *Coelastrella* sp. (46)[30], *Coelastrum astroideum* (72)[30], *Desmodesmus* sp. (37-80)[30], *Scenedesmus sp.* (33)[30], *Scenedesmus obliquus* (59)[30]	Biodegradation and photodegradation
Diclofenac	*Chlorella sorokiniana* (30)[17], (40-60)[12], *Chlorella vulgaris* (21)[17], Mixed consortia (55)[18], (92)[6]	Photodegradation, biodegradation
Diltiazem	Mixed consortia (72-77)[7]	Not determined
Diphenhydramine	*Chlorella sorokiniana* (73)[30], *Chlorella vulgaris* (98)[30], *Chlorella saccharophila* (93)[30], *Coelastrella* sp. (87)[30], *Coelastrum astroideum* (87)[30], *Desmodesmus* sp. (88-92)[30], *Scenedesmus sp.* (86)[30], *Scenedesmus obliquus* (85)[30]	Biodegradation
Enrofloxacin	Mixed consortia (75-77)[1]	Not determined
Erythromycin	Mixed consortia (85)[7], (63-86)[1]	Not determined
Estriol	*Scenedesmus dimorphus* (85)[2]	Biodegradation
Estrone	Mixed consortia (85)[1], *Scenedesmus dimorphus* (85)[2]	Biodegradation
Flecainide	*Chlorella sorokiniana* (71)[30], *Chlorella vulgaris* (100)[30], *Chlorella saccharophila* (100)[30], *Coelastrella* sp. (52)[30], *Coelastrum astroideum* (66)[30], *Desmodesmus* sp. (72-96)[30], *Scenedesmus sp.* (40)[30], *Scenedesmus obliquus* (93)[30]	Photodegradation
Fluconazol	Desmodesmus sp. (33)[30]	Bioadsorption
Fluoxastrobin	Synechococcus sp.[19]	Bioadsorption
Fluxonazole	Mixed consortia (25)[1]	Not determined
Hydrochlorothiazide	Mixed consortia (44-84)[7]	Not determined
Hydroxyzine	*Chlorella sorokiniana* (76)[30], *Chlorella vulgaris* (93)[30], *Chlorella saccharophila* (93)[30], *Coelastrella* sp. (80)[30], *Coelastrum astroideum* (96)[30], *Desmodesmus* sp. (87-100)[30], *Scenedesmus sp.* (73)[30], *Scenedesmus obliquus* (95)[30]	Biodegradation
Ibuprofen	*Chlorella sorokiniana* (100)[12], *Nannochloris* sp. (40)[13], Navicula sp. (60)[20], Mixed consortia (98)[7], (99)[6]	Bio-uptake and biodegradation
Ketoprofen	Mixed consortia (36-85)[7]	Not determined
Kresoxim-methyl	Mixed consortia [19]	Not determined
Levofloxacin	*Chlorella vulgaris* (10-90)[21]	Biodegradation
Lincomycin	Mixed consortia (80)[1]	Not determined
Lorazepam	Mixed consortia (30-60)[12]	Not determined
Memantine	*Chlorella sorokiniana* (87)[30], *Chlorella vulgaris* (100)[30], *Chlorella saccharophila* (100)[30], *Coelastrella* sp. (78)[30], *Coelastrum astroideum* (73)[30], *Desmodesmus* sp. (44-86)[30], *Scenedesmus sp.* (92)[30], *Scenedesmus obliquus* (86)[30]	Bioadsorption and biodegradation
Metoprolol	*Chlorella sorokiniana* (100)[12], *Chlamydomonas reinhardtii* [19], *Dictyosphaerium* sp. (99)[15]	Biodegradation
Mitrazapine	*Chlorella sorokiniana* (63)[30], *Chlorella vulgaris* (69)[30], *Chlorella saccharophila* (80)[30], *Coelastrella* sp. (70)[30], *Coelastrum astroideum* (67)[30], *Desmodesmus* sp. (55-85)[30], *Scenedesmus sp.* (77)[30], *Scenedesmus obliquus* (62)[30]	Bioadsorption and biodegradation
Naproxen	Mixed consortia (10-70)[7], (89)[6]	Biodegradation
Norfloxacin	Mixed consortia (41-53)[1]	Not determined
Norgestrel	*Chlorella pyrenoidosa* (60)[22], *Scenedesmus obliquus* (95)[22]	Biodegradation
Ofloxacin	Mixed consortia (43-52)[1], (66)[7]	Not determined
Orphenadrine	*Chlorella sorokiniana* (82)[30], *Chlorella vulgaris* (100)[30], *Chlorella saccharophila* (98)[30], *Coelastrella* sp. (78)[30], *Coelastrum astroideum* (66)[30], *Desmodesmus* sp. (75-82)[30], *Scenedesmus sp.* (79)[30], *Scenedesmus obliquus* (95)[30]	Bioadsorption
Paracetamol	*Chlorella sorokiniana* (41-69)[17], (100)[12], Mixed consortia (88-94)[1]	Biodegradation and photodegradation
Paroxetine	Mixed consortia (99)[7]	Not determined
Progesterone	*Chlorella pyrenoidosa* (95)[22], *Scenedesmus obliquus* (95)[22], Mixed consortia (83-87)[1]	Biodegradation

Table 1 (*continued*)

