

Biological activated carbon and advanced oxidation processes for the removal of cyanobacterial metabolites in drinking water treatment

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Abstract

Biological activated carbon (BAC) and advanced oxidation processes (AOPs) are often used in conjunction during drinking water treatment for the removal of trace organic compounds that are not effectively removed during traditional treatment processes such as coagulation, flocculation and sand filtration. These trace organic compounds include toxic cyanobacterial metabolites such as saxitoxins and taste and odour (T&O) causing compounds like geosmin and 2-methylisoborneol (2-MIB) which are produced by a number of bacterial species including cyanobacteria. At present, the Hamilton Drinking Water Treatment Plant (HDWTP) employs the use of BAC as part of the final stage of drinking water treatment for its municipal water supply. This article provides a general overview of the chemical and physical processes involved and a review of the current state of AOP technology.

Introduction

The use of carbon as a means to purify water dates back to antiquity, with Hindu documents dating from around 450 BC making references to the use of charcoal filters for this purpose. The use of activated carbon for this purpose, however, is a more recent advance and it was first used as a means to dechlorinate chlorinated drinking water in 1910. Since then, it has been applied to a wide range of treatment problems including the removal of taste and odour – (T&O) causing compounds, synthetic organic contaminants (SOCs) and disinfection by-products (DBPs).¹

Activated carbons (ACs) are porous carbonaceous materials capable of adsorbing a wide range of aqueous phase solutes. Because of their porosity and very high surface area (500-1500 m²g⁻¹), they have the potential to adsorb very large amounts of material.^{1,2}

The nature of the starting material, carbonisation conditions and activation process all contribute to the properties of the AC produced. Such properties include porosity, pore size, pore size distribution, surface functionality, and ash content.^{1,2} The surface functionality of ACs plays an important role in the adsorption of organic solutes and is comprised mainly of oxygen based functional groups such as acidic groups including strong and weak

carboxylic acids, phenols and carbonyls (α protons). Basic surface groups such as cyclic ethers are also generally present, with higher activation temperatures resulting in a more basic surface. Other components of ACs such as minerals, e.g. calcium, sulphate, and phosphate ions and ash (silica, alumina, iron oxides, and alkaline earth metals) also contribute to the surface activity.¹

While activated carbon is very good at removing problematic compounds from drinking water sources, due to the physical nature of the process and the finite number of absorption sites, the surface of the AC becomes saturated over time. Once the surface of the AC is saturated, adsorption no longer occurs (or is substantially reduced) and breakthrough of previously adsorbed compounds is observed.³ To remedy this situation, the AC must either be replaced or regenerated, both of which are costly processes.

A method to overcome this problem that has become increasingly exploited over the years, both in drinking and waste water treatment, is the use of biological activated carbon (BAC). In this mode of operation, microbial communities are allowed to colonise the AC media as the adsorption capacity becomes depleted. Once colonised, compounds that were previously removed by physical adsorption may now be metabolised enzymatically by the microorganisms that inhabit the AC surface.

Granular activated carbon in drinking water treatment

In drinking water treatment, the filter media in fixed bed carbon filters usually consists of granular activated carbon (GAC). Granular activated carbons generally have a particle size ranging from 0.2-5 mm and are designated by mesh sizes such as 8/20, 20/40, or 8/30 for such applications.^{1,4}

The use of GAC in drinking water treatment is a very common practice and is implemented with the aim of removing unwanted contaminants from source water intended for use as drinking water that cannot be removed via primary treatment.^{1,3,5} As such, the composition of the source water and the specific contaminants it may contain mean that GAC is employed for different reasons

depending on location.^{1,5} In Hamilton, GAC filtration was introduced as a precautionary measure for the removal of cyanobacterial metabolites, particularly cyanotoxins like microcystins (Fig. 1) and saxitoxins (Fig. 2), that may pose serious health risks during potential cyanobacterial blooms in the future.⁶ Additionally, GAC is extremely effective in the removal of T&O causing compounds¹ such as geosmin and 2-methylisoborneol (GSM and 2-MIB; Fig. 3) which are known to be present in the Waikato River and were another reason for the initial implementation of GAC at the Hamilton plant.⁷

