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TECHNOLOGIES FOR THE CONTROL OF EMERGING CONTAMINANTS IN DRINKING WATER TREATMENT PLANTS

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Abstract

In recent years, so-called emerging contaminants (ECs) have attracted growing interest as they have been detected in reservoirs and even in drinking water. The new proposal *Drinking Water Directive* (2018) provides for the introduction of new parameters relevant to the ECs category. As these contaminants today tend to be present in a growing number of water sources, provide treatment systems that ensure compliance with regulatory limits and the protection of public health has become essential. The aim of this paper is to provide essential information on five ECs (more precisely: haloacetic acids, microcystine-LR, Perfluoro Alkylated Substances, Bisphenol-A and Nonylphenol) and to explain useful processes for their removal in a DWTPs. For each contaminant, current and future legislation, health aspects and in particular a focus of the chemical and physical removal technologies already existing and under study are reported. The effectiveness of both conventional (e.g. chemical oxidation, coagulation/flocculation, adsorption on Granular Active Carbon (GAC), ion exchange) and advanced treatments (e.g. membrane filtration, AOPs) is presented and discussed.

Keywords: bisphenol, haloacetic acids, microcystins, nonylphenol, PFAS

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1. Introduction

In recent years, so-called emerging contaminants (ECs) have attracted growing interest. Teodosiu et al. (2018) reported the definition of ECs as substances detected in the environment but currently not included in routine environmental monitoring programmes and which may be candidate for future legislation due to their adverse effects and/or persistency. In addition, most ECs have been discharged into the environment for years, but their presence has only recently begun to be investigated (Dulio et al., 2018) or are only recently recognized as potential causes of adverse effects on ecosystems or humans (Houtman, 2010). Most of this ECs are not yet included in the current drinking water legislation (e.g. *Directive 98/83/EC of the European Council* (EC,

1998)) (Riva et al., 2018). ECs include more than 1000 substances (Teodosiu et al., 2018) such as pharmaceuticals, endocrine disruptors, perfluorinated compounds (PFAS), cyanotoxins, haloacetic acids (HAAs), surfactants, plastic products, chromium VI, emerging DBPs, radioactivity, 1,4-Dioxane and new pesticides (Adamson et al., 2017; Petrovic, 2003; Sharma et al., 2019; Sillanpää et al., 2018b; Ternes et al., 2015). ECs have been detected in reservoirs and even in drinking water and are today increasingly object of research thanks to better existing analytical techniques and new toxicological evidence (Khatibikamal et al., 2019; McCleaf et al., 2017; Sillanpää et al., 2018b; Westrick et al., 2010).

Based on the indications provided by the most recent World Health Organization guidelines (WHO, 2017a), the new proposal for a *Drinking Water*

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Directive (EC, 2018), hereinafter called DWD 2018, provides parametric values for some of the over 1000 ECs. Firstly, among the ECs inserted in the DWD 2018 proposal, those that were discussed in this paper were selected considering ECs classified as possible carcinogens (class 2B), namely: (i) HAAs-, more precisely Dichloroacetic acid (IARC, 2014); (ii) microcystin-LR (MC-LR) (IARC, 2010); (iii) Perfluoro Alkylated Substances (PFAS), more precisely Perfluorooctanoic Acid (IARC, 2017). Furthermore, among the endocrine disruptors (EDCs), the other contaminants analysed in this paper were Bisphenol-A (BPA) and Nonylphenol (NP) due to their health effects and their presence in natural and treated water (WHO, 2017a).

Regarding the five selected compounds, the new proposal of DWD 2018: (i) introduces the limit of 80 µg/L for the HAAs; (ii) indicates a limit for MC-LR of 1 µg/L according to the WHO suggestion; (iii) regulates the PFAS and Total PFAS with two new proposed limit of 0.10 µg/L and 0.5 µg/L respectively; (iv) prescribes 0.01µg/L as limit for BPA and finally regulates for the first time the NP with a limit of 0.3 µg/L. In order to comply with the requirements that will be provided by the new proposal for a *Drinking Water Directive* (EC, 2018), the following solutions can be applied: (i) identify new water sources of better quality, (ii) optimize the management of Drinking Water Treatment Plants (DWTPs) (Sorlini et al., 2015b) and (iii) identify new treatment solutions for ECs removal.

As previously reported, these contaminants tend to be present today in a growing number of water sources; therefore, providing treatment systems that ensure compliance with regulatory limits and the protection of public health becomes essential (Ternes et al., 2015). The ECs can represent a problem in DWTPs because their removal cannot always be efficient with conventional treatments (Simazaki et al., 2015). The conventional treatments include adsorption on activated carbon, sand filtration, ion exchange and chemical oxidation. In order to cope with the recalcitrant ECs, advanced treatments are also available. Among these processes, there are the

advanced oxidation processes (AOPs), membrane filtration and biological processes. In Fig. 1, a list of the treatments presented in the paper is reported.

In this paper, specific insights regarding HAAs, MC-LR, PFAS, BPA and NP are presented. For each parameter, the origin, the adverse effects on human health and some considerations about the presence in the environment are presented. Moreover, the removal technologies already existing and under study are also reported.