Emerging contaminant	Microalgal species (percentage removal efficiency)	Pathways
Roxithromycin	Mixed consortia (87-94)[1]	Not determined
Salicylic acid	*Chlorella sorokiniana* (73)[17], (93-98)[23], *Chlorella vulgaris* (25)[24], Mixed consortia (33)[7], (90)[18], (97)[1], *Nannochloris* sp. (60)[4], *Scenedesmus obliquus* (93)[24]	Bio-uptake and biodegradation
Salinomycin	Mixed consortia (71-79)[1]	Not determined
Sulfadiazine	Mixed consortia (52-75)[1]	Not determined
Sulfadimethoxine	Mixed consortia (56-78)[1]	Not determined
Sulfamethazine	Mixed consortia (18-48)[1], *Scenedesmus obliquus* (17)[25]	Not determined
Sulfamethoxazole	Mixed consortia (0-18)[1, 19], *Nannochloris* sp. (32)[4], (40)[13], *Scenedesmus obliquus* (29)[25]	Bioadsorption, biodegradation and photodegradation
Sulfapyridine	Mixed consortia (98)[1]	Not determined
Testosterone	Mixed consortia (100)[1]	Not determined
Tetrabromobisphenol-A	*Chlorella sphaericum* & *Scenedesmus quadricauda* (98)[22]	Biodegradation
Tetracycline	*Chlorella vulgaris* (69)[26]	Bioadsorption and photodegradation
Tramadol	*Dictyosphaerium* sp. (57)[15], *Chlorella vulgaris* (51)[30], *Desmodesmus* sp. (14-45)[30], *Scenedesmus obliquus* (91)[27]	Bio-uptake and biodegradation
Triclocarbon	Mixed consortia (81-99)[1]	Not determined
Triclosan	*Chlorella pyrenoidosa* (77)[28], *Microcystis aeruginosa* (46)[29], Mixed consortia (31-58)[1], (95)[6], *Nannochloris* sp. (72)[13], (100)[11], (100)[32]	Biodegradation and photodegradation
Trihexyphenidyl	*Chlorella sorokiniana* (40)[30], *Chlorella vulgaris* (100)[30], *Chlorella saccharophila* (95)[30], *Coelastrum astroideum* (54)[30], *Desmodesmus* sp. (63-73)[30], *Scenedesmus sp.* (49)[30], *Scenedesmus obliquus* (60)[30]	Bioadsorption
Trimethoprim	*Chlorella sorokiniana* (40-60)[12], (60)[17], *Dictyosphaerium* sp. (<4)[15], Mixed consortia (0-37)[1]	Not determined
Tylosin	Mixed consortia (75)[1]	Not determined

Note = [1]Zhou et al., (2014), [2]Zhang et al., (2014), [3]Hom-Diaz et al., (2015), Bai and charya (2019), [5]Guo et al., (2016), [6]Matamoro et al. 2016, [7]Hom-Diaz et al., 2017a,b,[8]Li et al., (2015),[9]Lui et al., (2015), [10]Ji et al., (2014), [11]Xiong et al., (2017a), [12]de Wilt et al., (2016), [13]Bai and Acharya (2016), [14]Chen et al., (2015), [15]Gentili and Fick (2017), [16]Pan et al., (2018), [17]Escapa et al., (2015), [18]Villar-Navarro et al., (2018), [19]Stravs et al., (2017), [20]Ding et al., (2017), [21]Xiong et al., (2017b), [22]Peng et al.,(2014a), [23]Escapa et al., (2017a), [24]Escapa et al., (2017b), [25]Xiong et al., (2018b), [26]de Godos et al., (2012), [27]Ali et al., (2018), [28]Wang et al., (2013),[29]Huang et al., (2016), [30]Gojkovic et al., (2019), [31]Maes et al., (2014), [32]Rühmland et al., (2015).

accumulators'. Species belonging to the genera *Anabaena* (*Dolichospermum*), *Chlorella*, *Cladophora*, *Oscillatoria* and *Scenedesmus* have already demonstrated 'hyper-accumulators' and 'hyper-adsorbents' properties with respect to heavy metal adsorption (Kumar et al., 2016; Bwapwa et al., 2017) and similar properties could potentially exist with these and other microalgal species for a range of ECs. Enhancement of the physico-chemical properties of the immediate adsorption environment, such as optimising pH and temperature for the given species and EC of concern, or stimulation of EPS secretions, may help to facilitate 'hyper-adsorbency' by the microalgae.

Modification of the microalgal cell surface through either physical (e.g. grinding, thermal drying, steaming and lyophilisation) or chemical (e.g. acid and alkaline conditions) pre-treatment processes may also be a viable method for enhancing EC bioadsorption by the microalgae. Ali et al. (2018) demonstrated a 70% higher bioadsorption rate with chemically (0.1 N NaOH) modified microalgal biomass compared to unmodified microalgal biomass for the pharmaceutical drug, tramadol. Increased adsorption rates were a result of chemical modifications of the microalgal cell surfaces that permitted hydrophilic interactions between the hydroxyl and carbonyl functional groups of the cell surface and the amino and carbonyl groups in the molecules (Ali et al., 2018). Similarly, cell surface chemical modification can result in enhanced electrostatic attraction between the EC ions and the cell surface functional groups (such as amines, carboxyls, and hydroxyls) by deprotonation, which increases the negative charge of the cell surface (Bilal et al., 2018). Other mechanisms for enhancing bioadsorption of ECs by microalgae include optimising temperature, optimising algal growth conditions and the exposure time. As bioadsorption is a thermodynamic process, changes in temperature will alter the rate of EC adsorption onto the microalgal cell surface. How temperature affects the adsorption rate will depend on whether the process is endothermic or exothermic. Increased temperature enhances the rate of bioadsorption for endothermic processes but has the opposite effect on exothermic processes., increase in temperature decreases biosorption in the case of exothermic sorption processes (Zeraatkar et al., 2016). Optimised growth conditions will increase the total numbers of microalgal cells thus increase the total available cell surface area for bioadsorption, while optimised exposure time will enhance the total removal rate of the EC and is dependent on both the hydraulic residence time of the body of water and the thickness of the boundary layer surrounding the cell.