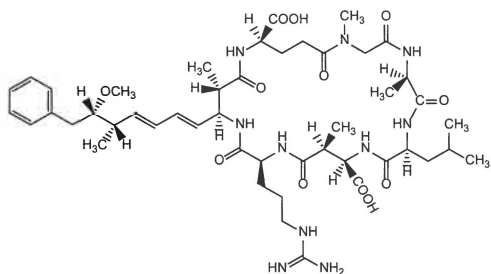
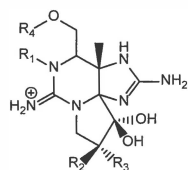


Fig. 1. Molecular structure of microcystin L-R



Toxin	Substituent Groups			
	R1	R2	R3	R4
STX	H	H	H	CONH ₂
GTX2	H	H	OSO ₃ ⁻	CONH ₂
GTX3	H	OSO ₃ ⁻	H	CONH ₂
C1	H	H	OSO ₃ ⁻	CONHSO ₃ ⁻
C2	H	OSO ₃ ⁻	H	CONHSO ₃ ⁻
dcSTX	H	H	H	H
dcGTX2	H	H	OSO ₃ ⁻	H

Fig. 2. General structure of saxitoxins and the substituents of some common analogues⁸⁻¹⁰

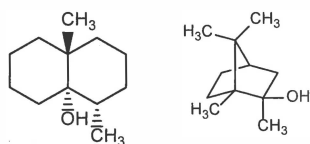


Fig. 3. Molecular structures of geosmin (left) and 2-methylisoborneol (right)

Biological activated carbon

The GAC filters currently in service at the HDWTP have been in use since 2007 following an extensive upgrade of the plant. Due to the length of time the filters have been operating, it is generally thought that adsorption processes have largely ceased and any removal of contaminants is a result of biological activity.⁷ Indeed, the long term plan for the use of these filter was for them to operate as BAC filters once adsorption capacity was exhausted and a biofilm was gradually established.¹¹

For successful operation of GAC filters operating in the BAC mode, certain operational criteria must be met in

order to achieve sufficient removal of the target compounds. These criteria include ensuring the influent target compounds are in a form that is readily biodegradable (biodegradable organic matter; BOM) by the filter microorganisms and allowing sufficient contact time to permit diffusion of target compounds to the surface bound bacterial colony for metabolism to occur.

Usually, to increase the BOM fraction of influent dissolved organic matter (DOM), an advanced oxidation process (AOP) such as ozonation is implemented prior to the BAC filter, with the "BAC process" referring to the coupled mode of operation. While this was initially considered during the upgrade of the HDTWP, it was not implemented at the time. However, the design of the upgrade allowed contingency for the addition of such a process in the future if required.¹¹

In order to provide sufficient time for the mass transport of these contaminants from the liquid phase into the bacterial cell for metabolism to occur, the contact time of water within the filter must be sufficiently long. In the operation of GAC and BAC filters, this is generally measured using the "effective empty bed contact time" (EBCT), which is a measure of the average time water would take to traverse the filter bed if the filter were empty. For BAC filters, an EBCT of greater than 7.5 minutes is generally thought to be sufficient if it is coupled to an AOP prior to the filter. Without the associated AOP, EBCTs of 10 minutes or more are considered more appropriate and this reflects the current operation of the filters at the HDWTP.

The general mechanism of removal of problematic compounds by bacteria occurs via secondary metabolic pathways acting upon the target compounds as secondary substrates due to their low concentration (ng L⁻¹), with the total organic carbon (TOC) which is present at much higher concentrations (mg L⁻¹) providing the primary substrate for primary metabolism. For example, GSM and 2-MIB are generally present in Hamilton source water at baseline levels of 5 to 50 ng L⁻¹ which is noticeable to many people, imparting an earthy or musty character to the water (Table 1). Hence, the degree of removal needs to be very good and provide high percentages of removal even when the influent concentration is very low. The degree of removal is also very important for compounds like cyanotoxins which are covered under the Drinking Water Standards for New Zealand (DWSNZ) where, for example, the maximum acceptable value (MAV) for microcystins is set at 1 µg L⁻¹.¹²

Table 1. Odour concentration threshold values for geosmin and 2-MIB¹³

Compound	Odour concentration threshold (ng L ⁻¹)
Geosmin	6-10
2-MIB	2-20

While the desired outcome of metabolic transformation of target compounds is, at a minimum, the loss of chemical functionality that imparts undesired properties to finished drinking water (taste and odour, colour, toxicity, etc.), this may not always be the case. For example, there is some evidence to suggest that during the degradation

of saxitoxins in biological filters, those with lower relative toxicity like C1, C2, GTX2 and GTX3 (Fig. 2) are converted to the more toxic STX, potentially leading to an increase in toxicity following biological filtration and in other environmental contexts.¹⁴⁻¹⁶ In situations where the influent water is known to contain high levels of saxitoxins, for example during a cyanobacterial bloom, it may be necessary to implement an AOP temporarily so as not to potentially exacerbate the problem.

