Review

Advanced oxidation processes (AOPs) based wastewater treatment - unexpected nitration side reactions - a serious environmental issue: A review

Manoj P. Rayaroth [a], Charuvila T. Aravindakumar [b], Noor S. Shah [c], Grzegorz Boczkaj [a,d,*]

[a] Gdańsk University of Technology, Faculty of Chemistry, Department of Process Engineering and Chemical Technology, 80-233, Gdańsk, G. Narutowicza 11/12 Str, Poland
[b] School of Environmental Sciences, Mahatma Gandhi University, Kottayam 686560, Kerala, India
[c] Department of Environmental Sciences, COMSATS University Islamabad, Vehari Campus 61100, Pakistan
[d] EkoTech Center, Gdansk University of Technology, G. Narutowicza St. 11/12, 80-233 Gdansk, Poland

ARTICLE INFO

ABSTRACT

Chemical compounds containing nitro group (nitro-products) are a one of toxic by-products, that can be formed during wastewater treatment processes. In case of presence of nitrite or nitrate ions, the formation of nitro-products during advanced oxidation processes (AOPs) is very common. It is caused by the reactive nitrogen species (RNs) such as nitrate radical ($NO_3^{\bullet}$), nitrite radical ($NO_2^{\bullet}$), nitrogen oxide radical ($NO^{\bullet}$) and peroxynirite ($ONOO–$). In fact, the oxidative degradation of N-containing pollutants releases nitrate, nitrite and ammonium ions. In some cases, secondary reactions of mineralised nitrogen species (nitrate and nitrite ions) with the parent or intermediate compound generate next several nitro-products. The nitro-products are more toxic comparing to the primary pollutants and act as the precursors of the nitrogenous disinfection by-products. Moreover, some studies reported unexpected nitro-products formation during the oxidative degradation. In case of such processes a special attention should be made to monitor and minimize these effects. De-nitration of the initial nitro-compounds induces the formation of various nitro-products in AOPs. It was observed for UV light driven, Fenton and persulfate based AOPs. The sonochemical nitrogen fixation is a key mechanism for the formation of nitro-compounds in ultrasounds based AOPs. Therefore, this paper is focused on comparison of various AOPs in terms of nitro-products formation mechanisms and the associated environmental issues.

1. Introduction

Lack of pure water is the one of major barriers in the global socio-economic development. The industrial discharge and other human activities release different kind of chemicals into the natural environment, contaminating available resources of water [1]. The chemicals included in the risk category are heavy metals, pesticides, chlorinated pollutants, pharmaceuticals and personal care products, and their transformation products [2–5]. These pollutants are persistent in the environment and thus the concentration of pollutants in the water body increases by their continuous discharge from their respective sources. The trace amounts of these pollutants are even toxic to aquatic environment. Therefore, tough regulation is being imposed every day to the effluent from the particular sources of pollution [6]. As a result, researchers have focussed

on the development of sustainable and suitable water treatment technologies to clean water. There are techniques such as biological and physicochemical processes for the removal of pollutants. Conventional physical and biological processes often fail because they are time consuming, require large space, pH sensitive and ineffective against non-biodegradable toxic pollutants. It also fails to treat wastewater containing high concentration of the pollutants. These issues were reported especially in the case of attempts for direct treatment via biological treatment plants of industrial effluents and, landfill leachates [7–9].

Advanced oxidation processes (AOPs) are considered as a one of the most effective methods for the removal of organic pollutants [10]. These processes are mainly based on non-selective character of reaction of hydroxyl radicals ($HO^{\bullet}$) having high oxidation potential with organic

pollutants at high reaction rates (generally between $10^8 - 10^{11}$ $M^{-1}s^{-1}$). These processes are therefore capable for the oxidation of many pollutants [10–19]. In addition to $^\bullet OH$, other reactive oxygen species (ROS) such as $SO_4^{\bullet-}$, $O_2^{\bullet-}$, $^1O_2$, and $HO_2^\bullet$ are also capable of degrading the pollutants [20]. The different kinds of AOPs and the ROS involved in each AOPs are given in Fig. 1.

Beside main reactions with target pollutants, side reactions can take place with primary as well as secondary ROS resulting in formation of wide variety of by-products. Some of them are further reacting with ROS finally forming carbon dioxide. Remaining by-products often can be more toxic than primary pollutants [21–23]. This risk is not well addressed in many papers about AOPs wastewater treatment. This aspect is particularly important in case of AOPs based treatment. If the chemical nature of some of the intermediate products are conducive for cross reactions or dimerization reactions, the entire efforts that lead to a complete removal of the pollutants will no longer be feasible, unless synergic protocols with other techniques are designed. In this context, a complete understanding of the nature of intermediate products is of paramount interest. A particular group of by-products that can be formed during various AOP based treatment cycles are nitro-products, especially in the presence of nitrite ions [24] . These by-products are usually more toxic than primary pollutant. Toxicity of these by-products depends on chemical structure of primary molecule and further depends on the number of $-NO_2$ functional groups in the structure. In such cases the toxicity of the solution after treatment can increase. Therefore, it is important to monitor the nitro-products during the degradation of pollutants to correlate the toxicity changes. Several reasons on occurrence of nitro-products can be listed. There have been several studies reported the evolution of nitro-products during the oxidative degradation of pollutants in the presence of nitrite ion and some natural photochemical reactions [24]. However, very recent reports have shown the evolution of intermediate nitro-products even in the absence of nitrite ions [25]. Their persistence to degradation under AOP conditions makes them very interesting in respect to safety of treated water discharge to the environment. Secondly, the risk of their formation can be included in comparison between alternative AOPs for selection of the optimal process. These aspects are discussed and summarized in this review. The main goals relate to comprehensive review of AOPs in respect to possibility of appearance of secondary nitration reactions, types of formed nitro-products and assessment of their environmental importance.
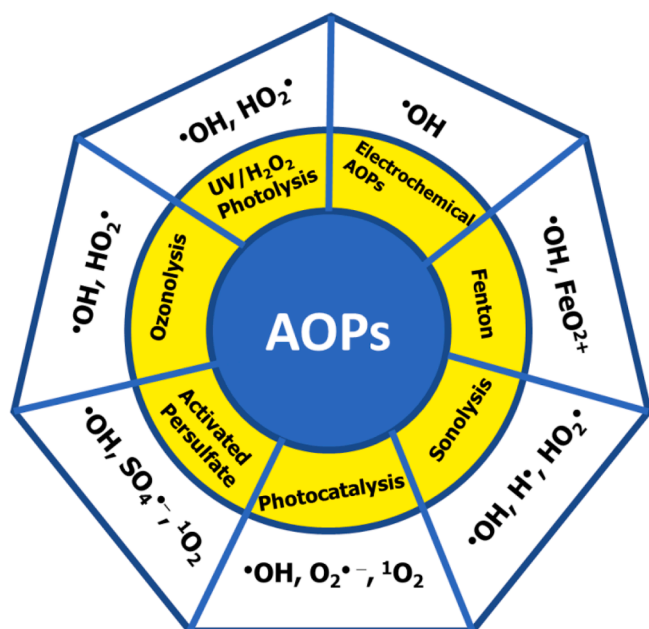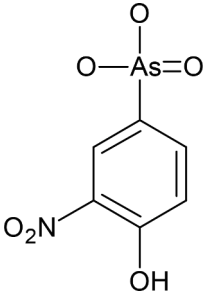
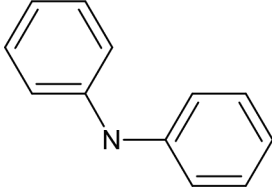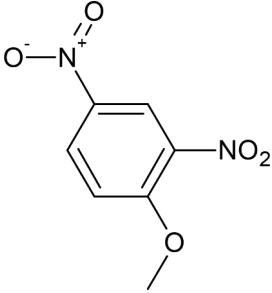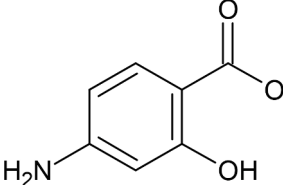## 2. Unexpected nitration in AOPs
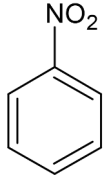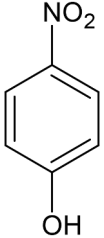
Reactive nitrogen species (RNs) are an important category of environmentally relevant free radicals formed in the natural water resources by the photochemical decomposition of nitrite and nitrate ions. The RNs include nitrate radical ($NO_3^\bullet$), nitrite radical ($NO_2^\bullet$), nitrogen oxide radical ($NO^\bullet$) and peroxynirite ($ONOO–$) [26,27]. Also, nitrate or nitrite ions present in the reaction medium reacts with hydroxyl radicals ($^\bullet OH$) and sulfate radicals ($SO_4^{\bullet-}$) during the oxidative treatment of contaminants to form respective RNs as secondary radicals as given in the Eqn 1 and 2 [28]. In addition, the nitrogen fixation reactions are also able to generate variety of RNs. Some studies for the compounds having N-functional groups (more specifically, $-NO_2$) reported that denitration releases $NO_2^\bullet$ and related RNs to the reaction medium.

$$NO_3^- + HO^\bullet / SO_4^{\bullet-} \rightarrow NO_3^\bullet \tag{1}$$

$$NO_2^- + HO^{\bullet/} SO_4^{\bullet-} \rightarrow NO_2^\bullet \tag{2}$$

In certain cases, the RNs played a significant role on the transformation of organic pollutants during wastewater treatment [24]. $NO_3^\bullet$ is a strong oxidant having the redox potential of 2.3 – 2.5 V, whereas $NO_2^\bullet$, and $NO^\bullet$ are weaker oxidants with redox potential of 1.03 and 0.39 V and acts as nitrating and nitrosating agent [28]. However, their reaction rate constants are lower than values reported for $^\bullet OH$. On the other hand, they are feasible towards the electrophilic substitution reaction with pollutants bearing electron-donating functional groups like phenol and aniline derivatives. The RNs, especially the $NO_2^\bullet$ rapidly hydrolyze in the aqueous medium to give another stable nitrating agent, nitrous acid (HNO_2) [29]. Therefore, the pollutants can undergo nitration reaction once the RNs are formed in the medium even though they have relatively similar lifetime of ROS [30,31]. Thus, the compounds like bisphenol A, estrone, and 17α-ethynylestradiol are rapidly reacting with RNs [32]. The RNs reacts with the phenolic compounds with a bimolecular rate constant of $1–10 \times 10^4$ M^{-1} s^{-1}, which is 10^5 times lower comparing to reaction with $^\bullet OH$ [33]. However, the comparable steady state concentration and longevity of these radical make it more reactive towards the pollutants. The reaction of pollutants like phenol, chlorophenol, nitrophenol, naphthalene, sulfamethoxazole with RNs resulted in the formation of respective nitro-products [24,31–34].

Generally, N-containing compounds such as amines, nitro and azo derivatives have found a variety of application in dye, pesticide, surfactants, and pharmaceutical production [35]. Toxicity studies of these nitrogenous compounds revealed that they are carcinogenic and included as priority pollutants. Therefore, many oxidative treatment methods have been demonstrated for the removal of this kind of pollutants from aqueous medium [36]. Detailed product analyses have also been reported for such compounds. There are many cases, where unexpected nitro-products are formed during their degradation. The list of pollutants generating nitro-products during the oxidative degradation is compiled in Table 1. As can be seen from the table, majority of the compounds have $-NO_2$ functional group in their structure (Eg: nitrobenzene (NB), p-nitrophenol (PNP), roxarsone (ROX), and 2,4-dinitroanisole (DNAN)) and others contain N as primary or secondary amine group. PNP, NB and their derivatives as well as diphenylamine (DPhA) are widely released into the aquatic environment from various industries as these chemicals are the major precursors in the production of pesticide, pharmaceuticals, and petrochemical products [37–39]. ROX is mainly used as a feed additive and is excreted into the animal manure. Since ROX is an organo arsenic compound, its environmental release leads to the Arsenic contamination [40]. Moreover, the PAS are pharmaceutically active compounds and mostly released into the aquatic environment from hospital waste, pharmaceutical industry and domestic sewages [41,42]. Therefore, several AOPs have been studied for the removal of these contaminants from aqueous medium. All the methods offered complete removal of pollutants, however the formation of some intermediate products and mechanism of their formation was reported.

Fig. 1. Various AOPs and the ROS involved.

Table 1

Details of the nitrogen compounds reviewed in this paper.

Compound (Abbreviation)	Structure	CAS	Applications
Nitrobenzene (NB)		98–95-3	Precursor in the production of pesticides, fertilizers, dyes, papers, plasticizers, pharmaceuticals etc.
Para-nitrophenol (PNP)		100–02-7	
Roxarsone (ROX)		121–19-7	Feed additive
Diphenylamine (DPhA)		122–39-4	Precursor of dyes, pesticides and many pharmaceuticals
2,4-dinitroanisole (DNAN)		119–27-7	Insensitive munitions compound
Para-amino salicylic acid (PAS)		65–49-6	An antibiotic

3. Degradation mechanism in AOPs

The mechanism in AOP involves the reaction of ROS with the organic pollutants for complete mineralisation [43,44]. A sequence of several reactions is needed to obtain complete mineralisation of one molecule of target pollutant and often this goal is not fully obtained. Generally, the •OH react with the organic pollutants via, hydrogen abstraction, one electron oxidation and electrophilic OH addition. Detailed description of the degradation mechanisms in AOPs can be found in dedicated review articles [23,44–46]. Finally, some kinds of by-products remaining in the effluents after treatment are more persistent and toxic than the parent compound. Therefore, detailed process control of the effluents is a must in many studies these aspects are only briefly addressed.

Researchers, aware of this risk, have used a variety of analytical techniques mainly based on high resolution chromatography and mass spectrometry techniques for the identification of intermediates as well as by-products. The degradation mechanism is finally proposed based on the products identified by these techniques. The major intermediates

identified in the treated samples are hydroxylated derivatives, products of ring cleavage, aliphatic acids, etc. The general mechanism involved in AOPs is summarized in Fig. 2.

The high electron density centers such as aromatic ring of the pollutants are highly susceptible to the electrophilic attack of the hydroxyl radical resulting the formation of phenolic compounds. These products are usually identified by an increase of 17 mass units comparing to the parent compound [47,48]. Further attack of the OH group to the monohydroxylated product is possible, which leads to the formation of di-, tri-hydroxylated products. Many of the oxidative degradation studies have monitored the time dependant formation of hydroxylated products. As an example, the time dependent formation of mono and di-hydroxylated methyl paraben, and benzene sulfonates have been examined during the sonochemical and the photocatalytic degradation of methyl paraben and benzene sulfonates respectively [48,49]. It is clear that the hydroxylated intermediate products are also degraded with time. As a strong electrophile, the •OH can attack at the ipso position of the C atom to release the group attached to the aromatic ring. This kind of mechanism is common for many compounds such as chlorophenol, nitrophenol, atenolol, 2,4-dichlorophenoxyacetic acid (2,4-D), etc. [50–52].