4. Microalgal bio-uptake of emerging contaminants

During bio-uptake, the contaminant is transported through the cell wall into the cell, where it binds to intracellular proteins and other compounds. Bo-uptake of contaminants into the cell occurs over hours to days, and unlike adsorption, it only occurs in living microalgal cells. Microalgal cells can uptake ECs by three major pathways: (1) passive diffusion; (2) passive-facilitated diffusion; or (3) energy-dependent/active uptake, across the cell membrane. Passive diffusion of ECs into the cell does not require any energy exertion from the cell as the EC diffuses through the membrane from a high (external) concentration to a low (internal) concentration. As the cell membrane is hydrophobic, low molecular weight EC that are non-polar and lipid-soluble material may potentially diffuse through the cell membrane, while polar molecules, molecules with high molecular weight and ions cannot pass through passively. Accumulation of the antibiotics triclosan and triclocarban by the filamentous green alga, *Cladophora* sp. and the anti-epileptic drug carbamazepine by the green alga, *Pseudokirchneriella subcapitata,* are two examples of ECs bio-uptake through passive cell membrane diffusion (e.g Coogan et al., 2007; Vernouillet et al., 2010). Passive diffusion can also result from changes to the cell membrane permeability as a result of expose to the EC. This process is not mediated by the microalgal cell itself but is a result of either depolarisation or hyperpolarisation of the membrane caused by the EC. Interference with the integrity of the cell membrane by the EC can lead to increased diffusion of the EC, or other contaminants present, into the cell. For example, several of

the compounds within the EC family, perfluorinated alkyl acids (PFAAs), have been shown to increase microalgal cell membrane permeability at concentrations well below that which affected cell viability (Liu et al., 2018). Exposure of a cyanobacterium, *Anabaena* CPB4337, to the PFAAs compounds, perfluorooctano sulphonate (PFOS) and perfluorooctanoic acid (PFOA) resulted in changed sensitivity to several herbicides, with some herbicides becoming more toxic and some less toxic to the cell (Rodea-Palomares et al., 2015). Passive-facilitated diffusion is the process where ECs diffuse across the cell membrane with the help of transporter proteins, whose role is to mediate the influx of polar molecules into the cell. The final mechanism is active transport of the EC across the cell membrane, which requires the use of energy by the cell. Often in active transport, the compound moves against a concentration gradient, although this is not always the case. Regardless of the mechanism, bio-uptake affected by the physico-chemical environment, including temperature and pH, the metabolic state, or health, of the cell, and the presence of any metabolic inhibitors (Wilde and Benemann, 1993).

Of EC treatment by microalgae, to date, bio-uptake is the least represented mechanism, with only 10% of studies featured in Table 1 showing bio-uptake to be at least partially involved in the treatment of 6 ECs, where removal mechanisms had been identified. However, several studies have demonstrated uptake as the main removal mechanism for some lipophilic pharmaceuticals by microalgae (e.g. Gattullo et al., 2012; Maes et al., 2014; Bai and Acharya, 2016). Bio-uptake accounted for approximately 23% removal of 17ά-ethinylestadiol by the green alga *Desmodesmus subspicatus* (Maes et al., 2014) and approximately 42% removal of triclosan by the green alga *Nannochloris* sp. (Bai and Acharya, 2016).

One of the challenges with bio-uptake is that the accumulation of ECs into the microalgal cell may likely result in overproduction of reactive oxygen species, which may lead to oxidative damage to biomolecules, cellular dysfunction and ultimately cell death (Zhang et al., 2011). This presents a number of challenges when considering bio-uptake as a viable bioremediation technology for ECs; including, but not limited to, re-release of unbound ECs back into the surrounding media following cell death, maintenance of a viable cell culture during bioremediation and efficiency of EC removal. It is, therefore, important to ensure that the EC concentrations are at levels that allow for accumulation within the cell, but not interrupt, or result in, unbalanced cellular redox status in the cell that may result in cell death. Microalgal bio-uptake is best suited for dilute concentrations of ECs where filtering and concentrating of the ECs for other treatment options would be cost-prohibitive.

4.1. Bio-uptake research opportunities

Opportunities for enhancing microalgal bio-uptake of ECs include selecting for strains that are both tolerant to anticipated concentrations of the EC of concern and have high uptake rates of that contaminant. Uptake rates of ECs vary among different species, genera and families of microalgae. For example, Gojkovic et al. (2019) found that the bio-uptake rate of amitriptyline was 32% in *Coelastrum astroideum*, 8% in *Chlorella saccharophyla* and 0% for *Chlorella vulgaris*, while uptake rate of clomipramine was 100% in *C. astroideum* and 0% for *C.saccharophyla* and *C. vulgaris* (see Table 1). In addition to determining optimum species, the lifecycle stage may also influence the amount of EC that is taken up by the cell. Lee et al. (2019) observed that the highest bio-uptake rates of the radionuclide caesium by the green alga *Haematococcus pluvialis* occurred when the cells were in the red cyst stage, while the lowest uptake rates occurred in the flagellate stage. Changes in the number of cellular potassium transporters at the different lifecycle stages is thought to explain the measured differences in the caesium uptake rates by this species (Lee et al., 2019). Both the cellular metabolic processes themselves and their rates are influenced by the external and internal physico-chemical environments that the cell experiences, such as pH and temperature. Optimisation of those physico-chemical parameters that affect both the rate and quantity of contaminant taken up by the cell, and/or protect the cell from any associated toxicity, will most likely enhance contaminant removal rates.

5. Microalgal biodegradation

Biodegradation or biotransformation, of ECs by microalgae provides one of the most promising technologies for the remediation of contaminants of concern. Unlike bioadsorption or bio-uptake, which simply acts as biological filters to concentrate the EC and remove it from the surrounding aqueous solution, biodegradation involves the transformation of complex compounds into simpler breakdown molecules through catalytic metabolic degradation. Biodegradation overcomes any issues associated with either the disposal of EC-laden microalgal biomass that is generated during bioadsorption or bio-uptake treatment. Microalgal biodegradation can occur via two principle mechanisms; either by metabolic degradation, in which the EC serves as the carbon source or electron donor/acceptor, for the microalga, or by co-metabolism, in which the EC is degraded by enzymes that are catalysing other substrates present (Tiwari et al., 2017). In the case of metabolic degradation, some microalgal species can employ mixotrophic growth strategies, where both organic carbon and dissolved inorganic carbon are simultaneously assimilated, meaning that they can operate both autotrophic and heterotrophic metabolisms co-currently. The microalgal biodegradation process can occur either intracellularly or extracellularly, or a combination of both, where initial degradation occurring extracellularly, and the breakdown products are further degraded intracellularly (Tiwari et al., 2017). Intracellular degradation relies on the bio-uptake of the EC by the cell (see above), while extracellular degradation relies on the excretion of enzymes, into the EPS, to function as an external digestive system. The EPS can also act as a surfactant and emulsifier to increase the bioavailability of the ECs for subsequent up-take by the cell (Xiong et al., 2018a).