Advanced oxidation processes

Advanced oxidation processes (AOPs) are often employed in drinking water treatment as a method of removing unwanted organic impurities and trace organic pollutants via chemical oxidation, with the ultimate aim of complete mineralization to C-O₂.¹⁷ In particular, AOPs are a useful method for increasing the BOM fraction of the TOC prior to BAC or another type of bio-filtration system as a means of allowing compounds resistant to biodegradation to be metabolised more effectively by the biofilm. Of course, as a living biomass is involved, sufficient time must be allowed for the oxidant residual to decrease to a level that will not affect the health of the biological media following the AOP treatment.¹⁸ Additionally, the AOP used must not contribute an increase in the trihalomethane (THM), haloacetic acid (HAA) or other disinfection by-product (DBP) formation potential, as these are tightly controlled under the DWSNZ.¹²

Although a range of AOPs are currently employed in various drinking and waste water treatment scenarios, almost all are based on the production of highly reactive radical intermediates, specifically the hydroxyl radical ([•]OH, Table 2).¹⁹ Under most conditions, [•]OH will react via addition to unsaturated carbon-carbon bonds, aromatic substitution, hydrogen abstraction, or mono-electronic oxidation.²⁰

Table 2. Standard half-cell potentials for some oxidants commonly used in water treatment^{5,21,22}

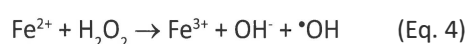
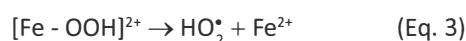
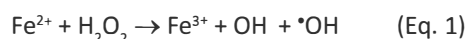
Oxidant	Reduction half-reaction	E ^o _{red} (V)
Titanium dioxide "hole"*	TiO ₂ (h ⁺) + e ⁻ → TiO ₂	3.20
Hydroxyl radical	[•] OH + H ⁺ + e ⁻ → H ₂ O	2.85
Ozone	¹ / ₃ O ₃ + H ⁺ + e ⁻ → ¹ / ₂ H ₂ + ¹ / ₂ O ₂	2.08
Hydrogen peroxide	¹ / ₂ H ₂ O ₂ + H ⁺ + e ⁻ → H ₂ O	1.78

* h⁺ = valence band hole produced by incident photons of sufficient energy

A range of AOPs are available and currently used in full-scale drinking water treatment plants worldwide. The use of AOPs as a mechanism for the removal of pollutants is applicable only in situations where the source water has a relatively low organic load (chemical oxygen demand; COD ≤ 5g L⁻¹). Hence, AOPs are ideally suited for the treatment of water intended for human consumption that has undergone primary treatment (coagulation, flocculation and filtration).¹⁷ Current AOPs can be characterised as catalytic processes, ozone-based processes or UV-based processes.

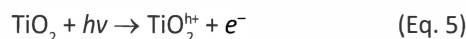
Catalytic AOPs

Catalytic AOPs utilize H₂O₂, UV or a combination thereof in conjunction with a solid semi-conductor or transition metal catalyst to produce [•]OH. Catalytic AOPs such as the Fenton (Eq. 1) and Fenton-like processes (Eqs. 2-4) are often confined to waste water treatment, as the catalytic activity of Fe²⁺/Fe³⁺ that is a feature of these processes requires strict pH control at fairly strong acidity (pH = 2.7-2.8) that is unlikely to be feasible for drinking water treatment applications.^{17,22,23} The rate of degradation of organic pollutants by a Fenton-like mechanism can be increased by the use of UV light, giving the so-called photo-assisted Fenton processes. However, the pH requirements are the same as for more traditional Fenton-like processes.

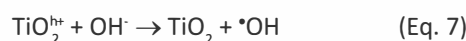
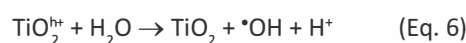


Photocatalysis: TiO₂/UV

More recently, photocatalytic AOPs based on TiO₂ (anatase) have been developed. The initial step in the TiO₂/UV type system involves the irradiation of TiO₂ followed by the formation of electron-hole pairs. This is achieved by employing incident photons of sufficient energy to produce conduction band electrons and valence band holes (Eq. 5).