The continuous attack of oxidizing species to the aromatic intermediates leads to the formation of polyhydroxylated and/or quinone forms, which undergoes further oxidation to short-chain aliphatic carboxylic acids [42,53]. The aliphatic acids formed during the oxidative degradation of pollutants were maleic acid, malic, pyruvic acid, glyoxilic acid, and oxalic acid depending on the structure of the parent compound [53].

3.1. Identification of the unexpected nitrated products in AOPs

The challenging task in AOPs is the identification of intermediates and by-products formed during the course of degradation [23,47]. Simple spectrophotometric methods are not useful for the identification of short-lived species. However, some studies have utilised fluoresce spectrometric techniques to identify the mono and di hydroxy products of benzene and naphthalene sulfonates during their photocatalytic degradation [49,54]. Still, this technique is not universal, as only compounds exhibiting fluorescence can be detected and identified. It can highlight specific transformation but without identifying the unexpected by-products or other non-target products. Chromatographic techniques are able to separate the individual components of the degraded samples. The intermediates can be identified with respect to their retention time values based on used "library" of retention times acquired for available standards. These techniques were helpful for identification of several types of by-products, such as phenol and its derivatives (chloro, nitro, etc.,), catechol, hydroquinones, benzoic acids, and aliphatic acids. Coupling of chromatography with mass spectrometry (MS) is now widely used in this kind of research to identify the unknown compounds based on their masses [43,55,56]. Further research is being implemented to MS analysers to offer the accurate masses. High resolution mass spectrometers such as time-of-flight (TOF), Orbitrap or Fourier-transform ion-cyclotron resonance (FT-ICR) are capable for providing the accurate masses of the individual components [57].

Among the above techniques, the nitro phenols formed during the persulfate (PS)-based oxidation of nitrobenzene, and phenols were analysed by LC-MS/MS techniques. The mass to charge ratio (m/z) values for the mono, di and tri and dinitrophenols were 138, 183 and 228 respectively. Three peaks for mono-nitrophenols, two peaks for
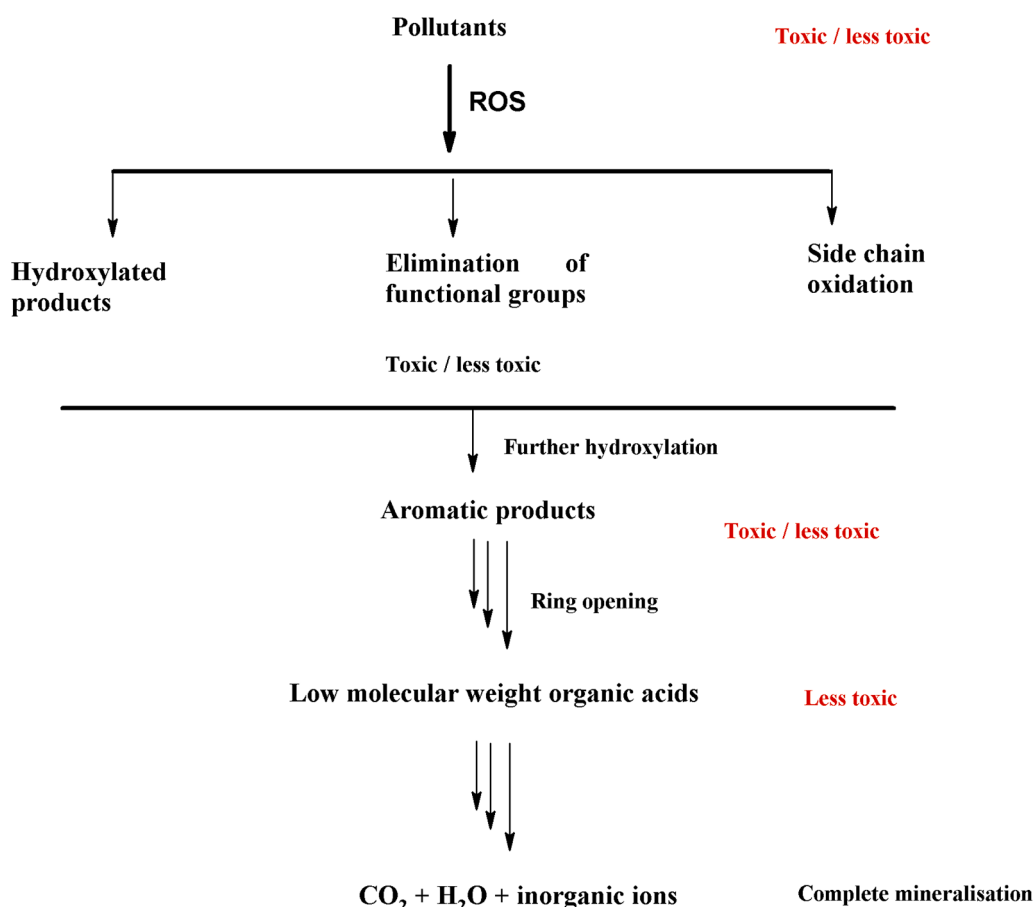

Fig. 2. Mechanistic pathways involved in the degradation of aromatic pollutant during AOPs before complete mineralisation [45].

dinitro-phenols, and one for trinitro-phenols were detected. Similarly, peaks for higher m/z values of 320 and 365 for the coupling products (nitrobiphenyls and nitrodiphenyl ether) were detected as well [58]. Same technique has been utilised for the identification of nitrophenols formed from ROX, and nitrated and nitrosated products of DPhA [59,60].
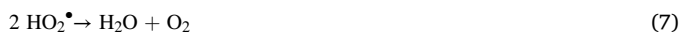
Rayaroth et al., utilised Q-ToF-MS for the identification of intermediates in the treated sample of PAS after sonolysis [25]. This technique provided the accurate mass, MS/MS spectra and the corresponding elemental composition. Various nitro-products have been detected by this technique including isomeric products. The m/z value of the PAS at 152 was obtained at ESI negative mode. Furthermore, products formed via hydroxylation and decarboxylation were identified based on their m/z value. However, many other products were observed with higher masses which neither formed from the hydroxyl radical reaction nor by the coupling reactions. Such products are having the m/z values 154, 181, 137, and 182. The elemental composition confirmed the presence of extra nitrogen in the structure. The MS/MS spectra showed a fragment corresponds to the loss of NO_2 indicates that all the products had nitro group in their structure. Another interesting aspect of this study was the identification of the isomeric products by energy resolved mass spectrometric (ERMS) techniques. In ERMS, the intensity of the fragment ions was plotted against the collision energy. The difference in the formation of fragmentation ions would be helpful in identifying the positional isomers formed during AOPs [61–63]. All the study revealed that MS is the most useful technique in the identification of unknown compounds in AOP.

3.2. Sonochemical degradation of PAS and DPhA

Sonolysis is considered as a green technology in water treatment as it doesn't require any extra chemicals [74–76]. The ultrasonic irradiation of aqueous solution leads to the formation of small cavities in the aqueous medium, which starts growing with time and finally implodes to generate an extreme condition of high temperature and pressure of temperature and pressure up to 5000 K and 200 atm. This process is called acoustic (or sono) cavitation. This condition caused the pyrolytic cleavage of water molecules to generate $^{\bullet}OH$ and $H^{\bullet}$ [4,77]. $^{\bullet}HO_2$ and H_2O_2 are generated from the successive reaction of $H^{\bullet}$ and $^{\bullet}OH$ in the aerated medium (Eqs 3–7). Furthermore, the combination of sonolysis with other AOPs such as sonocatalysis, sonophotocatalysis, sono-fenton, sono-ozonolysis, sono-oxidants, etc., enhanced the degradation by synergistic mechanism [76,78–83].

$$H_2O \text{ -)))} \rightarrow H^{\bullet} + {}^{\bullet}OH \tag{3}$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \rightarrow {}^{\bullet}OH + \tfrac{1}{2}\,O_2 \tag{4}$$

$$2H^{\bullet} \rightarrow H_2 \tag{5}$$

In the absence of any organic species,

$$2\,{}^{\bullet}OH \rightarrow H_2O_2 \tag{6}$$

$$2\,HO_2^{\bullet} \rightarrow H_2O + O_2 \tag{7}$$

Similar to other AOPs the major degradation products are formed from the reaction of primary pollutants with $^{\bullet}OH$ [46,84]. Moreover, degradation by mechanical cleavage, $H^{\bullet}$ reactions, and thermal degradation products are also possible [85,86]. However, some unusual nitro-products were reported to be formed during the sonochemical degradation of N containing pollutants [25,59]. Many nitro-products were formed during the sonochemical degradation process of PAS and DPhA and were not detected during the normal AOPs like UV/H_2O_2 method. The involvement of N species in the degradation of DPhA was confirmed by the scavenging experiment in the presence of 2-(4-phenyl)-4, 4, 5, 5-tetramethylimidazoline-1-oxyl 3-oxide, ferulic acid (FA). The unusual products detected using LC coupled with MS techniques (LC-MS/MS and

LC-Q-ToF-MS) are compiled in Table 2.

Some of the earlier studies demonstrated the evolution of RNs in the reaction medium by sonochemical nitrogen fixation processes [87–90]. In this phenomenon, the atmospheric nitrogen is converted into nitrogen species. The steps of this process include (i) dissolution of N_2 and O_2 in the water, (ii) formation of atomic oxygen by the thermal dissociation of O_2 in the highly reactive cavities, (iii) the reaction of atomic oxygen with nitrogen causes a formation of nitric oxide (is the rate determining step in the N-fixation), which can be further convert into nitrogen dioxide and (iv) finally all the N species form nitrate and nitrite ions released into the liquid region [91,92]. The complete steps are given in Fig. 3. The RNs formed in the reactive interface region of the cavitating bubbles are $NO^{\bullet}$, and $NO_2^{\bullet}$, which are capable for reacting with the pollutants via nitration and nitrosation reaction. The sonication would supplement more O_2 from the liquid region to interface region of the cavitating bubble and enhance the nitrogen fixation process [93]. The role of dissolved gas on the RNs as a function of respective ion was confirmed with different gases such as Ar, N_2, O_2 and air. It is reported that the evolution of nitrate/nitrite is more abundant in air saturated solution. Furthermore, their formation is inhibited if the system contain pure O_2 or N_2 and forms nitrate/nitrite in a mixture of O_2/N_2 [90].

In addition, the sonocavitation process induced the emission of photons with broad wavelength spectrum (called sonoluminescence) [94–96]. Photochemical activation of nitrate and nitrite ions results in the generation of RNs. Therefore, there is a slight chance for such reaction in sonocaviation process. This may induce the activation of acoustically generated nitrogen containing ions. However, there were no proper research made on this particular topic of sonoluminescene and the RNs formation likely due to the lower life time (pico-second range) of sonoluminescence.

The effect of various operational parameters such as initial concentration, frequency, power density, and pH on the formation of nitro-products has been evaluated. The formation of nitro-products is frequency dependant; 600 kHz (rate constant, $k = 2.035\ s^{-1}$) > 200 kHz (rate constant, $k = 0.968\ s^{-1}$) > 400 kHz (rate constant, $k = 0.924\ s^{-1}$) > 800 kHz (rate constant, $k = 0.428\ s^{-1}$). The size of the cavity reaches maximum but the number of bubbles and acoustic cycles become less at lower frequency (here 200 kHz) [97–99]. Therefore, N undergoes dissociation in the cavitating bubble which would result in the formation of RNs. It is inferred that lower frequencies are beneficial to the generation of RNs. So, the nitration likely occurs at a higher rate. But its decay is lower at this frequency. At high frequency even though the bubble collapse occurs with less violence, the availability of reaction site and thus the number of cavitational events becomes higher and more RNs are generated.

The formation and decay of the nitro-products were also varied with the power density. The bubble formation rate is increased by lowering the threshold limit of cavitation, which can be achieved by increasing the applied power. This will increase the number of cavitating bubbles. The energy of collapse and resonance size of the bubble increases with the applied power density [48,84,100]. This process intensifies the nitrogen fixation. The formation of nitro-products is maximal at neutral pH. But the formation and decay of the products is high under the acidic pH and low at alkaline pH. Since the pKa of HNO_2 is 3.37 and the structural changes of HNO_2 insignificant, the nitrosation reaction is not much influenced at this pH [101]. On the other hand, alkaline pH causes the dissolution of all the nitrosating agents followed by their conversion into respective ions [102]. Another interesting observation made by this study is the difference in the NDPhA formation in the presence of dissolved gases such as air and argon. The degradation of DPhA was not much affected by these gases, instead NDPhA formation was reduced in the presence of Ar. This study confirms that the major source of nitrosating agent is the N_2 and O_2 present in the medium.

