Toxicity and Removal of Parabens from Water: A Critical Review

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Review

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ABSTRACT

Parabens are biocides used as preservatives in food, cosmetics and pharmaceuticals. They possess antibacterial and antifungal activity due to their ability to disrupt cell membrane and intracellular proteins, and cause changes in enzymatic activity of microbial cells. Water, one of our most valuable natural resource, has become a huge reservoir for parabens. Halogenated parabens which are a result of chlorination/ozonation of water contaminated with parabens have shown to be even more persistent in water than other types of parabens. Unfortunately, there is dearth of data on their presence and fate in groundwater which serves as a major source of drinking water for a huge population in developing countries. An attempt to neglect the presence of parabens in water will expose man to it through contaminated food and direct ingestion of contaminated water. Although there are reviews on the occurrence, fate and behaviour of parabens in the environment, they largely omit toxicity and removal aspects. This review therefore, presents recent reports on the acute and chronic toxicity of parabens, their estrogenic agonistic and antagonistic activity and also their relationship with antimicrobial resistance. This article further X-rays several techniques that have been employed for the removal of parabens in water and their drawbacks including adsorption, biodegradation, membrane technology and advanced oxidation processes (AOPs). The heterogeneous photocatalytic process (one of the AOPs) appears to be more favoured for removal of parabens due to its ability to mineralize parabens in water. However, more work is needed to improve this ability of heterogeneous photocatalysts. Perspectives that will be relevant for future scientific studies and which will drive policy shift towards the presence of parabens in our drinking waters are also offered. It is hoped that this review will elicit some spontaneous actions from water professionals, scientists and policy makers alike that will provide more data and effective technologies that will address the growing threat of the presence of parabens in our environment with respect to human health.

1. Introduction

Parabens are alkyl esters of p-hydroxybenzoic acid (PHBA). They are inert, odourless, tasteless, colourless, lipophilic, and are stable over a wide range of solution pH (Tavares et al., 2009). The family of parabens mainly includes methylparaben (MeP), ethylparaben (EtP), n-propylparaben (PrP), isopropylparaben (iPrP), n-butylparaben (BuP), isobutylparaben (iBuP) and benzylparaben (BeP) (Piao et al., 2014; Yamamoto et al., 2011a). The chemical structure and a few properties of these parabens are shown in Table 1. These parabens are used as preservatives in food, cosmetics and pharmaceuticals. They have found wide application as antimicrobial preservatives in processed products like vegetables, baked goods, fats and oils, seasonings, sugar substitutes, coffee extracts, fruit juices, pickles, sauces, soft drinks and frozen dairy products at concentration between 450 and 2000 mg/kg (Ocaña-González et al., 2015; Piao et al., 2014). Parabens are widely used in pharmaceutical and personal care products (e.g., solar lotions, deodorants, hair gels, shampoos, creams and toothpastes). These parabens have antibacterial and antifungal activity due to their ability to disrupt cell membrane and intracellular proteins, and cause a change in the enzymatic activity of microbial cells. Iso-butylparaben and benzylparaben are known to possess antimicrobial activity against *E. coli* (Crovetto et al., 2017b) while a mixture of methylparaben and propylparaben (because of their antifungal property) have been used in the production of paper (Neves et al., 2009). It has been discovered that an increase in the length of the alkyl chain on the parabens causes an increase in the antimicrobial activity even though this decreases their water solubility (Piao et al., 2014).

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*Abbreviations*AhRaryl hydrocarbon receptor.BePbenzylparaben.BuPbutylparaben.Br_1BePmonobrominated benzylparaben.Br_2BePdibrominated benzylparaben.Br_2BuPdibrominated butylparaben.Br_2EtPdibrominated ethylparaben.Br_2PrPdibrominated propylparaben.Br_2MePdibrominated methylparaben.EtPethylparaben.iBuPisobutylparaben.ILionic liquid.iPrPisopropylparaben.MDHBmethyl 3,5-dichloro-4-hydroxybenzoate.MePmethylparaben.MNPsmagnetic nanoparticles.MWTACCmagnetic waste tyre activated carbon-chitosan.NOMnatural organic matter.pHBAp-hydroxybenzoic acid.PrPpropylparaben.PS/Fe_3O_4polystyrene coating of the magnetite.TODtransferred ozone dose.

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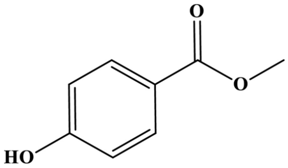
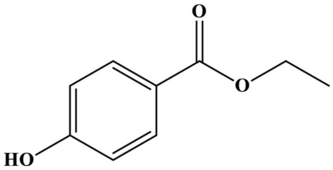
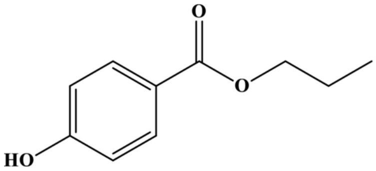
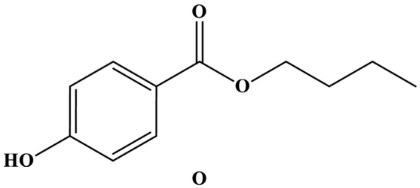
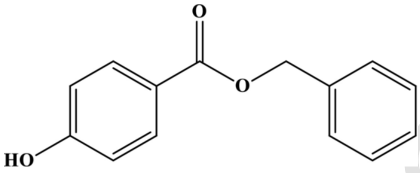
Table 1
Chemical structures and properties of parabens.

Compound name	Chemical structure	Molecular formula	Molecular weight	pKa
Methylparaben		$C_8H_8O_3$	152.15	8.17
Ethylparaben		$C_9H_{10}O_3$	166.17	8.22
Propylparaben		$C_{10}H_{11}O_3$	180.20	8.35
Butylparaben		$C_{11}H_{14}O_3$	194.23	8.37
Benzylparaben		$C_{14}H_{12}O_3$	228.25	8.50

Increasing use of pharmaceutical and personal care products have increased the concentration of parabens in our environment through wash off from human bodies, improper disposal of products with parabens content in toilets, sinks and trash cans. Water, which is one of the most important natural resources in the world, is fast becoming a huge reservoir for these parabens. The concentration of parabens in European waters were found to be low, up to 400 ng/L of methylparaben (Jonkers et al., 2009; Kasprzyk-Hordern et al., 2008). This may have increased significantly in recent years. Methylparaben and ethylparaben were reported to have the highest concentrations of 3142 and 1060 ng/L in Chinese rivers (Peng et al., 2008) while ethylparaben was predominantly observed in Indian waters (Ramaswamy et al., 2011b). A concentration of 2.9 mg/L was present in the influent of wastewater treatment plants and 60 μg/L in their effluents (Gomes et al., 2018). The occurrence of parabens in sea water is a concern in the aquatic environment because some parabens, especially BuP can cause complete coral bleaching at very low concentrations (Alcudia-León et al., 2013). Haman et al. in their review reported that methylparabens are predominantly found in aquatic systems than other parabens and that chlorinated parabens are more persistent in water than any other parabens (Haman et al., 2015).

Soils, groundwater and sludge also get polluted with parabens especially from irrigation process using water containing high levels of parabens and from the indiscriminate release of improperly treated wastewater (Błędzka et al., 2014; Ferreira et al., 2011; Viglino et al., 2011). However, it was recently reported that parabens levels ≥1000 mg/kg is unlikely to pose any serious threat to soil species like *Eisenia fetida* (earthworm) especially because >90% of this concentration degrade within three days (Samarasinghe et al., 2020). Parabens have also been found in life underwater as a result of their interaction with paraben-polluted water. For example, the level of parabens in adult fish in Manila Bay in the Philippines was reported to be 4700 ng/g while it was 2200 ng/g in the younger ones (Ramaswamy et al., 2011a). All of these will certainly influence, negatively, the health of humans in the long-term, when these polluted fishes are consumed as food. The concentrations of parabens present in aqueous matrices in some countries are shown in Table 2. In a recent study by Wei et al, (Wei et al, 2021) they concluded that even though human exposure levels to parabens is higher in the U.S. and in EU countries, than in India and China, this is likely to change with increasing production of parabens in these latter countries.

The cosmetic industry (which is the main driver of parabens pollution of aquatic systems) will grow by 7.2% in the next 6 years (https://www.gminsights.com/industry-analysis/cosmetics-preservative-market) which obviously will be driven by growth in world population. It is, therefore, evident that the concentration of parabens in the environment will continue to increase, portending more danger to the health of man and animals. Water, which remains a necessary commodity for all life on earth, will act as one major carrier of parabens to humans and animals. Although, there have been reviews for (Fransway et al., 2019; Kirchhof and de Gannes, 2013) and against (Crinnion, 2010; Haman et al., 2015) the use of parabens based on their occurrence and fate in the environment, yet it is evident currently that parabens are contaminants of concern and have a Category 1 status by the European Commission on Endocrine Disruption (https://davidsuzuki.org/queen-of-green/dirty-dozen-parabens/). Several countries across the world: Australia (Evans et al., 2016), China (Li et al., 2016; Li et al., 2015; Liu and Wong, 2013), Spain (González-Mariño et al., 2011), United States (Renz et al., 2013; Wang and Kannan, 2016), Japan (Terasaki et al., 2012; Yamamoto et al.,

Table 2
Concentration of parabens (ng/ml) in various aqueous matrices in different countries.

Sample matrix	Contaminant	Concentration range	Location	Reference
Drinking, river and waste water	MeP	0.00085–0.190	Spain & Morocco	(Azzouz and Ballesteros, 2014)
	EtP	0.00073–0.390		
	iPrP	0.0013–0.355		
	PrP	0.0047–0.300		
	iBuP	0.00098–0.110		
	BuP	0.00230–0.350		
	BeP	0.00061–0.195		
Sewage water	MeP	0.631–4.338	Chile	(Becerra-Herrera et al., 2019)
	PrP	2.455–14.905		
	BuP	0.44–0.895		
Tap, river & wastewater	MeP	0.037–3.259	Spain	(Blanco et al., 2009)
	EtP	0.030–0.202		
	PrP	0.044–0.756		
	BuP	0.083		
	BeP	0.09–0.655		
Swimming pool water	MeP	0.009–0.033	Spain	(Cacho et al., 2016)
	EtP	0.009–0.022		
	PrP	0.028–0.047		
Wastewater	MeP	0.0061–10	Spain	(González-Mariño et al., 2011)
	EtP	0.0098–1.600		
	PrP	0.021–2.800		
	BuP	0.039–0.270		
	iPrP	0.0056		
	iBuP	0.013–0.110		
	ClMeP	0.0069–0.061		
	Cl_2MeP	0.008–0.090		
River water	MeP	ND–0.525	Japan	(Kimura et al., 2014)
	EtP	ND–0.0736		
	PrP	ND–0.181		
Urban stream	MeP	0.025–0.676	Japan	(Yamamoto et al., 2011a)
	EtP	<0.0013–0.064		
	PrP	<0.0008–0.207		
	BuP	<0.0006–0.163		
	iPrP	<0.0016–0.046		
	iBuP	<0.0012–0.013		
	BeP	<0.0002–2.3		
River water	MeP	0.010–0.048	UK	(Kasprzyk-Hordern et al., 2008)
	EtP	0.004–0.008		
River water	MeP	0.0022–0.0173	USA	(Renz et al., 2013)
	PrP	ND-0.012		
	BuP	ND-0.002		
River water	MeP	0.0021–0.0054	Japan	(Terasaki et al., 2012)
	PrP	0.0049–0.025		
	BuP	<11–0.012		
Wastewater	MeP	1400–2400	Japan	(Terasaki et al., 2012)
	EtP	52–57		
	PrP	2200–2600		
	BuP	370–450		
	Cl_2MeP	2100–2300		
	Cl_2EtP	170–410		
River water	MeP	<0.0053–2.875	Brazil	(Santos et al., 2016)
	EtP	<0.0044–1.485		
	PrP	<0.0051–0.486		
	BuP	<0.0061–0.286		
	MeP	0.11–0.98		(Derisso et al., 2020)
	EtP	0.38–9.70		
	PrP	0.70–7.90		
	BuP	1.90–11.0		
Wastewater	MeP	0.0044–0.267	India	(Karthikraj et al., 2017)
	EtP	0.0019–0.0584		
	PrP	0.0028–0.583		
	BuP	0.0007–0.0105		
	HepP	ND–0.0174		
	BeP	ND–8.2		
River water	MeP	ND–0.0228	India	(Ramaswamy et al., 2011b)
	EtP	0.00247–0.147		
	PrP	ND–57.0		
Wastewater	MeP	211–1002	China (Beijing)	(Li et al., 2015)
	EtP	32.9–220		
	PrP	287–605		
	BuP	16.6–35.5		
	BeP	0.26		
	3,5-2Cl-MeP	7.55–30		
	3,5-2Cl-EtP	16.2–49.4		
River water	MeP	1.41–68.8	China	(Sun et al., 2016)
	PrP	1.91–69.9		
Swimming pool water	MeP	0.019–5.96	China	(Lu et al., 2017)
	EtP	0.0018–0.11		
	PrP	0.0010–0.32		
	iPrP	ND–0.44		
	BuP	ND–0.0031		
tWastewater	PrP	2.9	Netherlands	(Hernandez Leal, 2010)
	BuP	0.86		
Storm water	MeP	6.29	Australia	(Evans et al., 2016)
	EtP	21.37		
	PrP	2.87		
	BuP	4.35		
Urban river	MeP	3.63		
	EtP	7.33		
	PrP	2.70		
	BuP	4.26		
Effluent (residential)	MeP	7.61		
	EtP	4.70		
	PrP	2.87		
	BuP	4.54		
Drinking water	MeP	47.2	Egypt	(Radwan et al., 2020)
	PrP	15.7		
	BuP	22.6		

ND = not detected.

