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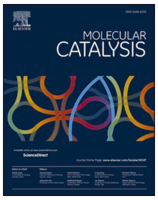

The application of advanced oxidation processes including photocatalysis-based ones for the off-flavours removal (GSM and MIB) in recirculating aquaculture systems

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ABSTRACT

Recirculating aquaculture system (RAS) popularity is threatened by the accumulation of off-flavour compounds such as geosmin (GSM) and 2-methylisoborneol (MIB) in the rearing water. Due to their lipophilic nature and the high bio-accumulation rate, they can be detected at very low concentrations in fish flesh, thus reducing product quality and marketability. The removal of these compounds often requires fish to be purged using high amounts of fresh and/or highly treated water before harvesting. A promising alternative is controlling the off-flavours throughout the production cycle by means of advanced oxidation processes (AOPs). In this review, the current state of the art of AOPs application to GSM and MIB degradation is reviewed under the perspective of their applicability to RASs. In particular the advantages of promising coupled processes such as photocatalytic ozonation have been highlighted. Finally, we critically reviewed the existing detection methods of off-flavour compounds in the rearing water, emphasising those allowing rapid and cheap measurements, in order to enable RAS plant managers to make real-time informed decisions, when off-flavours concentration increases above a certain threshold.

Introduction

Aquaculture is the world fastest growing food production system, currently providing more fish than wild capture fisheries for human consumption [1,2]. Most of its production is obtained by using open systems in which rearing water is continuously exchanged with the environment. This is the case of sea cages located both in and off-shore and flow-through tanks built on land along river streams. Even if, aquaculture proved to be the least impacting animal production with a minimal use of chemicals and antibiotics [3], the release of the aquaculture effluents in the environment may pose some concerns. High concentration of nitrogen and phosphorous as a result of the use of formulated feed and fish metabolism may result in eutrophication of water [4,5]. Residuals of chemicals (e.g. disinfectants) and antibiotics may lead to the spread of antibiotic resistance [6,7]. The high amount of water required goes in direct competition with other human activities and can be a limiting factor, especially during the period of drought which have become increasingly frequent due to climate change. Future aquaculture managing practices require policymakers, in concert with scientists and the industry, to anticipate changes of direction in production and consumption, in ways that sustain the health of human population, ecosystems and environmental quality for this generation and the ones to come [8].

In this context, recirculating aquaculture system (RAS), may gain interest as a low impacting fish farming technique. In the RAS, the replacement of water is substituted, to some extent, with water treatment techniques. As such, RAS may have the advantage of reducing water consumption, allowing more resilient farming techniques with a lower dependence on natural resources. In addition, being the reared animal isolated from the environment, they are less susceptible to pathogens and parasite coming from the wild (such as sea lice in salmon) and the risk of inbreeding with wild populations due to escapes is

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removed [9,10]. A typical water treatment plant of a RAS consists, in sequence, of a mechanical filter, a biological filter, a degasser, an oxygen enrichment unit and a disinfection unit [11]. However, the scaling up of RAS is facing mainly two problems. Firstly, a sophisticated water treatment with a high cost of capital is needed to ensure fish farming water quality and consequently, optimal fish health and welfare. Secondly, the production of off-flavour compounds that may accumulate in RAS water and in the lipid-rich tissue of fish, affecting taste and quality of the fillet [12–15].

Off-flavour compounds, also called taste and odour compounds (T&O), are a class of molecules which are responsible for an unpleasant taste profile. Out of the several compounds in this class such as geosmin (GSM), 2-methylisoborneol (MIB), 2-isobutyl-3-methoxypyrazine (IBMP), and 2-isopropyl-3-methoxypyrazine (IPMP), the first two are the most relevant, mainly responsible of causing off-flavours in fish flesh (Fig. 1). GSM and MIB are characterized by an earthy-musty odour and very low odour detection thresholds: between 10 and 20 ng L^{-1} in pure water and as low as 0.2 μg Kg^{-1} and 0.5 μg Kg^{-1} in fish flesh for MIB and GSM, respectively [16,17]. Off-flavour compounds are produced by enzymes (mainly terpene synthases) as secondary metabolites of a wide variety of microorganisms, such as actinomycetes, cyanobacteria, proteobacteria, and fungi [18–20]. These microorganisms find in the RAS biofilter the optimal conditions for their replication, having constant access to nutrients (e.g. nitrogen compounds from fish metabolism and organic matter) and oxygen [13,21,22]. GSM and MIB are very stable in water and are hardly degradable by the typical water treatment plant in a RAS. The current removal approach is to purge them from the fish prior to harvesting using high amounts of fresh and/or highly treated water [23]. The purging process throws up significant issues affecting RAS fish farms. Firstly, the purge of the fish can take up to 16 days [21], even though the exact period required to completely remove the compounds from the fish flesh is not known. The first cohorts of fish produced in a new RAS facility tend to require less purge time than the subsequent cohorts. This is likely due to the ever-increasing build-up of GSM and MIB in the bio-filters and the bio-film on the tank walls [12,24]. In addition, this purging process often requires starvation [13] and the double-handling of fish prior harvesting significantly increases stress and may results in poor flesh texture, which may lead to fillet gaping [25].

The control of the off-flavours compounds under a detectable threshold directly from the RAS rearing water can offer a solution for the further development of this technique. Several solutions have been developed based on chemical (e.g. algaecide, hydrogen peroxide and other chemical compounds), biological (e.g. biodegradation techniques using bacteria) and physical principles. Some of them are not viable in aquaculture, such as the use of chlorine or copper containing agents, being toxic to the fish. Those that are showing promising results for the treatment of GSM and MIB and represent the focus of this literature review are the Advanced Oxidation Processes (AOPs) [13,26,27]. AOPs is an umbrella term for a variety of new water treatment techniques in which highly reactive and short-lived species such as hydroxyl radicals are produced in water. Their high reactivity allows to degrade a large part of organic micropollutants. In addition, they have short life and are absent in the final product. Therefore, they are considered relatively safe for the fish and the final consumer. This literature review represents a comprehensive work reporting issues related to both detection of the off-flavours compounds in RAS plants and the application of advanced oxidation processes for their removal. A special focus has been dedicated to the latest developments in terms of coupling of AOPs (e.g. photocatalytic ozonation), and in Sections 3.1 and 5.4 readers can find information regarding the reasons why in our view the synergy shown between these two methods should be more carefully considered. Moreover, innovative detection methods based on machine learning and biosensors have been reviewed along with more traditional laboratory techniques such as gas chromatography coupled with mass spectrometry.

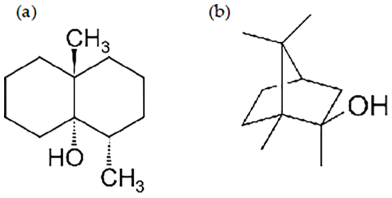

Fig. 1. Molecular structure of (a) geosmin and (b) 2-methylisoborneol.

Overview of AOPs

Advanced oxidation processes oxidize organic molecules by generating hydroxyl radicals and other unstable and short-lived reactive species, such as superoxide radical or singlet oxygen. The application of some AOP methods, such as ozone or ultraviolet irradiation (UV), have long been described in aquaculture research, while others are still in their infancy. Some of them only generate studies at pilot-scale or with few sampling points observations in full-scale systems that may not reflect a long-time follow-up in an operative, commercial RAS. Moreover, the scaling-up of AOP may face some problems. amongst them are the relatively high energy consumption, the influence of the RAS water quality (e.g. suspended solid and organic matter) on the efficacy of the process and the possible formation of dangerous by-products such as bromates [28,29]. Therefore, an effective AOP filtration unit to be installed on a RAS system has to comply with the requirements of being successful in off-flavours removal, cost effective and compatible with living animals. Regarding the cost effectiveness, several figures of merit have been proposed in literature discussing the running costs of different AOP methods. Many factors contribute to the running costs, such as the procurement and management of oxidants (e.g. hydrogen peroxide) and/or the replacement of catalysts. In most cases, however, the major expense of an AOP treatment is the consumption of electric energy. In this regard, Bolton et al. proposed two figures of merit to compare the consumption of electricity in the different AOP methods [30]. These are the *electric energy per mass* (E_{EM}) and the *electric energy per order* (E_{EO}). The first figure of merit assumes that the degradation-energy relationship is of zero order, which means that the mass of the degraded pollutant is proportional to the energy applied. This assumption occurs when the pollutant is present at high concentration in the water medium. The second figure of merit assumes that the degradation-energy relationship is first-order overall, which normally occurs when the pollutant is present at lower concentrations. Since GSM and MIB are present at very low concentrations in the RAS rearing water, we decided to focus this literature review based on this categorization. E_{EO} is defined as follows:

“Electric energy per order (E_{EO}) is the electric energy in kilowatt hours [kWh] required to degrade a contaminant C by one order of magnitude in a unit volume” [30].