The mechanism of nitrosated DPhA (NDPhA) formation during the sonochemical degradation of DPhA is given in Fig. 4. The RNs such as $NO^{\bullet}$, N_2O_3, and $NO_2^{\bullet}$ contributed to the formation of NDPhA by

Table 2
Unexpected products generated from the oxidative degradation of nitrogen containing compounds in deionized water.

| AOP	Pollutant	Experimental conditions	Unexpected product	Ref.
Photolysis	DNAN	$[DNAN]_0 = 109$ mg L^{-1}	methoxytrinitrophenols	[64]
Fenton	NB	$[NB]_0 = 1.20$ mM, $[H_2O_2]_0 = 7.5$ mM, $[Fe^{+2}]_0 = 0.1$ mM	1,3-dinitrobenzene	[65]
		$[NB]_0 = 0.75$ mM, $[H_2O_2]_0 = 2.7$ mM, $[Fe^{+3}]_0 = 0.32$ mM		
Fenton	NB	$[NB]_0 = 1.0$ mM; $[H_2O_2]_0 = 8.0$ mM; $[Fe^{2+}]_0 = 0.1$ mM (Fenton); $[Fe^{3+}]_0 = 0.1$ mM	1,3-dinitrobenzene	[66]
UV/PS	DNAN	$[DNAN]_0 = 40$ μM; pH = 7.0; [PS] = 5 mM; 15 W low pressure mercury (LP-Hg) lamp	2,4,6-trinitrophenol	[67]
Heat activated PS	NB	[NB] = 50 μM; [PS] = 2 mM;T = 60 °C; [Phenol] = 500 μM	2,6-DNP and 2,4-DNP	[68]
Heat activated PS in soil system	PNP	$[PNP]_0 = 93(\pm2)$ mg/kg, [PS] = 60 mM kg^{-1}	2, 4-dinitrophenol4-hydroxy-2′, 3, 4′-trinitrobiphenyl	[69]
Heat activated PS	PNP	$[NPs]_0 = 50$ μM, [PS]0 = 1.0 mM, $T = 60$ °C, pH = 7.0	2,4-DNP 2,6-DNP, 2,4,6-TNP, 2′-hydroxyl-2,3′,4,5′-tetranitrodiphenyl ether, 2,2′-dihydroxyl-3,3′,5,5′-tetranitrobiphenyl	[58]
Heat activated PS	ROX	$[ROX]_0 = 50$ mM, [PS] = 2.0 mM, Temp = 40–70 °C, pH = 7.0	2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrophenol (2,4-TNP)	[60]
PS co-activated with heat and metal ions	PNP	$[PNP]_0 = 0.72$ mM , $[Na_2S_2O_8] = [Fe^{2+}$ or $Cu^{2+}] = 30$ mM Temp = 70° C	2, 4-dinitrophenol 4-hydroxy-2′, 3, 4′-trinitrobiphenyl Dinitrophenyl trinitrobiphenyl	[70]
PMS activated with Co_3O_4-Y_2O_3	ROX	$[ROX]_0 = 50$ mM, initial solution pH = 7, $[PMS]_0 = 0.5$ mM, $[catalyst]_0 = 0.2$ g/L, Temp. = 25 °C	2-nitro-4-(2-nitrophenoxy)phenol 2,4-dinitrophenol	[71]
Peroxymonosulfate (PMS) and Hydroxylamine (HA)	Phenol	$[Phenol]_0 = 20$ μM, $[PMS]_0 = 600$ μM $[HA]_0 = 1200$ μM	Nitrophenol, nitrosophenol	[72]
nZVI/PS-HP	PNP	[nZVI]0 = 0.2 g L_1, [PNP]0 = 20 mg L^{-1}, $[H_2O_2/PDS$ (1 : 1)]0 = 2 mM.	2,4-dinitrophenol	[73]
Sonolysis	PAS	Frequency 350 kHz and power 80 W, $[PAS]_0 = 10^{-5}$ M	4-amino-3-nitrobenzoic acid 3-amino-4-nitrophenol 2-nitroaniline 4-hydroxy-3-nitrobenzoic acid	[25]
Sonolysis	DPhA	$[DPhA]_0 = 5.0 \times 10$–3 mol m-3, frequency = 600 kHz, power density = 0.19 W mL-1, T = 20.0 °C, initial pH = 7.0	*N*-nitroso-*N*-phenylaniline 2-nitro-*N*-phenylaniline 2,4-dinitro-*N*-phenylaniline 4-nitro-*N*-(4-nitrophenyl)aniline 4-nitro-*N*-phenylaniline	[59]
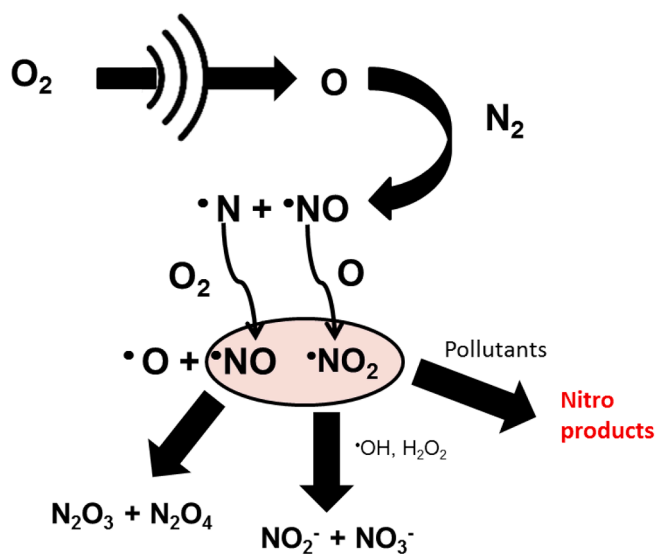
Fig. 3. Schematic representation of sonochemical N-Fixation process for the RNs formation.

different pathways in the cavitating bubble or liquid region. The attack of NO• on the N atom of DPhA and the subsequent release of •H leads to the formation of NDPhA. Whereas, the attack of N_2O_3 (path 2) and NO_2• (or N_2O_4) (path 3) on the N atom leads to the formation of planar five membered ring (TS1) and planar hexatomic ring (TS2) transition states respectively. The rearrangement of these transition states complex results the evolution of NDPhA.

3.3. Formation of Nitro-products in persulfate based AOPs

Persulfate ($S_2O_8^{2-}$) is the one of the emerging oxidants in AOPs because of their excellent oxidation ability with redox potential of 2.01 V [103]. The reactive species generated upon the decomposition of PS is $SO_4^{•-}$ ($E^0 = 2.6$ V), which is having the oxidative degradation capacity as that of •OH. In comparison with •OH, the $SO_4^{•-}$ reacts selectively with the target pollutants. Thus, PS based AOPs are effective for the degradation of nitroaromatic pollutants and other pharmaceuticals in the aqueous medium as well as the *in situ* remediation of contaminated sites [104–107]. The activators of PS are photoirradiation, heat, transition metals, electrochemical, ultrasound, etc. [20,108–114]. The $SO_4^{•-}$ some times generates •OH (Eqn. 8–9).

$$S_2O_8^{2-} + Activators \rightarrow 2\ SO_4^{•-} \tag{8}$$

$$SO_4^{•-} + H_2O \rightarrow SO_4^{2-} + {}^{•}OH + H^+ \tag{9}$$
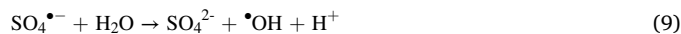
In contrast to sonolysis, many nitro-products have been detected during PS mediated degradation of nitro benzene, and nitrophenols as it is originated by denitration and renitration processes [68]. The $SO_4^{•-}$ mediated NB degradation led to the formation of a series of nitrophenols, including 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2,6-dinitrophenol (2,6-DNP), 2,4,6-trinitrophenol (2,4,6-TNP), and many other coupling products. Heat and Co_3O_4-Y_2O_3 activated peroxymonosulfate oxidation of ROX, also result in the formation of polynitrated by-products. In this case, 2,4,6-TNP is the major intermediate product (yield 41 to 48%). Small amount of DNP have been detected in degradation of PNP by H_2O_2 and PS activation of nZVI. However, this dinitro-products were not detected in Fenton reactions, as only •OH is formed [58,60,65–71,73].

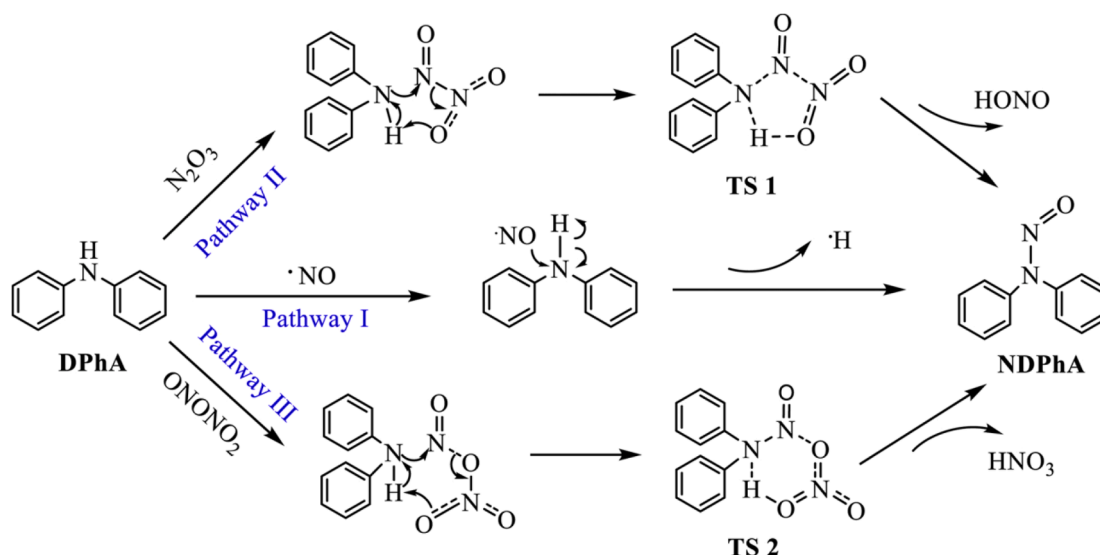The formation of hydroxylated products was explained by the usual

Fig. 4. Different pathways involved in the formation of NDPhA during the sonochemical transformation of DPhA [59].

$SO_4^{\bullet-}$ reaction. The one electron oxidation of the aromatic ring generates a radical cation, followed by a hydroxycyclohexadienyl radical by the hydrolysis reaction. Finally, hydroxylated products are formed by the addition of O_2 and subsequent elimination of HO_2. Moreover, the nitration products were formed due to the de-nitration and the re-nitration reactions. The initial de-nitration of the NP, results in the release of nitrite ions (NO_2^-). The generated NO_2^- would then react with the $SO_4^{\bullet-}$ and $^\bullet OH$ to form a strong nitration agent $NO_2^\bullet$. The rate constant for the reaction of NO_2^- with the reactive species is given below (Eq. 10 and 11). One electron oxidation of mononitrophenol generates a

nitrohydroxycyclohexadienyl radical and the subsequent nitration produce dinitro phenols (Fig. 5). The major dinitrophenol observed during such reactions is 2,4-DNP, it could be produced from both 2-NP and 4-NP, while 2,6-DNP would be generated only from 2-NP. Similar reactions on the di-nitro-products form tri-nitro-products (NP → DNP → TNP) and other coupling products (Fig. 5).

$$NO_2^- + SO_4^{\bullet-} \rightarrow NO_2^\bullet \ (k = 8.8 \times 10^8 \ M^{-1} \ s^{-1}) \ [28] \tag{10}$$

$$NO_2^- + {}^\bullet OH \rightarrow NO_2^\bullet \ (k = 8.8 \times 10^{10} \ M^{-1} \ s^{-1}) \ [28] \tag{11}$$
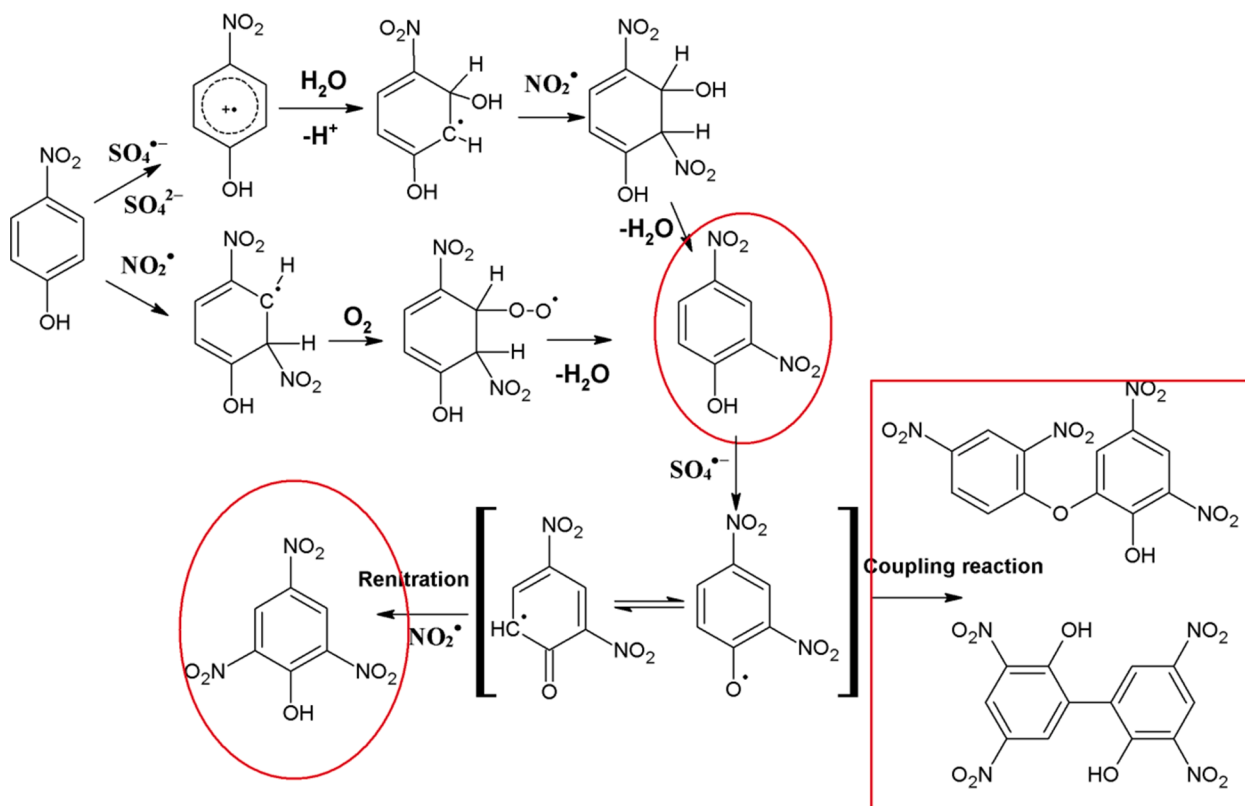
Fig. 5. Mechanism involved in the sulphate radical mediated denitration and renitration process for the formation of poly nitrated compounds and coupling products.

A more recent research on the PS activation by hydroxylamine for the degradation of phenol reported the formation of various nitro phenols [72]. In comparison with other PS based AOPs discussed in the previous section, denitration might not happen for this compound. Therefore, the nitration and nitrosation occurs by a different mechanism. Hydroxyl amine (NH_2-OH, HA), a widely used reducing agent, has been used for the activation of peroxides [115]. HA activates the PS to form $SO_4^{\bullet-}$ and aminoxyl radical ($NH_2O^{\bullet}/NH_3O^{\bullet+}$). The aminoxyl radical can further activate the oxidant to generate more reactive species. As a result, this process is employed in the removal of various contaminants like phenols, bisphenol, atrazine, etc. The aminoxyl radical can be converted into the gaseous N_2/N_2O or inorganic ions such as NO^-, NO_2^-, and NO_3^- and the complete reactions are given in Eqn 12–16 [116,117]. These ions would then react with ROS as given in the Eq. (10) and (11) to form RNs.
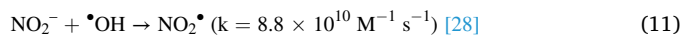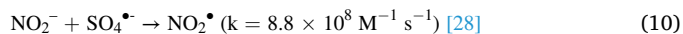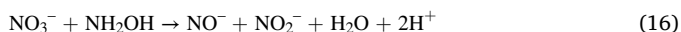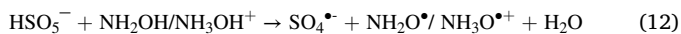
$$HSO_5^- + NH_2OH/NH_3OH^+ \rightarrow SO_4^{\bullet-} + NH_2O^{\bullet}/ NH_3O^{\bullet+} + H_2O \quad (12)$$

$$2NH_2O^{\bullet} \rightarrow N_2 + 2 H_2O \quad (13)$$

$$2HNO \rightarrow N_2O + H_2O \quad (14)$$

$$NH_2O^{\bullet} + oxidants \rightarrow NO_3^- \quad (15)$$

$$NO_3^- + NH_2OH \rightarrow NO^- + NO_2^- + H_2O + 2H^+ \quad (16)$$

This process caused the evolution of nitrosophenol as the major product (yield is 35%).