2011b), Brazil (Galinaro et al., 2015; Santos et al., 2016), Korea (Liao et al., 2013) and even Australia (Evans et al., 2016) have made attempts to monitor the presence of parabens in their waters and have used data obtained to established regulatory policies that limit the use of parabens and their release into their environment. For instance, the maximum allowable concentration of 0.4% and 1.0% parabens have been placed on cosmetics in China and Japan respectively (Shen et al., 2007), 0.4% for single parabens and 0.8% for a mixture of parabens in Europe (Błędzka et al., 2014). However, several developing countries, especially those in Africa are yet to set limits for this class of emerging contaminants perhaps because there is dearth of data on their presence in waters in these countries and there are no sufficient empirical reports on their toxicity to animals and humans alike.

There is no doubt, that parabens are becoming more ubiquitous in our environment due to an increase in their use and indiscriminate discharge of pharmaceutical and personal care products. More of their impact on human health is now being reported today. There is an existing report that presents a comprehensive review on the occurrence, fate and behaviour of parabens in aquatic environments (Haman et al., 2015). Even recently, a review on parabens as chemicals of emerging concern in the environment and humans was reported (Wei et al., 2021). These reviews do not address specifically the toxicity of this class of chemical contaminants to humans and other living species in the environment. In addition, they omit discussions related to their (parabens) relations with antimicrobial resistance and discussions on technologies that have been applied for the removal of these chemicals, their strength and their weaknesses. At the moment, parabens are classified as contaminants of emerging concern. Hence, to forestall an impending health crisis nationally and globally, there should be a critical understanding of the toxicity of these parabens and technologies that have been applied for their removal in water. This should trigger an appropriate regulatory framework and an adaptation of new and more efficient technologies to properly handle them in the environment in various continents of the world.

In the light of the foregoing, this paper critically examines the toxicity of parabens, their contribution to antibiotic resistance and several management strategies that have been used to reduce or remove them completely from water. It is hoped that, this article will spur some strong action from all stakeholders (water professionals, policy makers and scientists) to come up with more compelling data that will drive the development of sustainable solutions to the threat, this emerging pollutant (parabens) presents to our current world as we strive to avoid a global health situation that will not only be financially demanding but will likely cost human lives.

2. Data survey

The occurrence, removal and toxicity data of parabens used in this review were sourced from published articles that are available on database and search engines, such as google scholar, Elsevier, PubMed, Wiley Online Library, ACS Publication and MDPI. The keywords used in the search were "Occurrence of Parabens", "Paraben Concentration", "Paraben Determination", "Paraben Toxicity", "Paraben Biodegradation", "Paraben Photodegradation", "Paraben Adsorption" "Paraben EC50", "Paraben LC50", "Paraben Removal", "Paraben Estrogenicity", "Agonistic Activity of Parabens", "Antagonistic Activity of Parabens", "Paraben Aryl Hydrocarbon Receptor" and "Parabens and Antimicrobial Resistance". The data were sorted based on the following: exposure to or removal of single or mixed parabens; test carried out under laboratory conditions; endpoint and time of exposure/contact stated; removal efficiency stated.

3. Toxicity of paraben

Humans are exposed to these parabens through indiscriminate discharge of untreated industrial wastewater from the pharmaceutical, personal care products and paper industries (Liao and Kannan, 2014). Until recently, parabens were not seen as a threat to human and animal health because they are easily absorbed and converted to a less toxic compound, p-hydroxybenzoic acid (pHBA) by cutaneous carboxyesterases (Fransway et al., 2019; Soni et al., 2005). This has fuelled their application in the development of various products used by man today. Recently, scientific reports point strongly to their toxicities.

There are several reports on the toxicity of parabens using organisms. Dobbins et al. (Dobbins et al., 2009) reported the acute toxicity test of seven parabens on *Daphnia magna* and *Pimephales promelas*. The lethal concentration to kill 50% of the *Daphnia magna* and *Pimephales promelas* (LC_{50}) was between 4.0 mg/L to 24.6 mg/L for *D. magna* and 3.3 mg/L to >160.0 mg/L for *P. promelas.* At concentrations between 0.12 mg/L to 9.0 mg/L of these parabens, the growth of *D. magna* was affected while reproduction was negatively influenced at 1.5 mg/L to 6.0 mg/L. However, the growth of *P. promelas* was adversely affected at higher concentrations of between 1.0 mg/L to 25.0 mg/L. Of the seven parabens, Dobbins et al. observed that methylparaben was least

vein, Yamamoto et al. (Yamamoto et al., 2011a) reported the results of acute toxicity tests of seven parabens using *Oryzias latipes* (medaka), *Daphnia magna* and *Psuedokirchneriella subcapitata* (green algae). The LC_{50} values for algae, daphnia and medaka (fish) were: methylparaben (34 mg/L to 80 mg/L), ethylparaben (7.4 mg/L to 52 mg/L), *n*-propylparaben (2 mg/L to 36 mg/L), *i*-propylparaben (3.5 mg/L to 48 mg/L), *n*-butylparaben (1.9 mg/L to 9.5 mg/L), *i*-butylparaben (3.3 mg/L to 4.6 mg/L) and benzylparaben (0.73 mg/L to 2.1 mg/L). This indicates that the toxicity of parabens could increase with an increase in alkyl chain length or even with the presence of an aromatic ring attachment parabens molecule. Indeed, this was confirmed by studies carried out by Terasaki et al. (2015) showing the chronic toxicity of benzylparaben to *Ceriodaphnia dubia* when this organism was exposed to it as compared with propylparaben and isopropylparaben. Furthermore, the effect of parabens on the growth, reproduction and locomotion behaviour of organisms was studied with *Caenorhabditis elegans* (a soil nematode) and it was found to be in the order BuP > PrP > EtP > MeP after 72 h of exposure to these parabens (Nagar et al., 2020). In addition, this organism (*C. elegans*), in the presence of these parabens, showed high reactive oxygen species generation, anti-oxidant transcripts, evidence of oxidative stress, endocrine disruption and toxicity of the organism. In a further study with *Ceriodaphnia dubia*, its death rate and progeny reduction increased as the hydrophobicity of the parabens increased and decreased with an increase in chlorination of the parabens. Sasaki and Terasaki (2018) demonstrated the agonistic and antagonistic activity of benzylparaben on a yeast transfected with the human estrogen receptor α, which were weakened with increased bromination. Although, it is suggested that increased derivatization of parabens (from chlorination/halogenation of water contaminated with parabens) masks their apparent estrogenic activity (Gouukon et al., 2020), yet the resulting chlorinated compounds may represent a potential hazard to human and animal health. It is therefore expedient that further toxicity tests be performed to establish the true impact of halogenated derivatives of parabens on human cells.

Another potential factor that increases the toxicity of parabens in water systems, aside the inclusion of alkyl chains, aromatic rings and halogens, is their simultaneous presence in such systems. This is supported by the study of Lee et al. (2018b) who dosed a mixture of four parabens: Methylparaben, ethylparaben, propylparaben and butylparaben to *Aliivibrio fischeri*. The result from bioluminescence inhibition test suggests that toxicity to *A. fischeri* was stronger in the presence of mixed parabens than in the presence of single parabens even though all four parabens were toxic to the organism.

Aside from several scientific reports on the estrogenicity of parabens to organisms, there have been a few reports on their toxicity to human and animal, using cells. Parabens are now known to exhibit estrogenic activity that alter the function of the endocrine system in the body resulting in harmful consequences both to man and animals (Vo et al., 2011). They are now known to be endocrine disruptors, interfering with the endocrine by activating or hindering hormone receptors; synthesis, metabolism and clearance of endogenous hormones could also be affected, leading to the influence of hormone bioavailability (Damstra et al., 2002). This poses serious threat to the normal healthy life of an individual. Lately, parabens in rats have been linked with poor sperm development (Guerra et al., 2017; Oishi, 2002). Besides, parabens have been shown to enable multiple cancer hallmarks in human breast epithelial cells (Amin et al., 2019; Darbre and Harvey, 2014; Pan et al., 2016). Parabens can interact with different steroid sensitive tissues to cause malfunction of the central nervous system (Kim et al., 2011; Miodovnik et al., 2011) and the immune system, homeostasis of lipids (Raza et al., 2018), changes in glucose levels (Hectors et al., 2011), inhibition of proper functioning of the thyroid especially in relation to pregnant women (Aker et al., 2016) and telomere shortening (inability for cells to replicate) that leads to aging, cancer and possibly death (Finot et al., 2017). Only very recently, it has been suggested that exposure to parabens especially butylparabens, can trigger childhood overweight development through the altering of pro-opiomelanocortin-mediated neuronal appetite regulator (Leppert et al., 2020). Nowak et al. have provided a detailed review on the endocrine disruptive action of parabens in human bodies (Nowak et al., 2018). Fig. 1 presents a summary of the adverse effects and toxicity of parabens.

Sasaki and Terasaki (2018) investigated the estrogen agonistic and antagonistic activity of sixteen (16) brominated by-products of parabens by using a yeast transfected with the human estrogen receptor α. For the agonist assay, five C3–C4 alkylparabens and benzylparaben showed significant activity relative to that of 17β-estradiol, but none of the brominated alkylparaben exhibited agonistic activity. In the antagonist assay, 5 monobrominated and 7 dibrominated parabens showed significant antagonistic activity. The antagonist activity of C1–C4 alkylparabens increased with the number of bromine substitutions. These interruptive activities have the potential of causing reproductive and developmental defects in humans (Hu, 2015). The impact of parabens on human development with respect to obesity is fully discussed by Hu (2015).

The aryl hydrocarbon receptor (AhR) is a ligand-activated transcription factor that was seen as an indicator for environmental toxins (Gutiérrez-Vázquez and Quintana, 2018). The activation of AhR by environmental xenobiotics are described as a sensor for toxicity (Irigaray and Belpomme, 2010). Recently, investigation from Gouukon et al. (2020) showed the AhR agonist activity of brominated parabens, especially monobrominated parabens contrary to report by Sasaki and Terasaki (2018). AhR-mediated toxicity of brominated parabens is similar to that of polychlorinated biphenyls (PCBs) which possess AhR potency due to structural similarities of the molecules (Machala et al., 2004). Recent studies have already revealed the presence of dibrominated methylparaben (Br_2MP), ethylparaben (Br_2EP), propylparaben (Br_2PP), butylparaben (Br_2BP), benzylparaben (Br_2BnP), and monobrominated benzylparaben (Br_1BnP) in river water samples with concentration between 8.1 ng/L and 28 ng/L (Yoom et al., 2018). This suggests that long term ingestion of these polluted water could activate AhR that will trigger unpleasant biological responses in humans such as disruption of normal hormone signalling pathways, neuroendocrine, developmental and reproductive toxicity, immunotoxicity, mutagenicity and induction of the cytochrome P450 (CYPs) system (Giesy and Kannan, 1998; Poland et al., 1976; Safe, 2001). Ethylparaben, at concentration as high as 0.6 mM has been shown to cause apoptosis (cell death) in human placenta cells within 24 h (Kim et al., 2020) while Vero cells from monkey were found to show reduced proliferation rates when exposed to 500 μM propylparaben (Martín et al., 2010). Table 3 provides a list of species used for paraben toxicity test and the corresponding results.

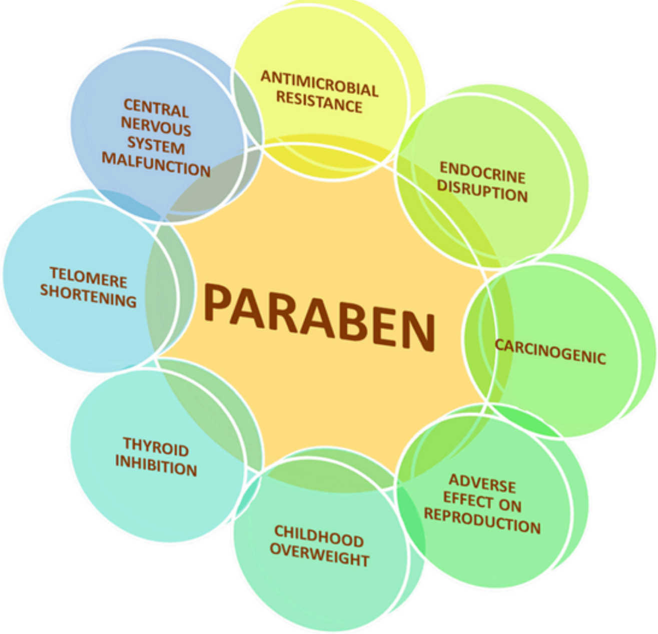


Fig. 1. Adverse effects and toxicity of parabens.