The extremely high oxidation potential of holes (denoted h⁺; Table 2) means that nearly all chemicals should be able to be oxidized, including the oxidation of adsorbed H₂O or OH⁻ to give [•]OH (Eqs. 6 & 7).



Similarly, direct oxidation of pollutants may also occur, via adsorption and subsequent oxidation at the TiO₂ surface, although this process is thought to play a very minor role in the oxidation of organic components, with respect to [•]OH (Eq. 8).²²



Additionally, the electrons produced in the initial step are able to reduce some metals and dissolved O₂ to give the superoxide radical, [•]O₂⁻.

This method has the advantage of potentially using solar radiation as a source of UV, thereby not requiring the implementation of UV lamps as part of the reactor. However, as this relies on consistently fine weather, this leads to inconsistent system performance. Additionally, standard TiO₂ only absorbs a narrow bandwidth of the total solar spectrum, meaning the overall quantum yield is low. To overcome this, the development of doped TiO₂ that is able to more effectively utilise wavelengths of the

solar spectrum available at ground level have been investigated as a means of reducing the need for specialised UV reactors.^{17,24} TiO₂-based AOPs have been investigated by a number of researchers as a means to remove cyanotoxins from drinking water including microcystins (Fig. 1), cylindrospermopsins and nodularins (Fig. 4) with good results.²⁵⁻²⁸

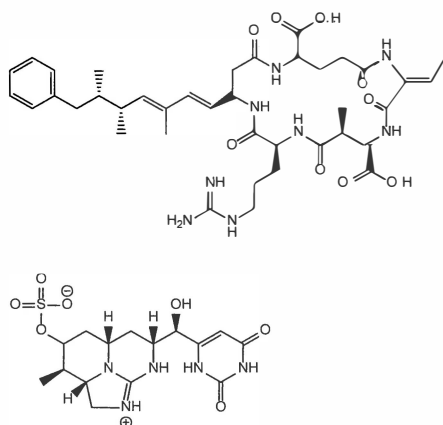


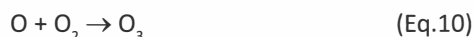
Fig. 4. Molecular structures of nodularin-R (top) and cylindrospermopsin (bottom)

Ozone- and UV-based AOPs

Ozone-based processes rely on the decomposition of ozone (O₃) to produce [•]OH. The yield of [•]OH can be increased by the use of H₂O₂ or UV in the system. The production of [•]OH in aqueous systems can also be achieved without the use of O₃ as is the case with UV-based processes like H₂O₂/UV and Cl₂/UV-based AOPs.

Ozone-based processes

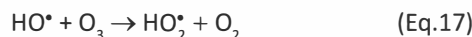
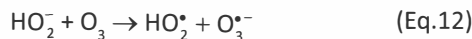
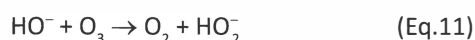
The use of O₃ as an oxidant requires the implementation of an on-site O₃ generator. Ozone is usually generated by an electrical discharge (8-20 kV) applied to molecular oxygen, air or oxygen enriched air as per Eqs. 9 & 10.⁵



The O₃ that is generated can then be introduced into solution via a suitable gas transfer device such as an in-line gas injection system or a multistage bubble contactor.⁵

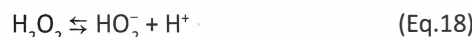
O₃ is highly reactive towards many compounds found in drinking water that contain specific functional groups including alkenes, activated aromatics, amines, sulfides and other organic compounds containing electron rich moieties.^{29,30} While this means direct use of ozone is likely to be minimally effective for the removal of many T&O causing compounds (Fig. 3), cyanotoxins are likely to be effectively oxidised due to their wide range of susceptible functionalities (Figs. 1,2,5).

Under the right conditions, O₃ will also spontaneously decompose via a chain reaction mechanism, which includes the production of [•]OH and [•]OOH (hydroperoxyl) radicals that are much less selective oxidants according to Eqs. 11-17.