Nitrophenol was also formed but the yield is nearly 10%. The time dependent study revealed that nitrosoproduct is decreasing gradually with time, but the concentration of nitrophenol remains constant. Nitroso products were formed for other phenolic products such as acetaminophen (AAP), bisphenol A (BPA), and bisphenol S (BPS). The effect of various factors such as HA concentration, and initial pH on the evolution of nitroso products were monitored. The yield of nitroso products was very high at pHs 4 and 5. These are stable even after 1 hr at pH 5. In addition, the nitrosoproduct formation increased with increase of HA: PMS concentration. The pKa for NH_2OH is 5.96 and exists as protonated form at lower pH [118]. The rate of reaction of oxidant with HA is rapid for the neutral form than the positively charged species (pH < 5). At high pH, the scavenging of $SO_4^{\bullet-}$ by HA is the predominant reaction and not able to degrade the target pollutant.

3.4. Photochemical and Fenton based AOPs

The formation of 1,3 DNB has been compared in various AOPs such as UV/H_2O_2, photo-Fenton, Fenton like and Fenton processes. Such nitro-products have also been observed in the UV/PS oxidation of DNAN.
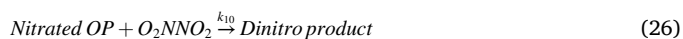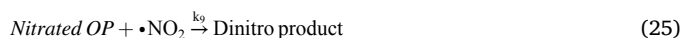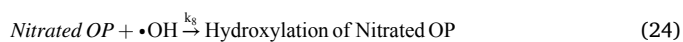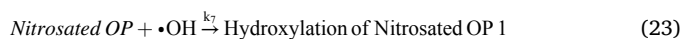
Photochemical oxidation of the oxidants generates the ROS by the cleavage of O-O bond on these oxidants. This process either used the light in the UV or visible region based on the molar absorptivity of the oxidant in this region [119–121]. Fenton reaction utilized certain oxidants (mainly H_2O_2) activated by transition metal ions (Fe^{2+}, Cu^{2+}, Co^{2+}, Mn, Ni, etc.,) to generate ROS [122–126]. This ROS generation would be enhanced by the introduction of light, called photo Fenton reaction. Moreover, the homogeneous Fenton catalyst has been replaced by heterogeneous catalyst containing transition metals. As discussed in the previous sections, de-nitration is the major phenomenon in the formation of nitrated products. De-nitration releases nitrite ions, which has shown good UV absorption. The photochemical reaction of nitrite ions forms different RNs, which induces nitration and nitrosation reactions in the medium. Among the reported AOPs, the 1,3 DNB formation is found in the order UV/H_2O_2 < Fenton < Fenton like < photo Fenton. The formation of 1,3 DNB is dependent on the reagent concentration such as Fe^{2+}, and H_2O_2. An increase of Fe^{2+}/Fe^{3+} concentration increases the degradation of NB with the formation of DNB. In another study, the photochemical reaction of DNAN forms methoxyl

dinitrophenol as the major intermediate because of the similar denitration and re-nitration processes [64].

The nitration reaction in the presence of nitrate/nitrite is a common reaction during the degradation of pollutants in natural water as it contains nitrate and nitrite ions [24,127–129]. The nitrate and nitrite ion has shown maximum absorbance at a wavelength of 300 nm and 350 nm, respectively [130,131]. Therefore, RNs are formed along with the reactive oxygen species depending on the wavelength of irradiation. The schematic representation of the photochemical formation of RNs is given in the Fig. 6.

4. Kinetics of nitro-product formation

To express the kinetics of nitro-product formation one should address the degradation of initial pollutant, and the formation of nitro-products. As reported for other AOPs, the degradation can be described by the pseudo first order kinetics. However, the kinetic studies were very limited for the nitro-product formation. Yao et al., proposed the kinetic models to propose such nitro-product formation [59]. It was proposed based on the assumption of involving both the ROS and RNs. The ROS is $^{\bullet}OH$ and RNs are $NO^{\bullet}$ and $NO_2^{\bullet}$. The sources of the reactive species such as the water, dissolved gases (N_2 and O_2) and their concentration are constant in the reaction medium. As a results, the concentration of reactive species and the final products such as $^{\bullet}OH$, $NO^{\bullet}$, N_2O_3, $ONONO_2$ ($NO_2^{\bullet}$) and O_2NNO_2 formed from these precursors are also the same. The OP would react with the $^{\bullet}OH$ to form the initial intermediate products, it takes place for all the AOP based reactions (k_1). The nitrosating agents such as $NO^{\bullet}$, and N_2O_3 reacts with the organic pollutants (OP) to form nitrosated products (k_2). Nitration agents such as $ONONO_2$ ($NO_2^{\bullet}$) and O_2NNO_2 causes formation of nitro-products, both mono and dinitro-products and nitrosation products (k_3, k_4, k_5, k_6, k_9 and k_{10}). All the representative reactions and the corresponding rate constant are given in the Eqns 17–26. Moreover, it should be noted that the rate constants corresponding to the reaction N_2O_3 can be neglected in AOPs other than sonolysis. In addition, the pyrolytic effect should be addressed in the sonochemical transformation. In the case of isomeric product formation, three more steps can be added similar to the Eqns. 24–26. Same can be done for other polynitrated products.

$$OP + {^{\bullet}OH} \xrightarrow{k_1} products \quad (17)$$

$$OP + {^{\bullet}NO} \xrightarrow{k_2} Nitrosated\ OP \quad (18)$$

$$OP + ONONO_2 \xrightarrow{k_3} Nitrosated\ OP \quad (19)$$

$$OP + N_2O_3 \xrightarrow{k_4} Nitrosated\ OP \quad (20)$$

$$OP + {^{\bullet}NO_2} \xrightarrow{k_5} Nitrated\ OP \quad (21)$$

$$OP + O_2NNO_2 \xrightarrow{k_6} Nitrated\ OP \quad (22)$$

$$Nitrosated\ OP + {^{\bullet}OH} \xrightarrow{k_7} Hydroxylation\ of\ Nitrosated\ OP\ 1 \quad (23)$$

$$Nitrated\ OP + {^{\bullet}OH} \xrightarrow{k_8} Hydroxylation\ of\ Nitrated\ OP \quad (24)$$

$$Nitrated\ OP + {^{\bullet}NO_2} \xrightarrow{k_9} Dinitro\ product \quad (25)$$

$$Nitrated\ OP + O_2NNO_2 \xrightarrow{k_{10}} Dinitro\ product \quad (26)$$
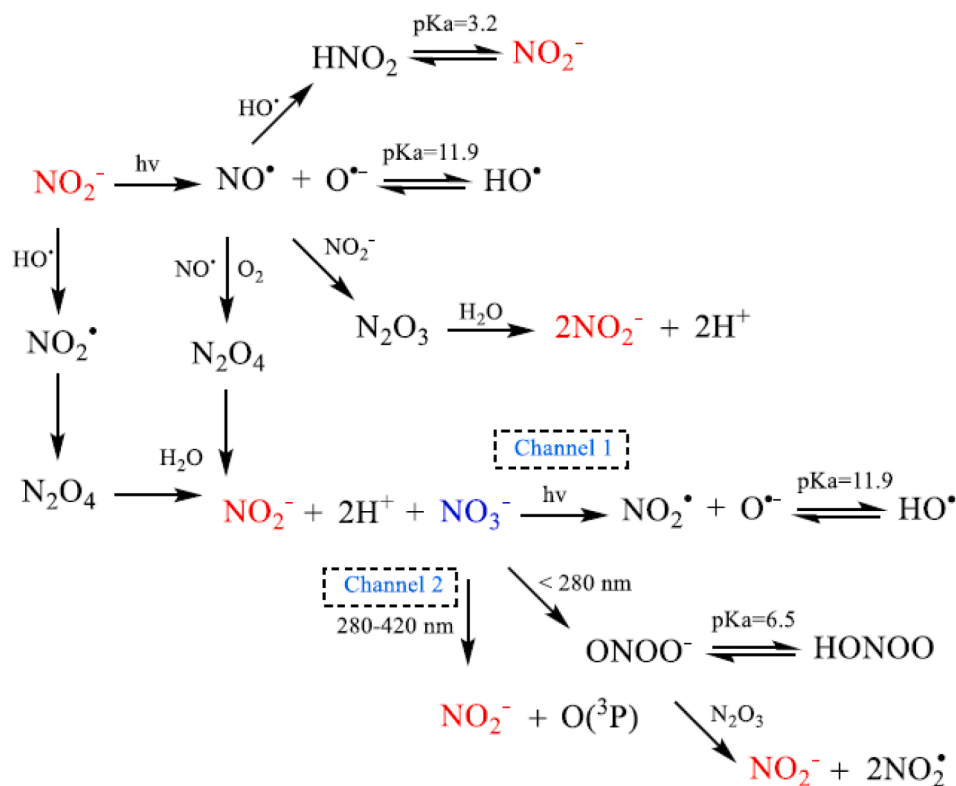
The rate of degradation and nitro product formation can be represented by

Fig. 6. Photochemical generation of reactive N species in solution containing NO_2^- ion [24].

$$\frac{d[OP]}{dt} = -(k_1[\bullet OH] + k_2[\bullet NO] + k_3[ONONO_2] + k_4[N_2O_3])[OP] - (k_5 + k_6)[NO_2^\bullet][OP] - (k_7 + k_8)[O_2NNO_2][OP]$$

(27)

$$\frac{d[Nitrosated - OP]}{dt} = (k_2[\bullet NO]) + k_3[ONONO_2] + k_4[N_2O_3][OP] - (k_7[HO^\bullet])[Nitrosated\ OP]$$

(28)

$$\frac{d[nitro - OP]}{dt} = k_5[2ON^\bullet] + k_6[O_2NNO_2][OP] - k_8[HO^\bullet] + k_9[NO_2^\bullet] + k_{10}[O_2NNO_2][nitro - OP]$$

(29)

All the above can be simplified as,

$$\frac{d[OP]}{dt} = -k_1'[OP]$$

(30)

$$\frac{d[Nitrosated - OP]}{dt} = k_2'[OP] - k_3'[nitrosated - OP]$$

(31)

$$\frac{d[Nitrated - OP]}{dt} = k_4'[OP] - k_5'[nitrated - OP]$$

(32)

Where k_1' represent the apparent rate constant for the degradation of OP.

$$k_1' = (k_1[\bullet OH] + k_2[\bullet NO] + k_3[ONONO_2] + k_4[N_2O_3] + (k_5 + k_6)[NO_2^\bullet] + (k_7 + k_8)[O_2NNO_2]$$

(33)

Nitrosation mediated apparent degradation of pollutants; $k_2' = k_2[\bullet NO] + k_3[ONONO_2] + k_4[N_2O_3]$, apparent degradation of nitrosated products by $\bullet OH$; $k_3' = k_7[\bullet OH]$, apparent degradation rate constants for the nitration of OP; $k_4' = k_5[NO_2^\bullet] + k_6[O_2NNO_2]$, and the apparent degradation rate constant for the nitrated OP $k_5' = k_8[\bullet OH] + k_9[NO_2^\bullet] + k_{10}[O_2NNO_2]$. The ratios of the apparent rate constants provide the contribution of the degradation via nitrosation and nitration. The nitrosation reaction can be obtained from the ratio of k_2' to k_1'. The ratio of $(k_4' + k_5') / k_1'$ represent the role of nitration reaction for the degradation of OP.

5. Fate of nitro-products during the oxidative treatment

As discussed in the previous section, various nitro-products were

generated during oxidative degradation. However, the ROS involved in the process would further rapidly react with the intermediate products. Therefore, the fate of these intermediate also needs to be addressed. Complete degradation of DPhA was reported during the sonolysis after 45 min with the formation of NDPhA and nitro-DPhA [59]. The concentration of nitrogen derivatives was very high in the first 15 min and slowly decayed with time. Moreover, these species remain in the treated medium even after 50 min of process. Likewise, the Fenton process leads to the complete degradation of 1 mM of nitrobenzene with the formation of intermediates such as nitrophenols, phenol and 1,3 DNB. The concentration of intermediates such as phenol and nitrophenol were 0.005 mM and 0.05 mM respectively. These products were completely degraded in short time and their concentrations were decreased below the detection limit after 6 min of treatment. On the other hand, the 1,3 DNB was formed with a concentration of nearly 0.08 mM. Their formation was increased linearly with time and were not degraded even after the complete degradation of parent compound and other intermediate products [66].