4. Parabens and antimicrobial resistance

Parabens being biocides, act as antimicrobials and are used as preservatives in products like food, paints, body care products and pharmaceuticals. As earlier mentioned these biocides (parabens) have been implicated with endocrine disruptions and more recently with antimicrobial resistance potentials (Chen et al., 2018; Maamar et al., 2020) especially because they are found in significant amounts in the environment. However, only a few studies have reported on parabens and their relationship with antimicrobial resistance. To support this, we visited the PubMed search engine and observed that only 551, 42 and 25 published articles were related to triclosan, paraben and triclocarban respectively, as at the end of the year 2020 even though there were 298,745 articles published on antimicrobial resistance in the same year. Antimicrobial resistance caused by the presence of parabens is one that is scarcely investigated.

The mechanisms of resistance to parabens developed by bacteria and fungi are similar to those of other antimicrobials and they include the use of efflux pumps, cell membrane modification (Flasiński et al., 2018), lack of target sites, expression of enzymes induced during exposure (Fahimipour et al., 2018; SCENIHR, 2009; Yadav et al., 2019). In 2018, Ashkaan investigated the relationships between the use of antimicrobial chemicals (triclosans, triclocarbans and parabens) in buildings and their impact on indoor microbial communities. The results showed bacteria were cross-resistant to three antibiotics: clarithromycin, ampicillin, and tetracycline (Fahimipour et al., 2018). Their findings implied that the chemicals impacted the microbial diversity within and outside such buildings as well as the occupants. This was supported by findings from Hartmann et al. (2016) who identified 17 known antibiotic resistance genes in building housing triclosans, triclocarbans and parabens products. Selvaraj et al. (2013) had reported the susceptibility of cultured *Staphylococcus aureus*, *Bacillus* sp., *Escherichia coli* and *Pseudomonas aeruginosa* to ≥5 mg of parabens. They indicated that Gram-negative bacteria showed less susceptibility to parabens than the Gram-positive ones. Although this study did not report the mechanism of resistance, an earlier study by Bredin et al. (2005) reported the induction of potassium efflux by *E. coli* due to propyl-paraben exposure and the presence of spermine in their membrane (a known OmpF channel-blocker) as mechanisms of resistance. However, there are no similar reports on the relationship between these biocides in water and antimicrobial resistance. This is a gap that needs to be filled in urgently with data from scientific experiments.

5. Removal of parabens

Having X-rayed the danger parabens portends for human health both now and in the future, the need for their complete removal in drinking water cannot be overemphasized. Over the years, there have been several methods employed for the treatment of water and wastewater. However, most treatment plants around the world, especially in developing countries, still rely on old technologies such as filtration, flocculation and precipitation to treat their water. These techniques do not sufficiently remove most emerging contaminants like parabens from water (Błędzka et al., 2014). However, several other techniques have been adopted for the removal of parabens in water. These techniques, their advantages and disadvantages are discussed further.

5.1. Physical removal technologies

5.1.1. Adsorption

Adsorption is a common method for the removal of organic pollutants and is mostly applied at the tertiary stage of water treatment. There are studies that have reported the removal of parabens in water samples through the use of adsorbents. Among these adsorbents, magnetic nanoparticles have received wide interest due to their nanoscale sizes of between 10 and 20 nm and relative efficiency. To maximize the adsorption capacity of magnetic nanoparticles, they are subjected to different physical and chemical modifications. For example, a synthesized magnetic nanoparticle modified with phenyl group from a polystyrene coating of magnetite (PS/Fe_3O_4) was used for the removal

Table 3
Toxicity of parabens on invertebrate, algae, bacteria, nematode, fish and different cell lines.

Compound	Taxonomic group	Species	Test duration/test type	Toxicity type	Conc. (mg/L)	Ref.
MeP, EtP, PrP, BuP	Invertebrate	*Daphnia magna*	24 h/growth inhibition LC_{50}	Acute	11.2–73.4	(Lee et al., 2018a)
	Bacteria	*Aliivibrio fischeri*	15 min/ bioluminescence inhibition EC_{50}	Acute	2.34–16.80	
MeP	Invertebrate	*Daphnia magna*	48 h/immobilization EC_{50}	Acute	36.731	(Lee et al., 2017)
			21 d/reproduction	NOEC		
MeP	Algae	Pseudopediastrum boryanum	72 h/growth inhibition EC_{50}	Acute	135	(Puerta et al., 2020)
		Desmodesmus communis	72 h/growth inhibition EC_{50}	Acute	170	
		Raphidocelis subcapitata	72 h/growth inhibition EC_{50}	Acute	92.8	
MeP, EtP, PrP, BuP, BeP	Invertebrate	*Daphnia magna*	48 h/immobilization EC_{50}	Acute	1.9–34	(Yamamoto et al., 2011a)
			21 d/reproduction	NOEC	0.8–2.4	
	Fish	*Oryzias latipes*	96 h/LC_{50}	Acute	0.73–63	
			14 d/vitellogenin	NOEC	0.02–0.16	
	Algae	*Psuedokirchneriella subcapitata*	72 h/growth inhibition EC_{50}	Acute	1.2–80	
			72 h/growth inhibition	NOEC	0.52–21	
MeP, PrP, Cl_2MeP, Cl_2PrP, BeP	Invertebrate	*Ceriodaphnia dubia*	7 d/reproduction EC_{50}	Chronic	0.047–12	(Terasaki et al., 2015)
MeP, ClMeP, EtP, ClEtP, PrP, ClPrP, BuP, Cl_2BuP, BeP	Bacteria	*Vibrio fischeri*	15 min/ bioluminescence inhibition EC_{50}	Acute	0.0038–5.9	(Terasaki et al., 2009)
	Invertebrate	*Daphnia magna*	48 h/immobilization EC_{50}	Acute	3.0–62	
MeP, EtP, PrP, BuP, BeP	Invertebrate	*Daphnia magna*	48 h/immobilization LC_{50}	Acute	4.0–24.6	(Dobbins et al., 2009)
			10 d/growth inhibition	LOEC	0.12–9.0	
			10 d/reproduction	LOEC	1.5–6.0	
	Vertebrate	*Pimephales promelas*	96 h/immobilization LC_{50}	Acute	3.3–>160	
			7 d/growth	LOEC	1.0–25	
MeP, EtP, PrP, BuP	Nematode	*Caenorhabditis elegans*	72 h/LC_{50}	Acute	131.88–278.1	(Nagar et al., 2020)
EtP	Nematode	*Caenorhabditis elegans*	Growth inhibition LC_{50}	Acute	>200	(Xue and Yang, 2016)
MeP	Fish	*Danio rerio*	96 h/growth inhibition LC_{50}	Acute	0.015	(Dambal et al., 2017)
PrP	Nematode	*Caenorhabditis elegans*	24 h/growth inhibition LC_{50}	Acute	0.09–9.1	(García-Espiñeira et al., 2018)
			24 h/reproduction LC_{50}	Acute	0.09–0.9	
MeP, EtP, PrP, BuP, BeP	Fish	*Oreochromis niloticus*	48 h/mortality LC_{50}	Acute	7.80–67.11	(Silva et al., 2018)
MeP	Fish	*Danio rerio*	72 h/growth inhibition LC_{50}	Acute	50	(Ateş et al., 2018)
MeP	Frog	*Xenopus laevis*	96 h/mortality LC_{50}	Acute	240	(San Segundo et al., 2013)
MeP, EtP, PrP, BuP, BeP	Invertebrate	*Daphnia magna*	48 h/growth inhibition LC_{50}	Acute	6–21	(Bazin et al., 2010)
	Invertebrate	*Tetrahymena thermophila*	28 h/growth inhibition LC_{50}	Acute	5.7–58	

Compound	Taxonomic group	Species	Test duration/test type	Toxicity type	Conc. (mg/L)	Ref.
MeP, EtP, PrP, BuP	Bacteria	*Escherichia coli*	6 h/growth inhibition EC_{50}	Acute	274–845	(Crovetto et al., 2017a)
MeP, EtP, PrP, BuP	Invertebrate	*Dugesia japonica*	96 h/mortality LC_{50}	Acute	7.3–77	(Crovetto et al., 2017a)
BuP	Human cell line	HepG2	24 h/cell viability IC_{50}	Toxic	58.3	Kizhedath et al., 2019)
		HDFn	24 h/cell viability IC_{50}	Toxic	58.3	
PrP	Mammalian cell line	Vero cell	24 h/cell viability	Acute	90.1	(Martín et al., 2010)
EtP	Human cell line	Human placental BeWo cells	24 h/cell viability IC50	Cell apoptosis	91.3	(Kim et al., 2020)
MeP, BuP	Mice cell line	Stromal stem cell, C3H10T1/2	–	Toxic	–	(Hu, 2015)

orption capacities of PS/Fe_3O_4 increased with increasing alkyl groups on the paraben. The adsorption capacities for the parabens were 19.5%, 42.4% and 63.7% for MeP, EtP and PrP respectively while the desorption capacities were 42.5%, 77% and 99.7% respectively after five reuse cycles. It was observed that the adsorption of the parabens on PS/Fe_3O_4 was independent of pH as their adsorption was via π–π electron-donor acceptor interactions (Chen et al., 2017a). Recently, a magnetic waste tyre activated carbon-chitosan (MWTACC) composite was prepared by co-precipitation method for the adsorption of parabens (Mashile et al., 2020). A high adsorption capacity of 85.9 mg/g and 90.0 mg/g for methylparaben and propylparaben respectively was obtained for the adsorbent. The magnetic adsorbent was stable for up to seven adsorption/desorption cycles with adsorption efficiency >95% up till the 8th reuse cycle but dropped to 87% efficiency after the 9th reuse cycle. The magnetic sorbent is reported to be cost-effective and could be easily separated from liquid solutions by an external magnetic field (Mashile et al., 2020). Also, recently, micro- and mesoporous silicas were synthesized from coal fly ash at different pH for the adsorption of parabens in aqueous media. Adsorption equilibrium was reached within 10 min and adsorption was more favoured for parabens with longer alkyl chains in the acidic medium (pH = 3.0) than in basic medium (de Oliveira et al., 2020). Increasing initial concentration of the parabens does increase the adsorption capacity (Forte et al., 2017).

Polymeric adsorbents have also found use in the removal of parabens from water. Chin et al. developed two crosslinked polymers for the removal of MeP, EtP, PrP and BeP from aqueous solution (Chin et al., 2010). They observed that crosslinking β-cyclodextrin with toluene-2,6-diisocyanate (TDI) made it a more efficient adsorbent for the removal of the parabens from aqueous solution than crosslinking with hexamethylene diisocyanate (HDMI) even though both adsorbents had high reusability and simple regeneration procedure (Chin et al., 2010). The benzylparaben (BeP) was completely removed from real water samples solution by β-cyclodextrin crosslinked with TDI. It is suggested that the efficient removal is because it is the least polar of the four parabens and least soluble in water and will therefore, easily adsorb into the cavity of β-CD due to its very strong solute-adsorbent interaction (Chin et al., 2010). In another example, polypropylene fibre (PPF) was found to act as a support material for the synthesis of a novel amphiphilic structured functionalized adsorbent (Ran et al., 2020). It was found that the adsorbent ($PP_{A\text{-}P}F\text{-}C_{12}$) with hydrophilic polyamines and hydrophobic linear alkyl chain groups, was efficient for the removal of butylparaben from aqueous solution. It retained a 90% removal efficiency of the parabens even after 10 reuse cycles (30 min each cycle) and a 98% desorption efficiency (using ethanol). Yusoff et al. also studied the effectiveness of a polymeric adsorbent (β-cyclodextrin-toluene-2,6-diisocyanate, β-CD-TDI) grafted on modified magnetic nanoparticles (MNPs) with ionic liquid (IL) loaded on the surface, for the removal of propyl, butyl and benzylparabens in water (Yusoff et al., 2018). They observed, using ^1H nuclear magnetic resonance (NMR) together with ultraviolet-visible (UV–vis) spectroscopic analysis, that adsorption of the parabens from water was facilitated by a π-π interaction between β-CD and parabens with a removal efficiency of between 60 and 90% (benzylparabens being the most adsorbed). With real wastewater, the adsorbent removed between 60 and 80% parabens (Yusoff et al., 2018) indicating its strong potential for use in the treatment of complex water matrices containing parabens.

Other inorganic- and organic-based materials such as fly-ash treated with acid and calcined African palm shell has been used to remove methyl, ethyl-, propyl- and butylparabens from water (de Oliveira et al., 2020; Moreno-Marenco et al., 2019). The removal of propyl- and butylparabens were more favoured at acidic pH (de Oliveira et al., 2020). In another study, a porous N grafted graphene-NiO (NiO@N-G) nanoparticles were used as an adsorbent for the removal of parabens (Husein, 2019). The choice of using NiO in this adsorbent is because it could act as a stabilizing agent against the aggregation of graphene layers (Khan et al., 2015). The NiO@N-G nanoparticle adsorbent achieved 39.2%, 56.6%, 69.5% and 79.3% removal of methyl-, ethyl-, propyl- and butylparaben respectively. An adsorption/desorption equilibrium was reached after 3 h. Desorption efficiency of 50.1%, 81.1%, 99% and 99.9% was achieved respectively with 100% ethanol and the adsorbent was stable for four adsorption/desorption cycles. Again, it is suggested that the π–π interactions via double bonds of graphene sheets and in the benzene rings in the paraben molecules is responsible for the adsorption of parabens (Husein, 2019).