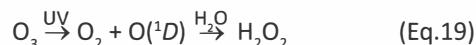


The chain reaction can be initiated in various ways including the presence of natural organic matter (NOM), Fe²⁺, H₂O₂, UV radiation and OH⁻ (Eq. 11; pH ≥ 8.5).^{5,17,23,30}

For example, the production of HO₂[•] from H₂O₂ in aqueous solution (Eq. 18) illustrates how the initiation of the chain decomposition to produce [•]OH may be enhanced, by increasing the quantity of HO₂[•] available to react with O₃ (Eq. 12).^{17,22,30}



Hence, oxidation by O₃ can be enhanced by the addition of H₂O₂ into the system. This can be achieved by directly introducing H₂O₂ into the system (O₃/H₂O₂), or by producing H₂O₂ *in situ* from O₃ using UV radiation (O₃/UV system).^{22,30} This is achieved via the UV irradiation of ozone, which produces molecular oxygen and excited singlet state oxygen (O(¹D)). The singlet oxygen rapidly combines with water to produce hydrogen peroxide (Eq. 19).



The H₂O₂ that is produced can then dissociate (Eq. 18) and initiate the chain reaction decomposition of O₃ (Eqs. 12-17).

The use of additives such as H₂O₂ or UV overcomes the need to maintain the O₃ system at low pH while still producing an adequate concentration of [•]OH to effect a reasonable rate of oxidation for a wide range of target contaminants. Reaction rates of oxidation by [•]OH of some T&O causing compounds are generally much higher than O₃ (Table 3), with the faster reaction rates of oxidation with O₃ limited to alkenes and activated aromatic compounds.²⁹

UV-based processes

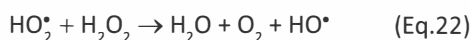
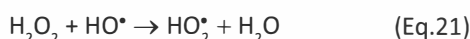
UV-based processes forego the use of ozone as an oxidant and instead aim to form [•]OH or other radical species from other oxidising agents or from water directly. These include UV/H₂O₂, UV/Cl₂ and vacuum UV (VUV).

UV/H₂O₂

This process aims to produce [•]OH from H₂O₂ by exploiting the absorption of UVC radiation by H₂O₂ between 100 and 280 nm.²⁰ As Hg lamps produce an emission line at 253.6 nm, these are most commonly used for this purpose.^{20,22} Initiation of the chain propagation reaction begins with homolytic photolysis of H₂O₂, yielding two [•]OH (Eq. 20), which then undergo a radical chain reaction via the Haber-Weiss mechanism (Eqs. 21 & 22).^{22,31}

Table 3. Reaction rate constants of taste and odour compounds via oxidation with O₃ or •OH²⁹

Compound	Reaction rate constant (k)	
	O ₃	•OH
β-cyclocitral	3890 M ⁻¹ s ⁻¹	7.42 × 10 ⁹ M ⁻¹ s ⁻¹
geosmin	0.10 M ⁻¹ s ⁻¹	7.80 × 10 ⁹ M ⁻¹ s ⁻¹
3-hexen-1-ol	5.4 × 10 ⁵ M ⁻¹ s ⁻¹	7.45 × 10 ⁹ M ⁻¹ s ⁻¹
β-ionone	1.6 × 10 ⁵ M ⁻¹ s ⁻¹	7.79 × 10 ⁹ M ⁻¹ s ⁻¹
2-isopropyl-3-methoxypyrazine	50.2 M ⁻¹ s ⁻¹	4.91 × 10 ⁹ M ⁻¹ s ⁻¹
2-methylisoborneol	0.35 M ⁻¹ s ⁻¹	5.09 × 10 ⁹ M ⁻¹ s ⁻¹
2,6-nonadienal	8.7 × 10 ⁵ M ⁻¹ s ⁻¹	10.49 × 10 ⁹ M ⁻¹ s ⁻¹
1-penten-3-one	5.9 × 10 ⁴ M ⁻¹ s ⁻¹	4.71 × 10 ⁹ M ⁻¹ s ⁻¹
2,6-di- <i>tert</i> -butyl-4-methylphenol	7.4 × 10 ⁴ M ⁻¹ s ⁻¹	3.20 × 10 ⁹ M ⁻¹ s ⁻¹
2,4,6-tribromoanisole	0.020 M ⁻¹ s ⁻¹	3.74 × 10 ⁹ M ⁻¹ s ⁻¹
2,4,6-trichloroanisole	0.057 M ⁻¹ s ⁻¹	5.10 × 10 ⁹ M ⁻¹ s ⁻¹