2. Emerging contaminants (ECs)

2.1. Haloacetic acids

The HAAs are a group of compounds of organic nature that are formed as disinfection by-products (DBPs) following the presence of Natural Organic Matter (NOM) in waters subjected to chlorination process (Collivignarelli et al., 2017; Wang et al., 2017). They are one of the largest groups of water DBPs, based on weight, and represent (with THMs) over 50% of total halogenated DBPs (EPA, 2018; WHO, 2017a; 2017b). The main factors influencing the formation of HAAs are: (i) the temperature, (ii) the pH, (iii) the contact time, (iv) the presence and concentration of halogen ions (e.g. Cl, Br and I) and (v) the presence of NOM (EPA, 2018; He et al., 2018; Postigo and Zonja, 2018; Xue et al., 2017).

HAAs are considered cytotoxic and genotoxic (Dad et al., 2018; Postigo and Zonja, 2018). The route of exposure to these contaminants is commonly the ingestion of drinking water containing HAAs. According to the Environmental Protection Agency (EPA, 2018), inhalation and dermal exposure can also occur but, given the chemical properties of these compounds (i.e. low volatility and high polarity), these exposure paths have a limited impact on the population. In the United States, according to EPA (2018), most of the population is exposed to HAAs. Referring to WHO (2017b), evidence of carcinogenicity to health is not completely clear for all HAAs compounds.

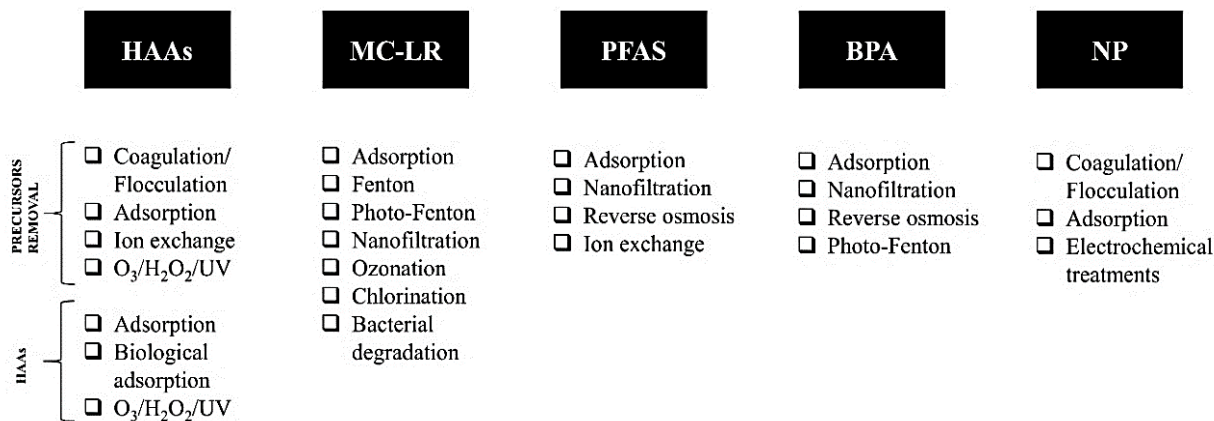


Fig. 1. List of the treatments suitable for ECs removal in DWTPs, presented in this paper

For some compounds, the possible carcinogenicity is demonstrated; for example, dichloroacetic acid is classified 2B by IARC. For others, e.g. monochloroacetic acid and trichloroacetic acid, there is still no direct evidence of carcinogenic properties on humans. For the bromoacetic acids, insufficient data are available for health effect classification.

Given the effects on public health, the World Health Organization (WHO, 2017a) suggested in its guidelines a limit of 80 µg/L for the sum of nine different compounds considered representative (mono-, di- and trichloroacetic acid, mono- and dibromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid and tribromoacetic acid). The new DWD 2018 (EC, 2018) fully incorporates the suggestions provided by the WHO (WHO, 2017a) and introduces this new parameter in Part B concerning chemical parameters.

In order to reduce the concentration of HAAs in drinking water, the types of intervention are essentially: (i) removal of precursors before disinfection, (ii) modification of disinfection operating practices and (iii) removal of HAAs after their formation (EPA, 2018). With regard to the removal of precursors, many techniques are available. For example, coagulation, by means of iron and aluminium based reagents, allows to eliminate on average between 20% and 75% of NOM and Dissolved Organic Carbon (DOC), precursors in the formation of HAAs (Sillanpää et al., 2018b; Zheng et al., 2015). Furthermore, the ion exchange technique shows excellent results in the field of precursor removal, with removal yields between 50% and 70% (EPA, 2018; Finkbeiner et al., 2018); higher values are obtained if this technique is combined with coagulation. In this case the coagulant consumption can be reduced up to 50% (Metcalf et al., 2015) and removal of up to 80% of the precursors can be achieved (EPA, 2018). Moreover, HAAs precursors can be removed also by AOPs, in particular O₃/H₂O₂/UV (Sillanpää et al., 2018a). The main objective of this treatment is oxidizing the organic matter by high reactive and non-selective species (OH•) produced in the process (Giannakis et al.,

2016). In this case the HAAs formation potential can be reduced up to 70% (Sillanpää et al., 2018a).

Regarding the operational changes, pre-oxidation with chlorine could be replaced by potassium permanganate, hydrogen peroxide or ozone (EPA, 2018). Another alternative may be to replace chlorination with chloramination that reduces the formation of HAAs but the production of N-DBPs (nitrogenous disinfection by-products) is increased (Bond et al., 2011). Also, the chlorine dioxide (ClO₂) if used in the presence of NOM does not lead to the formation of HAAs but can however form other DBPs such as chlorites and chlorates (Sorlini et al., 2015a, 2016). UV rays are also excellent candidates for complete or partial replacement of chlorine (Wang et al., 2015). However, they have no persistence and are therefore unable to provide coverage in the water distribution network (EPA, 2018).