Microalgal biodegradation of ECs involves a complex enzymatic process that involves both Phase I and Phase II enzyme families. Phase I of the biodegradation involves cytochrome P450 enzymes, which includes monooxygenase, dioxygenase, hydroxylase, carboxylase, and decarboxylase enzymes (Thies et al., 1996; Pflugmacher and Sandermann, 1998). In biodegradation, the main role of these enzymes is to make a contaminant more hydrophilic, through the addition, or unmasking of a hydroxyl group through either hydrolysis, oxidation, or reduction reactions (Xiong et al., 2018a). In Phase II, enzymes, such as gluthathione-S-transferases, catalyse the conjugation of glutathione with a wide group of compounds possessing electrophilic centres, resulting in the opening of the epoxide ring to protect against oxidative damage in the cell (Xiong et al., 2018a). A large number of enzymes have been reported as having a role in cellular protection, deactivation and/or degradation of a range of organic compounds that induce cellular stress in microalgae (Wang et al., 2019). These include superoxide dismutase, catalase, glutamyl-tRNA reductase, malate/pyruvate dehydrogenase, mono(di)oxygenase, pyrophosphatase, carboxylase/decarboxylase, dehydratase, alkaline and acid phosphatase, transferase, and hydrolases (Elbaz et al., 2010; Xiong et al., 2018a; Wang et al., 2019). Several of these enzymes, including superoxide dismutase and catalase, have shown increased activity in several microalgal species, when the cells were exposed to human and

veterinary antibiotics (Aderemi et al., 2018; Wang et al., 2019). Microalgal biodegradation of ECs is regarded as being highly complex and the exact role of the multiple enzymes in both the Phase I and Phase II enzyme families are not fully understood (Xiong et al., 2018a) and both the enzymes involved, and their respective roles is likely to differ, at least in part, between different microalgal species.

One enzyme thought to play a role in microalgal biodegradation of contaminants is the extracellular glycoprotein laccase (EC 1.10.3.2, p-diphenol: O_2 oxidoreductases). Laccase glycoproteins are multi-copper oxidases that catalyse the one-electron oxidation of a wide range of substrates such as mono- and poly-phenols and aromatic amines to radicals, which may undergo cross-linking or depolymerization reactions thereafter (Claus, 2004, Otto and Schlosser, 2014). While laccase-mediated biodegradation of aromatic compounds by fungi and bacteria has been studied intensively, the role of laccase in microalgal biodegradation is still in the early stages of investigation (Otto and Schlosser, 2014). Laccase glycoproteins have been identified as playing a major role in the microalgal-mediated biodegradation of both phenol and industrial dyes (Kılıç et al., 2011, Otto and Schlosser, 2014). Increased secretion and activity of laccase and polyphenol oxidase has been reported in cultures of the cyanobacterium *Phormidium valderianum* during the biodegradation of phenol (Shashirekha et al., 1997), while laccase-mediated biodegradation of industrial dyes has been reported in the green alga *Gonium* sp (Kılıç et al., 2011). However, laccase has also been shown to have no role in microalgal biodegradation of other compounds, such as ρ-chlorophenol, while the enzymes that were responsible had not been determined (Forootanfar et al., 2013). One reason for this is that there is very limited information available with respect to the behaviour of laccase or other enzymes during microalgal-mediated biodegradation of ECs and therefore further investigations are required (Xiong et al., 2018a).

Pharmaceuticals and personal care products are some of the more frequently studied contaminants for microalgal biodegradation (Norvill et al., 2016). Over the last five years, biodegradation of ECs by microalgae has been well reported in the literature, with 47% of studies featured in Table 1 showing biodegradation to be at least partially involved in the remediation of 28 EC compounds, where the removal mechanism had been identified by the authors. For example, microalgal biodegradation of the hormone progesterone and norgestrel has been successfully demonstrated in the two freshwater microalgae, *Scenedesmus obliquus* and *Chlorella pyrenoidosa* (Peng et al., 2014a), while Hom-Diaz et al. (2015) reported biodegradation of the hormones 17β-estradiol and 17ά-ethinylestradiol by the microalgae *Selenastrum capricornutum* and *Chlamydomonas reinhardtii*. Peng et al. (2014a) identified the main reactions involved in the microalgal transformation of the progesterone and norgestrel as being reduction (hydrogenation), hydroxylation, oxidation (dehydrogenation) and side-chain breakdown. Xiong et al. (2017a) successfully demonstrated co-metabolic removal of ciprofloxacin by the green alga *Chlamydomonas mexicana* under laboratory conditions. The electron donating properties of sodium acetate is thought to have enhanced the efficiency of *C. mexicana's* co-metabolism of the antibiotic, but the exact mechanisms were unknown, while the addition of other sources of carbon were either inhibitory, or had no effect, suggesting limited, or no, mixotrophic metabolism (Xiong et al., 2017a). For the flame retardant tetrabromobisphenol-A (TBBPA), sulfation, glucosylation and *O*-methylation and debromination were identified as the main transformation mechanisms utilised by six freshwater green microalgae during TBBPA biodegradation (Peng et al., 2014b). Other contaminants that have been biodegraded by microalgae include salicylic acid and paracetamol by *Chlorella sorokiniana* (Escapa et al., 2015), the antimicrobial agent triclosan by *Chlorella pyrenoidosa* (Wang et al., 2013), and the chemical bisphenol A by *Chlamydomonas mexicana* and *Chlorella vulgaris* (Ji et al., 2014).