Ji et al., monitored the time dependant evolution of polynitrophenols during the degradation of NP by heat activated PS [58,68]. Complete degradation of 2-NP was observed after 6 hr of treatment. The DNPs (2,4-DNP and 2,6-DNP) were formed as initial nitro-products during the initial time of reaction and their concentration is increased linearly even after the complete removal of initial NP. The concentration of 2,4-DNP and 2,6 DNP were 2.82 μM and 1.44 μM respectively after 8 hr. Same pattern was observed for 4-NP with the formation of 2,4DNP as the major product. Thereafter the concentration of these DNPs was decreased with time with the formation of trinitrophenols (TNPs). TNPs were persistent to degradation, even after 16 hr of treatment. In the case of NB, complete degradation was observed only after 300 min. In this case 2,4-DNP and 2,6-DNP were also formed during the course of the reaction. These species were slowly degraded and remained present in the medium until 480 min of reaction [68]. All these reports reveal that the generated nitro-products are more persistent to degradation via AOPs than the initial compounds.
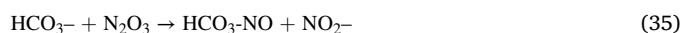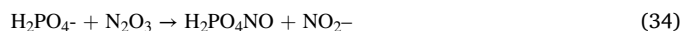
Furthermore, we have calculated the ecotoxicity of other nitro-derivatives towards aquatic organisms such as Fish, Daphnia, and green algae using Ecological Structure Activity Relationships (ECOSAR v1.10) software from U.S. Environmental Protection Agency. The toxicity values of the primary pollutants and their unexpected nitro-products towards the aquatic organisms are given in Table 3 and Table 4 respectively. The acute toxicities and the chronic toxicities are presented in this Tables. The nitro-products and nitroso products are mutagenic and highly toxic [128]. If the treated water contains any of these species, it may cause notorious effect to ecosystem and human. The NPs such as 2-NP, 4-NP, 2,4-DNP, 2,6-DNP, and 2,4,6-TNP are categorised as highly toxic compounds. The toxicological studies revealed that the poly nitro-products are more toxic than the mononitro-products [128,129]. Anaerobic toxicity studies revealed that the substituted phenols are more toxic than that of the mono substituted NPs. The exposure of these NPs to humans affects the central nervous system, lung, kidney, and other circulatory systems [132–135]. However, the ecotoxicity values of NB and PNP calculated in this review using ECOSAR were lower than that of polynitro-products. The acute toxicity values of ROX are 6.39×10^6, 2.30×10^6, 2.57×10^5 mg L^{-1} and the chronic toxicity values are

3.46×10^5, 62479.98, and 24225.75 mg L^{-1} towards Fish, Daphnia, and green algae respectively. At the same time the intermediate nitro-products are more toxic than the parent ROX. In this case the LC50 values were decreased. Likewise, the nitrosoderivatives of DPhA are highly toxic to the aquatic organisms compared to other nitrogen containing byproducts. Among the degradation byproducts of PAS, nitro-aniline, and 3-amino-4-nitrophenol are more toxic than the parent compound. It is noted that the toxicity of the above derivatives is reported for the individual cases and thus their toxicity will further increase in the case of mixture of derivatives. Therefore, in this case, more detailed investigation is needed to evaluate the cumulative effect of the mixed nitroderivatives. 67/548/EEC) as LC$_{50}$ > 100 or EC$_{50}$ > 100 (Not harmful), 10 < LC$_{50}$ < 100 or 10 < EC$_{50}$ < 100 (Harmful), 1 < LC$_{50}$ < 10 or 1 < EC$_{50}$ < 10 (Toxic), and LC$_{50}$ < 1 or EC$_{50}$ < 1 (Very toxic), While chronic toxicities assessed based on the Chinese hazard evaluation criteria for new chemical substances (HJ/T154–2004), i.e., ChV > 10 (Not harmful), 1 < ChV < 10 (Harmful), 0.1 < ChV < 1 (Toxic), and ChV < 0.1 (Very toxic)

6. Effects of water matrix on the nitro-product formation

Water matrix also had a prominent role on the formation of nitration processes. In one of the studies, the NDPhA formation has been monitored in the presence of different inorganic ions such as Br-, HCO$_3^-$, PO$_4^{3-}$, NH$_4^+$ and Fe^{2+} at a concentration level of 10^{-2} M. All the selected ions except Br$^-$ slightly retarded the degradation of DPhA, on the other hand these ions had a substantial effect on the NDPhA formation. The ions such as HCO$_3^-$, PO$_4^{3-}$, NH$_4^+$ and Fe^{2+} inhibited the NDPhA formation and their effect followed the order of HCO$_3^-$ ≫ Fe^{2+} > PO$_4^{3-}$ > NH$_4^+$ [59]. The inhibitory effect of these ions is due to the scavenging of sonochemically generated nitrosating agent. The observed effect is due to the scavenging of nitrosating agent by these ions like other radical based reactions [59]. Thus, common composition of real matrix with presence of inorganic ions can be beneficial in respect to inhibitory (positive) effect on formation of nitro-products.

The PO$_4^{3-}$ would react with the one of the nitrosating agent N$_2$O$_3$ to form H$_2$PO$_4$NO. This product has a five membered ring and doesn't possess the nitrosating ability as that of the primary species [136]. HCO$_3$ has bigger potential to scavenge the N$_2$O$_3$ than that of PO$_4^{3-}$ under neutral condition [137]. It follows from the inhibitory effect. Likewise, Fe^{2+} scavenges NO$^\bullet$ from the aqueous solution to form an iron complex, FeNO^{2+} [138]. All the scavenging reactions are presented in the Eqns 34–36

$$H_2PO_4^- + N_2O_3 \rightarrow H_2PO_4NO + NO_2– \quad (34)$$

$$HCO_3– + N_2O_3 \rightarrow HCO_3\text{-}NO + NO_2– \quad (35)$$

$$Fe^{2+} + NO^\bullet \rightarrow FeNO^{2+} \quad (36)$$

The NH$_4^+$ ions have shown different mechanism on the nitro-product formation. The NH$_4^+$ can scavenge the $^\bullet$OH to form the NH$_2^\bullet$ [139]. The reactive species can neutralise the RNs to gaseous N$_2$ and N$_2$O. But the rate of scavenging reaction is very low and their inhibitory effect is minimal. This is clear from the NDPhA formation during the sonochemical degradation of DPhA in the presence of NH$_4^+$ ions [59]. On the other hand, NH$_4^+$ ions promoted the formation of nitro-products in PS

Table 3

Estimating ecotoxicities of nitrogen compounds towards aquatic organism in the units of mg/L*.

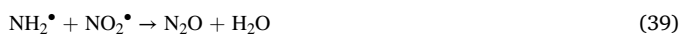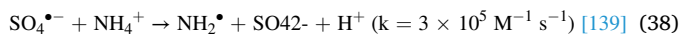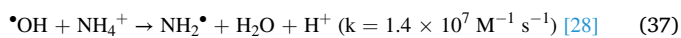| Compound	Fish (LC$_{50}$)	Daphnia (LC$_{50}$)	Green Algae (EC$_{50}$)	Fish (ChV)	Daphnia (ChV)	Green Algae (ChV)
NB	14276.82	6501.36	1944.87	1075.71	343.09	311.59
PNP	3695.81	310.00	1884.43	245.06	59.24	918.04
ROX	6.39×10^6	2.30×10^6	2.57×10^5	3.46×10^5	62479.98	24225.75
DPhA	2.87	1.94	2.98	0.34	0.30	1.15
DNAN	2.69×10^6	9.90×10^5	1.23×10^5	1.58×10^5	28906.51	12270.59
PAS	1044.02	539.35	271.84	91.28	40.43	57.68

MOST WIEDZY Downloaded from mostwiedzy.pl

Table 4

Estimating ecotoxicities unexpected products towards aquatic organism in the units of mg/L*.

Compound	Fish (LC$_{50}$)	Daphnia (LC$_{50}$)	Green Algae (EC$_{50}$)	Fish (ChV)	Daphnia (ChV)	Green Algae (ChV)
Methoxytrinitrophenol (Photolysis/DNAN)	3.94×10^7	3.66×10^5	3.59×10^6	1.27×10^6	70466.43	1.86×10^6
1,3-dinitrobenzene (Fenton/NB)	2.70×10^6	9.87×10^5	1.19×10^5	1.57×10^5	28235.07	3.94×10^5
1,3-dinitrobenzene (Fenton/NB)	2.70×10^6	9.87×10^5	1.19×10^5	1.57×10^5	28235.07	3.94×10^5
2,4,6-trinitrophenol (UV/PS/DNAN)	2.57×10^7	2.58×10^5	2.49×10^6	8.46×10^5	49636.52	1.29×10^6
2,6-DNP (Heat/PS/NB)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
2,4-DNP (Heat/PS/NB)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
2,4- dinitrophenol (Heat/PS in Soli/PNP)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
4-hydroxy-2′, 3, 4′-trinitrobiphenyl (Heat/PS in Soli/PNP)	1.55×10^6	34248.32	2.79×10^5	66394.80	6577.32	1.41×10^5
2,4-DNP (Heat/PS/PNP)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
2,6-DNP (Heat/PS/PNP)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
2,4,6-trinitrophenol (Heat/PS/PNP)	2.57×10^7	2.58×10^5	2.49×10^6	8.46×10^5	49636.52	1.29×10^6
2′-hydroxyl-2,3′,4,5′-tetranitrodiphenyl ether (Heat/PS/PNP)	3.15×10^8	1.88×10^6	2.04×10^7	8.76×10^6	3.63×10^5	1.70×10^7
2,2′-dihydroxyl-3,3′,5,5′-tetranitrobiphenyl (Heat/PS/PNP)	3.16×10^6	7.98×10^8	6961.60	6.58×10^6	5.06×10^8	256.59
2,4-DNP (Heat/PS/ROX)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
2,4,6-TNP (Heat/PS/ROX)	2.57×10^7	2.58×10^5	2.49×10^6	8.46×10^5	49636.52	1.29×10^6
2,4-DNP (Co-activated/PS/PNP)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
4-hydroxy-2′, 3, 4′-trinitrobiphenyl (Co-activated/PS/PNP)	1.55×10^6	34248.32	2.79×10^5	66394.80	6577.32	1.41×10^5
dinitrophenyl (Co-activated/PS/PNP)	2.70×10^6	9.87×10^5	1.19×10^5	1.57×10^5	28235.07	11669.43
trinitrobiphenyl (Co-activated/PS/PNP)	1.67×10^7	5.76×10^6	5.47×10^5	9.06×10^5	1.04×10^5	47317.15
2-nitro-4-(2-nitrophenoxy)phenol (PMS/ Co$_3$O$_4$-Y$_2$O$_3$/ROX)	56478.18	2818.62	19189.01	3157.16	539.71	9487.46
2,4-dinitrophenol (PMS/ Co$_3$O$_4$-Y$_2$O$_3$/ROX)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
Nitrophenol (PMS-HA/Phenol)	3695.81	310.00	1884.43	245.06	59.24	918.04
Nitrosophenol (PMS-HA/Phenol)	62.97	14.40	70.34	5.80	2.74	33.30
2,4-dinitrophenol (nZVI/PS-HP/PNP)	3.18×10^5	9224.71	70682.64	14864.16	1769.82	35489.69
4-amino-3-nitrobenzoic acid (Sonolysis/PAS)	86341.63	40905.72	14412.86	6816.55	2410.10	2521.93
3-amino-4-nitrophenol (Sonolysis/PAS)	316.97	5.12	207.52	68.79	18.47	13.28
2-nitroaniline (Sonolysis/PAS)	3987.05	1.07	9.69	24.60	0.15	12.81
4-hydroxy-3-nitrobenzoic acid (Sonolysis/PAS)	59769.82	4755.60	29242.92	3895.05	909.07	14267.81
N-nitroso-N-phenylaniline (Sonolysis/DPhA)	6.57	0.89	0.56	0.25	0.08	0.20
2-nitro-N-phenylaniline (Sonolysis/DPhA)	1689.25	867.22	425.87	146.61	63.89	89.10
2,4-dinitro-N-phenylaniline (Sonolysis/DPhA)	2.83×10^5	1.17×10^5	23052.06	18945.32	4655.92	2955.10
4-nitro-N-(4-nitrophenyl)aniline (Sonolysis/DPhA)	2.83×10^5	1.17×10^5	23052.06	18945.32	4655.92	2955.10
4-nitro-N-phenylaniline (Sonolysis/DPhA)	1689.25	867.22	425.87	146.61	63.89	89.10

* Acute toxicities based on the European Union criteria (described in Annex VI of Directive

based AOPs. In this case, the one electron oxidation of NH_4^+ ions resulted the formation of $NH_2^\bullet$. These $NH_2^\bullet$ reacts with the O_2 molecule to form the stable aminoperoxy radical ($NH_2O_2^\bullet$). Further reaction of this long-lived species with the reactive species result in the formation of RNs (Eqns 37–43). These processes enhanced the nitro-product formation. Yang et al., reported the formation of nitro-products such as mono-nitro and di-nitro phenols during the degradation of phenolic compounds by the PS based AOPs in the presence of NH_4^+ ion [140].

$\bullet OH + NH_4^+ \rightarrow NH_2^\bullet + H_2O + H^+$ (k = $1.4 \times 10^7 M^{-1} s^{-1}$) [28] (37)

$SO_4^{\bullet -} + NH_4^+ \rightarrow NH_2^\bullet + SO42- + H^+$ (k = $3 \times 10^5 M^{-1} s^{-1}$) [139] (38)

$NH_2^\bullet + NO_2^\bullet \rightarrow N_2O + H_2O$ (39)

$NH_2^\bullet + NO^\bullet \rightarrow N_2 + H_2O$ (40)

$NH_2^\bullet + O_2 \rightarrow NH_2O_2^\bullet$ (41)

$NH_2O_2^\bullet \rightarrow NO^\bullet + H_2O$ (42)

$NO^\bullet + \bullet OH/SO4^{\bullet -} \rightarrow NO_2^\bullet$ (43)

But the halide ions (X⁻) scavenge the primary reactive species $\bullet OH$/$SO_4^{\bullet -}$ to form secondary species ($\bullet X$). These species in turn reacts with the NO$^\bullet$ to form a stronger nucleophilic nitrosatig agent, NOX and

enhance the nitrosation reaction (Eqns 44–46). This is evident from the sonochemical degradation of DPhA and the decomposition of phenol by PS activation by hydroxylamine. In the first case, the Br⁻ ion enhanced the formation of NDPhA and in the latter case the Cl⁻ ion increase the nitrophenol content in the treated solution [59,72].

$\bullet OH/SO_4^{\bullet -} + Br- \rightarrow \bullet BrOH-$ (44)

$\bullet BrOH- \rightarrow \bullet Br + OH–$ (45)

$\bullet Br + NO^\bullet \rightarrow NOBr$ (46)

Like inorganic ions, organic matrix (NOM) also has the prominent role on the radical based water treatment process and the product formation. These NOM can scavenge the reactive species and reduce the degradation rate of parent compounds and affect the intermediate product formation. Ji et al., studied the effect of NOM on the degradation of NPs during the PS based degradation. The NOM reduced the formation of 2,4-DNP due to the scavenging of RNs by the phenolic moieties present in the NOM, which further slowed down the 2,4,6-TNP formation [58].

Important outcome highlighted in this section was that various components present in the real matrix lowered the AOPs effectiveness, but on the other hand it will inhibit formation of hazardous by-products. However, the trend is not uniform in all AOPs that further depends on

the process and the oxidant used. In addition, the rate of nitro-product formation may vary in the presence of complex mixture. Thus, a detailed investigation on the influence of real wastewater matrix on the nitro-product formation in AOPs is a must and a one of challenges for future studies.

7. Environmental impacts of unexpected nitration and their minimisation possibilities

Chemical oxidation processes are widely used to treat the contaminated water and soil. Various AOPs including *in situ* chemical oxidation were studied for treatment of wastewater containing nitrogen derivatives. All these methods are efficient in the successful degradation of the target pollutants as well as for their complete mineralisation. However, incomplete mineralisation led to the release of intermediate products as some of the products are more toxic than the parent compound. Chlorinated and nitrated by-products are generally more toxic compared to primary pollutant and their formation needs to be avoided in this kind of processes. However, in many studies chlorinated and nitrated by-products were formed as oxidation by-products during the oxidative degradation in the presence of Cl^- and NO_2^- [21–24].