The unit volume is commonly taken as one cubic metre. It is worth underlining the assumption that the overall reaction is first-order with respect to electrical energy consumption. Under this hypothesis, the energy consumption, E, is linked to the concentration of the pollutant X according to Eq. (1):

$$\log\frac{[X]}{[X]_0} = -kE \tag{1}$$

The plot representing Eq. (1) is a straight line in a logarithmic graph, as shown in Fig. 2. It can be seen that reducing the pollutant concentration by one order of magnitude requires the same energy regardless of the initial concentration. Therefore, the amount of energy required is proportional to the amount of degradation in terms of orders of magnitude, hence the term electric energy per order. This approach is frequently reported in the existing AOPs literature. Miklos et al.

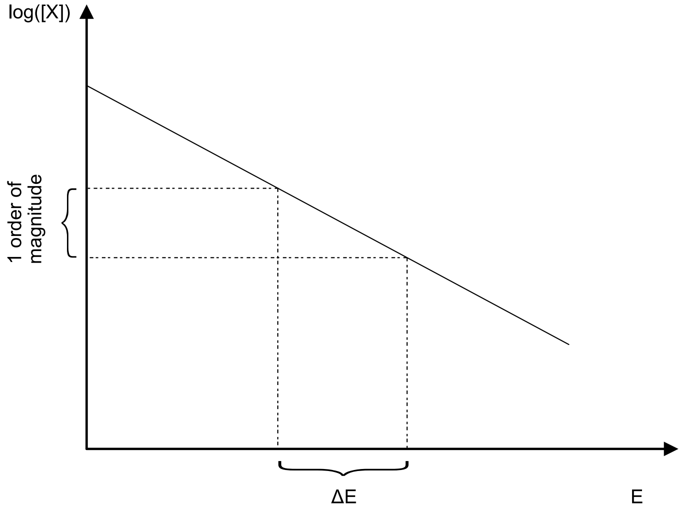

Fig. 2. Degradation of a pollutant X as a function of electrical energy, under the assumption of first order behaviour.

proposed a comparative screening of E_{EO} values for different AOPs [31]. Even though this screening did not specify which pollutant were tested with the different AOP treatments, the resulted outcome are useful for comparative purposes and are shown in Fig. 3 [31]. The results are nonetheless indicative of general trends in electrical efficiency of various AOPs and can be summarized as it follows: (i) the E_{EO} figure spans seven order of magnitude, (ii) data for ozonation are very scattered, which reflects its high dependency on the water matrix (still, ozonation is one of the most energy efficient treatments), (iii) most processes have an average E_{EO} between 0.1 and 10 kWh m^{-3}, (iv) microwave and ultrasound treatments are the least efficient processes.

A limitation of the reported values for the E_{EO} is that the energy required to produce consumables such as hydrogen peroxide is not considered, thus making the figure of merit less accurate in these cases. Müller et al. proposed to solve this problem by introducing an "electricity equivalent" for hydrogen peroxide but this practice is not widespread in the literature [32].

In this review we have divided the currently existing AOP methods into three categories, according to the source of energy utilized as oxidant input (Table 1). The first category consisted of oxidant-based AOP, in which the energy is introduced by an oxidising precursor of radicals (e.g. ozone or hydrogen peroxide). The second category consisted of irradiation-based AOPs, in which the energy is introduced by physical means, using photons, sound waves or electric currents. The third category includes the combination of oxidant-based and irradiation-based AOPs, which have been found to have a synergistic effect.

Oxidant-based AOPs

Ozonation

Ozonation is commonly used in RAS, for the disinfection of drinking water and for the degradation of organic pollutants [33,34]. Ozone (O_3)

Table 1
Classification of AOPs reviewed in this work.

Oxidant-based AOPs
Ozonation
Catalytic ozonation
$O_3 + H_2O_2$ (*peroxone* process)
Fenton reaction
Irradiation-based AOPs
UV irradiation
Cold plasma
Photocatalysis
Sonication
Combined oxidant and irradiation AOPs
UV/O_3
UV/H_2O_2
Photo-Fenton
Photocatalytic ozonation

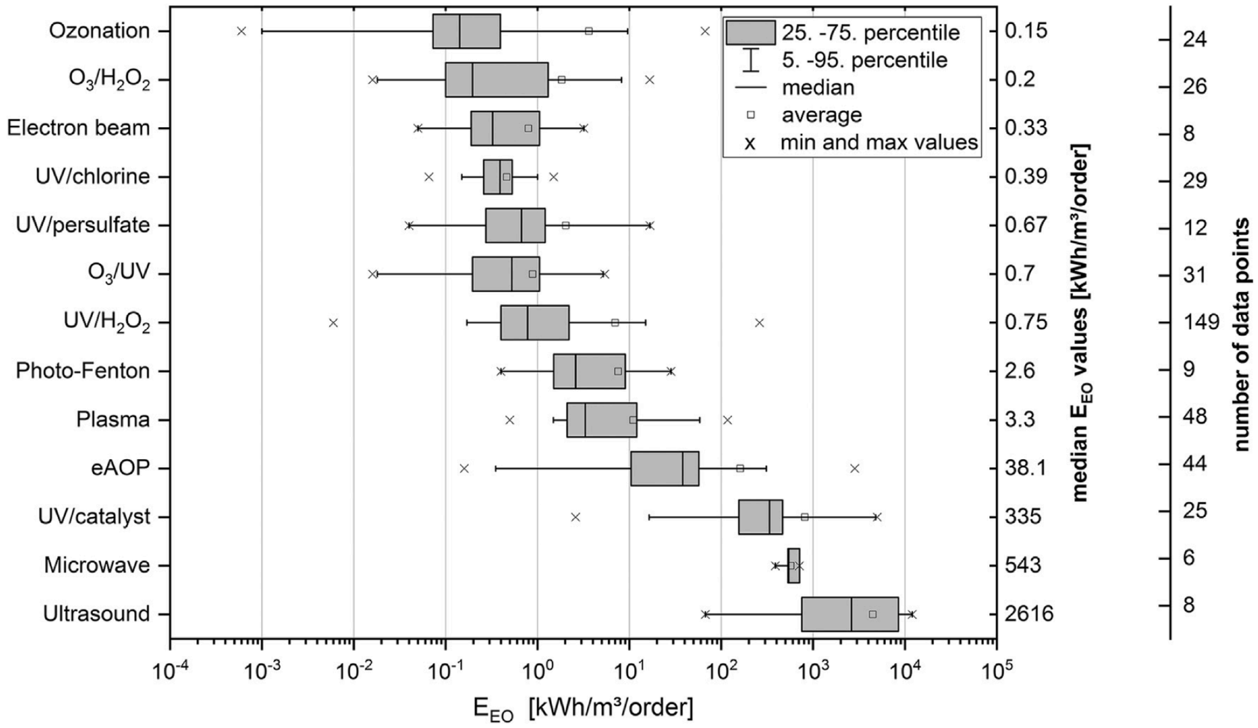

Fig. 3. E_{EO} comparison for various AOPs.