One of the challenges associated with screening microalgae for potential biodegradation of ECs is that the enzymes responsible may not be active at the time of screening and the microalga may require a threshold concentration of the EC before the degrading enzymes can be triggered. Production and maintenance of these enzymes are metabolically expensive to the cell and comes at the cost of growth and reproduction. Aderemi et al. (2018) found that cellular energy budget and growth rates were significantly reduced in the microalga, *Raphidocelis subcapitata*, following exposure to four different antibiotics. The authors concluded that the decreased cellular energy budget was in response to the induction of superoxide dismutase production by the cells following antibiotic exposure. Pre-acclimation of the microalgal strains to sub-toxic concentrations the contaminant of concern may be an important initial step required prior to undertaking any biodegradation potential screening. Studies have shown that microalgae acclimated to contaminants showed enhanced photosynthesis, growth rates, metabolic functions and/or other cellular processes (e.g. Osundeko et al., 2014; Cho et al., 2016). It is plausible to suggest that, for some microalgae, their tolerances increase in response to chronic exposure due to the induction of enzymatic pathways to counteract the toxic effects. Chen et al. (2015) reported that the removal efficiency of the antibiotic cefradine by *Chlorella pyrenoidosa* increased when it was pre-exposed to the antibiotic. Similarly, Xiong et al. (2017b) found that the biodegradation of the antibiotic, levofloxacin, significantly increased when *Chlorella vulgaris* was pre-acclimated to the antibiotic. Both authors reported that the acclimation mechanism included increased xanthophyll pigment production. These pigments acts as antioxidants, membrane stabilizing agents and protectant against damaging radiation (Xiong et al., 2017b).

Another challenge for biodegradation is that while the breakdown products are often less toxic to aquatic biota or human health, this may not always the case. For example, Tadros et al. (2000), found that the hydroxylamino intermediates formed during the transformation of TNT, 24DNT, and 26DNT exerted elevated toxic effects on the microalga, *Selenastrum capricornutum*. Isolation, identification and screening for toxicity and fate of the breakdown products is, therefore, an important step in developing microalgal biodegradation treatment systems.

5.1. Microalgal-assisted bacterial biodegradation

Microalgae may also play a role in enhancing bacterial biodegradation of ECs. In microalgae-bacteria coupled treatment systems, such as wastewater high rate algal ponds (HRAPs), microalgal photosynthesis provides the necessary oxygen, a key electron acceptor, for aerobic bacterial degradation of the organic compounds, which, in turn, provides the CO_2 required for microalgal photosynthesis (Sutherland et al., 2015). For example, different microalgae-bacteria consortium have been used for the degradation of black oil (Safonova et al., 1999), acetonitrile (Muñoz et al., 2005), salicylate (Guieysse et al., 2002) and the detoxification of industrial wastewater (Safonova et al., 2004), where the microalgae provided the oxygen to support aerobic bacteria degradation. Microalgae can also enhance bacterial-mediated degradation of ECs through the release of dissolved organic matter (DOM), which can provide the necessary substrates for bacterial co-metabolism of the contaminant, although the exact mechanism for enhanced biodegradation is not fully understood. For example, Wolfaardt et al. (1994) observed increased removal of the contaminant diclofop methyl by bacteria when grown in the presence of algae or their metabolites. Similarly, Matamoros et al. (2016) observed

enhanced biodegradation of ibuprofen and caffeine in the presence of microalga-bacteria consortia than just bacteria alone. Matamoros et al. (2016) postulated that the enhanced biodegradation was a result of microalgae either releasing exudates, such as enzymes, or oxygen that aided degradation, or microalgal uptake of the compounds. However, microalgae-bacteria relationships with respect to EC degradation may not necessarily be beneficial, as both are capable of inhibiting each other, depending on the species present.

Investigations into the role microalgae play in bacterial-mediated biodegradation of contaminants of concern, or vice versa, are important for developing enhanced treatment systems for effective bioremediation of ECs. Understanding which exudates released by the microalgae enhance bacterial biodegradation, the mechanisms behind this enhancement, and the physico-chemical conditions that stimulate their release will most likely further increase the degradation rate of a given contaminant, or contaminants.

5.2. Microalgal biodegradation research opportunities

For microalgal species with demonstrated biodegradation capacity abilities, optimising the physico-chemical environment to stimulate degradation of the contaminant of concern is an important first step for the development of this technology. Research opportunities include enhancing both the enzyme activation and metabolism of the contaminant, as well as enhancing growth of the microalga and therefore efficiency of biodegradation. Further understanding on the role of enzymes produced in the presence of pollutants and their behaviour during degradation or detoxification, may offer some insight into the enzymatic pathways for microalgal biodegradation of other ECs. Understanding these pathways will allow for the development of treatment systems that are operated for optimal enzyme production and therefore maximal biodegradation.

Once EC degrading enzymes have been identified, research into how culture conditions can be manipulated to stimulate overproduction of the enzymes will help to increase the efficiency of microalgal biodegradation of the contaminant of concern. For example, Otto et al. (2010) demonstrated that laccase-like enzyme activity in the microalgal *Chlamydomonas moewusii* biodegrading phenolic compounds, was enhanced with the addition of 20 μM of $CuSO_4$ to the culture media, whereas 10 μM was not sufficient to further enhance laccase production while 30 μM resulted in acute toxicity to the cell. However, one of the challenges with optimising conditions that stimulate enzyme production is applicability of a full-scale system. Both cost and downstream environmental consequences need to be taken into consideration. In the above example of $CuSO_4$ addition for laccase-like enzyme production, copper concentrations in the discharge would exceed regulatory aquatic environmental guidelines.

Other research opportunities for enhancing microalgal biodegradation of emerging contaminants includes inducing gene expression and genetic transformation. Inducing elevated production of enzyme activity in the target microalga can be achieved through enhanced gene expression techniques, including exposing the cells to high levels of UVC irradiance to induce random mutagenesis, or targeted gene editing. Genetic modification, for example, the insertion of a fungal or bacterial gene into the microalga, may be an effective means of improving biodegrading enzyme production. However, for many countries, the use of genetically modified organisms for bioremediation at full-scale is not a viable option at present due to restrictions on their use (Manamsa et al., 2016).