Finally, as suggested by EPA (2018), another alternative is to continue to use chlorine as an oxidizing agent and to remove HAAs after their formation by, for example, filtration using biologically active (EPA, 2018) or not biologically active (Jiang et al., 2017) granular activated carbon (GAC). Jiang et al. (2017) studied the adsorption on AC of chlorinated water according to a different approach from the traditional one in which the precursors of the formation of DBPs are removed. DBPs, including the HAAs, are removed only once they have been formed. Their results indicate that the new approach is substantially more effective in controlling halogenated DBPs than the traditional approach. Also, in this case, as reported by Matilainen and Sillanpää (2010), the application of O₃/H₂O₂/UV can be effective (50-90%) in HAAs reduction if applied in DWTPs. They also explained that the presence into drinking water of humic acids can interfere with the decomposition of HAAs by the process reducing the yields by 20-40% (Matilainen and Sillanpää, 2010). In fact, humic acids could cause the H₂O₂ accumulation and the decrease in rate constants of HAAs decomposition (Wang et al., 2009). In Table 1, examples of suitable treatments for HAAs and precursors removal in DWTPs are reported.

Table 1. Examples of suitable treatments for HAAs and precursors removal in DWTPs. ^a: ADS= adsorption, CF= coagulation/flocculation, IE= ion exchange. ^b: L= laboratory scale, F= full-plant scale. ^c: DW= drinking water; R= real drinking water, S= synthetic drinking water. ^d: PAC= powdered activated carbon; GAC= granular activated carbon; HL= Hydraulic load. n.a.= not available

Target compounds	Treatment ^a	Scale ^b	Source	Type of DW ^c	Parameters ^d	Summary of results	References
HAAs precursors	ADS	L	Surface water	R	type of PAC= TiO ₂ NB 550 or TiO ₂ NB 700; TiO ₂ = 1.5 g/L	TiO ₂ NB 550: reduction of HAAs formation potential= 50%; TiO ₂ NB 770: reduction of HAAs formation potential= 25-30%	Gora and Andrews (2019)
HAAs precursors	ADS	L	Surface water	R	type of GAC= CJ15; HL= 4 m/h; period = 7-10 d; GAC= Φ1.5 mm × 5 mm; H = 1500 mm	HAAs precursors removal= 9 ± 20%	Chen et al. (2007)

HAAs precursors	ADS	L	Surface water	R	adsorption on GAC; HL= 2 m/h; EBCT= 30 min	HAAs precursors removal= 5-15% (rapid exhaustion)	Amini et al. (2018)
TCAA	ADS	L	n.a.	S	spherical cellulose adsorbent; solid-to-solution ratio of 1.0 g/L; initial TCAA= 50 mg/L; reaction time= 5 h; pH > 5	TCAA removal= 80-100%.	Lin et al. (2016)
HAAs precursors	CF	L	Surface water	R	coagulant= FeCl ₃ ; FeCl ₃ = 17-25 mg/l	HAAs precursors removal= 21 ± 10%	Chen et al. (2007)
HAAs precursors	IE	L	Surface water	R	HL= 2 m/h; EBCT= 30 min	HAAs precursors removal (DOC)= 80%	Amini et al. (2018)
HAAs precursors	IE+CF	L	Surface water	R	coagulant= Al ₂ (SO ₄) ₃ ·(14-16)H ₂ O; IE resin in slurry form= 1-6 mL/L	Reduction of HAAs formation potential > 60%	Levchuk et al. (2018); Singer et al. (2002)
TCAA+DCAA	O ₃ /H ₂ O ₂ /UV	L	n.a.	S	O ₃ = 0.3 mg/min; H ₂ O ₂ = 2.5 mg/L; UV at 254 nm; t= 3 min	TCAA removal > 50%. DCAA removal > 90%	Matilainen and Sillanpää (2010)
HAAs precursors	O ₃ /H ₂ O ₂ /UV	L	Surface water	R	O ₃ = 1-2 mg/mgDOC; H ₂ O ₂ = 10 mg/L; UV at 254 nm	Reduction of HAAs formation potential= 45%	Sillanpää et al. (2018a)
HAAs precursors	O ₃ /H ₂ O ₂ /UV	L	Groundwater	R	O ₃ = 0.5 mg/L; H ₂ O ₂ = 10 mg/L; UV at 254 nm; UV fluence= 0.6 and 3 J/cm ²	Reduction of HAAs formation potential= 68%	Sillanpää et al. (2018a)

2.2. Microcystin-LR

Cyanobacteria are able to produce a large variety of bioactive substances. Some of these, cyanotoxins, are toxic to humans (WHO, 2015). To date, over 80 different types of cyanotoxins are known including microcystins that are produced by several species of common planktonic cyanobacteria. The most common, as well as the most toxic, in surface waters is the microcystin-LR (MC-LR where L is leucine and R is arginine) (Antoniou et al., 2018; Takumi et al., 2017), a cyclic heptapeptide toxin (Takumi et al., 2017). The most common types of cyanobacteria that can produce microcystins are *Microcystis*, *Nodularia*, *Oscillatoria*, *Nostoc*, *Planktothrix* e *Anabaena* (Takumi et al., 2017; Westrick et al., 2010; WHO, 2017b). Acute symptoms due to ingestion of contaminated water are episodes of gastroenteritis, fever and skin, eyes, throat and respiratory tract irritation and neurotoxicity (ISS, 2011; WHO, 2015). However, the liver is the main target of the toxicity of the microcystin (ISS, 2011; WHO, 2017b; Woolbright et al., 2017). Long-term chronic effects, on the other hand, also include genotoxicity and carcinogenicity (IARC, 2010).