is a strong oxidant, presenting also disinfectant properties [35]. In addition it helps the flocculation of suspended solids, thus reducing the load on the filtration systems, resulting particularly useful in a RAS [36]. Since O_3 spontaneously decays into O_2, it must be generated on-site. Most ozonisers work by exciting the oxygen present in the air via an electric arc (corona discharge) to form ozone. However, reactive nitrogen species and nitrogen oxides, which are toxic for the fish, are also formed. For this reason, typical ozonisers used in a RAS system utilize pure oxygen to produce ozone [37]. Ozone degrades organic pollutants in two different ways. First of all, ozone directly attacks the electron-rich groups such as the unsaturated bonds in the target molecules. This first degradation led to an incomplete mineralization and takes place mainly at acidic pH values. The second degradation is boosted indirectly, upon ozone degradation, which gives rise to highly reactive species (e.g. OH radicals and reactive oxygen species) capable of oxidising the target organic molecules. This second is less prevalent in a RAS system, since the formation of OH radicals increases with increasing pH values and is more effective at pH ≥ 9 [34], which is not in the pH range of a RAS system rearing water. If the aqueous matrix of the RAS is complex, as always occurs in real applications, several other reactions are possible, both with organic and inorganic species. The presence of organic matter is reported to influence both positively and negatively the efficiency of ozonation. On one side, organic matter reacts with ozone to form OH radicals, thus acting as an OH initiator [34]. On the other hand, this acts as an OH radical scavenger, promoting its oxidation. The two effects are conflicting, and the resulting outcome are difficult to estimate depending on the concentration and on the chemical nature of the organic matter [34,38]. Overall, in a fully operative RAS system, the organic load is considered a key parameter to keep under a certain threshold of concentration, because it influences the oxidant activity of ozone [39]. Another important drawback of ozonation is the oxidation of bromide into bromate ions. Bromide is considered safe, naturally present in both freshwater and especially seawater, where it is necessary to some marine organisms [26]. On the other hand, bromate ions are moderately toxic for aquatic organisms [40] and carcinogenic (group 2b in IARC classification) with a regulated concentration threshold in drinking water of only 10 $\mu g\ L^{-1}$ in both EU and USA. The direct pathway of formation of bromate ions from ozone and bromide ions is expressed by the following overall reaction (Eq. (2)):

$$Br^- + 3O_3 \rightarrow BrO_3^- + 3O_2 \quad (2)$$

Indirect pathways are also possible in which the OH radicals (deriving from ozone degradation) take part to the reaction. In all cases, the formation of bromate is a multi-step reaction where hypobromous acid is a key intermediate [38].

At the concentration normally used in a RAS system ($< 1\ \mu g\ L^{-1}$ of treated water), ozonation is not very effective in removing GSM and MIB. High concentration of ozone may be more effective, however, the production of bromate ions becomes too important [41] resulting in toxicity for the farmed species [42]. The reasons for the low efficacy of ozonation in removing GSM and MIB is the lack of a direct route, since these compounds are aliphatic in nature and, therefore, do not have in their structure electron-rich groups that could be attacked by ozone. Removal of GSM and MIB can be improved by combining ozone with UV light or hydrogen peroxide, which promotes the formation of hydroxyl radicals. However, the most successful coupling, in our opinion, could be the one reported in greater detail in Section 5.4 of this work, i.e. ozone-heterogeneous photocatalysis by TiO_2. In fact, in this case not only are OH radicals produced, which can intensify the mineralization of GSM and MIB, but the formation of the carcinogenic bromate ion species is also prevented.

Catalytic ozonation

The combination of ozonation with a catalytic membrane made out of Al_2O_3 or TiO_2 was tested at pilot scale in a RAS system [43] and for the depuration of drinking water from MIB [44,45]. Catalytic ozonation resulted in higher degradation rate compared to ozonation alone. Authors justified this finding because of the high amount of oxygen species, mainly OH radicals, generated upon interaction of ozone and the surface of the catalyst. Therefore, the adsorption of MIB at the surface of the catalyst facilitates its oxidation. amongst aluminium oxides, γ-Al_2O_3 showed the best performance [46]. The reaction appeared faster when the pH of the solution approached the zero charge point of the catalyst [45]. Catalytic ozonation is advantageous compared to ozonation alone as it increases the rate of degradation of the organic compounds, it allows the use of smaller quantities of ozone and, consequently it reduces the formation of bromate ions. However, its commercial application is hampered by the uncertainties about the mechanism and the efficacy [47]. Moreover, additional studies are needed to assess the scalability and the reusability of the catalysts [48] and there is a lack of information regarding the possible effects of fouling of the catalyst in a full operative RAS system. Coupling ozonation with other catalysts such as granular activated carbon (GAC) is also utilized in RAS systems and its efficacy has been successfully investigated on the degradation of a model pollutant, the 4-nitrophenol [49]. GAC has a catalytic effect on the decomposition of O_3, increasing the ozonation rate. Ozone can degrade not only the small molecules in solution, but also those adsorbed onto the GAC, which, therefore, can be simultaneously regenerated. Moreover, the use of GAC allowed processing larger volumes of water with respect to sole ozonation.

Peroxone process

The combination of ozonation and hydrogen peroxide (H_2O_2) is also known as the peroxone process. Its application in aquaculture has been demonstrated in flow through systems, both for the disinfections of the inlet water [50] and for the treatment of wastewater [51]. To the best of our knowledge, no application has been demonstrated yet in RAS systems. The synergistic effect of this process is due to the reaction between deprotonated H_2O_2 (the peroxide anion HO_2^-) and ozone to form OH radicals, resulting in an oxidizing effect on the organic compounds. First, protonated superoxide and $O_3^{\cdot-}$ are formed (Eq. (3)). The superoxide radical anion then reacts with ozone to form another $O_3^{\cdot-}$ anion (Eq. (4)). Once protonated, $O_3^{\cdot-}$ anions decomposes finally forming hydroxyl radicals (Eq. (5)) [52]. The synergy is optimal with the molar ratio of $H_2O_2/O_3 = 0.5$ [31].

$$HO_2^- + O_3 \rightarrow HO_2^{\cdot} + O_3^{\cdot-} \quad (3)$$

$$O_2^{\cdot-} + O_3 \rightarrow O_2 + O_3^{\cdot-} \quad (4)$$

$$HO_3^{\cdot} \rightarrow O_2 + {}^{\cdot}OH \quad (5)$$

The peroxone process is advantageous in terms of control of bromate ions, because O_3 is more readily degraded, thus limiting the conversion of bromide to bromate. Moreover, H_2O_2 can reduce hypobromous acid back to bromide (Eq. (6)) [53].

$$H_2O_2 + HOBr \rightarrow H^+ + Br^- + H_2O + O_2 \quad (6)$$

Because of its strong oxidizing capacity on the organic compounds, the peroxone process is able to deplete GSM and MIB. However, the degradation of GSM and MIB can be improved with further addition of H_2O_2, which significantly increases the degradation rate of the organic compounds. The efficiency increases proportionally with the amount of H_2O_2 added and the temperature. However, the addition of H_2O_2 must be limited to leave sufficient residual ozone to achieve disinfection [54]. Due to the concerns in terms of cost, risks, and difficulties of handling concentrated H_2O_2, the electro-peroxone process may be an alternative where H_2O_2 is electrochemically generated *in situ*, using a cathode immersed in water. This approach is not different from the traditional peroxone process, from a chemical point of view, but it has the advantage of running on-demand and of being easily integrated into an ozonation system [41]. The drawbacks of peroxone and electro-peroxone processes are the reduced disinfectant effectiveness of the ozonation (because of the reaction to form OH radicals) and the residual H_2O_2. This last is an important concern in an operative RAS system because of its toxicity for the farmed animals. The safety threshold level of H_2O_2 has been reported to be 70–100 mg L^{-1} for salmonids for up to two hours of exposure [55] but some additional treatments for the degradation of residual H_2O_2 may be implemented in case safe levels are exceeded [41].

Fenton reaction

The combination of H_2O_2 with Fe^{2+} salts, known as Fenton reaction, catalyses the formation of OH radicals resulting in an oxidizing effect on the organic compounds. The degradation efficacy of this technology on GSM and MIB has been successfully demonstrated by [42]. Fenton reaction has been applied in the depuration of aquaculture effluents which contain high amount of organic pollutants [56,57] but no application has been demonstrated yet on a RAS systems. In a pure aqueous solution, H_2O_2 slowly disproportionate to oxygen and water (Eq. (7)) [58]. This reaction alone does not form OH radicals; therefore it does not qualify as an AOP. However, as seen in the previous section, the use of other agents in combination with H_2O_2 can greatly alter the mechanism of decomposition.

$$H_2O_2 + H_2O_2 \rightarrow O_2 + 2H_2O \tag{7}$$

This is the case of the Fenton reaction, in which the addition of Fe^{2+} salts to H_2O_2 solutions causes the decomposition of the peroxide to OH radicals (Eq. (8)):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-} \tag{8}$$

The reaction is generally carried out under acidic conditions (ideally at pH = 3) to avoid the precipitation of ferric oxy-hydroxide. It is not practical to achieve and maintain this acidic pH in water treatment processes, so additives are being developed to keep the iron in solution at a near-neutral pH [59].