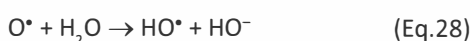
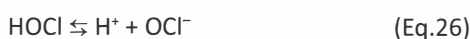
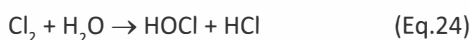
Stoichiometrically, it would seem that the photolysis of 1 mol of H₂O₂ would yield 2 mol of •OH, and experiments in the gas phase do agree with this where the quantum yield of •OH (Φ_{OH}[•]) has been shown to be 2.09 ± 0.36. However, in the liquid phase this is not true, where Φ_{OH}[•] ≈ 1 and this indicates that only approximately 50% of H₂O₂ is converted to free •OH. This is often explained by the solvent “cage” effect, whereby newly created radicals in the liquid phase are surrounded by a solvent cage which promotes recombination of the radical species (Eq. 23).^{20,22,31}



The UV/H₂O₂ system is quite commonly used, and has the advantage of requiring fewer oxidants and dosage systems compared with O₃/H₂O₂ systems, while still providing high enough concentrations of •OH to achieve reasonable degrees of removal of pollutants at the commonly used dosages in water treatment of 2 – 10 mg L⁻¹.²²

UV/Cl₂

The UV/Cl₂ process is based on UV-induced photo-dissociation of species present in aqueous solutions of chlorine which is produced by introducing chlorine gas to water (Eqs. 24 – 28).^{32,33}



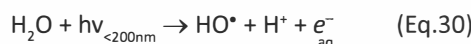
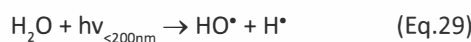
While the yield of •OH is theoretically higher than the

UV/H₂O₂ process, the UV/Cl₂ process is pH dependent, with optimum yield being realised at pH < 6.³² As the pH of the influent water used at the HDWTP is approximately 7,³⁴ pH adjustment would be required to achieve optimum •OH yield. However, at neutral pH, the process is kinetically comparable to the UV/H₂O₂ in the oxidation of trace organic contaminants.³² Additionally, as many water treatment plants, including Hamilton, already employ Cl₂ as a disinfectant, this method may provide a cost effective alternative AOP to O₃ and H₂O₂ based processes which require the installation of new infrastructure. Although this may be a good option in some cases, and has been shown to degrade GSM and 2-MIB quite effectively,³² it may be more prone to radical scavengers and quenching than the UV/H₂O₂ process, depending on the composition of the influent water.³⁵

Vacuum UV

Vacuum UV (VUV) is an “oxidant free” AOP that degrades organic pollutants by the formation of reactive species like •OH, •H, e_(aq)⁻, •HO₂ and •O₂ via the direct photolysis of water by irradiation with short wavelength (< 200 nm) UV radiation.²²

Two main reactions initiate a series of chain reactions (Eqs. 29 & 30).



Photons with wavelengths in the VUV region can be produced in a number of ways, most commonly via the use of excimer (excited dimer) lamps and low-pressure Hg lamps (VUV-Hg). Excimer lamps, which contain inert gases like xenon, argon and krypton, emit VUV radiation at various wavelengths, depending on the gas used. For example, Xe₂-excimer lamps emit at 172 nm with around 5 to 40% efficiency. One problem with the use of these lamps is the fact that water has a very high absorptivity (550 cm⁻¹) at this wavelength. While VUV-Hg lamps provide radiation at 185 nm where the absorptivity of water is lower (1.80 cm⁻¹), this still means that most of the emitted photons are absorbed within 0.3 cm of the water surface. Possible ways to circumvent this problem may be to increase the level of turbulence in the VUV reactor or bubbling oxygen or air through the system via some form of diffuser or aerator.^{22,36,37}

More than 30 reactions are known to occur during VUV photolysis of water, and while the direct photolysis of dissolved organic compounds is possible, it is unlikely to be significant compared to the oxidation of these compounds by the radicals produced from water during the VUV process, which is present at a concentrations many orders of magnitude higher.²²

At present, VUV technology is still at the laboratory stage and in pilot plant development for application to large scale water treatment, although it looks to be a promising technology for future applications in this area.

Summary

AOPs provide a means of mineralising problematic organic contaminants commonly associated with cyanobacteria. When complete mineralisation is not achieved, AOPs may also pre-treat influent water for a downstream bio-filtration system such as BAC by oxidising these problematic compounds and presenting them in a more biodegradable form. While some of these AOPs are well established and used routinely in full scale treatment facilities, some promising new technologies are emerging that minimise the use of chemical oxidants or employ photocatalytic reagents providing greener, more sustainable options.

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