Many pollutants (pharmaceuticals, dyes, pesticides, etc) contain nitrogen in their structure either attached to the side chain (primary) or azo group, nitro group or in heterocyclic ring. The oxidative cleavage leads to the release of ammonia or nitrate ions depending on the attached functional groups. The released ammonia or nitrate ions can further be converted into nitrite/nitrate ions. Lopez et al., have reported 14 % and 16% of nitrogen from 5-methyl-1,3,4-thiadiazole-2-thiol (MMTD), 5-methyl-1,3,4-thiadiazole-2-methylthiol (Me-MMTD), respectively, was recovered as nitrate during their degradation by UV/H_2O_2 photolysis [141,142]. Photocatalytic degradation of sulfonamide drugs such as sulfa dimethoxine, sulfa merazine and sulfathiazole leads to the 70%, 18%, and 90% recovery of nitrogen [143]. The release of NH_4^+ indicates the breakage of heterocyclic ring present in these compounds. Electrochemical oxidation of pharmaceuticals like paracetamol, and sulfachloropyridazine also release nitrogen as ammonia and nitrate ions [53,144,145]. Sonochemical degradation of pharmaceuticals like atenolol, PAS, released nitrite, nitrate and ammonium ions [25,47]. Moreover, their interference on the further degradation/transformation of the parent pollutants is not addressed well. In addition, in case of real aqueous matrix, there could be many nitrogens based ionic species including the ammonium. Being a radical process, AOPs can initiate several RNs in the presence of these species. It has been reported that nitrate and nitrite ions acts as sensitizers and undergo photolysis under the natural conditions to form RNs and ROS and further contribute to the transformation of parent compounds to nitro-products [24]. Many pharmaceuticals such as sulfamethoxazole, many beta blockers undergo nitration/nitrosation reactions to produce toxic, carcinogenic and mutagenic nitrated/nitrosated products [33,146].

The nitro-products are reported to be the precursors of nitrogeneous disinfection by-products (N-DBPs) [147,148]. Like the parent pollutants, N-DBPs also gained an increasing attention as they shown adverse health effects. Toxicological studies revealed that some of the N-DBPs cause cancer, liver diseases, reproductive problems etc [149]. N-DBPs are generally formed by the reaction of disinfectants, such as chlorine, chloramines, chlorine dioxide, etc., with NOM, inorganic ions and many other pollutants [150,151]. Inorganic ions like nitrite ions lead to the formation of many nitrated products during the degradation/disinfection products. The nitrated products act as the precursor of many N-DBPs [152]. Therefore, special consideration also should be given to the oxidative degradation of N-containing compounds and to verify if the primary pollutants get mineralised without any nitro by-products remaining in the medium after treatment process.

As given in the previous sections, the key species in the unexpected nitro-product formation are the nitrite ions. Therefore, to minimise the formation of nitro-product the nitrite ion generation should be controlled. The coupling of more than one AOPs would be an option to minimise the nitro-product formation. Electrochemical methods and ozonolysis are an important choice in this aspect [153–155]. Electrochemical AOPs (EAOPs) provided rapid oxidation of parent compounds and minimisation of their inter-crossing reaction with the released ions. Another important advantage of EAOP is that the *in situ* generated nitrite ions could be oxidised to nitrate ions at the electrode surface. Another oxidant, ozone is effective in oxidising the NO_2^- to nitrate ions. This may reduce the generation of RNs. Thus, it is proposed that hybrid process such as sono-EAOP, sono-ozonolysis, PS-EAOP, PS-Ozonolysis, etc, will be effective in minimising the unexpected nitration of the pollutants during their oxidative degradation.

8. Conclusions

This review made an effort to understand the mechanisms of unexpected nitro-product formation and its environmental impacts during the oxidative degradation of pollutants via AOPs. Denitration and the subsequent renitration of the nitrophenols were the major mechanism for the nitro product formation in most of the AOPs including persulfate-based methods. While the nitrite ion is released from the hydroxylamine by the reaction with oxidants, it leads to the nitro-products formation for phenolic products in hydroxylamine-based water treatment. This product further leads to the formation of another toxic products N-DBPs.

After review of wide variety of papers on AOPs as material for this manuscript, it must be stated that the risk of nitro-products formation is currently not included in most of the studies. Highlighted in these papers mechanisms clearly indicate that this aspect must be evaluated in case of serious and comprehensive research articles. Nitro-products can be controlled by several modern analytical techniques. Even simple HPLC system equipped with UV diode array detector will provide first tentative information about their presence in post-processed samples. Other approach that could be included in process control is determination of nitrite and nitrate ions and the determination of nitrogen mass balance during degradation. It is possible to apply simple analysis via spectrometric colorimetric tests or by ion chromatography.

To further trace reports on unexpected nitro-products formation, future papers should focus on aspects of aeration of processed samples comparing to application of inert gas, as it was reported that removal of oxygen and nitrogen allows to minimize this undesired effect. Most of the reviewed studies were performed for model wastewater, currently the literature lacks of data about nitro-products formation in real case scenario. On the other hand, the individual components of real wastewater matrix had some effect on the undesirable nitration phenomenon. The HCO_3^- inhibited the nitration process, but on the other hand halide ions increased the nitration reaction.

Finally, nitro-products are known to be often toxic. Thus, in case of risks on their presence in water or wastewater after treatment, a toxicity tests should be performed to prove that formed by-products are not more toxic comparing to primary pollutants. Well addressed above mentioned aspects should allow to obtain in next few years deeper knowledge about nitro-product formation during AOP water and wastewater treatment.

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.

Acknowledgements

References

[1] A.O. Ibrahim, K.A. Adegoke, R.O. Adegoke, Y.A. AbdulWahab, V.B. Oyelami, M. O. Adesina, Adsorptive removal of different pollutants using metal-organic framework adsorbents, J. Mol. Liq. 333 (2021), 115593.

[2] M.l. Farré, S. Pérez, L. Kantiani, D. Barceló, Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment, TrAC -, Trends Anal. Chem. 27 (2008) 991–1007.

[3] M. Edelstein, M. Ben-Hur, Heavy metals and metalloids: Sources, risks and strategies to reduce their accumulation in horticultural crops, Sci. Hortic. 234 (2018) 431–444.

[4] P. Chowdhury, T. Viraraghavan, Sonochemical degradation of chlorinated organic compounds, phenolic compounds and organic dyes – A review, Sci. Total Environ. 407 (2009) 2474–2492.

[5] R. Chow, R. Scheidegger, T. Doppler, A. Dietzel, F. Fenicia, C. Stamm, A review of long-term pesticide monitoring studies to assess surface water quality trends, Water Res. X 9 (2020), 100064.

[6] M. Patel, R. Kumar, K. Kishor, T. Mlsna, C.U. Pittman, D. Mohan, Pharmaceuticals of Emerging Concern in Aquatic Systems: Chemistry, Occurrence, Effects, and Removal Methods, Chem. Rev. 119 (2019) 3510–3673.

[7] M.R. Heidari, M. Malakootian, G. Boczkaj, X. Sun, Y. Tao, S.H. Sonawane, H. Mehdizadeh, Evaluation and start-up of an electro-Fenton-sequencing batch reactor for dairy wastewater treatment, Water Resour. Ind. 25 (2021), 100149.

[8] N. Filipowicz, M. Momotko, G. Boczkaj, H. Cieśliński, Determination of phenol biodegradation pathways in three psychrotolerant yeasts, Candida subhashii A011, Candida oregonensis B021 and Schizoblastosporion starkeyi-henricii L012, isolated from Rucianka peatland, Enzyme Microb. Technol. 141 (2020), 109663.

[9] V. Homem, L. Santos, Degradation and removal methods of antibiotics from aqueous matrices – A review, J. Environ. Manag. 92 (2011) 2304–2347.

[10] JIAN.LONG. WANG, LE.JIN. XU, Advanced Oxidation Processes for Wastewater Treatment: Formation of Hydroxyl Radical and Application, Crit. Rev. Environ. Sci. Technol. 42 (3) (2012) 251–325.

[11] G. Boczkaj, P. Makoś, A. Fernandes, A. Przyjazny, New procedure for the examination of the degradation of volatile organonitrogen compounds during the treatment of industrial effluents, J. Sep. Sci. 40 (2017) 1301–1309.

[12] G. Boczkaj, A. Przyjazny, M. Kamiński, New Procedures for Control of Industrial Effluents Treatment Processes, Ind. Eng. Chem. Res. 53 (2014) 1503–1514.

[13] Y. Fu, L. Wang, W. Peng, Q. Fan, Q. Li, Y. Dong, Y. Liu, G. Boczkaj, Z. Wang, Enabling simultaneous redox transformation of toxic chromium(VI) and arsenic (III) in aqueous media—A review, J. Hazard. Mater. 417 (2021), 126041.

[14] A. Fernandes, P. Makoś, Z. Wang, G. Boczkaj, Synergistic effect of TiO2 photocatalytic advanced oxidation processes in the treatment of refinery effluents, Chem. Eng. J. 391 (2020), 123488.

[15] G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review, Chem. Eng. J. 320 (2017) 608–633.

[16] V.K. Landge, S.H. Sonawane, M. Sivakumar, S.S. Sonawane, G. Uday Bhaskar Babu, G. Boczkaj, S-scheme heterojuction Bi2O3-ZnO/Bentonite clay composite with enhanced photocatalytic performance, Sustain. Energy Technol. Assess. 45 (2021), 101194.

[17] M. Sayed, A. Khan, S. Rauf, N.S. Shah, F. Rehman, A.A. Al-Kahtani, J.A. Khan, J. Iqbal, G. Boczkaj, I. Gul, M. Bushra, Bismuth-Doped Nano Zerovalent Iron: A Novel Catalyst for Chloramphenicol Degradation and Hydrogen Production, ACS Omega 5 (2020) 30610–30624.

[18] G. Boczkaj, A. Fernandes, P. Makoś, Study of Different Advanced Oxidation Processes for Wastewater Treatment from Petroleum Bitumen Production at Basic pH, Ind. Eng. Chem. Res. 56 (2017) 8806–8814.

[19] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84.

[20] R. Yuan, Z. Jiang, Z. Wang, S. Gao, Z. Liu, M. Li, G. Boczkaj, Hierarchical MnO2 nanoflowers blooming on 3D nickel foam: A novel micro-macro catalyst for peroxymonosulfate activation, J. Colloid Interface Sci. 571 (2020) 142–154.

[21] I.A. Ike, T. Karanfil, J. Cho, J. Hur, Oxidation byproducts from the degradation of dissolved organic matter by advanced oxidation processes – A critical review, Water Res. 164 (2019), 114929.

[22] A. Sharma, J. Ahmad, S.J.S. Flora, Application of advanced oxidation processes and toxicity assessment of transformation products, Environ. Res. 167 (2018) 223–233.

[23] D. Fatta-Kassinos, M.I. Vasquez, K. Kümmerer, Transformation products of pharmaceuticals in surface waters and wastewater formed during photolysis and advanced oxidation processes – Degradation, elucidation of byproducts and assessment of their biological potency, Chemosphere 85 (2011) 693–709.

[24] Y. Wu, L. Bu, X. Duan, S. Zhu, M. Kong, N. Zhu, S. Zhou, Mini review on the roles of nitrate/nitrite in advanced oxidation processes: Radicals transformation and products formation, J. Clean. Prod. 273 (2020), 123065.

[25] M.P. Rayaroth, U.K. Aravind, C.T. Aravindakumar, Role of in-situ nitrite ion formation on the sonochemical transformation of para-aminosalicylic acid, Ultrason. Sonochem. 40 (2018) 213–220.

[26] F.C. Fang, Antimicrobial reactive oxygen and nitrogen species: concepts and controversies, Nat. Rev. Microbiol. 2 (10) (2004) 820–832.

[27] S. Goldstein, J. Rabani, Mechanism of Nitrite Formation by Nitrate Photolysis in Aqueous Solutions: The Role of Peroxynitrite, Nitrogen Dioxide, and Hydroxyl Radical, J. Am. Chem. Soc. 129 (2007) 10597–10601.

[28] P. Neta, R.E. Huie, A.B. Ross, Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution, J. Phys. Chem. Ref. Data 17 (1988) 1027–1284.

[29] A. Kroflič, M. Huš, M. Grilc, I. Grgić, Underappreciated and Complex Role of Nitrous Acid in Aromatic Nitration under Mild Environmental Conditions: The Case of Activated Methoxyphenols, Environ. Sci. Technol. 52 (23) (2018) 13756–13765.

[30] P. Attri, Y.H. Kim, D.H. Park, J.H. Park, Y.J. Hong, H.S. Uhm, K.-N. Kim, A. Fridman, E.H. Choi, Generation mechanism of hydroxyl radical species and its lifetime prediction during the plasma-initiated ultraviolet (UV) photolysis, Sci. Rep. 5 (2015) 9332.

[31] G. Marussi, D. Vione, Secondary Formation of Aromatic Nitroderivatives of Environmental Concern: Photonitration Processes Triggered by the Photolysis of Nitrate and Nitrite Ions in Aqueous Solution, Molecules 26 (2021) 2550.

[32] Y. Huang, M. Kong, D. Westerman, E.G. Xu, S. Coffin, K.H. Cochran, Y. Liu, S. D. Richardson, D. Schlenk, D.D. Dionysiou, Effects of HCO3– on Degradation of Toxic Contaminants of Emerging Concern by UV/NO3–, Environ. Sci. Technol. 52 (2018) 12697–12707.

[33] R.C. Scholes, C. Prasse, D.L. Sedlak, The Role of Reactive Nitrogen Species in Sensitized Photolysis of Wastewater-Derived Trace Organic Contaminants, Environ. Sci. Technol. 53 (2019) 6483–6491.

[34] D. Vione, V. Maurino, C. Minero, E. Pelizzetti, Nitration and Photonitration of Naphthalene in Aqueous Systems, Environ. Sci. Technol. 39 (2005) 1101–1110.

[35] L. Oliviero, J. Barbier, D. Duprez, Wet Air Oxidation of nitrogen-containing organic compounds and ammonia in aqueous media, Appl. Catal. B: Environ. 40 (2003) 163–184.

[36] A.P. Bhat, P.R. Gogate, Degradation of nitrogen-containing hazardous compounds using advanced oxidation processes: A review on aliphatic and aromatic amines, dyes, and pesticides, J. Hazard. Mater. 403 (2021), 123657.

[37] R. Fatima, M.N. Afridi, V. Kumar, J. Lee, I. Ali, K.-H. Kim, J.-O. Kim, Photocatalytic degradation performance of various types of modified TiO2 against nitrophenols in aqueous systems, J. Clean. Prod. 231 (2019) 899–912.

[38] Z. Xiong, H. Zhang, W. Zhang, B. Lai, G. Yao, Removal of nitrophenols and their derivatives by chemical redox: A review, Chem. Eng. J. 359 (2019) 13–31.