Irradiation-based AOPs

Ultraviolet irradiation

Ultraviolet (UV) irradiation is widely used in RAS aquaculture to reduce bacteria load and as a broad-spectrum bugs control. Depending on the wavelength of the radiation, different effects are obtained. The common classification of the UV spectrum is summarized in Table 2. UV-A and UV-B irradiation, in the presence of suitable sensitizers, has been repeatedly shown generating OH radicals and other oxidants, as also explained in Sections 4.3 and 5.1 – 5.3. UV-C radiation alone is an effective germicide. It works by damaging nucleic acids, thus hindering proper DNA transcription. Cells have mechanisms to counteract DNA damage, however sufficient exposure to UV radiation can overwhelm them and lead to cell death [60]. UV-C disinfection is a proven technology for the disinfection of the rearing water in RAS system. In a standard RAS system it is the last treatment before the reintroduction of the water to the fish tanks [13]. Both UV-A and UV-B radiation alone cannot degrade organic compounds such as GSM and MIB. UV-C in the 200 - 280 nm wavelength region, can have an effect on the degradation of GSM and MIB although, due to low absorbance at these wavelengths, the treatment is ineffective [61]. On the contrary, vacuum UV (VUV) irradiation, with wavelengths ranging between 200 and 100 nm, can be used for this purpose. VUV can be produced by common low-pressure mercury vapour lamps, which emits radiation mainly at 254 nm but also at 185 nm (with intensity 8 % compared to the main emission line). It should be noted that the low-pressure mercury vapour lamp acts as a VUV source only if it is equipped with a special glass transparent to the radiation at such low wavelengths. The mechanism responsible for the degradation of GSM and MIB with VUV is not the direct photolysis of the off-flavour molecules, but the indirect degradation due to OH radicals formed from water according to Eq. (9).

Table 2
UV radiation classification according to ISO 21348.

UV denomination	Wavelength range (nm)
UV-A	400–315
UV-B	315–280
UV-C	280–200
Vacuum UV (VUV)	200–100

$$H_2O \xrightarrow{h\nu} {}^{\cdot}OH + H^{\cdot} \quad \lambda < 180\ nm \tag{9}$$

The OH radicals can therefore degrade the pollutants in a similar way to what happens using other techniques [62]. Bromate ions are not an issue with VUV irradiation, because VUV radiation can reduce bromate to bromide ions, according to Eqs. (10)–(12) [62].

$$2\ BrO_3^- \xrightarrow{h\nu} 2BrO_2^- + O_2 \tag{10}$$

$$2BrO_2^- \xrightarrow{h\nu} 2BrO^- + O_2 \tag{11}$$

$$2BrO^- \xrightarrow{h\nu} 2Br^- + O_2 \tag{12}$$

The main disadvantage of this technique is represented by the low depth of penetration of the VUV into the water. In addition, like other UV irradiation, VUV can convert nitrates into harmful nitrites (Eq. (13)) [62].

$$2NO_3^- \xrightarrow{h\nu} 2NO_2^- + O_2 \tag{13}$$

The E_{EO} value for GSM and MIB appear to be less than 0.5 kWh m^{-3} in pure water and less than 1.5 kWh m^{-3} in raw water (taken from a drinking water tank, dissolved organic carbon 3.0 mg L^{-1}) [62]. The not very high efficiency of this process is caused by the presence of NOM, which scavenges the hydroxyl radicals [61] and is a limiting factor of the efficacy of VUV irradiation in RAS system.

Plasma

Plasma techniques use a non-thermal plasma discharge to generate reactive species. Its application for the treatment of RAS rearing water has never been demonstrated but there is a wide range of application in food industry which make it a promising AOP method for the degradation of organic compounds [37,63,64]. Non-thermal plasma (NTP) is a plasma whose constituents (non-ionized, ionized species, and free electrons) are not in thermal equilibrium. It is also called cold plasma because its temperature is close to the ambient one. Various sources of cold plasma are possible, using direct current, low frequency alternating current (AC), radio frequency and microwave discharges. Amongst the low frequency techniques, the corona discharge and the dielectric barrier discharge are the most important ones [63].

The simplest treatment consists of a discharge of glowing cold plasma in the air, at atmospheric pressure, just above the free surface of water. Discharge can generate ozone, reactive oxygen and nitrogen species, and OH radicals. These species can migrate to the bulk of the liquid, which therefore is called plasma-activated. The migration processes are quite complex, as reviewed by [64]. The main active species present in plasma-activated water (PAW) are, in decreasing order of concentration, hydrogen peroxide, nitrite, nitrate, ozone, superoxide and peroxyl nitrite [64]. In this gas-phase plasma approach, the critical aspect to consider is to ensure a good diffusion of the species generated in the liquid. The plasma discharge can also be generated directly in the liquid phase. This approach, however, has the disadvantage of being energy inefficient and presents the risk of leaching of the electrode metals into the water [37]. Jo et al. investigated the effect of cold plasma on the degradation of MIB [37]. The plasma was generated in the gas phase inside a porous hydrophobic ceramic tube, permeable to gases but not to water. The tube was surrounded by flowing water (Fig. 4). Due to a pressure difference, the gas bubbles migrated from the inside of the tube to the surrounding liquid, carrying the active species into the water. The initial concentration of GSM and MIB was 500 ng L^{-1} each. The extent of degradation depended on the total energy applied to the system, regardless of power. The energy consumption reported was of the order of 3–8 kJ L^{-1} for a degradation of 90 %. This means an E_{EO} figure of the order of 1 kWh m^{-3}. The system was also able to decompose cyanobacteria cells.

Photocatalysis

The oxidation of GSM and MIB by heterogeneous photocatalysis (PC) has been extensively reported in the literature and its application has already been tested on a RAS system [65,66]. The photocatalyst is a semiconductor, which, when irradiated at suitable energy, allows the generation of electron (e^{-}) - hole (h^{+}) pairs. These charges can migrate to the surface of the photocatalyst where complex energy or electron transfer reactions with adsorbed molecules can take place [67]. In particular, OH radicals are generated through oxygen reduction, with intermediate production of hydrogen peroxide (Eqs. (14)–(16) and/or water oxidation induced by holes (Eq. (17)) [68]:

$$O_2 + e^- + H^+ \rightarrow HO_2^{\cdot} \tag{14}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{15}$$

$$H_2O_2 + e^- + H^+ \rightarrow {}^{\cdot}OH + H_2O \tag{16}$$

$$H_2O + h^+ \rightarrow {}^{\cdot}OH + H^+ \tag{17}$$

The most studied photocatalytic system is TiO_2 irradiated with UV light, which is effective in the degradation of GSM and MIB. TiO_2 has the advantages of low cost, photochemical stability and non-toxicity [49]. The photocatalytic degradation of GSM and MIB follows pseudo-first order kinetics [69], with OH radicals as the main active species [70]. Unlike other UV-based methods, which require shorter wavelengths, UVA radiation is sufficient to photo-excite TiO_2. Moreover, in TiO_2 photocatalysis the bromide concentration is generally stable, and no bromates are formed. In fact, while hydroxyl radicals oxidize bromide ions to bromine radicals (Eq. (18)), superoxide radicals have the opposite effect, reducing bromine radicals to bromide ions (Eq. (19)) [71].