While the adsorption technique has shown very good efficiency for removal of parabens from water, it is however faced with the challenge of having significant efficiency reduction in real polluted water systems and the high cost involved in the use of ethanol for regeneration of the adsorbents. This is aside the fact that the performance of the adsorbent depends on the type of material used to prepare it. Furthermore, other organic molecules, if present alongside parabens in water, will definitely compete for adsorption sites and thus reduce the efficiency of the adsorbent for parabens. In addition, the high investment cost required to set up an adsorption system (as a unit operation system) for treatment of large volume of water is prohibitive. Table 4 presents some of the adsorbents that have been used for the removal of parabens in water and some operating variables required for the adsorption process.

5.1.2. Membrane technology

Membrane technology is one of the most efficient for water treatment except for the disadvantage of frequent membrane fouling. Till date, only very few reports are available on the use of membrane filters for the removal of parabens in water. Two nanofiltration membranes (NF-90 and DE-SAL-HL) were developed for the removal of MeP, EtP, PrP and BuP from aqueous solution and it was observed that both membranes achieved >90% removal of the PrP and BuP from water. The addition of a magnetic anionic exchanger resin to both membranes resulted in a 100% removal of both parabens from water (López-Ortiz et al., 2018), this is as a result of the resins affinity for hy-

Table 4
Contaminant concentration, pH, dosage, contact time and removal efficiency of some adsorbents.

Contaminant	CC mg/L	Opt. pH	Dosage g/L	Contact time (min)	Adsorbent	Removal efficiency (%)	Reference
MeP, PrP	2	6.5	1.2	35	MWTACC	100	(Mashile et al., 2020)
MeP, EtP, PrP, BuP	5	3.0	0.05	30	FA-AT7	–	(de Oliveira et al., 2020)
PrP, BuP, BeP	10	6.0	1.0	80	IL-MNP-βCD-TDI	60–90	(Yusoff et al., 2018)
MeP, EtP, PrP	50	3.0–7.0	10.0	1440	PS/Fe_3O_4	19.5–63.7	(Chen et al., 2017a)
MeP	7.6	5.0	4.3	60	Polyacrylonitrile (PAN) beads	>60	(Forte et al., 2017)
EtP, BuP, OcP	200	5.0	0.7	30	$PP_{A\text{-}P}F\text{-}C_{12}$	90	(Ran et al., 2020)
MeP, EtP, PrP, BuP	10	5.0	2.5	90	NiO@N-G	39.2–79.3	(Husein, 2019)
MeP, EtP, PrP, BeP	100	–	1.0	120	β-CD-TDI	33.56–100	(Chin et al., 2010)
MeP, PrP	20	6.0	1.0	120	PiH-activated carbon	>84	(Nodeh et al., 2020)
MeP	20	7.0	1.1	120	(Fe_3O_4@SiO_2-NH_2)	98	(Mohammadi et al., 2018)
BuP	10	7.0	4.0	180	CBAC	>97	(Atheba et al., 2018)
MeP, EtP, PrP, BuP	0.5	5.0	0.7	–	MWCNTs/SiO_2/β-CD	95	(Ding et al., 2018)

drophilic and hydrophobic dissolved organic compounds (Boyer, 2015). Recently, CuO/TiO_2 coated ceramic ultrafiltration membrane (which is less often fouled compared with polymeric membranes) was developed for the removal of parabens from water. It showed a removal efficiency of >99% and toxicity test of treated water showed less impact on ovarian teratocarcinoma (PA-1) cell lines than untreated water (Bhattacharya et al., 2021). The membrane technology, is no doubt, highly efficient for water treatment. However, the high energy requirement and the high cost of maintenance has made it unattractive especially in developing countries.

5.2. Chemical removal technologies

Advanced oxidation processes (AOPs) is the main chemical removal technology that have been applied for the removal of parabens in water. It has found application in the degradation of organic pollutants. It is known that AOP process is based on the generation of highly reactive species, basically hydroxyl radical ($^{\cdot}OH$) that can degrade organic pollutants found in water and lead to their mineralization (Derikvandi and Nezamzadeh-Ejhieh, 2017; Dhaka et al., 2017). According to Sharma et al. (2018), there are two broad classifications of AOPs. These are non-photochemical and photochemical methods.

5.2.1. Non-photochemical methods

In non-photochemical method, there are four possible ways of producing OH radical without light:

1. Ozonation at elevated pH,
2. Catalytic ozonation,
3. The combination of ozone and hydrogen peroxide (O_3/H_2O_2), and
4. Fenton system (H_2O_2/Fe^{2+}).

In the first case, the decomposition of ozone is initiated in the presence of hydroxyl ion (OH^-), which causes reactions that lead to OH radical ($HO^{\bullet}$) formation. The $HO^{\bullet}$ formed has a short half-life but it is a very strong oxidizing agent. Superoxide anion radical ($O_2^{\bullet-}$), hydroperoxyl radical ($HO_2^{\bullet}$) and ozonide anion radical ($O_3^{\bullet-}$) are also formed in the process.

$$3O_3 + OH^- + H^+ \rightarrow 2HO^{\bullet} + 4O_2 \tag{1}$$

To test this method, ozonation of MeP, EtP, PrP and BuP was carried out by Tay et al. (2010). They showed that pH does influence the rate of the ozonation reaction such that the dissociated parabens reacted 10^4 more than the undissociated and 10^7 times more than the protonated parabens. The ozonation process gave rise to degradation by-products which were formed mainly from hydroxylation (Tay et al., 2010). However, authors did not carry out any toxicity test on the treated water to ascertain its safety.

The second way of generating $HO^{\bullet}$ is through catalytic ozonation. Catalytic ozonation is divided into two; homogeneous and heterogeneous catalytic ozonation. In homogeneous catalytic ozonation, transition metal ions (Fe^{2+}, Mn^{2+}, Ni^{2+}, Ag^+) present in water could act as a catalyst for the decomposition of ozone (O_3) to produce MO^{2+} in the process (e.g. O_3/Fe^{2+}). The MO^{2+}produced, transfers an electron to H_2O^+ to form $HO^{\bullet}$ (Eqs. (2)–(3)).

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{2}$$

$$FeO^{2+} + H_2O^+ \rightarrow Fe^{3+} + HO^{\cdot} + OH^- \tag{3}$$

However, the heterogeneous catalytic ozonation involves the use of solid catalysts like titanium oxide, alumina, iron oxides or their combination with ozone or any other oxidant. Gomes et al. used Ag, Pt, Pd, Au-doped TiO_2 to remove parabens from water in the presence of ozone (Gomes et al., 2017a). The best material was Au-doped TiO_2 which completely removed the parabens from water. The process required the use of Ultraviolet A irradiation and a small amount of ozone to reduce the degradation time. Low mineralization was observed but the treated water showed reduced toxicity to *Vibrio fischeri*, *Lepidium sativum* and *Corbicula fluminea*. Again, hydroxylation was suggested as the pathway for the photodegradation process (Gomes et al., 2017a). However, the factors to consider in selecting catalysts for this process are density, surface area, and pore size.

The third way is through the use of a combination of ozone and hydrogen peroxide (O_3/H_2O_2). When ozone (O_3) and peroxide (H_2O_2) combine (known as perozone), HO_2^-, a conjugate base of H_2O_2 reacts with O_3 to generate OH radical (Staehelin and Hoigne, 1985) as shown in Eqs. (4)–(6).

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{4}$$

$$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet} \tag{5}$$

$$O_3 + H_2O_2 \rightarrow 2HO^{\bullet} + O_3^{\bullet} \tag{6}$$

Pipolo et al. used ozone and various ozone-based technologies to remove parabens from water (Pipolo et al., 2017). They observed that increasing ozone concentration increased degradation of the parabens up to 98%. The addition of H_2O_2 (co-oxidant) to deal with saturated organic rings further oxidized by-products from the ozonation process. However, increasing the concentration of H_2O_2 to 5 mg/L reduced the efficiency of the system since H_2O_2 can also scavenge $HO^{\bullet}$ from the reaction system. Ozone is known as an electrophilic molecule highly reactive with compounds having high electronic density sites like aromatic rings present in parabens (Pipolo et al., 2017). The only drawback with this technique is the relatively high cost of the volume of H_2O_2 needed for the process and the cost of generating O_3 in-situ.

The fourth non-photochemical method is the use of the Fenton system (H_2O_2/Fe^{2+}). Hydroxyl radical is produced from the reaction between ferrous ions and peroxide.

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + HO^{\bullet} \quad (7)$$

Fenton process has been used to remove methylparaben, ethylparaben, propylparaben, and butylparaben from water and a photodegradation of between 85 and 94% of the parabens after 48 h was reported (Domínguez et al., 2014). Martins et al. also achieved excellent results with using the Fenton process for removal of parabens from water while the treated water showed reduced toxicity for *V. fischeri* and *C. fluminea* (Martins et al., 2016). It is suggested that an increased amount of ferric ion and the presence of natural organic matter (NOM) like humic acid does enhance Fenton reaction even at neutral pH (Christoforidis et al., 2015). However, the main disadvantages of the Fenton process in the treatment of water are its narrow working pH range, the relatively high cost of H_2O_2 and the high amount of ferric sludge produced in the neutralization step of the treated solution before disposal (Zhang et al., 2019b).

5.2.2. Photochemical methods

5.2.2.1. Ultraviolet-assisted advanced oxidation processes This involves the application of ultra-violet light together with peroxide, ozone, and/or ferrous ion to produce hydroxyl radicals. Unlike with the non-photochemical AOP technique, the photochemical AOP technique have five distinct mode. The first photochemical method is the ozone- ultraviolet radiation. In this method, ozone absorbs UV light to generate peroxide which produces $HO^{\bullet}$ (Eqs. (8)–(9)).

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \quad (8)$$

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad (9)$$

Secondly, we have hydrogen peroxide-ultraviolet radiation. In this case, the bonds in hydrogen peroxide undergoes homolysis when it absorbs ultraviolet light, to produce hydroxyl radicals which eventually form peroxy radical, oxygen and water molecules (Eqs. (10)–(12)).

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad (10)$$

$$H_2O_2 + HO^{\bullet} + h\nu \rightarrow H_2O + HO_2^{\bullet} \quad (11)$$

$$H_2O_2 + HO_2^{\bullet} + h\nu \rightarrow H_2O + O_2 + HO^{\bullet} \quad (12)$$

Thirdly, there is the ozone-hydrogen peroxide-ultraviolet light process. Rapid generation of hydroxyl radical occurs as peroxide increases the rate of ozone decomposition under ultraviolet light as shown in Eq. (6).Fourthly, Photo-Fenton/Fenton-like systems which is the application of ferrous ions and hydrogen peroxide with UV/visible light. Hydroxyl radical is produced as Fe^{3+} undergoes reduction to Fe^{2+}, which also reacts with H_2O_2.