The current European Directive 98/83/CE (EC, 1998) does not include a limit neither on microcystins nor on MC-LR. Because of the dangers on human health due to the toxicity, evidenced since 2003 (Antoniou et al., 2018; Takumi et al., 2017), some member states provided autonomous provisional limit values over the years. For example, Italy (IMH, 2012) introduced a limit of 1 µg/L as an equivalent MC-LR referring to the sum of the concentrations of the different microcystins congeners present in the sample. In 2017 the WHO (2017b) recommended a

temporary limit on the MC-LR of 1 µg/L. This value was confirmed in the support document to the revision of the Annex I Council Directive 98/83/EC (WHO, 2017a) and fully incorporated in the revision of the DWD 2018 with a proposed value of parameter of 1 µg/L. The main approaches related to the removal of MC-LR, such as cyanotoxins in general, can be: (i) removal of cyanobacteria responsible for the production of MC-LR or (ii) removal of toxins present in the water (Vlad et al., 2014; Westrick et al., 2010). For the first and easiest approach, the WHO (2015, 2017b) suggests coagulation/flocculation, sand filtration and micro and ultrafiltration (MF and UF) as effective treatments. The study by Westrick et al. (2010) showed percentages of intact cyanobacteria cell removal, with coagulation/flocculation, sand filtration and (MF/UF) of 99.5%, 99.5% and 98%, respectively, thus demonstrating the efficiency of these treatments for eliminating directly the cyanobacteria cells.

Regarding the removal of extracellular MC-LR, more critical approach but also more effective because it acts on the free toxin present in the drinking water, WHO (2015, 2017b) suggests membrane filtration and adsorption on AC as optimal treatments. Not all types of membrane filtration are useful for MC-LR removal. As reported by Eke et al. (2018) the molecular weight of MC-LR is approximately 1kDa, while the literature molecular weight cut-off for UF and nanofiltration (NF) ranges from 10kDa-100kDa and 1kDa-10kDa, respectively. Therefore, they found that the concentration of MC-LR is not influenced by UF while NF can partially remove the toxin. The study by Cermakova et al. (2017) confirms the possibility of adequately removing organic nitrogen compounds, with a very low molecular weight (e.g. cyanobacterial

toxins and therefore also MC-LR), through adsorption on AC. These results are also confirmed by the study of Guerra et al. (2015) that reaffirm the use of AC as a very effective solution in the removal of MC-LR.

The study of Sorlini and Collivignarelli, (2011) and Sorlini et al., (2018) confirms removals between 80% and 90% of cyanotoxins, in particular MC-LR, by means of adsorption on AC. For MC-LR, the literature also noted that an adjustment of the solution pH conditions, to low pH, results in an enhanced adsorption of free toxins (Sorlini et al., 2018). Instead, Lopes et al. (2017) evaluated the removal efficiency of MC-LR from drinking water using a combined treatment that included Fenton oxidation, an AOPs, sand filtration and GAC adsorption. They concluded that the Fenton process in combination with a GAC filter is a viable and effective option for purifying water containing even high concentrations of MC-LR. Oxidation with ozone and chlorine is reported as a possible treatment for the removal of MC-LR (Westrick et al., 2010); but this solution can also be a possible cause of the release of new cyanotoxins in the treated water (WHO, 2015).

Furthermore, in recent years the photo-Fenton process, another AOPs, has been applied to remove MC-LR in DWTPs. For instance, Karci et al. (2018)

studied the influence of H₂O₂ and Fe²⁺ concentration on removal efficiencies and noted that higher yields can be obtained increasing concentrations of H₂O₂ and Fe²⁺. The main disadvantage due to the photo-fenton process is the production of chemical sludge that must be properly treated and disposed of with an increase in the costs of managing the DWTPs (Collivignarelli et al., 2019b; Sillanpää et al., 2018a).

Recently biological degradation became a promising technology (Kumar et al., 2019; Thees et al., 2019; Yang et al., 2014). The *Sphingomonas sp.* was the first strain reported to degrade MC-LR (Jin et al., 2018); moreover, some others naturally occurring bacterial species, such as *Arthrobacter sp.* and *Rhodococcus sp.*, showed a fast removal rate of MC-LR (up to 100%) (Kumar et al., 2019, Thees et al., 2019).

This treatment method is currently under study, but it potentially can be applied in the DWTPs as biological activated carbon filter or biosand filter. In fact, biological processes present some advantages over physicochemical treatment. They are: (i) more economical, (ii) more effective and (iii) they produce fewer toxic by-products (Kumar et al., 2019). In Table 2, examples of suitable treatments for MC-LR removal in DWTPs are reported.