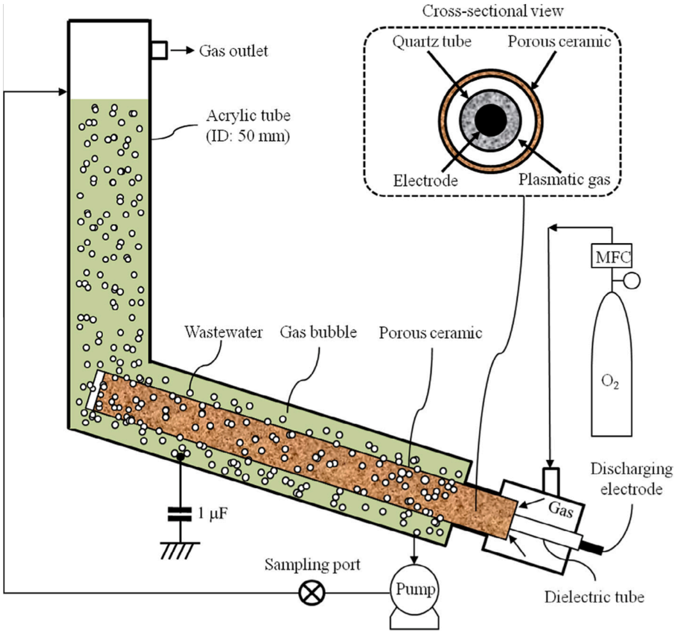

Fig. 4. The experimental apparatus used in Jo et al. (2014).

$$Br^- + {}^{\cdot}OH + H^+ \rightarrow BrOH^- + H^+ \rightarrow Br^{\cdot} + H_2O \tag{18}$$

$$Br^{\cdot} + HO_2^{\cdot} \rightarrow Br^- + H^+ + O_2 \tag{19}$$

One problem that hinders the industrial application of TiO_2 photocatalysis in a RAS system is the low quantum yield, which results in slow kinetics and lower energy efficiency than other AOPs (Fig. 3). Rodriguez-Gonzalez et al. integrated a PC batch reactor into a RAS facility to study how it performs in a realistic scenario [13]. The PC reactor used immobilized TiO_2 to avoid introducing nanocrystals into the aquarium. It was placed downstream of the moving bed bioreactor. The reactor was able to remove 61 % of GSM and 72 % of MIB. Degradation of the MIB was achieved after 6 h of contact in a batch process that was found to perform better [13].

Sonication

Ultrasonic irradiation is a technique that has been used successfully for multiple applications, especially water oxidation, wastewater treatment, and microorganism control [72].

The ultrasound activity is based on the phenomenon of acoustic cavitation. Ultrasounds consist of pressure waves with a frequency greater than 20 kHz. In a water treatment plant, the waves are generated with a piezoelectric transducer, and transmitted to the liquid. These waves interact with the microscopic gas bubbles that are always present in a liquid with dissolved gases. The pressure oscillations cause the bubbles (called cavitation bubbles) to expand, wobble and eventually collapse. The collapse is almost adiabatic, reaching temperatures of 5000K and pressures of 100MPa [73]. Under these conditions, radicals are formed in the water and organic molecules can be thermally dissociated. Shock waves and turbulent flow are also generated [74]. This AOP has the advantage of not requiring the addition of chemical reagents. Furthermore, it does not rely on optical radiation, which makes it particularly suitable for the treatment of murky water [72]. The combination of chemical and mechanical action is also interesting. The main problem is the low energy efficiency compared to other methods, so much so that water heating becomes a problem [74]. The technique has been tested for the abatement of GSM and MIB. The degradation followed first order kinetics [72]. High (850 kHz) and low (20 kHz) frequencies were tested. The highest frequency was the most effective, resulting in an 80 % reduction in GSM after 15 min of sonication [74]. Pyrolysis was the main degradation mechanism, unlike other AOPs in which OH radicals play an important role [74]. This is advantageous because it obviates the detrimental effect of the OH scavengers present in the water matrix, such as humic substances. This explains why similar performance was achieved in different matrices such as tap water and water sampled from RAS. Huang et al. found that sonication also has an inhibitory effect on the growth of cyanobacteria, which are the main producers of GSM and MIB [75]. However, the consequences of this effect on aquaculture are not discussed. Living fishes are unlikely to tolerate ultrasound, so any treatment involving the use of sound waves should be applied in a separate tank.

Combined AOPs

UV/O_3

O_3 shows an absorption band centred at 254 nm, therefore under suitable UV irradiation it decomposes to form singlet oxygen and an excited O atom as expressed by Eq. (20) (state ${}^{1}_{0}D$ using spectroscopic notation):

$$O_3 \xrightarrow{h\nu} {}^1_0O_2 + O\left({}^1_0D\right) \tag{20}$$

Singlet oxygen is itself an oxidant, while the excited oxygen atom readily reacts with water to form hydrogen peroxide (Eq. (21))

$$O\left({}^1_0D\right) + H_2O \rightarrow H_2O_2 \tag{21}$$

Hydrogen peroxide can be photolyzed as discussed in the following paragraph. It can also react with dissolved ozone to form OH radicals as expressed by Eq. (22) [76].

$$H_2O_2 + 2O_3 \rightarrow 2^{\cdot}OH + 3O_2 \tag{22}$$

Collivignarelli et al. [77] investigated the performance of the UV/O_3 method for the degradation of GSM and MIB in water. 0.5 μg L^{-1} of GSM and 0.4 μg L^{-1} of MIB were added to the water. While ozonation alone was unable to degrade GSM and MIB beyond 70 % in 20 min, ozonation coupled with 254 nm irradiation achieved complete removal. Moreover, ozonation under irradiation with light at 254 nm resulted in a 40 % reduction in bromate ions compared to ozonation alone.

UV/H_2O_2

Hydrogen peroxide is dissociated by UV light to form hydroxyl radicals according to Eq. (23) [78]:

$$H_2O_2 \xrightarrow{h\nu} 2^{\cdot}OH \quad \lambda < 405\ nm \tag{23}$$

Once generated, OH radicals also degrade H_2O_2 molecules according to the chain reactions 24–25 [76]:

$$^{\cdot}OH + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{24}$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow H_2O + O_2 + {}^{\cdot}OH \tag{25}$$

Park et al. studied the degradation performance of the UV/H_2O_2 treatment for GSM and MIB [79]. Compared to UV irradiation alone (254 nm), the degradation efficiency improved of 38 % for GSM and of 52 % for MIB (Fig. 5).

Photo-Fenton

The OH radical production from the Fenton reaction can be enhanced by UV irradiation. UV rays activate two more reactions (Eqs. (23), (26)) that complement the Fenton reaction (Eq. (8)) to produce OH radicals from hydrogen peroxide [78]. In particular, Fe^{2+} ions are regenerated. The regeneration of Fe^{2+} ions, however, has a low quantum yield.

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + {}^{\cdot}OH + H^+ \quad \lambda < 405\ nm \tag{26}$$

The chain degradation of H_2O_2 initiated by OH radicals, as in Eqs. (24) and (25), it is also active. The Photo-Fenton reaction can also occur in the presence of sunlight in an open pond, thus reducing the energy requirement [80].

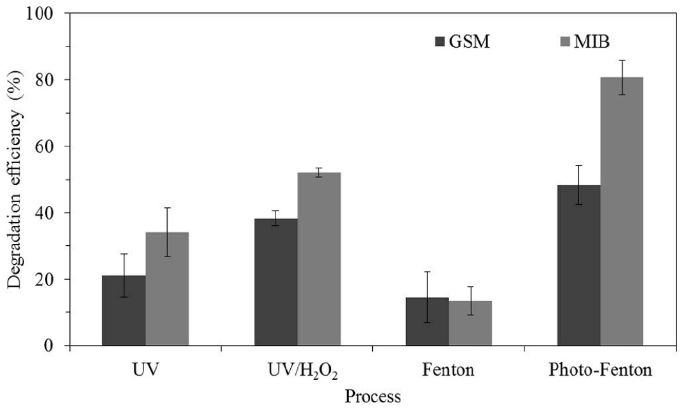

Fig. 5. Comparison of AOP processes.

Park et al. compared photo-Fenton and Fenton processes [79]. The experiments were conducted in distilled water with 20 mg L^{-1} of H_2O_2 and 100 ng L^{-1} of GSM and MIB. The degradation efficiency was significantly higher for both GSM and MIB degradation compared to the Fenton process, as shown in Fig. 5. The tests were done at pH values 9, 7, 5 and 3 and an increase in the efficiency was noticed as the pH decreased. The effect of the presence of natural organic matter was also investigated. It was found that this acts as a hydroxyl radical scavenger and absorbs some of the UV radiation, resulting in a decrease in the efficiency of degradation.