6. Photodegradation and volatilisation

If an EC of concern is not able to be bioremediated by microalgae through either bioadsorption, bio-uptake or biodegradation, microalgae may still play a role in its successful remediation. Two EC remediation processes that can be further enhanced by either the presence of microalgae, or the microalgal treatment system itself, are photodegradation and volatilisation. Photodegradation of an EC can occur by either photolysis or photooxidative degradation of the compound (Abo et al., 2016). Photolysis occurs when the contaminant absorbs light, directly resulting in the chemical alteration and subsequent degradation of the contaminant, while photooxidative degradation involves the degradation of the contaminant through interactions with hydroxyl radicals, or other similar oxidants, that are formed due either dissolved organic molecules, or nitrate, reactions with light (Castro-Jiménez and Van de meent, 2011, Abo et al., 2016). Photodegradation of ECs is dependent on several factors including the physico-chemical properties of the contaminant, the intensity and wavelength of light exposure, and the physico-chemical properties of the waterbody. While light exposure is fundamental to photodegradation processes, light in a microalgal treatment system is highly attenuated, as the cells either absorb or scatter the light as it passes through the water column. Such high light attenuation may have negative impacts on the rate of photodegradation; however, both the design and operation of the treatment system can be modified to help alleviate some of the light limitation that impedes photodegradation (discussed further below). Photodegradation may also be enhanced in microalgal treatment systems through the increased presence of dissolved organic molecules (DOM). DOM is collective term for a range of organic compounds comprising of molecules such as hydrophilic organic acids, hemicellulose, humic acids and fulvic acids. Microalgal release DOM into the surrounding culture medium and this matter may play a role in enhancing photodegradation through various mechanisms, including catabolic processes, redox cycling, via production of hydroxyl radicals, or in inhibiting photo-oxidation by competitive reaction with radicals (Van Trump et al., 2006, Norvill et al., 2016). This occurs as a result of the photosensitised transformation of low light absorbing ECs following chemical reaction with the various DOMs. de Wilt et al. (2016) suggested that indirect photodegradation in the presence of microalgal dissolved organic matter was the possible pathway for the removal of the pharmaceutical drug ibuprofen in a microalgal bioreactor. Photodegradation of ECs can be successfully coupled with nutrient removal by wastewater treatment microalgal treatment systems. For example, the photodegradation of several ECs has been successfully demonstrated in wastewater treatment HRAPs, including the pharmaceuticals tetracycline (de Godos et al., 2012), ciprofloxacin (Hom-Diaz et al., 2017a,b) and diclofenac (Villar-Navarro et al., 2018).

Volatilisation of ECs is the loss of volatile organic compounds from the liquid phase into the atmosphere. The process is dependent on both the physico-chemical properties of the EC of concern (e.g. Henry's law constant) as well as the operating conditions of the treatment system (for example, aeration or agitation rates, temperature and atmospheric pressure) (Tran et al., 2018). In microalgal-based treatment systems high aeration rates provided by the mixing devices (e.g. paddlewheel, bubble lift column, stirrers), coupled with high sunlight and temperatures (compared to conventional wastewater treatment systems) may help enhance the removal of volatile ECs. Matamoros et al. (2015) found that for hydrophobic, volatile compounds, such as musk fragrances, volatilisation during the summer-time operations, where both sunlight and temperatures were higher.

6.1. Photodegradation research opportunities

Microalgal treatment systems are designed to increase light exposure through the water column including the use of short path-lengths, such as thin layer cascades and algal turf scrubbers, turbulent mixing, such as HRAPs, or a combination of them both, such as photobioreactors, specifically for the purpose of increased microalgal biomass. However, further research into both the intensity and duration of light exposure for successful photodegradation of the EC of concern is needed for selecting the optimal microalgal treatment system for enhanced photodegradation. Similarly, changes in the operation of the microalgal treatment system that alter the chemical and physical environment, such as, hydraulic retention time, depth, mixing speed and frequency, CO_2 augmentation, species control and effluent recycling, may result in improved conditions for enhanced photodegradation of EC. For example, Hom-Diaz et al., 2017a,b observed increased photodegradation of the antibiotic ciprofloxacin in a pilot-scale HRAP when the hydraulic retention time was reduced from 7 to 3 days. Further research into how these operational factors impact on photodegradation is needed to develop a cost-effective EC remediation system.

In situations where microalgal-mediated dissolved organic matter (DOM) plays a significant role in the photodegradation of EC of concern, better understanding of the conditions that stimulate release of this matter in microalgal-based treatment systems will allow for enhanced remediation. Dissolved organic matter is released extracellularly by some microalgae either in response to a physico-chemical stress, such as nutrient limitation, low light, or unfavourable temperature or pH, bacterial or viral infections, or through cell decay, while other species may also release DOM under optimal growth conditions (Villacorte et al., 2015). Better understanding of the role of DOM and its production in relation to photodegradation will aide in developing a cost-effective treatment system.

7. Full-scale systems

Much of the research that has been undertaken, to date, on microalgal bioremediation of ECs has been undertaken within a laboratory setting, under batch culture conditions with long hydraulic retention times (Table 2). One of the challenges with laboratory based batch culture conditions is its translation to full-scale systems. While low volume point source supply of emerging contaminants, such as discharge from industry manufactures or contaminated sites, could potentially be treated under batch conditions, municipal wastewater treatment plants, even at regional and rural scales, are unable to be operated under batch culture conditions due to the large volume and daily supply of wastewater influent. An algal-based treatment system for emerging contaminants for wastewater streams will need to be operated under semi-continuous, or continuous conditions, with a daily inflow and outflow of at least part of the wastewater. How this may affect treatment of the ECs is unclear.

There are two studies that have demonstrated removal of ECs, in particular pharmaceutical and PCPs, from pilot-scale wastewater treatment HRAPs, one outdoor and one indoor, and one study from a constructed treatment wetland that contained both plants and algae (Table 2). These systems were operated on a semi-continuous culture condition where a proportion of the culture medium was exchanged daily (e.g. 12.5% exchange on an eight day HRT). Percentage removal rates of the pharmaceuticals Diclofenac and Salicylic acid were similar in the outdoor HRAP and in laboratory based batch cultures, despite the sometimes longer HRT in the laboratory cultures (Tables 1 and 2). Further investigations on the removal rates in outdoor HRAPs, with mixed microalgal species, over seasonal scales is required to justify microalgal-based EC treatment systems.