Table 2. Examples of suitable treatments for MC-LR removal in DWTPs. ^a: ADS= adsorption, UF= ultrafiltration, NF= nanofiltration, PF= photo-fenton, BD= bacterial degradation. ^b: L= laboratory scale, F= full-plant scale. ^c: DW= drinking water; R= real drinking water, S= synthetic drinking water; ^d: PAC= powder activated carbon. n.a.= not available

Target compounds	Treatment ^a	Scale ^b	Source	Type of DW ^c	Parameters ^d	Summary of results	References
MC-LR	ADS	L	Surface water	R	mesoporous PAC; PAC= 20 mg/L; BET surface area= 257 m ² /g; initial MC-LR= 5 µg/L; pH= 3.2-8.0; t= 10 min	MC-LR removal= 80-90%	Park et al. (2017)
MC-LR	ADS	L	n.a.	S	adsorption on PAC-Fe(III); PAC= 500 mg/L; initial MC-LR= 10 mg/L; pH= 4-10	MC-LR removal= 70%	Dai et al. (2018)
MC-LR	ADS	n.a.	n.a.	n.a.	<i>Moringa oleifera</i> Lam. seeds powder (PAC); PAC= 0.25–1.0 g/L; MC-LR= 15–120 mg/L; t= 15-360 min; pH= 2-7	MC-LR removal= 98%	Yasmin et al. (2019)
MC-LR	UF or NF	L	n.a.	S	membrane in cellulose acetate; P _{UF} = 2.76 bar; P _{NF} = 4.83 bar; initial MC-LR= 10 mg/L; pH > 7	UF: MC-LR removal= 10%; NF: MC-LR removal= 40%	Eke et al. (2018)
MC-LR	O ₃	n.a.	n.a.	n.a.	initial MC-LR= 21 µg/L; O ₃ = 1.2 mg/L; t= 5 min	MC-LR removal= 73%; (O ₃ residual= 0.13 mg/L)	Hitzfeld et al. (2000)
MC-LR	O ₃	L	n.a.	S	Initial MC-LR= 12 mg/L; O ₃ = 0.4 mg/L; t= 4 min; pH > 7,	MC-LR removal= 100%	Eke et al. (2018)
MC-LR	O ₃	n.a.	n.a.	n.a.	initial MC-LR= 9 µg/L; O ₃ = 1 mg/L; t= 5 min	MC-LR removal= 50%	Hitzfeld et al. (2000)
MC-LR	PF	L	n.a.	S	initial MC-LR= 1 mg/L; Fe ²⁺ = 7.2 µM; H ₂ O ₂ = 300 µM; UV= 70 mW/cm ² ; pH=5.7	MC-LR removal= 80-100%	Karci et al. (2018)
MC-LR	BD	L	Surface water	R	<i>Arthrobacter spp.</i> ; initial MC-LR= 5 µg/L; t= 2d	MC-LR removal= 84%	Kumar et al. (2019)
MC-LR	BD	L	n.a.	S	<i>Stenotrophomonas acidaminiphila</i> strain MC-LTH2; initial MC-LR= 21.2 mg/L; T= 30°C; pH= 6-8; t= 7d	MC-LR removal= 100%	Yang et al. (2014)
MC-LR	BD	L	n.a.	S	<i>Bacillus sp.</i> ; initial MC-LR= 0.22 mg/L; bacterial= 8.3 × 10 ⁶ CFU/mL; T= 12d;	MC-LR removal= 74%	Kansole and Lin (2016)

2.3. PFAS

The acronym PFAS (Perfluoro alkylated Substances) refers to a family of persistent organic pollutants (POPs) consisting of chains of carbon atoms, linear or branched, of variable length and linked to fluorine atoms and other functional groups (Buck et al., 2011; Xiao et al., 2013). The most studied and known PFAS molecules are those composed of 8 carbon atoms, namely Perfluorooctanoic Acid (PFOA) and Perfluorooctylsulfonic Acid (PFOS) (Appleman et al., 2014; Banzhaf et al., 2017; Flores et al., 2013; Sun et al., 2016). Given the particular chemical properties, (the C-F bond is very stable), these molecules are decisively resistant to the environment.

For this reason, over the years PFAS molecules have seen an ever-increasing use in the industrial sector especially as chemicals in industrial processing or as additives in consumer products (Buck et al., 2011; Sharma et al., 2016; Sun et al., 2016; Xiao et al., 2013). However, PFAS are highly persistent but unlike many other pollutants (e.g. dioxin) are soluble in water (Appleman et al., 2014). Therefore, the major concern given by the PFAS is aroused by the long time it takes for a person to dispose of them from his body. They can cause liver damage and are considered potential toxic agents for human reproduction (IARC, 2017; WHO, 2017a). In fact, for instance in 2017 the IARC inserted the PFOA in the list of possible carcinogenic compounds - class 2B (IARC, 2017).

Currently there is no European legislation on this type of pollutants. The DWD currently in force does not provide for any limit value. The suggestion of WHO (2017a) is to introduce a limit values of 0.4 µg/L for PFOS and 4 µg/L for PFOA. The new parameter values proposed in DWD 2018 are 0.1 µg/L for the individual PFAS and 0.5 µg/L for PFAS-Total (this is the sum of per- and polyfluoro alkyl substances). This is because the European Commission defines as a priority the application of the precautionary principle already adopted for example to set parameter values of pesticides (EC, 2018).

Regarding the possible treatments for removing the PFAS from contaminated water, in recent years, research has focused both on the application of conventional treatments and on the study of advanced treatments. It is necessary to highlight that conventional treatments, except ion exchange resins, give contrasting results depending on the type of compound considered. The coagulation/flocculation allows a very low removal of PFOA and PFOS (10-30%) when the contaminant concentrations is in the order of µg/L (Appleman et al., 2014; Xiao et al., 2013). Instead, the impact of filtration on GAC has been studied by Eschauzier et al. (2012). While for the PFOA and PFOS a reduction of about 50% and over 90% respectively can be noted, for the PFXa, PFXs and PFNA the removal is negligible. Indeed, the PFBA and the PFBS are easily

released by the filter, making this type of treatment inapplicable for their removal.