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH \quad (13)$$

A detailed review on Fenton process for organic wastewater treatment has been provided by Zhang et al. (2019b).The fifth photochemical method is photocatalytic oxidation, combining a metal oxide semiconductor like TiO_2 and ZnO with UV. The semiconductors absorb UV light that initiates valence band holes and conduction band electrons which combine to develop what is known as an electron–hole pair (e^-/h^+). The conduction band electron (e^-_{cond}) is available for reduction, and the valence band hole ($h_{vb}{}^+$) is available for oxidation.All five photochemical methods have been used to remove parabens from water. Álvarez et al. studied the efficiency of different oxidation processes on the photodegradation of parabens (Álvarez et al., 2020). The study focused on direct photolysis with UV radiation, UV/H_2O_2, UV/$S_2O_8{}^{2-}$ and UV/Fe^{2+}/H_2O_2. Direct photolysis of EtP with UV radiation was slow, with only 18.8% of parabens degraded after 10 min of irradiation. Higher degradation of 83.9% and 95.4% was observed with UV/H_2O_2 and UV/$S_2O_8{}^{2-}$ respectively after 10 min of irradiation. Degradation was highest with photo-Fenton (UV/Fe^{2+}/H_2O_2): 98.1% was achieved. Complete photodegradation was observed as the concentration of $S_2O_8{}^{2-}$ was increased and the time required to degrade 90% ethylparaben also reduced. The UV/$S_2O_8{}^{2-}$ process showed better mineralization of EtP (58%) compared with UV/H_2O_2 process (48%) or UV (4%) (Álvarez et al., 2020). In both UV/$S_2O_8{}^{2-}$ and UV/H_2O_2 process, the degradation rate increased with an increase in the concentration of the oxidants. The treated water was found to be non-toxic to cultured human embryonic kidney cell line (HEK-293).Asgari et al. (2020) conducted a study on photocatalytic ozonation of parabens using ZnO coupled with some ozone methods, and UV. Adsorbed ozone can function as a strong electrophilic agent that can produce ozonide radicals in the presence of metallic oxide semiconductor and UV radiation, which could go on to generate hydroxyl radicals in the adsorption layer (Rajeswari and Kanmani, 2009) as shown in Eqs. (14)–(17).

$$ZnO + h\nu \rightarrow e^- + h^+ \quad (14)$$

$$O_{3(ads)} + e^-_{cb} \rightarrow O_3^{-\cdot} \quad (15)$$

$$O_3^{-\cdot} + H^+ \rightarrow HO_3^{-\cdot} \quad (16)$$

$$HO_3^{-\cdot} \rightarrow HO^{\cdot} + O_2 \quad (17)$$

The conduction band electrons ($e^-{}_{cb}$) are from the valence band and they are taken up by the adsorbed ozone on the metallic oxide semiconductor (ZnO) and converted to ozonide. Each trapped electron produces one hydroxyl radical. In the study, the maximum removal efficiency of parabens was observed in alkaline pH (pH 9.0). The combination of O_3/UV/ZnO had the highest removal efficiency of 98%, 97%, 97%, 96%, 96% for methyl-, ethyl-, propyl-, butyl-, and benzylparaben respectively followed by O_3/UV with 65%, 62.5%, 60%, 58% and 53%, and O_3 with 52%, 50%, 49%, 48% and 47% respectively for the above parabens. The removal efficiency increased with an increase in reaction time. A combination of ZnO with O_3 in the presence of UV radiation is a much better process compared with O_3/UV, with high removal efficiency and mineralization of up to 42% in 20 min.Cuerda-Correa et al. studied eight different ozone combined advanced oxidation processes (Cuerda-Correa et al., 2016). The processes studied were single ozonation (O_3), two binary systems (O_3/H_2O_2 and O_3/UV), three ternary systems (O_3/H_2O_2/Fe^{2+}, O_3/UV/TiO_2 and O_3/UV/H_2O_2) and two quaternary systems (O_3/UV/H_2O_2/Fe^{2+} and O_3/UV/H_2O_2/TiO_2). Among the systems without UV, ozonation alone proved to be more efficient while those with the UV had O_3/UV/H_2O_2/TiO_2 being the most efficient and very fast for the removal of parabens. The influence of UV on the quick removal of parabens in the ozone system is attributed to the photolysis of ozone by UV. In addition, the degradation process was faster due to the introduction of a semiconductor (TiO_2) and hydroxyl radical generator (H_2O_2).Sulfate radical ($SO_4{}^{\cdot -}$) can be considered a good alternative to hydroxyl radical owing to its high redox potential of 2.5–3.1 V and longer lifetime of $3.0–4.0 \times 10^{-5}$ s (Ghanbari et al., 2016). Persulfate anion ($S_2O_8{}^{2-}$) is known to produce $SO_4{}^{\cdot -}$ if the peroxide bonds undergo homolysis when exposed to heat, UV light, bases, transition metals and ultrasound. Persulfate (PS) anion is a strong, aqueous stable, selective, and cheap oxidant which can be used in the pH range of 1.2–12.0 (Criquet and Leitner, 2009).

$$S_2O_8{}^{2-} + \mathit{activator} \rightarrow SO_4{}^{-\bullet} + (SO_4{}^{-\bullet} \text{ or } SO_4{}^{2-}) \quad (18)$$

$$SO_4{}^{-\bullet} + OH^- \rightarrow SO_4{}^{2-} + HO^{\bullet} \quad (19)$$

In support of sulphate radical being a good alternative to $HO^{\bullet}$, Dhaka et al. recorded 10% removal of methylparaben using only persulfate, 34% removal using UV irradiation only and 98.9% removal using a combination of UV/persulfate (Dhaka et al., 2017). Although a good removal efficiency was observed with UV/persulfate, the time of reaction was longer (90 min) with a 30.7% photo-mineralization as against 4.8% with UV only. In the degradation of parabens using UV-C lamps with and without H_2O_2, UVC/H_2O_2 demonstrated a better efficiency. Degradation of parabens using UVC/H_2O_2 was not only fast (30 min) but achieved higher photo-mineralization (66%) compared to the use of UVC only, which was slow (8 h) and achieved a 25% photo-mineralization (Gmurek et al., 2015b). In another study by Dhaka et al. (2018), a different oxidant, peroxymonosulfate (PMS), was used as part of UV-C mediated advanced oxidation processes. The efficiency of UV/PMS was compared with UV/PS and UV/H_2O_2. An 81.3% degradation of ethylparaben was observed with UV/PMS, 97.0% with UV/H_2O_2 and 98.1% with UV/PS, and photo-mineralization of 29%, 31% and 34% respectively.Persulfate absorbs mostly at 254 nm, which makes the use of UV-C light appropriate and widely used (Scheme 1). However, UV-C light has low penetration, it also makes use of a mercury vapour lamp and therefore cannot be seen as environmentally friendly (Chevremont et al., 2012). In view of this, the use of UV-A light-emitting diodes (LED) for the photodegradation of propylparaben in the presence of persulfate was employed owing to its very high efficiency with low power consumption. The study showed that UV-A radiation from LED or solar light can activate persulfate, producing hydroxyl and sulfate radicals needed for the degradation of parabens (Ioannidi et al., 2018). In a separate study, the effect of heating temperature on the oxidation of methyl and ethylparaben using persulfate, was studied. Increasing the temperature of the reactor from 20 °C to 60 °C increased the degradation rates from 3.5% and 2.7% to 94.8% and 95.3% respectively after 240 min (Chen et al., 2017b). Dealkylation of the methyl unit in MeP, decarboxylation of the carboxylic group, and subsequent hydrolysis were proposed as mechanism for the degradation of MeP (Chen et al., 2017b).A serious challenge with UV-based AOPs is the cost of the energy required to drive the lamps. According to the photochemistry commission of International Union of Pure and Applied Chemistry (IUPAC), energy consumption of a process can be measured through the electrical energy per order (E_{EO}). The E_{EO} is defined as the electrical energy in KW/h required for the degradation of 90% (one order magnitude) of the contaminant in 1 m^3 stream. It can be calculated using Eq. (20):

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log \frac{C_i}{C_f}} \tag{20}$$

where P is the power rating of the system in kW, t is the irradiation time in minutes, V is the volume of the reactor in litres, C_i and C_f are initial and final concentrations of the target contaminant respectively (Azarpira et al., 2019). Energy consumption for AOPs depends on water quality and the properties of the contaminants. In the presence of NOM, an AOP require higher electrical energy (Paredes et al., 2019). E_{EO} for a photocatalytic process is often lower than in photolysis due to the generation of radicals that aid the rate of degradation as shown in Table 5.Other equations that have developed for the calculation of specific energy consumption (SEC) include for photolysis (Eq. (21)):

$$SEC = \frac{P \times t}{V \times \left(COD_0 - COD_t\right)} \tag{21}$$

For ozone-based process (Eq. (22))

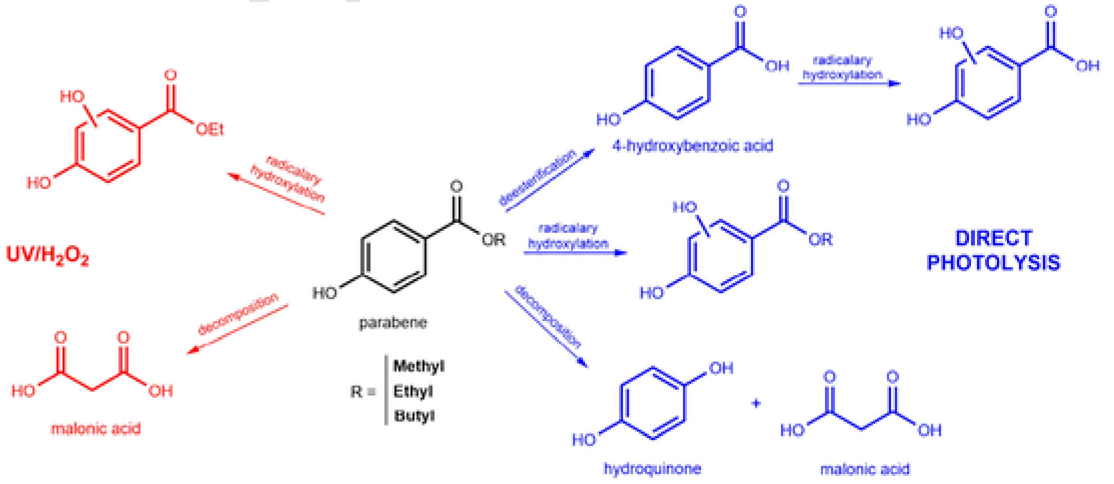
$$SEC = \frac{P \times t + r \times TOD}{V \times \left(COD_0 - COD_t\right)} \tag{22}$$

where P is the nominal electric power (kW) of the photochemical system, t is the reaction time (h), r is the energy requirement for O_3 production (15 kW h/kg O_3) (Gmurek et al., 2019).In a separate study, Gmurek et al. (2019) showed that of the various AOPs used for the removal of mixtures of parabens from aqueous solution: O_3, H_2O_2/Fe^{2+}, H_2O_2/UVC, O_3/H_2O_2, O_3/UVA, O_3/H_2O_2/UVA, UVA/catalyst, O_3/catalyst and O_3/UVA/catalyst, the H_2O_2/UVC mode was the most efficient with high rate for paraben removal and least energy consumption. Aside the energy consumption requirement, harmful by-products formed from the process, especially those assisted with oxidants like peroxide, oxalic acid etc. are cause for much concern.

5.2.2.2. Heterogeneous photocatalysis Heterogeneous photocatalysis involves activation of a catalyst by photon from light (UV or visible), leading to excitation of electrons (e^-) and formation of positive holes (h^+). These short-lived and highly reactive species are able to non-selectively oxidize organic pollutants. Due to its low cost and toxicity, high stability, reusability, chemical resistance and photoactivity compared to other semiconductors, TiO_2 is the most used photocatalyst. However, it suffers from a high band gap energy of 3.2 eV and it is most active under ultraviolet radiation (300–390 nm) (Centi and Perathoner, 2014). The band gap of TiO_2 could be reduced and its activity shifted towards the visible region through some modifications. Catalyst doping is a technique used for this purpose. It involves the inclusion of different semiconductor materials like (e.g. Ag@AgCl, $BiVO_4$, Bi_2WO_6, $Bi4Ti_3O_{12}$, Cu_2O, CuO, etc.) and non-metals (e.g. B, C, N) into the catalyst, capable of interacting with the conduction and valence band and cause modification of the band gap energy, also shifting its activity into the solar spectrum (>400 nm) (Pham and Lee, 2017; Rimoldi et al., 2018). For instance, the addition of persulfate to Al-doped TiO_2 had a positive effect on its rate of degradation of the parabens (Kotzamanidi et al., 2018). It is believing that doping TiO_2 with metals or non-metals improves charge separation (through transition of energy levels between TiO_2 and the dopant orbitals) and also the energy range of photoexcitation (Yang et al., 2011). Doping TiO_2 with Al was found to reduce its bandgap and permit its absorption in the visible region. Lee et al., proposed a simpler and less costly method for the preparation of WO_3/TiO_2 bi-component electrode (Lee et al., 2013).Activation of TiO_2 semiconductor occurs through a mechanism that involves reactive species, through the following reactions (Eqs. (23)–(28)):

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{(CB)} + h^+_{(VB)}) \tag{23}$$

$$OH^- + h^+_{(VB)} \rightarrow HO\bullet \tag{24}$$



Scheme 1. Decomposition pathways observed for parabens using different AOPs.(Reproduced from Álvarez et al. (2020) with permission from Elsevier.)

Table 5
The electrical energy per order, EEO, (kWh/m^3) for UV and UV/H_2O_2 treatments of parabens in wastewater with 95% confidence interval indicated.