8. Other research opportunities

One area that is often overlooked in studies assessing microalgae bioremediation of ECs is the potential interactions of multiple ECs on the bioremediation process. In most instances, municipal and industrial wastewater streams, landfill leachate, or urban aquatic surface and groundwater environments, have multiple ECs in their discharge (Tran et al., 2018). The numbers of known ECs have been reported to range up to 200 individual compounds, while the number of potential ECs present but currently not tested for, or are newly emerging onto the market, is unknown. Multi-contaminants may result in either competition for the binding sites or changes in the stability of the EC ion-microalgae interactions (Pradhan and Rai, 2001), interference amongst contaminants (Saavedra et al., 2018), or the antagonistic, synergistic or additive toxicity of multiple contaminants on the microalgal cell (Zhang et al., 2017). How multi-contaminants interact with each other, the environment or the microalgae itself, highlights the need for undertaking contaminant removal assessments under conditions that are realistic to the environment for which they will be applied. Different microalgal species most likely have different tolerances, bioadsorption or biodegradation properties for each contaminant. In situations where there are more than one contaminant of concern requiring bioremediation, microalgal treatment systems comprised of a consortia a species that each have their target contaminant would likely offer a more cost-effective and efficient means of remediation than a single species treatment system.

Many of the studies on microalgal bioremediation of EC, to date, have focused on species form the genera *Chlamydomonas, Chlorella* and *Scenedesmus*. Of the studies listed in Table 1, 25% of species listed were from the genus *Chlorella*, 25% from *Scenedesmus*/Desmodesmus and 12% from the genus *Chlamydomonas* (Table 3). *Chlorella sorokiniana*, *Scenedesmus obliquus* and *Chlorella vulgaris* are the most frequently reported species for EC treatment, treating 21, 20 and 17 ECs, respectively (Table 3). Each of these three species has demonstrated bioadsorption, biodegradation and bio-uptake pathways (Table 3). As well as often being recorded in wastewater treatment ponds, the species listed in Table 3 are often regarded as model species for laboratory studies for several reasons including availability, established cultures and growth conditions, as well as a wealth of information on their genome, photosynthetic and metabolic pathways. However, given the high diversity of phenotypes across both microalgae and cyanobacteria, high through-put screening programmes that test a wide range of species against chemically diverse contaminants are needed to help fast track the development of microalgal based EC treatment systems.

9. Conclusions

Microalgae have demonstrated ability to filter, concentrated, remove or biotransform a range of emerging contaminants. Direct treatment options include bioadsorption, bio-uptake, and biodegradation by the microalgal cells, while photodegradation and volatilisation can be enhanced in a microalgal treatment system. Further research is needed to exploit microalgal species for EC bioremediation properties, increase bioadsorption, enhance biodegrading enzymes and optimising growth conditions. When coupled with nutrient removal, such as HRAPs, microalgal treatment of EC can be a cost-effective viable option for the reduction of

Table 2
Culture and operation conditions for studies on microalgal treatment of a range of emerging contaminants. For a list of contaminants and microalgal species refer to Table 1.