The most recent study of McCleaf et al. (2017) has confirmed the most efficient removal, by means of adsorption on AC, of compounds such as PFOS and PFOA in spite of compounds such as PFBA which instead can give rise to the desorption phenomenon. Also, the study of Sun et al. (2016) confirms the greater simplicity in removing long chain PFAS (e.g. PFOS, PFOA) with powder activated carbon (PAC) in spite of those with short chain (e.g. PFBA). Appleman et al. (2014) demonstrated that conventional chemical oxidation treatments and AOPs do not have significant oxidative power against PFAS. PFOS and PFOA are slightly removed through processes such as UV/H₂O₂ and even treatments such as ozonation are counterproductive.

It is worth to note that UV-alone process gives encouraging results (about 35%) on PFOS removal (Appleman et al., 2014). With regard to membrane processes, it was found that MF and UF are not effective in removing PFAS (Appleman et al., 2014; Flores et al., 2013). Instead, NF and reverse osmosis systems are able to ensure a high effectiveness of removal of both short chain PFAS (e.g. PFBA) and long chain PFAS (e.g. PFOA and PFOS) (Hopkins et al., 2018). In fact, Flores et al. (2013) obtained a reduction of over 99% of long chain PFAS by reverse osmosis.

In recent years, several studies showed a significant effectiveness of ion-exchange resins in the removal of PFAS (both long and short chain) (Appleman et al., 2014; Hopkins et al., 2018; McCleaf et al., 2017; Woodard et al., 2017) overcoming some limits related to the use of AC (Eschauzier et al., 2012). Pilot-scale experiments, made by Conte et al. (2015), demonstrated that all tested materials (resins A600E, PAD500, PAD428 and MN102) removed the long chain PFAS (PFOA and PFOS) with almost 100% efficiency for long time, although they evidenced significant differences in the short chain PFAS (e.g. PFBA) removal.

Despite the excellent yields, to date the disadvantages of ion-exchange resins are essentially two: (i) exhausted resin must be managed and (ii) performances strongly depend on resin properties (Hopkins et al., 2018). In Table 3, examples of suitable treatments for PFAS removal in DWTPs are reported.

2.4. Bisphenol A and Nonylphenol

Bisphenol A (BPA) and Nonylphenol (NP) are two chemicals used in the production of polycarbonate plastics, epoxy resins and other polymeric materials (Chen et al., 2016; Lee and Choi, 2006). Polycarbonate plastic materials are used, for example, for the production of food and beverage containers, water containers and information technology equipment (Chen et al., 2016; Muhamad et al., 2016; Seachrist et al., 2016).

Table 3. Examples of suitable treatments for PFAS removal in DWTPs. ^a:ADS=adsorption, CF=coagulation/flocculation, SF= sand filtration, IE=ion exchange, NF=nanofiltration, RO=reverse osmosis. ^b:L= laboratory scale, F=full-plant scale. ^c:DW= drinking water; R=real drinking water, S= synthetic drinking water. ^d:GAC= granular activated carbon; HL=Hydraulic load. n.a.=not available

Target compounds	Treatments ^a	Type of plant ^b	Source	Type of DW ^c	Parameters ^d	Summary of results	References
PFOS	ADS+Cl ₂	F	Groundwater	R	adsorption on GAC; PFOS= 29-59 ng/L	PFOS removal= 7%	Rahman et al. (2014)
PFOS	CF+SF+O ₃ +A DS+SF	F	Surface water	R	adsorption on GAC; PFOS= 8.2 ng/L	PFOS removal= 97%	Rahman et al. (2014)
PFOA	SF+ADS+Cl ₂	F	Surface water	R	adsorption on GAC; PFOA= 67-92 ng/L	PFOA removal= 90-92%	Rahman et al. (2014)
PFBS	CF+SF+O ₃ +A DS+SF	F	Surface water	R	adsorption on GAC; PFBS= 35 ng/L	PFBS removal= 43%	Rahman et al. (2014)
PFOS, PFOA, PFBS, PFBA	IE	L	Groundwater	R	IE resins Purolite [®] A600E, A520E, A532E; resin= 1 g/L total capacity= 0.85-1.6 eq/L; PFOS= 27 ng/L; PFOA= 430 ng/L; PFBS= 171 ng/L; PFBA= 212 ng/L	PFBS and PFBA removal= 100% (with 20000 bed volumes); PFOS and PFOA removal= 100% (with > 60000 bed volumes)	Zaggia et al. (2016)
PFOS, PFOA, PFBS, PFBA	ADS	F	Groundwater	R	adsorption on GAC; minimum iodine number= 900-1100 mg/g; HL= 10-11 m/h; EBCT= 10-11 min; PFOS= 27 ng/L; PFOA= 430 ng/L; PFBS= 171 ng/L; PFBA= 212 ng/L	PFOS adsorption capacity= 2.4-4.1 µg/L; PFOA adsorption capacity= 17.3-39.6 µg/L; PFBS adsorption capacity= 6.8-8.1 µg/L; PFBA adsorption capacity= 3.8-4.3 µg/L	Zaggia et al. (2016)
PFOS	NF and RO	L	n.a.	S	NF in crossflow at 1.37 L/min; PFOS= 10 mg/L; P= 1379 kPa; pH= 4	NF: PFOS removal= 90-99%; RO: PFOS removal= 99%	Tang et al. (2007)
PFOS PFOA	ADS and IE	L	Groundwater	R	adsorption on GAC; EBCT _{GAC} = 20 min; EBCT _{IE} = 7.5 min; PFOS= 26 µg/L; PFOA= 12 µg/L	GAC: PFOS and PFOA removal= 99%; IE: PFAS and PFOA removal= 99%; (IE removed over four times as much total PFAS/g as GAC before significant breakthrough was observed)	Woodard et al. (2017)