Contaminant	UV	UV/H_2O_2	References
Methylparaben	13.9 ± 0.2	8.1 ± 0.6	(Hansen and Andersen, 2012)
Ethylparaben	15.9 ± 0.7	5.3 ± 0.3	(Hansen and Andersen, 2012)
Propylparaben	19.1 ± 1.1	6.4 ± 0.4	(Hansen and Andersen, 2012)
Isobutylparaben	14.2 ± 1.6	7.0 ± 0.4	(Hansen and Andersen, 2012)
Butylparaben	28.0 ± 2.9	7.9 ± 0.4	(Hansen and Andersen, 2012)

$$O_2 + e^- \rightarrow O_2^{-\bullet} \quad (25)$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet} \quad (26)$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \quad (27)$$

$$H_2O_2 + O_2^{-\bullet} \rightarrow OH^- + HO^{\bullet} + O_2 \quad (28)$$

TiO_2 has been widely used as a photocatalyst for the degradation of parabens. A study on the photocatalytic degradation of propylparaben with TiO_2 using a high-pressure mercury lamp as the light source (Fang et al., 2013) was reported. Although mercury lamps have the advantages of being more energy efficient than incandescent and most fluorescent lights coupled with its long bulb life, it is not environmentally friendly. In another study of methylparaben degradation with TiO_2 using UV light, 50% removal was observed with 80% mineralization under 360 min (Lin et al., 2009).Ozone has been effectively combined with heterogeneous photocatalysis (photocatalytic ozonation) as shown by Gomes et al. (2017a). Ozone is a strong oxidant with a high potential of oxidation ($E^o = 2.07$ V) to oxidize large number of organic compounds). The combination of ozone with heterogeneous catalysts enhances the generation of more hydroxyl radicals (Gomes et al., 2017b). One other advantage of combining heterogeneous photocatalysis with ozonation processes is that the use of the photocatalyst in this process requires a lower amount of transferred ozone dose (TOD), a term used to describe the ozone transfer efficiency in the photocatalytic system. This is a more cost-effective approach which was effectively utilized by Gomes et al. when they investigated the effect of Ag and Pt as dopants on TiO_2 for the photocatalytic ozonation of parabens (Gomes et al., 2017b, 2017c). Increasing the metal loading from 0.1% to 0.5% resulted in lower TOD and better degradation efficiency even though the Ag-doped photocatalyst demonstrated a better efficiency than Pt-doped photocatalyst. The potential industrial application of TiO_2 for the photocatalytic degradation of parabens was studied by Gomes et al. (2019a) through the application of TiO_2 nanotubes, which is known for its high specific surface area and adsorption capacity. The photocatalytic oxidation process was studied using UVA and sunlight (solar) as irradiation sources and varying the number of catalytic plates. Degradation of about 80% was achieved with solar photocatalytic oxidation which was much better than with UVA. This efficiency was improved on by increasing the number of catalytic plates which provides more active sites for hydroxyl radical generation. In another study, Martins et al. reported the photoelectrocatalytic degradation of propylparaben using TiO_2 nanotubes (TiO_2-NT) electrode prepared through chemical anodization and modified with WO_3 by electrodeposition (Martins et al., 2017). About 99% propylparaben removal was achieved within 30 min and very high mineralization (94%) was achieved in 60 min. Although TiO_2 nanotubes have the advantages of good adsorption capacity and large surface area, it is however, costly. To reduce its cost, Ti/TiO_2-WO_3 photoanode composite was prepared through electrochemical deposition of WO_3 films on Ti substrate (Martins et al., 2019). Under optimized conditions of pH of 2.0 and +0.5 V, 100% mineralization was achieved in 180 min.Photocatalytic materials based on perovskite and ilmenite type oxides are known for exhibiting good stability, having simple structure and demonstrating good photocatalytic efficiency. They have general formula ABO_3 and include tantalates, niobates, titanates, vanadates and ferrite perovskite (Kanhere and Chen, 2014). Nickel and cobalt titanates ($NiTiO_3$ and $CoTiO_3$) possess ilmenite type structure with band gap energy between 2.14 and 2.5 eV and 2.25 and 2.6 eV respectively depending on their size, morphology and method of synthesis. This gives them the ability to function in visible regions of light and solar light (Inceesungvorn et al., 2014; Mao et al., 2017). Porous $Co_xNi_{1-x}TiO_3$ nanorods were prepared for the photocatalytic degradation of ethylparaben under a simulated solar irradiation. A 92% degradation occurred after 300 min under solar irradiation which decreased to 48% when only the visible part of the radiation was used (Moschogiannaki et al., 2020).Graphitic carbon nitride (g-C_3N_4) is a photocatalyst with advantages like good thermal and chemical stability, metal-free, tunable electronic structure, large surface area, and a two-dimensional planar conjugation structure which can allow coupling with other species. Graphite-like carbon nitride has a band gap of ~2.7 eV. It is a metal-free semiconductor that can be activated under visible light irradiation (Lima et al., 2018). It can be prepared by solvent-free, thermal polymerization of carbon- and nitrogen-rich compounds (Earth-abundant elements) at a low-cost (Ong et al., 2016). Nanohybrid of g-C_3N_4/$FeVO_4$ supported on biochar (CIB) have been used for the removal of methylparaben under three conditions; adsorption followed by photodegradation (AP); simultaneous adsorption and photocatalysis (SAP); and SAP + O_3 (Kumar et al., 2017). About 90.1% removal of methylparaben was observed with the AP technique. For the adsorption and photocatalysis (SAP) technique degradation of MeP was 98.4% with 74.2% mineralization in 90 min while 99.8% degradation was observed with the addition of ozone to SAP processes in 60 min. Ozonation, in the absence of the photocatalyst (CIB), achieved 41.2% removal. Metal-free graphite-like carbon nitride was used to achieve complete photocatalytic degradation of methyl-, ethyl- and propylparaben under light emitting diode (LED) irradiation in 20 min (Fernandes et al., 2020b). However, graphite-like carbon nitride suffers from low quantum efficiency and also the photo-generated electron-hole pairs recombine very fast which can be solved by coupling with other semiconductors (Ge et al., 2012; Hou et al., 2013). The efficiency of a metal-free graphite-like carbon nitride (GCN-500) in photodegradation of either isolated or mixture of parabens was found to be far more efficient than the commercial Degussa (TiO_2 P25) where the former achieved a total degradation of the parabens in 20 min and the latter in 120 min under visible light ($\lambda_{exc} = 417$ nm) LED excitation. Superoxide radicals were found to be the prominent reactive oxygen species that caused the photodegradation of the parabens (Fernandes et al., 2020b).Bismuth vanadate ($BiVO_4$) is a photoactive material with a narrow band gap of ~2.4 eV, chemically stable in aqueous solution with low toxicity but also suffers from low photocatalytic activity as a result of its high rate of recombination of photo-generated electron-hole pairs. To improve the photoactivity of $BiVO_4$, it was combined with CoO_x (CoO_x/$BiVO_4$) for the degradation of propylparaben under simulated solar irradiation (Petala et al., 2019). The synthesized material (CoO_x/$BiVO_4$) achieved 97% degradation of propylparaben under simulated solar irradiation and 89% degradation under visible-light irradiation.A novel Iodine-doped $Bi_4O_5Br_2$ photocatalyst was developed through a facile microwave synthesis route for the degradation of four parabens. Compared with the pure $Bi_4O_5Br_2$, the Iodine-doped $Bi_4O_5Br_2$ has a larger specific surface area and a relatively lower band gap energy. The Iodine-doped $Bi_4O_5Br_2$ photocatalyst had up to 27 times the activity of $Bi_4O_5Br_2$ photocatalyst for the degradation of the parabens while achieving up to 80% photodegradation of the parabens after 180 min and 64% mineralization after 60 min (Xiao et al., 2017).Ag_3PO_4 is another promising photocatalyst that is receiving much attention. It is active in the visible-light region and able to degrade and mineralize organics in water. It has found application in the degradation of parabens in aqueous media. In a study carried out by Frontistis et al., Ag_3PO_4 was able to degrade 73.3% of ethylparaben after 30 min (Frontistis et al., 2017a). However, Ag_3PO_4 like several other photocatalyst, suffers from facile photo-corrosion and high rate of recombination of photo-generated electron-hole pairs. Like many other photocatalysts, the efficiency of Ag_3PO_4 can be improved on by coupling with other semiconductors. For example, when Ag_3PO_4 was coupled with AgCl for the degradation of methylparaben under visible-light irradiation, a 100% photodegradation was achieved within 40 min of irradiation (Guo et al., 2018). In another citrate complexes under simulated sunlight was enhanced with the addition of oxalic acid. Approximately 99% degradation was observed after 30 min (Feng et al., 2014). Ma et al. (2020) also reported the successful use of a mesoporous exfoliated bentonite (EB)/Ag_3PO_4/AgBr (30%) (a heterojunction photocatalyst) for the removal of methylparaben in water. 0.2 g/L methylparaben was completely photodegraded over the EB/Ag_3PO_4/AgBr (30%) in 40 min under visible-light irradiation. After five reuse cycles, the photocatalyst showed 91% efficiency. The enhanced photocatalytic activity and photo-stability of EB/Ag_3PO_4/AgBr (30%) are ascribed to the stable structural characteristics, enlarged surface area, high absorption ability, and improved light absorption ability from loading Ag_3PO_4 onto exfoliated bentonite. Hydroxyl radicals and holes were shown to be responsible for the photodegradation (Ma et al., 2020) as shown in Fig. 2.Just as there are a few studies focused on the occurrence of chlorinated and brominated parabens, so there are even fewer investigations on their removal. However, synthesized cadmium sulfide/reduced graphene oxide/bismuth oxyiodide (CdS/rGO/BiOI) photocatalyst has been used for the photodegradation of chlorinated parabens under visible-light irradiation and at pH 9.0. It is suggested that rGO acts as the electronic shuttle between the two semiconductors, CdS and BiOI (the reduction and oxidation photocatalyst respectively) (Ma et al., 2019). Table 6 presents some of the various heterogeneous photocatalysts that have been used to degrade parabens in water under different operating conditions.It is true that heterogeneous photocatalysis holds a promising potential for efficient removal of organic contaminants from water including parabens. Indeed it is more preferred to other techniques because of its ability to convert organic contaminants in water to CO_2, H_20 and other less harmful by-products. However, its disadvantage includes low mineralization and development of harmful by products. Also, the application of this technique in treatment of real wastewater is still a challenge.

5.2.2.3. Electrochemical advanced oxidation processes (EAOPs) In EAOPs, hydroxyl radicals can be generated in situ for the degradation and mineralization of organic contaminants (Mandal et al., 2017). Some of the advantages of EAOPs are; high reaction rates, use of clean species as reagent (electron), small amounts of reagents are required, low sludge is produced in the process, renewable energy source can be used, could be coupled with other treatment technologies while the disadvantages are; could be costly, electrolytes may be needed if conductance of water is low, catalysts cannot be reused, and intermediate products could be more toxic than parent compounds (Seibert et al., 2020). Electrochemical oxidation and electro-Fenton are examples EAOPs that are flexible alternatives for the removal of organic contaminants in water (Brillas and Martínez-Huitle, 2015).Electrochemical oxidation involves the migration of electrons from an electron donor (reductant) to an electron acceptor (oxidant), thereby leading to a chemical reaction that generates radicals responsible for degradation of organic contaminants (Radha and Sirisha, 2018). In electrochemical oxidation, degradation occurs at the surface of the anode and/or by physisorbed hydroxyl radical M($^\bullet$OH) formed by water oxidation at high applied current (Panizza and Cerisola, 2009) as shown in Eq. (29). Aside the fact that electrochemical oxidation can occur directly through the action of hydroxyl radical generated on the anode, indirect oxidation could also take place by primary and secondary oxidants (chlorine, hypochlorous acid and hypochlorite or hydrogen peroxide/ozone) present in the system (Särkkä et al., 2015).

$$M + H_2O \rightarrow M(^\bullet OH) + H^+ + e^- \tag{29}$$

where M is the anode.Electro-Fenton, as one of the EAOPs, involves the reduction of dissolved oxygen in the cathode which produces H_2O_2 that react with ferrous ions to generate free $HO^\bullet$ (Nidheesh and Gandhimathi, 2012).

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{30}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + H_2O + HO^\bullet \tag{31}$$

$$HO^\bullet + \text{Organic molecule} \rightarrow CO_2 + H_2O + \text{by-products} \tag{32}$$

The free $HO^\bullet$ is able to degrade organic molecules like parabens (Eqs. (30)–(32)).Photoelectron-Fenton is another electrochemical advanced oxidation process that involves irradiation of the treated solution with UV-A light. The processes involved in the irradiation are: (i) photo-reduction of Fe^{3+} leading to the generation of hydroxyl radical (Eq. (33)) (Sun and Pignatello, 1993) (ii) photolysis of the complexes of Fe^{3+} and organics (Eq. (34)) (Moreira et al., 2017).

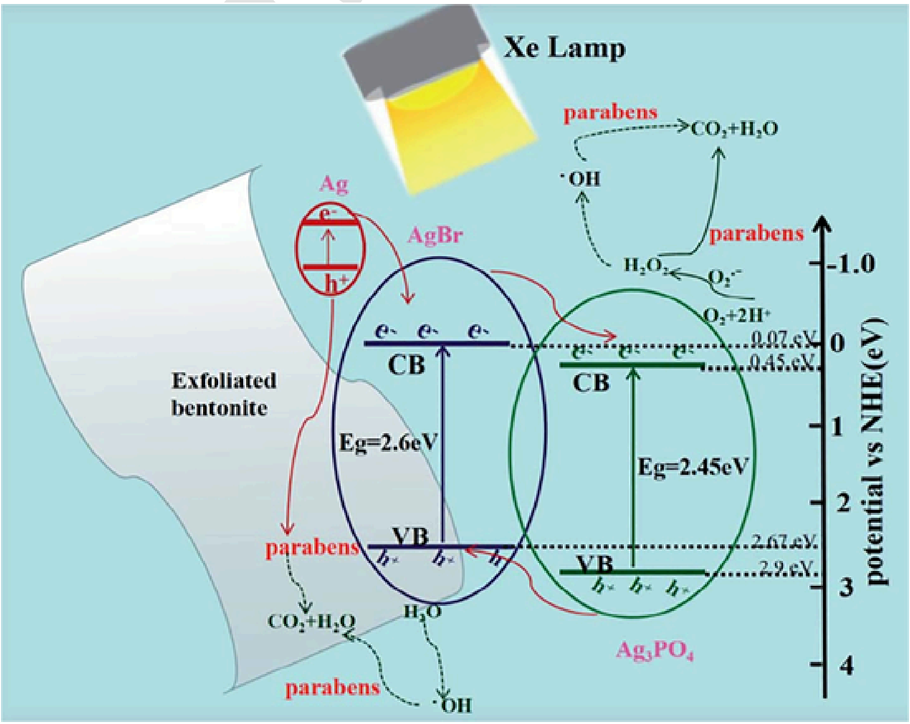


Fig. 2. The photodegradation mechanism of methylparaben on EB/Ag_3PO_4/AgBr (30%).(Reproduced from Ma et al. (2020) with permission from the Royal Society of Chemistry.)