The process described above is homogeneous photo-Fenton. The photo-Fenton reaction can also proceed in the presence of heterogeneous catalysts. In the latter case, a solid catalyst containing iron is generally used. However, to the best of our knowledge, the efficiency of this process for the degradation of GSM and MIB has not yet been investigated.

Photocatalytic ozonation

The coupling between photocatalysis and ozonation (photocatalytic ozonation, PO) allows to remove the specific weaknesses of the single technologies, namely the slow kinetics for photocatalysis and the low reactivity with some organic species (GSM and MIB amongst others) and unwanted by-products for ozonation [28].

When the two techniques are coupled, a synergy is observed whereby the extent of degradation is greater than that determined by the sum of the two processes taken alone. The intensification factor, E_i, has been defined as in Eq. (27), to quantify the extent of synergy. PC, OZ, and PO stand for photocatalysis, ozonation, and photocatalytic ozonation, respectively [28]:

$$E_i = \frac{\text{oxidation rate in PO}}{\text{oxidation rate in OZ} + \text{oxidation rate in PC}} \tag{27}$$

The synergy in PO depends on the relative weight of the rates of the two processes (δ = photocatalysis rate/ozonation rate) if performed individually under the same experimental conditions. By plotting the intensification factor E_i as a function of the parameter δ (Fig. 6), it was found that the synergy is maximized up to 60 % at a fixed relative weight of the two processes. The specific value for this weight is reaction specific, but generally a smaller fraction of the photocatalysis allows maximum synergy [28].

The synergy in PO can be explained by the interaction between ozone and the photocatalyst. Ozone can be adsorbed at the surface through three types of interactions: physical adsorption, hydrogen bonding, and Lewis acid site adsorption. After adsorption, the interaction with the photogenerated electrons leads to the production of ozonide radicals $O_3^{\cdot-}$

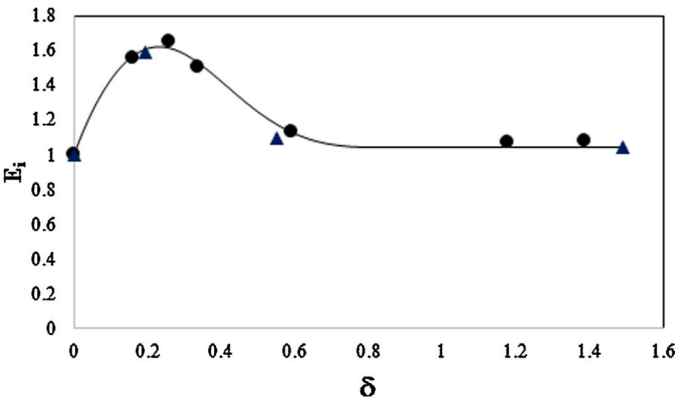

Fig. 6. Intensification factor E_i in PO as a function of the relative weight of ozonation δ.

(Eq. (28)), whose protonated species in turn decomposes and forms hydroxide radicals (Eq. (5)).

$$O_{3(ads)} + e^- \rightarrow O_3^{\cdot -} \quad (28)$$

Moreover, the presence of adsorbed oxygen also increases the numbers of electron acceptors on the surface reducing the recombination rate [81].

It is worth to mention that the formation of bromate ions can be effectively controlled during PO, as reported by Parrino et al. [29]. To the best of our knowledge, no studies are currently available for the degradation of GSM and MIB by photocatalytic ozonation. Camera-Roda et al. [26] tested the technique for water purification in a seawater aquarium. The PO apparatus was integrated into a water purification system comprising a protein skimmer, a biological filter, a denitrification solution and activated carbon unit. The tests lasted several months and indicated that high water quality could be achieved. An optimization of the ozonation and PO cycles made it possible to prevent the accumulation of bromate. This study provides a basis for future investigations into the applicability of photocatalytic ozonation for RAS.

It was previously mentioned (Catalytic ozonation) that ozonation acts synergistically with GAC adsorption. The same authors studied the performance of photocatalysis-GAC and photocatalytic ozonation-GAC. The combined PO-GAC process proved to be more effective than the combined OZ-GAC and PC-GAC [49].

Degradation pathways

Many of the articles cited in this review also provide some insights about the GSM and MIB degradation pathways. AOPs may differ in the mechanism that generates radicals and also in their nature, therefore the degradation pathways should be examined separately for each process. However, it has been observed that in the case of GSM and MIB the decomposition is mainly driven by hydroxyl radicals. The photocatalytic degradation of GSM was investigated by Bamuza-Pemu and Chirwa [70]. Dehydration products are mainly formed as intermediates which, along with GSM itself, quickly undergo ring opening reactions triggered by OH radicals. Initial elimination of methane is also possible, followed by dehydration (Fig. 7).

The degradation intermediates compounds of MIB were identified by means of gas chromatography-mass spectrometry [39,82]. These compounds can be divided into three groups (Fig. 8): the first group results from the oxidation of side chains of MIB (camphor is between these products) by action of hydroxyl radicals. The second group derives from the opening of the double ring of MIB to form single-ring compounds. The third group comprises compounds obtained from the opening of the single ring forming linear compounds (aldehydes, ketones, and

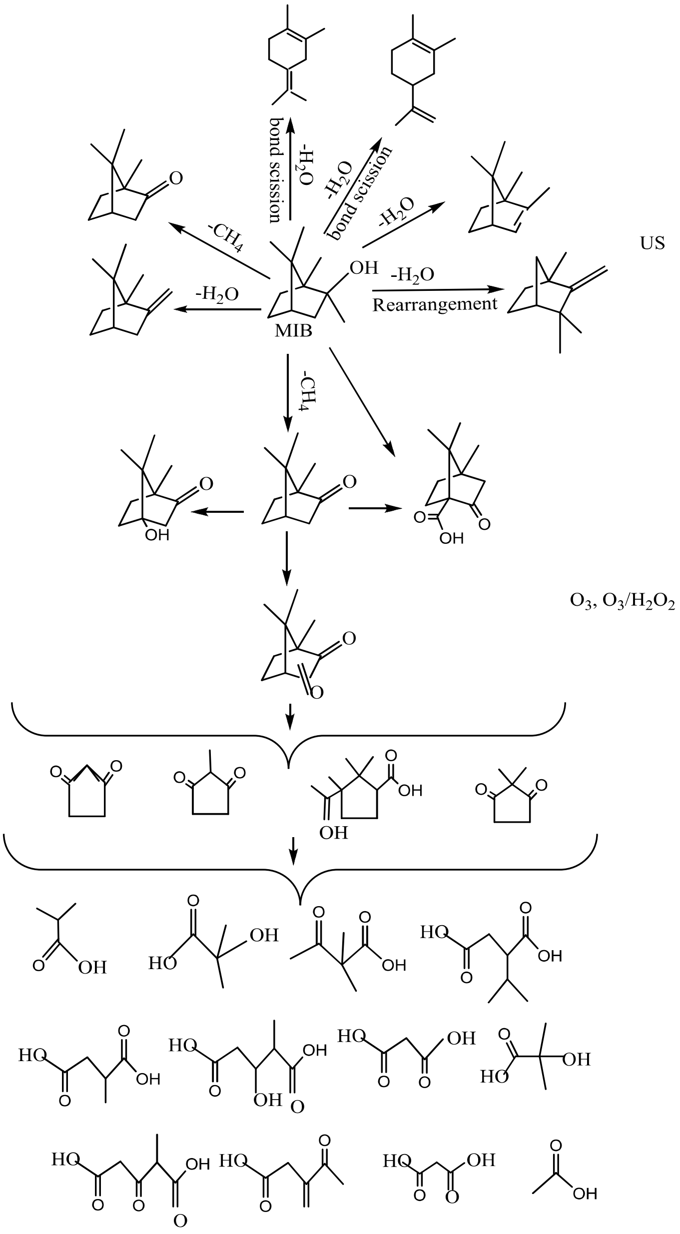

Fig. 8. Degradation pathways of MIB.