Epoxy-phenolic resins based on BPA are also used as protective coatings for tanks and drinking water pipes (Chen et al., 2016). Furthermore, NP is a biodegradation product of nonylphenol ethoxylate (NPE) which is the most common non-ionic surfactant used daily (Khatibikamal et al., 2019) BPA and NP, as well as all EDCs, have for years been the subject of a strong scientific controversy regarding their health risk. For example, the European CHemicals Agency (ECHA) in 2017 issued a unanimous verdict on BPA defining it as an EDC with probable serious effects on human health (ECHA, 2017). Also, in the case of the

BPA, Arnold et al. (2013) conducted a comprehensive research study, describing BPA concentrations in drinking water-using the data contained in 65 papers (31 of North America, 17 of Europe and 17 of Asia) to assess the relevance of drinking water as a source of human exposure and risk.

On the contrary, they have been able to assert that the data indicate that ingestion of drinking water represents the source of only 2.8% of the total intake of BPA by monitored human individuals. Although the WHO (2017a), according to this vision, has declared that currently there are no proven health risks

deriving from the presence of BPA and NP in drinking water, the DWD 2018 provides for the introduction for these parameters of the specific limit values of 0.01 µg/L for BPA and 0.3 µg/l for NP (EC, 2018). In Table 4, examples of suitable treatments for BPA and NP removal in DWTPs are reported. Regarding the removal of BPA, the conventional treatment technologies applied in the drinking water treatment plants have a satisfactory yield of 76-99% (Arnold et al., 2013). For example, Stackelberg et al. (2007)

obtained a 76% removal of BPA in a typical potabilization plant composed of clarification with ferric chloride, primary disinfection with sodium hypochlorite, sand filtration, GAC and secondary disinfection. In this study, it is also noted that the adsorption on GAC is responsible for more than 50% of the BPA removed. Membranes are another technology that can significantly remove BPA; however, the removal yields are sensibly dependent on the type of the membrane material.

Table 4. Examples of suitable treatments for BPA and NP removal in DWTPs. ^a: ADS= adsorption, NF= nanofiltration, RO= reverse osmosis, PF= photo-fenton, CF= coagulation/flocculation, SF= sand filtration. ^b: L= laboratory scale, F= full-plant scale. ^c: DW= drinking water; R= real drinking water, S= synthetic drinking water; ^d: GAC= granular activated carbon; PAC=powdered activated carbon. n.a.= not available

Target compounds	Treatment ^a	Type of plant ^b	Source	Type of DW ^c	Parameters ^d	Summary of results	References
BPA	ADS	L	n.a.	S	adsorption on GAC; GAC from Macauba palm; surface area= 907.0 m ² /g; GAC= 10 g/L; initial BPA= 100 mg/L; T= 25-80 °C; pH= 3-9;	BPA removal= 50-100%	Moura et al. (2018)
BPA	ADS	L	n.a.	S	adsorption on biobased surface functionalized cellulose fibers; fiber loading = 1 g/50 mL; initial BPA= 15 mg/L; t= 60 min; pH= 5	BPA removal= 70-80%	Tursi et al. (2018)
BPA	ADS	n.a.	Surface water	n.a.	adsorption on PAC; PAC= 5-15 mg/L; PAC breakthrough= 19597 bed volume; initial BPA= 45 ng/L; EBCT= 1.5-3 min	BPA removal= 68%	Hernández-Leal et al. (2011)
BPA	NF	n.a.	n.a.	S	membrane NF90 and NF270 (Dow Filmtec); initial BPA= 20 mg/L	NF270: BPA removal= 55%; NF90: BPA removal= 94%	Muhamad et al. (2016)
BPA	RO	n.a.	n.a.	S	membrane TW30-1812-100 (Dow Filmtec); initial BPA= 50 mg/L; P= 408.1 kPa; flow rate= 1.172 L/min; pH= 8	BPA removal= 87.3 %	Muhamad et al. (2016)
BPA	PF	n.a.	n.a.	S	initial BPA= 43.8 µmol/L; H ₂ O ₂ = 4x10 ⁻⁴ mol; Fe ²⁺ = 4x10 ⁻⁵ mol; UV= 320-410 nm on 0.5 mW/cm ² ; t= 9 min; pH= 4.0;	BPA removal= 100%	Liang et al. (2015)
NP	CF+SF	F	Surface water	R	initial NP= 0.1-7.3 µg/L; T=12-28 °C	NP removal= 62-95%	Shao et al. (2005)
NP	ADS	LS	n.a.	S	adsorption on GAC; GAC= coal-based Calgon Filtrasorb® 400 and coconut shell-based PICA TIF TE; iodine number= 1000 mg/g and 1237 mg/g; SA BET= 1030 m ² /g and 1156 m ² /g; initial GAC= 13-16 mg/L; initial NP= 500 ng/L	NP removal= 90% (with both type of GAC)	Yu et al. (2008)
NP	ADS	n.a.	Surface water	n.a.	adsorption on coal-based PAC; PAC breakthrough= 44,141 bed volume; initial NP= 15 µg/L; EBCT= 15 min	NP removal= 50-90%	Hernández-Leal et al. (2011); Yang et al. (2017)

Yüksel et al. (2013) tested UF and reverse osmosis with the aim of identifying the optimal material for BPA abatement. The result is a better rejection of BPA with polyamide membranes compared to cellulose acetate membranes. Furthermore, it has been shown that up to 98% removal can be achieved with reverse osmosis (Yüksel et al., 2013). These excellent results have been confirmed by the study of Albergamo et al. (2019) that have obtained more than 75% rejection of BPA. Rodriguez-Narvaez et al. (2017) have instead tested the removal of BPA thanks to a Photo-Fenton process, an AOP. The result is a removal of about 98% in just 20 minutes of treatment.