Table 6
Contaminant concentration, pH, dosage, reaction time, radiation source and removal efficiencies of some photocatalysts.

C	CC (mg/L)	Catalyst	Opt. pH	Dosage (g/L)	Radiation source	RxN time (min)	Removal efficiency (%)	Mineralization (%)	Reference
EtP	0.25	Porous $Co_xNi_{1-x}TiO_3$ nanorods	–	–	Visible light	300	92	–	(Moschogiannaki et al., 2020)
MeP, EtP, PrP, BuP		Fe (III)-citrate	6.0	–	Visible light	30	99	–	(Feng et al., 2014)
MeP, EtP, PrP	1.22	GNC-500	–	1.0	Visible light	20	100	–	(Fernandes et al., 2020b)
MeP	20	$AgCl/Ag_3PO_4$	8.0	0.5	Visible light	40	100	–	(Guo et al., 2018)
MeP	20	g-$C_3N_4/FeVO_4/Fe@NH_2$-biochar	5.5	0.5	Sunlight	90	98.4	74.2	(Kumar et al., 2017)
MDHB	20	CdS/rGO/BiOI	9.0	0.2	Visible light	120	80	–	(Ma et al., 2019)
PrP	0.2	$CoO_x/BiVO_4$	6.0	1.0	Visible light	150	97	–	(Petala et al., 2019)
PrP	50	TiO_2-NT/WO_3	3.0		UV/Visible light	30	99	94	(Martins et al., 2017)
EtP	0.3	N-TiO_2	6.5	0.75	Visible light	60	98	–	(Petala et al., 2015)
MeP	1.0	Aeroxide TiO_2 P-25	5.2	0.5	Visible light	35	100	42	(Velegraki et al., 2015)
EtP	20	ZnO	6.0	1.0	Visible light	240	100	–	(Frontistis et al., 2017b)
PrP	10	I-$Bi_4O_5Br_2$	–	1.0	Visible light	60	94.5	80	(Xiao et al., 2017)
MeP, EtP PrP, BuP, BeP	10	O_3/Ag-TiO_2	5.7	0.07	UV-A light	120	100	43	(Gomes et al., 2017c)
MeP	10	TiO_2	9.0	2.5	UV light	180	80	–	(Lin et al., 2009)
MeP, EtP, PrP, BuP, BeP	50	0_3/N-TiO_2	7.0	0.14	UV-A light	60	100	34.1	(Fernandes et al., 2020a)
PrP	0.42	Al-TiO_2	6.0	0.25	Visible light	90	90	–	(Kotzamanidi et al., 2018)
PrP	50	Ti/TiO_2-WO_3	4.0	–	UV/Visible light	60	100	78.3	(Martins et al., 2019)
MeP	30	RGOCdS	3.0	0.75	Visible light	90	100	–	(Mohan et al., 2021)
BeP	15	UV/ZnO-H_2O_2 (UZH)	9.0	1.0	UV-C light	90	100	55	(Sheikhmohammadi et al., 2020)
BuP	14	UV/ZnO-H_2O_2 (UZH)	9.0	1.0	UV-C light	90	100	37	(Asgari et al., 2020)
EtP	0.5	Ag_2CO_3	6.0	0.75	Solar	120	100	–	(Petala et al., 2020)
MeP, EtP, PrP, BuP, BeP	10	O_3/UV/ZnO	9.0	1.0	UV	20	98	42	(Asgari et al., 2019)
MeP	20	EB/Ag_3PO_4/AgBr	–	0.1	Visible light	40	100	–	(Ma et al., 2020)
MeP	10	AgBr@m-WO_3	–	1.0	Visible light	180	85	–	(Suliman et al., 2019)
EtP	10	Ag_2S-TiO_2	2.87	3	UV light	120	95	–	(Liu et al., 2020)
MeP	10	I-doped BiOCl	–	–	Visible light	60	91.2	–	(Zhang et al., 2019a)
MeP	30	UV-C/TiO_2	9.0	0.5	UV/visible light	60	100	78	(Doná et al., 2018)
PrP, EtP	1.0	ZVI/PS	2.1	0.04	UV-A light	15	97.5	–	(Palharim et al., 2020)
MeP, EtP, PrP	90	TiO_2-NT	–	–	Sunlight	60	80	–	(Gomes et al., 2019a)

Note: C = contaminant; CC = contaminant concentration; RxN = reaction; NT = nanotube; Opt. pH = optimum pH.

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \quad (33)$$

$$Fe^{3+}(L)_n + h\nu \rightarrow Fe^{2+}(L)_{n-1} + L^{\bullet}_{ox} \quad (34)$$

Several anodes have been used in electrochemical oxidation processes, such as Pt, PbO_2, TiO_2, IrO_2 and different Ti-based alloys. One of the anodes that is most often used in recent time is the boron-doped diamond (BDD), as it is effective in the removal and mineralization of organic contaminants in water. At high potential, highly reactive hydroxyl radicals are generated at the surface of the anode which can cause mineralization when it reacts with organics (Särkkä et al., 2015; Sirés and Brillas, 2012) as depicted by Eqs. (35)–(36).

$$BDD + H_2O \rightarrow BDD\ (HO^{\bullet}) + H^+ + e^- \quad (35)$$

$$Organics + BDD\ (HO^{\bullet}) \rightarrow CO_2 + H_2O \quad (36)$$

Currently, there are few researches on the electrochemical oxidation of parabens. In a study carried out by Frontistis et al. (Frontistis et al., 2017c), ethylparaben was subjected to electrochemical oxidation over a boron-doped diamond (BDD) anode. Degradation was faster in the presence of NaCl as electrolyte compared with $HClO_4$ or

This is due to an indirect oxidation of ethylparaben mediated by chlorine radicals formed from reaction between $HO^{\bullet}$ and Cl^-. So aside from hydroxyl radical, chlorine radical also played a role in the photodegradation of ethylparaben, a process which was achieved within 15 min. The various schemes leading to the formation of chlorination, dealkylation, decarboxylation and formation of chlorinated and non-chlorinated dimers are shown in Figs. 3 and 4.In another two separate studies employing BDD as the anode, electrochemical and hybrid of electrochemical and sonoelectrochemical oxidation were compared for the degradation of methylparaben using K_2SO_4 as an electrolyte (Steter et al., 2014a, 2014b). While both processes proved efficient, mineralization was higher (approximately 60%) with the use of sonoelectrochemical oxidation. In another study, the electrochemical oxidation of butylparaben on platinum and glassy carbon electrode. Electrochemical oxidation of butylparaben was more efficient in acidic medium, in the presence of $K_4P_2O_7$ as electrolyte and cetyltrimethylammonium chloride (CTAC) as surfactant. Approximately 95% degradation was observed after 2.5 h (Gomes et al., 2016).Steter et al. (2018) attempted the use of solar photoelectro-Fenton for removal of mixtures of parabens. The performance of the solar photoelectro-Fen-

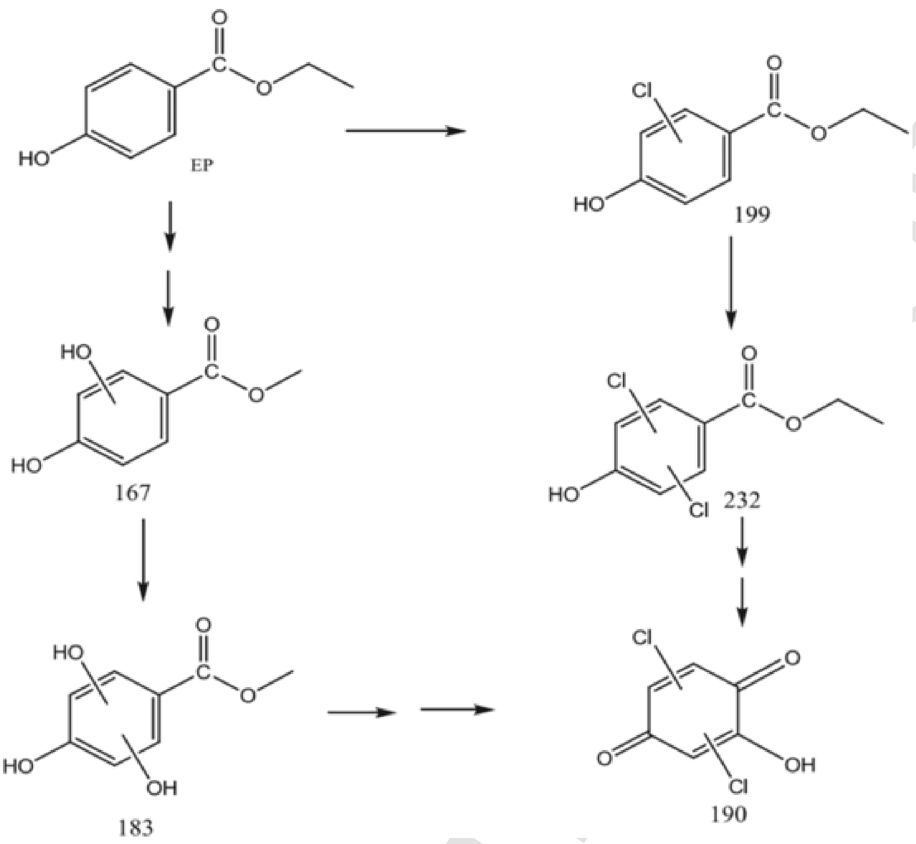


Fig. 3. Chlorination, dealkylation and hydroxylation pathways of EP electrochemical oxidation in the presence of NaCl. The mass marked below each structure corresponds to the $[M\text{-}H]^-$ pseudo-molecular ions.[Reproduced from Frontistis et al., 2017c with permission from Elsevier.]

was replaced with a less expensive anode (RuO_2) degradation was slower but a higher mineralization of 70% was achieved after 480 min. Although both BDD and RuO_2 anodes demonstrate very high performance in electrochemical oxidation, they are expensive, unstable during wastewater treatment and difficult to prepare (Yu et al., 2014).In trying to improve the EAOPs, Rosales et al. used graphite felt (GF) as the cathode in an electro-Fenton process (Rosales et al., 2018). An almost complete degradation MeP was observed after 1 h. To improve the process, heterogeneous electro-Fenton was subsequently carried out. In the heterogeneous electro-Fenton, iron activated with H_2SO_4 was introduced to the cathode. A 100% degradation of MeP was achieved after 30 min and 98.7% mineralization after 120 min at operational conditions of 100 mg/L MeP, 0.01 M Na_2SO_4, airflow of 1 L/min and pH of 3.0 (Rosales et al., 2018).The efficiency of the electrochemical oxidation of methylparaben was carried out using cheap, robust and dimensionally stable DSA®-Cl_2 (mixed metal oxide electrode) anode and a hybrid of DSA®-Cl_2 with UV light radiation (Dionisio et al., 2020). The degradation of methylparaben was enhanced by the production of hydroxyl radicals and active chlorine species (Cl_2, HClO, ClO^-). Degradation of methylparaben was fast in both processes but irradiation with UV improved the mineralization by facilitating the degradation of the by-products. Active chlorine species produced by electrochemical processes are activated to more oxidizing species ($OH^\bullet$ and $Cl^\bullet$) under UV irradiation to achieve a 40% increase in mineralization rate compared to simple electrolysis. MeP oxidation was via chlorination and hydroxylation (Dionisio et al., 2020). Bosio et al. also employed the use of Ti/Pt anode for the electrochemical oxidation of a mixture of parabens. A complete degradation of parabens was observed at a higher current density (125 A m^{-2}) and 3. 0 g/L of NaCl as electrolyte in 10 min (Bosio et al., 2020).As useful and efficient as EAOPs are, their drawback include relatively high cost, need for electrolytes may be needed if conductance of water is low and this can negatively influence the anode/cathode of the system, high cost of developing anodes, the high cost of energy requirements of the process, irreversibility of most spent anodes for reuse, and formation of intermediate products which could be more toxic than parent paraben compounds (Seibert et al., 2020).