[39] O. Drzyzga, Diphenylamine and derivatives in the environment: a review, Chemosphere 53 (8) (2003) 809–818.

[40] K. Christen, Sci. Technol. 35 (9) (2001) 184A–185A.

[41] Tuberculosis 88 (2008) 137–138.

[42] N. Oturan, C.T. Aravindakumar, H. Olvera-Vargas, M.M. Sunil Paul, M.A. Oturan, Electro-Fenton oxidation of para-aminosalicylic acid: degradation kinetics and mineralization pathway using Pt/carbon-felt and BDD/carbon-felt cells, Environ. Sci. Pollut. Res. 25 (2018) 20363–20375.

[43] S. Hisaindee, M.A. Meetani, M.A. Rauf, Application of LC-MS to the analysis of advanced oxidation process (AOP) degradation of dye products and reaction mechanisms, TrAC -, Trends Anal. Chem. 49 (2013) 31–44.

[44] W.J. Cooper, C.J. Cramer, N.H. Martin, S.P. Mezyk, K.E. O'Shea, C.v. Sonntag, Free Radical Mechanisms for the Treatment of Methyl tert-Butyl Ether (MTBE) via Advanced Oxidation/Reductive Processes in Aqueous Solutions, Chem. Rev. 109 (2009) 1302–1345.

[45] M.P. Rayaroth, U.K. Aravind, C.T. Aravindakumar, Degradation of pharmaceuticals by ultrasound-based advanced oxidation process, Environ. Chem. Lett. 14 (2016) 259–290.

[46] P. Liu, Z. Wu, A.V. Abramova, G. Cravotto, Sonochemical processes for the degradation of antibiotics in aqueous solutions: A review, Ultrason. Sonochem. 74 (2021) 105566, https://doi.org/10.1016/j.ultsonch.2021.105566.

[47] K.K. Nejumal, P.R. Manoj, U. Aravind, C.T. Aravindakumar, Sonochemical degradation of a pharmaceutical waste, atenolol, in aqueous medium, Environ. Sci. Pollut. Res. 21 (2014) 4297–4308.

[48] S. Sasi, M.P. Rayaroth, D. Devadasan, U.K. Aravind, C.T. Aravindakumar, Influence of inorganic ions and selected emerging contaminants on the degradation of Methylparaben: A sonochemical approach, J. Hazard. Mater. 300 (2015) 202–209.

[49] E. Szabó-Bárdos, O. Markovics, O. Horváth, N. Törő, G. Kiss, Photocatalytic degradation of benzenesulfonate on colloidal titanium dioxide, Water Res. 45 (2011) 1617–1628.

[50] E. Lipczynska-Kochany, Degradation of nitrobenzene and nitrophenols by means of advanced oxidation processes in a homogeneous phase: Photolysis in the presence of hydrogen peroxide versus the Fenton reaction, Chemosphere 24 (1992) 1369–1380.

[51] M.P. Rayaroth, U.K. Aravind, C.T. Aravindakumar, Effect of inorganic ions on the ultrasound initiated degradation and product formation of triphenylmethane dyes, Ultrason. Sonochem. 48 (2018) 482–491.

[52] J. Peller, O. Wiest, P.V. Kamat, Mechanism of Hydroxyl Radical-Induced Breakdown of the Herbicide 2,4-Dichlorophenoxyacetic Acid (2,4-D), Chemistry – A, European Journal 9 (21) (2003) 5379–5387.

[53] A. Dirany, I. Sirés, N. Oturan, A. Özcan, M.A. Oturan, Electrochemical Treatment of the Antibiotic Sulfachloropyridazine: Kinetics, Reaction Pathways, and Toxicity Evolution, Environ. Sci. Technol. 46 (7) (2012) 4074–4082.

[54] E. Szabó-Bárdos, Z. Zsilák, G. Lendvay, O. Horváth, O. Markovics, A. Hoffer, N. Törő, Photocatalytic Degradation of 1,5-Naphthalenedisulfonate on Colloidal Titanium Dioxide, J. Phys. Chem. B 112 (46) (2008) 14500–14508.

[55] A. Agüera, María.Jesús. Martínez Bueno, A.R. Fernández-Alba, New trends in the analytical determination of emerging contaminants and their transformation products in environmental waters, Environ. Sci. Pollut. Res. 20 (6) (2013) 3496–3515.

[56] D. Panda, B.P. Dash, S. Manickam, G. Boczkaj, Recent advancements in LC-MS based analysis of biotoxins: Present and future challenges, Mass Spec, Rev, 2021.

[57] M.W. Lam, S.A. Mabury, Photodegradation of the pharmaceuticals atorvastatin, carbamazepine, levofloxacin, and sulfamethoxazole in natural waters, Aquat. Sci. 67 (2) (2005) 177–188.

[58] Y. Ji, Y. Shi, Y. Yang, P. Yang, L. Wang, J. Lu, J. Li, L. Zhou, C. Ferronato, J.-M. Chovelon, Rethinking sulfate radical-based oxidation of nitrophenols: Formation of toxic polynitrophenols, nitrated biphenyls and diphenyl ethers, J. Hazard. Mater. 361 (2019) 152–161.

[59] J. Yao, H. Zhang, L. Chen, W. Liu, N. Gao, S. Liu, X. Chen, F. Rao, The Roles of Sono-induced Nitrosation and Nitration in the Sono-degradation of Diphenylamine in Water: Mechanisms, Kinetics and Impact Factors, J. Hazard. Mater. 402 (2021) 123720, https://doi.org/10.1016/j.jhazmat.2020.123720.

[60] Y. Ji, Y. Shi, D. Kong, J. Lu, Degradation of roxarsone in a sulfate radical mediated oxidation process and formation of polynitrated by-products, RSC Adv. 6 (85) (2016) 82040–82048.

[61] O. Laprévote, P. Ducrot, C. Thal, L. Serani, B.C. Das, Stereochemistry of Electrosprayed Ions. Indoloquinolizidine Derivatives, J. Mass Spec. 31 (1996) 1149–1155.

[62] D. Lemaire, L. Serani, O. Laprévote, V. Ovcharenko, K. Pihlaja, G. Stájer, Energy-resolved electrospray mass spectrometry of diexo-norbornane and norbornene derivatives containing a fused, phenyl-substituted, 1,3-oxazine ring: competitive retro-Diels–Alder fragmentation processes, Eur. J. Mass Spec. 5 (1999) 253–257.

[63] A.B. Attygalle, J. Ruzicka, D. Varughese, J.B. Bialecki, S. Jafri, Low-energy collision-induced fragmentation of negative ions derived from ortho-, meta-, and para-hydroxyphenyl carbaldehydes, ketones, and related compounds, J. Mass Spec. 42 (2007) 1207–1217.

[64] A. Halasz, J. Hawari, N.N. Perreault, New Insights into the Photochemical Degradation of the Insensitive Munition Formulation IMX-101 in Water, Environ. Sci. Technol. 52 (2018) 589–596.

[65] L. Carlos, D. Fabbri, A.L. Capparelli, A.B. Prevot, E. Pramauro, F.S.G. Einschlag, Intermediate distributions and primary yields of phenolic products in nitrobenzene degradation by Fenton's reagent, Chemosphere 72 (2008) 952–958.

[66] L. Carlos, D. Nichela, J.M. Triszcz, J.I. Felice, F.S. García Einschlag, Nitration of nitrobenzene in Fenton's processes, Chemosphere 80 (2010) 340–345.

[67] Y. Yang, Y. Ji, P. Yang, L. Wang, J. Lu, C. Ferronato, J.-M. Chovelon, UV-activated persulfate oxidation of the insensitive munitions compound 2,4-dinitroanisole in water: Kinetics, products, and influence of natural photoinducers, J. Photochem. Photobiol. A: Chem. 360 (2018) 188–195.

[68] Y. Ji, Y. Shi, L. Wang, J. Lu, Denitration and renitration processes in sulfate radical-mediated degradation of nitrobenzene, Chem. Eng. J. 315 (2017) 591–597.

[69] X. Chen, M. Murugananthan, Y. Zhang, Degradation of p-Nitrophenol by thermally activated persulfate in soil system, Chem. Eng. J. 283 (2016) 1357–1365.

[70] M. Zhang, X. Chen, H. Zhou, M. Murugananthan, Y. Zhang, Degradation of p-nitrophenol by heat and metal ions co-activated persulfate, Chem. Eng. J. 264 (2015) 39–47.

[71] C. Chen, L. Liu, Y. Li, L. Zhou, Y. Lan, Efficient degradation of roxarsone and simultaneous in-situ adsorption of secondary inorganic arsenic by a combination of Co3O4-Y2O3 and peroxymonosulfate, J. Hazard. Mater. 407 (2021) 124559, https://doi.org/10.1016/j.jhazmat.2020.124559.

[72] Z. Dong, C. Jiang, J. Duan, J. Jiang, S.-yan. Pang, Y. Zhou, Y. Gao, Z. Wang, J. Li, Q. Guo, Formation of nitrosated and nitrated aromatic products of concerns in the treatment of phenols by the combination of peroxymonosulfate and hydroxylamine, Chemosphere 282 (2021) 131057, https://doi.org/10.1016/j.chemosphere.2021.131057.

[73] J. Du, Y. Wang, F. Faheem, T. Xu, H. Zheng, J. Bao, Bao, Synergistic degradation of PNP via coupling H2O2 with persulfate catalyzed by nano zero valent iron, RSC Adv. 9 (35) (2019) 20323–20331.

[74] M. Gągol, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based on cavitation – A review, Chem. Eng. J. 338 (2018) 599–627.

[75] X. Sun, W. You, X. Xuan, L. Ji, X. Xu, G. Wang, S. Zhao, G. Boczkaj, J.Y. Yoon, S. Chen, Effect of the cavitation generation unit structure on the performance of an advanced hydrodynamic cavitation reactor for process intensifications, Chem. Eng. J. 412 (2021) 128600, https://doi.org/10.1016/j.cej.2021.128600.

[76] E. Cako, K.D. Gunasekaran, R.D. Cheshmeh Soltani, G. Boczkaj, Ultrafast degradation of brilliant cresyl blue under hydrodynamic cavitation based advanced oxidation processes (AOPs), Water Resour, Ind. 24 (2020), 100134.

[77] K. Makino, M.M. Mossoba, P. Riesz, Chemical effects of ultrasound on aqueous solutions. Evidence for hydroxyl and hydrogen free radicals (.cntdot.OH and. cntdot.H) by spin trapping, J. Am. Chem. Soc. 104 (1982) 3537–3539.

[78] M. Gągol, E. Cako, K. Fedorov, R.D.C. Soltani, A. Przyjazny, G. Boczkaj, Hydrodynamic cavitation based advanced oxidation processes: Studies on specific effects of inorganic acids on the degradation effectiveness of organic pollutants, J. Mol. Liq. 307 (2020), 113002.

[79] R.D.C. Soltani, Z. Miraftabi, M. Mahmoudi, S. Jorfi, G. Boczkaj, A. Khataee, Stone cutting industry waste-supported zinc oxide nanostructures for ultrasonic assisted decomposition of an anti-inflammatory non-steroidal pharmaceutical compound, Ultrason. Sonochem. 58 (2019), 104669.

[80] K. Fedorov, X. Sun, G. Boczkaj, Combination of hydrodynamic cavitation and SR-AOPs for simultaneous degradation of BTEX in water, Chem. Eng. J. 417 (2021), 128081.

[81] M. Gągol, R.D.C. Soltani, A. Przyjazny, G. Boczkaj, Effective degradation of sulfide ions and organic sulfides in cavitation-based advanced oxidation processes (AOPs), Ultrason. Sonochem. 58 (2019), 104610.

[82] M. Gągol, A. Przyjazny, G. Boczkaj, Effective method of treatment of industrial effluents under basic pH conditions using acoustic cavitation – A comprehensive comparison with hydrodynamic cavitation processes, Chemical Engineering and Processing - Process Intensification 128 (2018) 103–113.

[83] R.D.C. Soltani, M. Mashayekhi, M. Naderi, G. Boczkaj, S. Jorfi, M. Safari, Sonocatalytic degradation of tetracycline antibiotic using zinc oxide nanostructures loaded on nano-cellulose from waste straw as nanosonocatalyst, Ultrason. Sonochem. 55 (2019) 117–124.

[84] M.P. Rayaroth, U.K. Aravind, C.T. Aravindakumar, Sonochemical degradation of Coomassie Brilliant Blue: Effect of frequency, power density, pH and various additives, Chemosphere 119 (2015) 848–855.

[85] H. Cao, W. Zhang, C. Wang, Y. Liang, Sonochemical degradation of poly- and perfluoroalkyl substances – A review, Ultrason. Sonochem. 69 (2020), 105245.

[86] A.V. Mohod, P.R. Gogate, Ultrasonic degradation of polymers: Effect of operating parameters and intensification using additives for carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA), Ultrason. Sonochem. 18 (3) (2011) 727–734.

[87] A.I. Virtanen, N. Ellfolk, NITROGEN FIXATION IN AN ULTRASONIC FIELD, J. Am. Chem. Soc. 72 (2) (1950) 1046–1047.

[88] V. Míšík, P. Riesz, Nitric Oxide Formation by Ultrasound in Aqueous Solutions, J. of Phys. Chem. 100 (45) (1996) 17986–17994.

[89] Supeno, P. Kruus, Kruus, Fixation of nitrogen with cavitation, Ultrason. Sonochem. 9 (1) (2002) 53–59.

[90] J. Yao, L. Chen, X. Chen, L. Zhou, W. Liu, Z. Zhang, Formation of inorganic nitrogenous byproducts in aqueous solution under ultrasound irradiation, Ultrason. Sonochem. 42 (2018) 42–47.

[91] C.A. Wakeford, R. Blackburn, P.D. Lickiss, Effect of ionic strength on the acoustic generation of nitrite, nitrate and hydrogen peroxide, Ultrason. Sonochem. 6 (3) (1999) 141–148.

[92] H.S. Glick, J.J. Klein, W. Squire, Single-Pulse Shock Tube Studies of the Kinetics of the Reaction N2+O2⇌2NO between 2000–3000°K, The Journal of Chemical Physics 27 (4) (1957) 850–857.

[93] L.-M. Kwedi-Nsah, T. Kobayashi, Sonochemical nitrogen fixation for the generation of NO2− and NO3− ions under high-powered ultrasound in aqueous medium, Ultrason. Sonochem. 66 (2020) 105051, https://doi.org/10.1016/j.ultsonch.2020.105051.

[94] E.N. Harvey, Sonoluminescence and Sonic Chemiluminescence, J. Am. Chem. Soc. 61 (9) (1939) 2392–2398.