NP, as well as BPA, is removed quite easily with conventional treatments such as AC adsorption. Yang et al. (2017) showed removal from 50 to 90% using GAC. Studies are also looking for alternative adsorbents optimized for the removal of EDCs, such as NP. For example, Khatibikamal et al. (2019) found 67% removal of NP from drinking water using poly (amidoamine) coated magnetic iron oxide nanoparticles as adsorbent substance. Conventional chemical oxidation processes (e.g. ozonation), remove only around 30% of NP (Barrera-Díaz et al., 2018). On the contrary, electrochemical treatments, which can also be used for the removal of other pollutants from wastewater (e.g. heavy metals) (Collivignarelli et al., 2019a), allow a reduction of NP concentration of 70% from drinking water (Barrera-Díaz et al., 2018).

3. Summary and future outlooks of the research

- **HAA:** the removal of HAAs precursors solves only partially the problem due to the HAAs formation. In fact, yields of HAAs precursors removal are in the range of 50-80%. At the same time, focus the attention only to directly HAAs removal can be low effective; in fact, if high concentration of NOM is present in the water, HAAs will be present in too high concentration to be completely removed. Therefore, both types of interventions should be studied in deep with further research, particularly the ion exchange and activated carbon techniques, which show excellent results in the field of precursor and HAAs removal respectively. Regarding operational changes, chlorine could be replaced by other oxidants, but it must be considered that other DBPs can be formed (for example by dosing ozone or chlorine dioxide) and that other oxidants (e.g. UV rays) may not have persistence in the drinking water distribution network.

- **MC-LR:** currently, the research is focusing in particular on the removal of extracellular MC-LR, more critical approach but also more effective because it acts on the free toxin present in the drinking water. Adsorption and chemical oxidation provide good removal yields while not all types of membrane filtration are useful for MC-LR removal: the concentration of MC-LR is not influenced by UF while NF can only partially remove the toxin. Moreover, in future an interesting point could be

analyse better the combined effect of MF or UF with PAC. In fact, PAC would be able to remove effectively MC-LR toxin and, at the same time, MF or UF would allow to remove cyanobacteria (for preventive purpose) and separate the PAC from drinking water. Recently, also the biological degradation became a promising technology. However, further studies are needed on the application of biological treatments for the removal of free MC-LR toxin, in particular about the factors that can influence the degradation process in such a way as to maximize the process performance.

- **PFAS:** in general, PFAS removal from drinking water still remains a significant problem, especially for short chain PFAS (e.g. PFBA). Research is focusing in particular on the removal by ion exchange resins and membranes (NF and reverse osmosis), that ensure higher removal yields both for long and short chain PFAS, while other processes such as chemical treatments don't have enough oxidative power against PFAS. AC ensure good removal yields on long chain PFAS, but the main gap is related with the ineffective removal of short chain PFAS. The perspective of future research in this field could be also the integration of AC with NF or reverse osmosis in order to ensure the compliance with the new limits introduced by the proposal of DWD 2018. The research on AC application could be implemented studying new adsorbent materials and optimizing the configuration of the reactors.

BPA and NP: BPA and NP are removed easily with conventional treatments, such as AC adsorption or coagulation/flocculation. Currently, studies are focusing on: (i) research alternative adsorbents (e.g. derived from palm or coconut shell) optimized for the removal of BPA and NP in order to increase removal yields, (ii) evaluate the efficiency of AOPs (in particular Photo-Fenton process) and (iii) search and test optimal materials for membranes (e.g. polyamide), considering that this aspect significantly influences the efficiency of removal.

4. Conclusions

This paper presented the results of the application of conventional and advanced treatments for the removal of emerging contaminants (ECs). In particular, the following contaminants were investigated: HAAs, MC-LR, PFAS, BPA and NP. The comparison of more than 100 documents, articles and reviews showed that for some ECs it is possible to operate in different ways. For example, for HAAs the target can be directly the contaminant or the precursor responsible for its generation. At the same way, MC-LR can be directly removed as toxins (critical aspect), after they have been dissolved in water, or it is possible to act on the removal of suspended cyanobacteria that are responsible for their release in water.

Overall, it can be asserted that while for some ECs (e.g. HAAs, MC-LR, BPA, NP) conventional

remediation treatments can be considered highly effective, for others (e.g. PFAS) these may not be enough. In these cases, it is necessary to adopt advanced treatments in order to allow compliance with the limits set by legislation and therefore the protection of public health.

In some cases, also advanced processes have a limited effectiveness and new researches are necessary for identifying effective solutions. However, while for HAAs the number of applicable treatments is higher, as regards the removal of MC-LR, PFAS, BPA and NP further studies are needed to optimize the performance of those already identified and to search for further effective treatments.

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