Study	Reactor	Culture conditions	Operation	Hydraulic retention time (duration)
[1]Zhou et al., (2014)	Culture flask	Filtered wastewater, maintained at 25 ± 1 °C under an illumination intensity of 60 μmol m^{-2} s^{-1}, with a 12 h/12 h light/dark cycle.	Batch culture	7 days
[2]Zhang et al., (2014)	Culture flask	Autoclaved wastewater. 24 h light	Batch culture	7 days
[3]Hom-Diaz et al., (2015)	Culture flask	BG-11 medium or P49 medium (species specific) 24 h irradiance at 172 ± 18 μmol m^{-2} s^{-1} at 25 ± 1 °C.	Batch culture	10 days
[4]Bai and Acharya (2019)	Culture flask	Autoclaved wastewater. 24 h light	Batch culture	7 days
[5]Guo et al., (2016)	Culture flask	BM, BBM and BG-11 mediums (species specific) cultured under a 12/12 light/dark cycle at 200 μmol m^{-2} s^{-1}. Cultures were incubated at a temperature of 26 ± 1 °C and a CO_2 (2.5%) aeration rate of 0.2 vvm.	Batch culture	16 days
[6]Matamoro et al., (2016)	Culture flask	Raw and synthetic wastewater medium cultured under a 12/12 light/dark cycle at 150 μmol m^{-2} s^{-1}. Aeration of the reactors was ensured by using an air flow of 50 L h^{-1}	Batch culture	10 days
[7]Hom-Diaz et al., (2017)	Outdoor photobioreactor	Primary settled toilet water	Semi-continuous culture	8 days
[8]Li et al., (2015)	Culture flask	BG-11 medium cultured at 25 ± 1 °C and 40 μmol m^{-2} s^{-1} on a 12:12 light:dark cycle.	Batch culture	48 h
[9]Lui et al., (2015)	Culture flask	BG11 medium at 25 ± 1 °C under a 16:8 light:dark cycle at an intensity of 40 μmol m^{-2} s^{-1}.	Batch culture	7 days
[10]Ji et al., (2014)	Sealed serum bottles	BBM growth medium incubated at 27 °C and 150 rpm, under white fluorescent light illumination (16:8 light/dark cycle) at an intensity of 45–50 μmol m^{-2} s^{-1}.	Batch culture	10 days
[11]Xiong et al., (2017a)	Culture flask	BBM culture medium incubated at 150 rpm and 27 °C under white fluorescent light illumination (light/dark periods of 16/8 h) of 45–50 μmol m^{-2} s^{-1}.	Batch culture	11 days
[12]de Wilt et al., (2016)	Culture flask	Urine and synthetic urine medium. Cultures maintained at 35 °C with a continuous average illumination of 68 μmol m^{-2} s^{-1}. The incubator headspace was enriched with 3% CO_2 (v/v).	Batch culture	31 days
[13]Bai and Acharya (2016)	Culture flask	F/2 culture medium, 12 h light/dark cycle, culture maintained at 23 ± 1 °C	Batch culture	14 days
[14]Chen et al., (2015)	Culture flask	BG-11 medium maintained at 25 ± 1 °C under an illumination intensity of 2000 lux, with a 12 h/12 h light/dark cycle.	Batch culture	48 h
[15]Gentili and Fick (2017)	Open outdoor photobioreactor	Municipal wastewater, with CO_2 addition	Batch culture	7 days
[16]Pan et al., (2018)	Culture flask	BG11 culture medium incubated at 25 °C under the constant shake of 150 rpm. Irradiance supplied at 3000 lux with a dark/light cycle of 12h:12h	Batch culture	12 days
[17]Escapa et al., (2015)	Bubbling column photobioreactors	Mann and Myers medium and cultures maintained at pH 7.5 ± 0.5 through CO_2 addition. The irradiance maintained at 370 μmol photons m^{-2} $s^{-1}$and the photoperiod maintained at 12:12-h light/dark and the temperature at 25 ± 1 °C.	Batch culture	17–19 days
[18]Villar-Navarro et al., (2018)	Outdoor high rate algal pond	Wastewater. Ambient air temperature was 18.6 ± 5.7 °C.	Semi-continuous culture	3–9 days
[19]Stravs et al., (2017)	Culture flask	Modified WC medium incubated at 20 ± 1 °C with illumination supplied at 100 μE (m^2 s).	Batch culture	5 days
[20]Ding et al., (2017)	Culture flask	D1 and BG11 medium, incubated at 23 ± 1 °C in an incubator with illumination by fluorescent lamps (4000 lux, light: dark of 12: 12 h).	Batch culture	96 h
[21]Xiong et al., (2017b)	Culture flask	BBM culture medium incubated at 150 rpm and 27 °C under white fluorescent light illumination (light/dark periods of 16/8 h) of 45–50 μmol m^{-2} s^{-1}.	Batch culture	11 days
[22]Peng et al., (2014a)	Culture flask	BG11 medium, incubated at 25 °C in an incubator with illumination by fluorescent lamps (3000 lux, light: dark of 12: 12 h).	Batch culture	5 days
[23]Escapa et al., (2017a)	Bubbling column photobioreactors	Mann and Myers medium and cultures maintained at pH 7.5 ± 0.5 through CO_2 addition. The irradiance maintained at 370 μmol photons m^{-2} $s^{-1}$and the photoperiod maintained at 12:12-h light/dark and the temperature at 25 ± 1 °C.	Batch culture	16 days
[24]Escapa et al., (2017b)	Bubbling column photobioreactors	Mann and Myers medium and cultures maintained at pH 7.5 ± 0.5 through CO_2 addition. The irradiance maintained at 370 μmol photons m^{-2} $s^{-1}$and the photoperiod maintained at 12:12-h light/dark and the temperature at 25 ± 1 °C.	Batch culture	17–19 days
[25]Xiong et al., (2018b)	Culture flask	BBM culture medium incubated at 150 rpm and 27 °C under white fluorescent light illumination (light/dark periods of 16/8 h) of 45–50 μmol m^{-2} s^{-1}.	Batch culture	11 days
[26]de Godos et al., (2012)	Indoor high rate algal pond	Synthetic wastewater for the culture medium. Illumination provided by daylight fluorescent tubes and UV tube.	Semi-continuous culture	7 days
[27]Ali et al., (2018)	Culture flask	Chemically treated biomass	n/a	n/a
[28]Wang et al., (2013)	Culture flask	TAP medium shaken at 120 rmp and incubated at 22 °C with a 16/8-h light/dark photoperiod under a light intensity of 4000 lux.	Batch culture	24 h
[29]Huang et al., (2016)	Culture flask	BG11 medium maintained at 25 °C, under a 12 h/12 h day/night cycle at an intensity of 2000 lux.	Batch culture	96 h
[30]Gojkovic et al., (2019)	Flat panel photobioreactors	Bold Basal media, illumination provided by white LED lights on 12 h light/12 h dark regime. The culture was maintained at pH 7.2 ± 0.5 through CO_2 sparging.	Batch culture	12 days
[31]Maes et al., (2014)	Culture flask	M4 growth medium incubated at 20 ± 2 °C and subjected to a 16/8 h light/dark cycle at 15 μE/(m^2 s).	Batch culture	72 h
[32]Rühmland et al., (2015)	Constructed wetland	Treated wastewater.	Semi-continuous culture	5.5 days

Table 3
List of microalga species used for emerging contaminant treatment investigations featured in Table 1.

Microalgal species	Number of emerging contaminants	Number of pathways identified	Number of studies
Chlamydomonas sp.	1	2	1
Chlamydomonas mexicana	3	3	1
Chlamydomonas reinhardtii	2	2	1
Chlorella pyrenoidosa	3	1	3
Chlorella saccharophila	12	4	1
Chlorella sorokiniana	21	4	4
Chlorella sphaericum	1	1	1
Chlorella sp.	1	2	1
Chlorella vulgaris	17	4	5
Coelastrella sp.	10	4	1
Coelastrum astroideum	11	3	1
Mixed consortia	56	4	7
Desmodesmus subspicatus	2	2	1
Desmodesmus spp.	14	4	1
Dictyosphaerium sp.	4	0	1
Microcystis aeruginosa	2	2	2
Mychonastes sp	1	1	1
Nannochloris sp.	10	4	4
Navicula sp.	1	1	1
Scenedesmus dimorphus	2	1	1
Scenedesmus obliquus	20	4	7
Scenedesmus quadricauda	1	1	1
Scenedesmus sp.	10	4	1
Selenastrum capricornutum	2	2	1
Synechococcus sp	1	1	1

contaminant pollution in waterways.

Declaration of interest

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

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