[95] J. Lee, M. Ashokkumar, S. Kentish, F. Grieser, Determination of the Size Distribution of Sonoluminescence Bubbles in a Pulsed Acoustic Field, J. Am. Chem. Soc. 127 (48) (2005) 16810–16811.

[96] M. Wall, M. Ashokkumar, R. Tronson, F. Grieser, Multibubble sonoluminescence in aqueous salt solutions, Ultrason. Sonochem. 6 (1-2) (1999) 7–14.

[97] L. Yang, J.Z. Sostaric, J.F. Rathman, L.K. Weavers, Effect of Ultrasound Frequency on Pulsed Sonolytic Degradation of Octylbenzene Sulfonic Acid, J. Phys. Chem. B 112 (3) (2008) 852–858.

[98] C. Petrier, A. Jeunet, J.L. Luche, G. Reverdy, Unexpected frequency effects on the rate of oxidative processes induced by ultrasound, J. Am. Chem. Soc. 114 (8) (1992) 3148–3150.

[99] D. Sunartio, M. Ashokkumar, F. Grieser, Study of the Coalescence of Acoustic Bubbles as a Function of Frequency, Power, and Water-Soluble Additives, J. Am. Chem. Soc. 129 (18) (2007) 6031–6036.

[100] W. Xie, Y. Qin, D. Liang, D. Song, D. He, Degradation of m-xylene solution using ultrasonic irradiation, Ultrason. Sonochem. 18 (5) (2011) 1077–1081.

[101] C. Lee, J. Yoon, UV-A induced photochemical formation of N-nitrosodimethylamine (NDMA) in the presence of nitrite and dimethylamine, J. Photochem. Photobiol. A: Chem. 189 (2007) 128–134.

[102] E. Barnes, CCCLXIII.—The action of nitric oxide on alkaline hydroxides, Journal of the Chemical Society (Resumed) 0 (0) (1931) 2605–2620.

[103] I.M. Kolthoff, I.K. Miller, The Chemistry of Persulfate. I. The Kinetics and Mechanism of the Decomposition of the Persulfate Ion in Aqueous Medium1, J. Am. Chem. Soc. 73 (1951) 3055–3059.

[104] J. Wang, S. Wang, Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants, Chem. Eng. J. 334 (2018) 1502–1517.

[105] M.P. Rayaroth, C.-S. Lee, U.K. Aravind, C.T. Aravindakumar, Y.-S. Chang, Oxidative degradation of benzoic acid using Fe0- and sulfidized Fe0-activated persulfate: A comparative study, Chem. Eng. J. 315 (2017) 426–436.

[106] M.P. Rayaroth, D. Oh, C.-S. Lee, Y.-G. Kang, Y.-S. Chang, In situ chemical oxidation of contaminated groundwater using a sulfidized nanoscale zerovalent iron–persulfate system: Insights from a box-type study, Chemosphere 257 (2020), 127117.

[107] M.-W. Zhang, K.-Y.-A. Lin, C.-F. Huang, S. Tong, Enhanced degradation of toxic azo dye, amaranth, in water using Oxone catalyzed by MIL-101-NH2 under visible light irradiation, Sep. Purif. Technol. 227 (2019), 115632.

[108] Y. Qian, X. Guo, Y. Zhang, Y. Peng, P. Sun, C.-H. Huang, J. Niu, X. Zhou, J.C. Crittenden, Perfluorooctanoic Acid Degradation Using UV–Persulfate Process: Modeling of the Degradation and Chlorate Formation, Environ. Sci. Technol. 50 (2016) 772–781.

[109] R.H. Waldemer, P.G. Tratnyek, R.L. Johnson, J.T. Nurmi, Oxidation of Chlorinated Ethenes by Heat-Activated Persulfate: Kinetics and Products, Environ. Sci. Technol. 41 (2007) 1010–1015.

[110] K. Fedorov, M. Plata-Gryl, J.A. Khan, G. Boczkaj, Ultrasound-assisted heterogeneous activation of persulfate and peroxymonosulfate by asphaltenes for the degradation of BTEX in water, J. Hazard. Mater. 397 (2020), 122804.

[111] R.D.C. Soltani, M. Mahmoudi, G. Boczkaj, A. Khataee, Activation of peroxymonosulfate using carbon black nano-spheres/calcium alginate hydrogel

matrix for degradation of acetaminophen: Fe3O4 co-immobilization and microbial community response, Journal of Industrial and Engineering Chemistry 91 (2020) 240–251.

[112] A. Fernandes, P. Makoś, J.A. Khan, G. Boczkaj, Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based advanced oxidation processes, J. Clean. Prod. 208 (2019) 54–64.

[113] N.S. Shah, J.A. Khan, M. Sayed, Z.U.H. Khan, A.D. Rizwan, N. Muhammad, G. Boczkaj, B. Murtaza, M. Imran, H.M. Khan, G. Zaman, Solar light driven degradation of norfloxacin using as-synthesized Bi3+ and Fe2+ co-doped ZnO with the addition of HSO5−: Toxicities and degradation pathways investigation, Chem. Eng. J. 351 (2018) 841–855.

[114] R. Yuan, M. Jiang, S. Gao, Z. Wang, H. Wang, G. Boczkaj, Z. Liu, J. Ma, Z. Li, 3D mesoporous α-Co(OH)2 nanosheets electrodeposited on nickel foam: A new generation of macroscopic cobalt-based hybrid for peroxymonosulfate activation, Chem. Eng. J. 380 (2020), 122447.

[115] J. Duan, S.-yan. Pang, Z. Wang, Y. Zhou, Y. Gao, J. Li, Q. Guo, J. Jiang, Hydroxylamine driven advanced oxidation processes for water treatment: A review, Chemosphere 262 (2021) 128390, https://doi.org/10.1016/j. chemosphere.2020.128390.

[116] J. Lind, G. Merényi, Kinetic and Thermodynamic Properties of the Aminoxyl (NH2O•) Radical, J. Phys. Chem. A 110 (2006) 192–197.

[117] M.D. Johnson, B.J. Hornstein, The Kinetics and Mechanism of the Ferrate(VI) Oxidation of Hydroxylamines, Inorganic Chemistry 42 (2003) 6923–6928.

[118] R.A. Robinson, V.E. Bower, THE IONIZATION CONSTANT OF HYDROXYLAMINE, J. Phys. Chem. 65 (1961) 1279–1280.

[119] J.O. Tijani, O.O. Fatoba, L.F. Petrik, A Review of Pharmaceuticals and Endocrine-Disrupting Compounds: Sources, Effects, Removal, and Detections, Water Air and Soil Pollution 224 (2013).

[120] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B-Environ. 47 (4) (2004) 219–256.

[121] B.A. Wols, C.H.M. Hofman-Caris, Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water, Water Res. 46 (9) (2012) 2815–2827.

[122] P.V. Nidheesh, Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review, RSC Adv. 5 (51) (2015) 40552–40577.

[123] A. Dhakshinamoorthy, S. Navalon, M. Alvaro, H. Garcia, Metal Nanoparticles as Heterogeneous Fenton Catalysts, ChemSusChem 5 (1) (2012) 46–64.

[124] Venny, S. Gan, H.K. Ng, Ng, Current status and prospects of Fenton oxidation for the decontamination of persistent organic pollutants (POPs) in soils, Chem. Eng. J. 213 (2012) 295–317.

[125] E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry, Chem. Rev. 109 (12) (2009) 6570–6631.

[126] X.-J. Yang, X.-M. Xu, J. Xu, Y.-F. Han, Iron Oxychloride (FeOCl): An Efficient Fenton-Like Catalyst for Producing Hydroxyl Radicals in Degradation of Organic Contaminants, J. Am. Chem. Soc. 135 (2013) 16058–16061.

[127] Y. Ji, L. Wang, M. Jiang, J. Lu, C. Ferronato, J.-M. Chovelon, The role of nitrite in sulfate radical-based degradation of phenolic compounds: An unexpected nitration process relevant to groundwater remediation by in-situ chemical oxidation (ISCO), Water Res. 123 (2017) 249–257.

[128] P. Yang, L. Qian, Y. Cheng, Y. Ji, J. Lu, D. Kong, Formation of nitrophenolic byproducts in soils subjected to sulfate radical oxidation, Chem. Eng. J. 403 (2021), 126316.

[129] P. Yang, Y. Ji, J. Lu, Q. Huang, Formation of Nitrophenolic Byproducts during Heat-Activated Peroxydisulfate Oxidation in the Presence of Natural Organic Matter and Nitrite, Environ. Sci. Technol. 53 (2019) 4255–4264.

[130] H.O.N. Tugaoen, S. Garcia-Segura, K. Hristovski, P. Westerhoff, Challenges in photocatalytic reduction of nitrate as a water treatment technology, Sci. Total Environ. 599–600 (2017) 1524–1551.

[131] A.D. Shah, A.D. Dotson, K.G. Linden, W.A. Mitch, Impact of UV Disinfection Combined with Chlorination/Chloramination on the Formation of Halonitromethanes and Haloacetonitriles in Drinking Water, Environ. Sci. Technol. 45 (2011) 3657–3664.

[132] Z. She, M. Gao, C. Jin, Y. Chen, J. Yu, Toxicity and biodegradation of 2,4-dinitrophenol and 3-nitrophenol in anaerobic systems, Proc. Biochem. 40 (2005) 3017–3024.

[133] B.A. Donlon, E. Razo-Flores, J.A. Field, G. Lettinga, Toxicity of N-substituted aromatics to acetoclastic methanogenic activity in granular sludge, Appl. Environ. Microbiol. 61 (1995) 3889–3893.

[134] V. Uberoi, S.K. Bhattacharya, Toxicity and degradability of nitrophenols in anaerobic systems, Water Environ. Res. 69 (1997) 146–156.

[135] S. Morales-Torres, A.M.T. Silva, A.F. Pérez-Cadenas, J.L. Faria, F.J. Maldonado-Hódar, J.L. Figueiredo, F. Carrasco-Marín, Wet air oxidation of trinitrophenol with activated carbon catalysts: Effect of textural properties on the mechanism of degradation, Appl. Catal. B: Environ. 100 (2010) 310–317.

[136] L. Xu, Z. Sun, Q.M. Liu, Y.D. Liu, R.G. Zhong, F. Wu, The Influence of Phosphate Buffer on the Formation of N-Nitrosodimethylamine from Dimethylamine Nitrosation, J. Chem. 2013 (2013) 1–9.

[137] J.L. Caulfield, S.P. Singh, J.S. Wishnok, W.M. Deen, S.R. Tannenbaum, Bicarbonate Inhibits N-Nitrosation in Oxygenated Nitric Oxide Solutions*, J. Biol. Chem. 271 (42) (1996) 25859–25863.

[138] K. Kustin, I.A. Taub, E. Weinstock, A Kinetic Study of the Formation of the Ferrous-Nitric Oxide Complex, Inorg. Chem. 5 (6) (1966) 1079–1082.

[139] X. Zhang, P. Ren, W. Li, Y. Lei, X. Yang, E.R. Blatchley, Synergistic removal of ammonium by monochloramine photolysis, Water Res. 152 (2019) 226–233.

[140] P. Yang, Y. Ji, J. Lu, Transformation of ammonium to nitrophenolic byproducts by sulfate radical oxidation, Water Res. 202 (2021) 117432, https://doi.org/10.1016/j.watres.2021.117432.

[141] A. Lopez, A. Bozzi, G. Mascolo, R. Ciannarella, R. Passino, UV and H2O2/UV degradation of a pharmaceutical intermediate in aqueous solution, Annali di chimica 92 (2002) 41–51.

[142] A. Bozzi, A. Lopez, G. Mascolo, G. Tiravanti, Pharmaceuticals degradation by UV and UV/H2O2 treatments, Water Supply 2 (2) (2002) 19–26.

[143] P. Calza, C. Medana, M. Pazzi, C. Baiocchi, E. Pelizzetti, Photocatalytic transformations of sulphonamides on titanium dioxide, Appl. Catal. B: Environ. 53 (2004) 63–69.

[144] E. Brillas, I. Sirés, C. Arias, P.Lluís. Cabot, F. Centellas, R.María. Rodríguez, José. A. Garrido, Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode, Chemosphere 58 (4) (2005) 399–406.

[145] M. Haidar, A. Dirany, I. Sirés, N. Oturan, M.A. Oturan, Electrochemical degradation of the antibiotic sulfachloropyridazine by hydroxyl radicals generated at a BDD anode, Chemosphere 91 (9) (2013) 1304–1309.

[146] S. Zhou, L. Li, Y. Wu, S. Zhu, N. Zhu, L. Bu, D.D. Dionysiou, UV365 induced elimination of contaminants of emerging concern in the presence of residual nitrite: Roles of reactive nitrogen species, Water Res. 178 (2020), 115829.

[147] T. Bond, M.R. Templeton, N. Graham, Precursors of nitrogenous disinfection by-products in drinking water—A critical review and analysis, J. Hazard. Mater. 235–236 (2012) 1–16.

[148] J. Fang, J. Ma, X. Yang, C. Shang, Formation of carbonaceous and nitrogenous disinfection by-products from the chlorination of Microcystis aeruginosa, Water Res. 44 (2010) 1934–1940.

[149] S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chinn, M. J. Sclimenti, G.D. Onstad, A.D. Thruston, Occurrence of a New Generation of Disinfection Byproducts, Environ. Sci. Technol. 40 (2006) 7175–7185.

[150] T. Bond, N.H. Mokhtar Kamal, T. Bonnisseau, M.R. Templeton, Disinfection by-product formation from the chlorination and chloramination of amines, J. Hazard. Mater. 278 (2014) 288–296.

[151] L. Deng, C.-H. Huang, Y.-L. Wang, Effects of Combined UV and Chlorine Treatment on the Formation of Trichloronitromethane from Amine Precursors, Environ. Sci. Technol. 48 (2014) 2697–2705.

[152] N. Merlet, H. Thibaud, M. Dore, Chloropicrin formation during oxidative treatments in the preparation of drinking water, Sci. Total Environ. 47 (1985) 223–228.

[153] W. Baozhen, T. Jinzhi, Y.I.N. Jun, S.H.I. Guangmei, Ammonia, Nitrite and Nitrate Nitrogen Removal from Polluted Source Water with Ozonation and BAC Processes, Ozone: Science & Engineering 11 (1989) 227–244.

[154] M. Ying, M. Zhang, Y. Liu, Z. Wu, Ozone-assisted catalytic oxidation of aqueous nitrite ions on HZSM-5 zeolites, Sci. Rep. 9 (2019) 14322.

[155] Y. Wang, E. Laborda, R.G. Compton, Electrochemical oxidation of nitrite: Kinetic, mechanistic and analytical study by square wave voltammetry, J. Electroanaly. Chem. 670 (2012) 56–61.