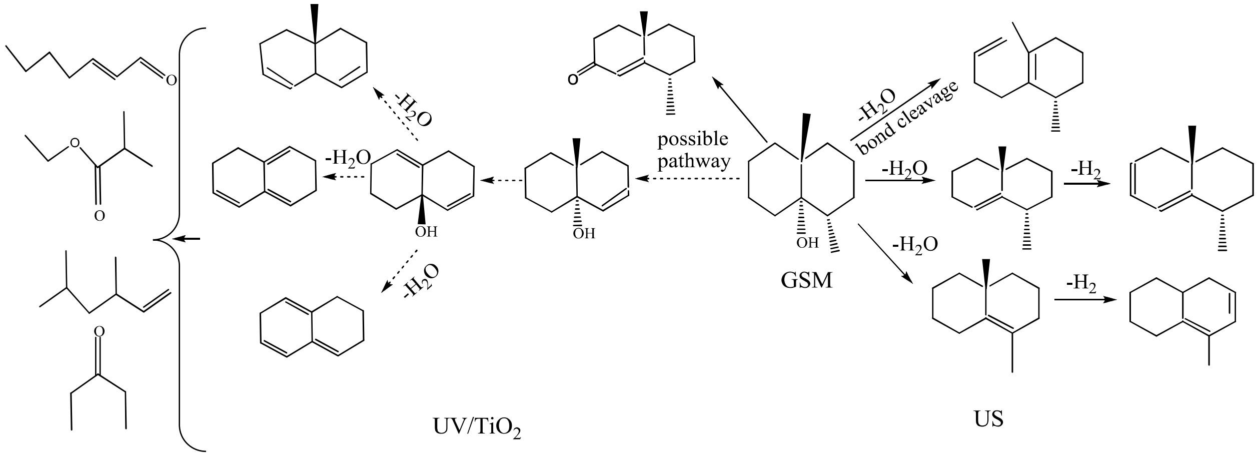

Fig. 7. Degradation pathways of geosmin under various AOPs.

carboxylic acids), which eventually can undergo mineralization to CO_2 and H_2O.

Detection methods of GSM and MIB in water medium

Depending on the water temperature and chlorine levels, the presence of GSM and MIB, defined as human odour threshold concentrations (OTCs), can be appreciated, as said previously, from 5 ng L^{-1} and 15 ng L^{-1}, respectively [83]. For trace analysis, the reference technique for the quantitative assessment of these organic compounds in water medium is the gas chromatography-mass spectrometry (GC/MS) coupled with a variety of extraction methods [84]. GC/MS remains the most selective and sensitive method, but other rapid and cheap solutions based on electronic tongues, bioelectronic noses, microwave spectroscopy and chemiluminescence reaction can have a big role in the real-time monitoring of the off-flavours compounds during the busy operational setting of a RAS system. Rapid solutions generally involve mathematical signal processing procedures and statistical tools as multivariate calibration and machine learning techniques. As a results, in this section of the review we focus on the currently existing detection methods of GSM and MIB, emphasising those rapid and cheap that would allow RAS plant managers to make real time informed decision if off-flavours concentration increases above a certain threshold. These last, developed mainly at a laboratory level and under controlled conditions, cannot be comparable in terms of GSM and MIB detection limits to complex reference techniques. However, the proposed solutions could be the starting point for a discussion on potential future steps.

Gas chromatography-mass spectrometry (GC/MS)

GC/MS is the reference technique for trace analysis of pollutants and consists of three separate steps: extraction, separation and detection [85–87]. The extraction step is basically a pre-conditioning of the sample to the further separation step, in which the analytes, GSM and MIB, are extracted from the water phase and concentrated. Different separation methods have been developed, for the sake of reviewing, these are: closed-loop stripping analysis (CLSA), resin adsorption (RA), liquid-liquid extraction (LLE), solid phase extraction and micro-extraction (SPE and SPME), stir-bar sorptive extraction (SBSE), liquid-phase microextraction (LPME), purge and trap (P and T) and static and dynamic headspace (SH and DH) [87]. Amongst these, solid phase microextraction (SPME) is a simple and inexpensive method for the extraction of volatile and semi-volatile compounds present in a wide variety of food, water and environmental matrices [86]. In literature, SPME technique has been used for GSM and MIB extraction from the RAS rearing water and from fish fillets [23,86,88]. SPME consists of two steps: firstly, the partitioning of the analyte between the extraction phase and the sample matrix and secondly, the desorption of the analyte into the analytical instrument [87]. The analyte is trapped by using a syringe plunger through a fibre coated with a suitable absorbent phase, either a liquid polymer or a solid sorbent or a combination of both. The target analyte molecules (GSM and MIB) are trapped and absorbed into the silica fibre which are then desorbed using either thermal or liquid desorption, into the injection port of a gas chromatograph for the further separation step [86]. This is a physical separation method, in which the components in a mixture are selectively distributed between the mobile phase, which is an inert carrier gas, and a stationary phase, which is present as a coating of either column packing particles or the inner column wall [89]. The separation process occurs as a result of repeated sorption/desorption steps during the movement of the analytes along the stationary phase by the carrier gas. Once all the components of the water mixture (including GSM and MIB) are separated in the gas chromatography column, the detection is performed by using a mass spectrometer with EI ionization. The ruling principle of this technique is the production of gas-phase ions that are subsequently separated according to their mass-to-charge (m/z) ratio and detected [89,90]. Despite of being time consuming and requiring expensive equipment, GC/MS coupled with solid-phase microextraction is a reliable, selective and solvent free method that can be easily automated for routine water analysis [87]. The method is able to detect GSM and MIB in both rearing water and fish fillets at concentration as low as 0.01 and 0.1 μg L^{-1}, respectively [17], far below human sensory thresholds.

E-tongues

Electronic tongues or e-tongues have recently come into prominence in food safety and quality field because they can simulate the human taste mechanism, in particular the physics-chemical interaction occurring between food molecules and the human tongue [91]. The simulation of the human taste perception presents some advantages such as the elimination of the time-consuming panel assessment process and the possibility of tasting unsafe and toxic molecules in a continuous monitoring approach. According to the definition provided by Vlasov and Legin, e-tongue systems are based on an array of nonspecific, low selective chemical sensors characterised by cross-sensitivity to the multiple components present in solution [92]. These systems are combined with data signal processing tools or pattern recognition methods, in order to extract features for both qualitative and quantitative assessments. E-tongues can be classified on the basis of the principle involved during the interaction between the sensors and the molecule under test. The most diffused taste sensors are voltametric, potentiometric and impedimetric arrays. With regards to the water medium, e-tongues were set up for different purposes, such as the assessment of organic pollutants in water samples [93], screening of cyano-bacterial microcystin toxins in potable water [94], and the discrimination of mineral waters according to the geographical origin based on chloride, sulphate and magnesium concentration [95], or their brand classification [96]. Starting from 83 spring water samples, Partial Least Squares (PLS) algorithm with orthogonal signal correction was also combined with a four noble electrodes voltametric system for the setting up of predictive models of concentrations of nitrate, sulphate, fluoride, chloride, sodium and pH [97].

With regards to GSM and MIB, their presence in drinkable water (at low, 20 to 100 ng L^{-1} and high concentration, 0.25 to 10 mg L^{-1}) was explored by using a potentiometric system based on 8 low-selective polymeric membrane (PVC-based solvent) and chalcogenide-glass electrodes combined with Partial Least Squares discriminant analysis (PLS-DA) [94]. A discrimination (from 20 ng L^{-1}) between artificially and not artificially contaminated samples with GSM and MIB were also conducted by combining the electrical capacitance response of a system of five sensors (1 bare microelectrode-S1 and 4 types of polymeric sensors) with a Principal Component Analysis (PCA) [87] and PCA and a fuzzy controller for a sample classification [98].

Bioelectronic noses

As known, human smell systems can identify odours at low concentration levels. According to the existing literature, it is possible to simulate the process and the mechanisms of the human odour detection with devices called electronic noses. These devices are characterized by an array of non-selective sensors and a pattern recognition system. The huge amount of literature dedicated to these tools testify the importance of the assessment of the volatile compounds in different sectors as medical diagnostic, food industry, environmental analytics and monitoring, and pharmaceutical analysis [99,100]. Starting from the pioneering works conducted by Göpel, the sensitivity and the selectivity of these devices have been improved by depositing on the sensor surface sensitive elements, particular biomolecules directly connected with the sensor related to odour detection [101,102]. Olfactory receptors (OR) are the biological materials used as the sensitive element in bioelectronic noses. ORs can be based on olfactory cells where the production of a signals cascade due to ionic transport from outside into inside of the cell is measured, on peptides or proteins, or on nanovesicles (combination of the solutions employing cells and proteins) as well described in the review by Wasilewski et al. [103]. Electrochemical, resonant, or optical transducers are then used to identify and change into analytically useful ones the specific signal generated by the bio sensitive element. Based on the different types of the signals microelectrodes, field-effect transistor (FET), surface plasmon resonance (SPR) sensors, microelectrodes, electrochemical impedance spectroscopy (EIS), quartz-crystal microbalance (QCM), conducting polymers, carbon nanotubes, and graphene can be considered examples of sensor detectors [104]. A bioelectronic nose with human-like performance was proposed for real-time and simultaneously monitoring of both GSM and MIB in water samples [105]. Authors functionalized olfactory nanovesicles produced from mammalian cells (HEK-293 cell) expressing the selected hORs on the cell surface with single-walled carbon nanotube (swCNT) field-effect transistor (FET) in order to convert the biological signals to electric ones. hOR51S1 and hOR3A4 were selected as specific receptors for the selective recognition of GSM and MIB, respectively. Main results evidenced the ability of the sensor in the selectively detection of the two organic pollutants (detection limit of 10 ng L^{-1}) and the feasibility of applying the tool for the assessment of real samples (such as tap, bottle and river water). Moreover, a cheaper solution based on graphene field-effect transistor (GFET) using a target-specific aptamer was proposed by Park et al. for the real-time monitoring of GSM in real water samples [106]. The proposed device was able to linearly detect the contaminant from 0.01 nM to 1 μM with a detection limit of 0.01 nM.

Microwave spectroscopy

Within the context of other real-time GSM and MIB detection techniques, those based on the assessment of the dielectric behaviour or on the polarization effect due to the interaction with an electromagnetic field appear also promising. As known, the dielectric permittivity ε^*, is a complex number characterized by a real (ε') and an imaginary part (ε'') and is influenced by the material properties, by the temperature and by the frequency of the oscillating field (j is the imaginary unit) [107]:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{29}$$

According to the electromagnetic wave propagation, the transmission and the reflection processes are related to the real part of the dielectric permittivity (ε'), that represents a measure of how much energy is stored in the material, and the imaginary part (ε'') represents the measure of how dissipative or lossy a material is.

The dielectric permittivity relative (ε_r) to free space (ε_0) is calculated by:

$$\varepsilon_r = \frac{\varepsilon^*}{\varepsilon_0} = \varepsilon'_r - j\varepsilon''_r \tag{30}$$

These properties can be assessed through different measurement techniques as the coaxial probe, the transmission line, the free space, the resonant cavity, the parallel plate. The choice of the right techniques is influenced by many factors mainly associated to the material properties and form, explored frequency range, expected values and accuracy of the measurement, temperature and cost. With regards to water, dielectric properties have been widely explored with the aim of monitoring drinkable and non-drinkable water quality. Some examples of these research works refer to the possibility of discriminating between different water quality samples by using an open-ended coaxial probe from 1 GHz to 18 GHz (contaminations with soil or sand) [108], parallel plates from 3.0 to 4.6 GHz (sodium chloride or bovine serum albumin) [109], an open-ended rectangular waveguide from 8 GHz to 12.5 GHz (different salinity) [110] a cavity resonator tuned at 1.91 GHz (nitrates and sulfite) [111]. A recent study conducted by Ryecroft et al., focused on the possibility of differentiating between samples characterized by methanol (from 5 mg L^{-1} to 20 mg L^{-1}) and distilled water contaminated with four levels of GSM (5 ng L^{-1}, 10 ng L^{-1}, 0.5 mg L^{-1} and 1 mg L^{-1}) by means of a resonant cavity device working in the microwave region of frequencies [112]. Based on the results, obtained by processing data with machine learning algorithms as K-Nearest Neighbour, Support Vector Machines and Random Forest, the range of frequency 6.4 GHz - 6.5 GHz appeared to be useful in the identification of the level of the GSM contamination in the methanol water solution. In order to implement techniques based on dielectric properties in fully operative RAS plants, further studies are necessary to understand the role of the other possible water contaminants or constituents on the interaction with the electromagnetic waves and in the futures extraction.

Chemiluminescence reaction

Another rapid method for the assessment of GSM and MIB in water medium is based on chemiluminescence and was proposed by Sato and Tanaka [113]. The proposed solution adopts a luminol-hydrogen peroxide (H_2O_2)-potassium peroxydisulfate ($K_2S_2O_8$) co-oxidation system in alkaline solution as chemiluminescence reaction. Luminol is a well-known luminogenic molecule susceptible to oxidation and its light emission is a consequence of the production of chemiexcited intermediates [114]. As known, in the H_2O_2 chemiluminescence reaction, redox reactions of ROS ($^{\cdot}OH$, $^1O_2$, $O_2^{\cdot-}$) can be appreciated, and in a luminol-H_2O_2-$K_2S_2O_8$ system, H_2O_2 and $K_2S_2O_8$ work as co-reactance by generating, respectively, ROS and $SO_4^{\cdot-}$ [115]. In detail, the concentration of GSM and MIB is quantified through the inhibitory effect on the above cited chemiluminescence reaction.

As expected, results evidenced the negative relationship between the chemiluminescence intensity and the concentration of GSM and MIB and the detection limits were 5.5×10^{-11} M for GSM and 1.2×10^{-10} M for 2-MIB in pure water samples. Nevertheless, the assessment appeared negatively influenced by the presence of other organic compounds in the water samples. Authors suggested to combine the proposed method with liquid chromatography for mutual separation of GSM and MIB [113].

Conclusions

This study provided a review of the issues related to the detection and degradation of GSM and MIB in aquaculture systems. While generally not an issue with traditional aquaculture, control of off-flavour compounds is a major obstacle to the diffusion of the more efficient and less polluting recirculating aquaculture systems. The most desirable solution for off-flavour control is to remove the compounds from the water, preventing their accumulation in the flesh of the farmed species. It has been shown that this task cannot be achieved with conventional water-treatment strategies, with the partial exception of adsorption on activated carbon. On the other hand, the efficacy of advanced oxidation processes for the removal of GSM and MIB has been repeatedly confirmed in the literature. After having examined each AOP relevant to this application, the relative strengths and weaknesses could be compared. Plasma-based techniques have been mainly applied in laboratory and issues related to scale-up of this technology are rather unknown. Processes based on the use of hydrogen peroxide (peroxone, or Fenton-like reactions) are particularly difficult to implement in RAS due to handling issues related to this compound, and to possible side effects on the health of fishes caused by oxidizing agents dissolved in water. Ozone-based AOPs are more favourable in this regard, due to the following reasons: first, ozonation is a mature technology, which also presents the added benefits of disinfection and suspended solids flocculation. Second, ozonation has a relatively low electrical energy consumption, and avoids the undesirable handling of hydrogen peroxide. However, ozonation by itself is marginally effective in the degradation of GSM and MIB, therefore it needs to be combined with other technologies, such as UV and photocatalytic treatments. Photocatalytic ozonation limits a peculiar disadvantage of ozonation, i.e. the formation of bromate. Moreover, compared to UV/O_3, it also has the advantage of requiring lower energy UV irradiation. Finally, by coupling photocatalysis and ozonation it is possible to confine the effects of the oxidizing species close to the photocatalytic bed, thus avoiding detrimental effects on the health of fishes. Therefore, in our opinion coupling photocatalysis and ozonation could be a viable solution for the removal of off-flavour compounds in RASs.

The current state of the art for the measurement of GSM and MIB concentration has also been reviewed. The setting up of real time solutions combined with mathematical signal processing procedures and statistical tools for the rapid assessment of GSM and MIB appear to have a big role in the real-time off-flavour control processes, even if detection limits cannot be comparable to gas chromatography-mass spectrometry reference technique.

CRediT authorship contribution statement

Vittorio Zorzi: Methodology, Data curation, Writing – original draft. **Andrea Bertini:** Conceptualization, Methodology, Data curation. **Andrew Robertson:** Conceptualization, Writing – review & editing. **Annachiara Berardinelli:** Writing – review & editing. **Leonardo Palmisano:** Writing – review & editing. **Francesco Parrino:** Conceptualization, Writing – review & editing.

Declaration of Competing 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.

Data availability

Data will be made available on request.

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