5.2.2.4. Miscellaneous techniques There are few other works which suggests that the removal of parabens from water were by other techniques aside those already discussed. For example some authors have used photosonochemical method to degrade parabens in water (Daghrir et al., 2014). It was observed that the addition of biochar improved sonochemical degradation of propylparaben by acting in two ways: as an adsorbent for propylparaben using the π-π interaction and serving as a nucleation site for the formation of radicals (Nikolaou et al., 2020).Comparing the efficiency of ultrasonication, direct photolysis and photosonolysis processes in the degradation of butylparaben, photosonolysis method showed a better degradation efficiency of ca. 99.2% and mineralization of 43.3% (at a power rating of 40 W and frequency of 518 kHz in 120 min) over ultrasonication and direct photolysis (Daghrir et al., 2014). Sasi et al. (2015) investigated the sonochemical degradation of methylparaben at 350 kHz and power density of 22.75 W/mL. A 98% mineralization after 90 min of sonolysis was recorded and this increased with time. Using the LC–TOF–MS to understand the mechanism of sonochemical degradation, it was observed that the sonochemical degradation of EtP occurs through dealkylation of the ethyl chain to form methylparaben, while successive hydroxylation of the aromatic ring yields 4-hydroxybenzoic, 2,4-dihydroxybenzoic and 3,4-dihydroxybenzoic acids (Papadopoulos et al., 2016). Although, the sonochemical technique is quite useful and yields high mineralization, its major drawback is associated with the energy cost of the process.In another process, some authors used the dye-sensitized photo-oxidation technique (which requires the use of photosensitizers) to remove parabens from water. Gmurek et al. used the *meso*-tetraphenylporphyrin (TPP) immobilized on polyurethane nanofiber material to remove BuP and benzylparabens (BeP) from water (Gmurek et al., 2015a). The dye-sensitized nanomaterial released singlet oxygen as its reactive oxygen species that was responsible for the degradation of BuP (50%) and BeP (70%). The main mechanism of photodegradation, as al-

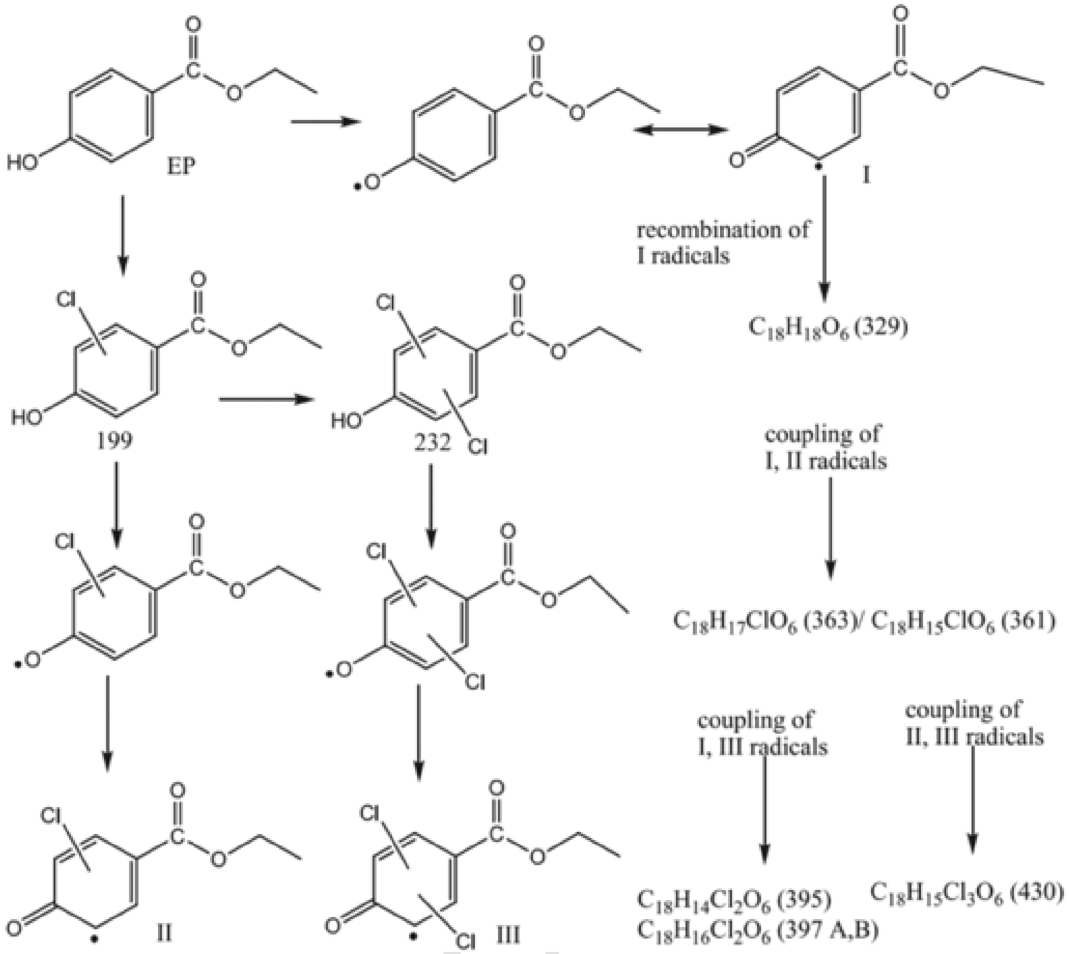


Fig. 4. Dimerization pathways of EP electrochemical oxidation in the presence of NaCl. The mass marked below each structure corresponds to the [M-H]$^-$ pseudo-molecular ions.[Reproduced from Frontistis et al. (2017c) with permission from Elsevier.]

ways, was by hydroxylation with the main photodegradation products being 4-hydroxybenzoic acid and monohydroxy parabens (Gmurek et al., 2015a).

5.3. Biological removal

5.3.1. Biodegradation

There are also reports on the degradation of parabens by microorganisms. In the study by Amin et al., two microorganisms isolated from non-sterile methylparaben and propylparaben solution were found to degrade the respective parabens (Amin et al., 2010). The microorganisms were identified to be *Pseudomonas beteli* and *Burkholderia latens* respectively. *P. beteli* could degrade methylparaben (100%) while propylparaben degradation was very low (5.12%) after 10 days. *B. latens* completely degraded both parabens (Amin et al., 2010). Onuche et al. also reported the biodegradation of methylparaben in shampoo and hair dressing salon wastewater by bacteria from sewage treatment sludge. *Klebsiella planticola* and *Proteus vulgaris* degraded 94.4% of methylparaben after 13 days of incubation in the Shampoo solution. *Vibro cholera*, *Pseudomonas beteli* and *Escherichia coli* degraded 90.5% of methylparaben after 4 days of incubation (Onuche et al., 2016). Recently, the removal of methylparaben and propylparaben from domestic sewage by free-flowing aquatic macrophytes: *Landoltia punctata* and *Lemna minor*, was reported (Anjos et al., 2019). *L. punctata* achieved 90.8% and 90.6% removal of methylparaben at daylight and in the evening respectively while *L. minor* achieved 88.0% and 90.5% removal of propylparaben at daylight and in the evening, respectively.

5.3.2. Biocatalytic degradation

Zhu and Wei in their recent study demonstrated, for the first time, the successful enzyme-mediated removal of parabens from water (Zhu and Wei, 2018).

The new biocatalyst (named as SDFsC), developed by expressing the enzyme, *Fusarium solani pisi* cutinase (FsC), on the cell surface of Baker's yeast, *Sacchromycese cerevisiae*, preferentially degraded parabens with relatively long alkyl or aromatic side chains (Fig. 5). Results from their study suggest that biodegradation of parabens with SDFsC could effectively deactivate the estrogenic effects of parabens. This was confirmed using a mass spectrometer analysis of the by-product of degradation in SDFsC treated water. It was observed that the ester bond of parabens was cleaved by SDFsC via a hydrolysis pathway and yielded 4-hydroxy benzoic acid and corresponding alcohols, which have negligible estrogenic activity. In a system where all three parabens (PrP, BuP and BeP) were present in the water simultaneously, >98% of PrP and all of BuP and BeP were removed within 48 h using the SDFsC biocatalyst (Zhu and Wei, 2018). When applied to wastewater, it was observed that wastewater matrix effect and simultaneous presence of metal ions had negligible effects on the efficiency of the SDFsC biocatalyst. Even after six cycles of reuse, the SDFsC biocatalyst maintained a high degradation efficiency of parabens in water at 90% (Zhu and Wei, 2018). The advantages of the use of SDFsC biocatalyst include its ability to operate at ambient temperature and pressure, zero chemical reagent requirement, high efficiency with real-world secondary effluents, good stability after several reuse and easy recoverability. As an additional advantage, the SDFsC biocatalytic treatment could either be

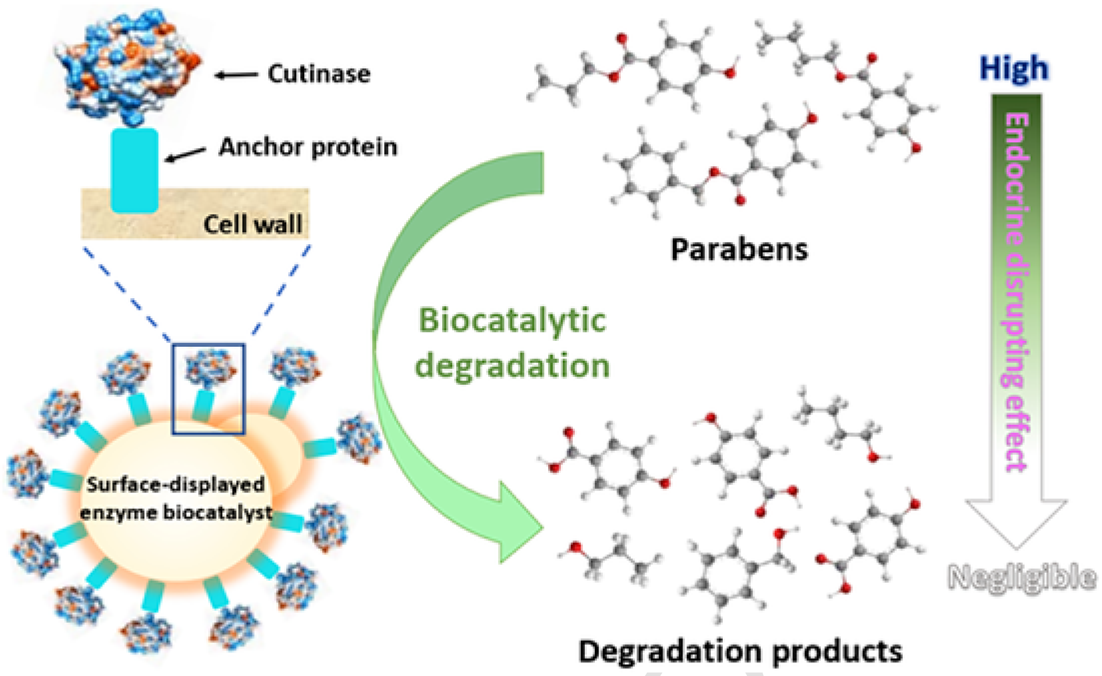


Fig. 5. Simple diagrammatic pathway for biocatalytic degradation of paraben.(Reprinted (adapted) with permission from Zhu and Wei (2018) American Chemical Society).

operated alone or in combination with other treatment technologies as a polishing step (Zhu and Wei, 2018).

In another study, Song et al. used periphyton (a microbial aggregate composed mainly of microalgae and bacteria, which commonly develops on submerged surfaces in the aquatic ecosystem) to remove methyl- ethyl-, propyl-, butyl-, and two chlorinated methylparabens. They reported that temperatures above environmental conditions enhanced the removal of all parabens, while dark condition favoured the removal of the chlorinated methylparabens (Song et al., 2017a).

In some other studies, parabens in water were biodegraded in activated sludge under aerobic and anaerobic conditions with the former yielding better results than the latter (Lu et al., 2018; Wu et al., 2017). While Wu et al. (2017) observed that the major by-product of aerobic biodegradation of MeP and PrP is benzoic acid and minor amounts of phenol, Lu et al. (2018) and Song et al. (2017b) observed transesterification of PrP to MeP, PrP to EtP and BuP to EtP occurred with addition of methanol or ethanol to their aerobic biodegradation system. It is suggested that amano lipase from *Pseudomonas fluorescens* catalyze transesterification of parabens (Wang et al., 2018). In the aerobic activated sludge with alcohol, MeP formed bulk of the transformation product arising because of its lower rate of degradation in the activated sludge (14. 7 h to reach 90% degradation) as compared with EtP, PrP and BuP (5 h to reach 90% degradation). Even in aerobic granular sludge, a similar trend was observed (Argenta et al., 2021). This suggests that the longer alkyl ester chain undergo faster degradation than shorter ones (Lu et al., 2018).

These efficiencies no doubt are impressive and suggest the potential that the biodegradation techniques holds for the future. However, there are several weaknesses of this technique that needs to be addressed. Biodegradation of highly chlorinated parabens might pose a serious challenge for microbial community in the system. Furthermore, the conditions under which an optimum efficiency can be obtained from the process still need to be research into. Biodegradation is a research-intensive technology that requires a thorough prior understanding of microbial processes. Else, the consequences could be more severe than the original contaminant to the ecosystem.

6. Effect of some variables on photodegradation of parabens

The photodegradation method has no doubt gained more attention than other methods that have been discussed in this article. It is, however, important that we understand how some operating variables within the photocatalytic system, influence the efficiency of the process in the removal of parabens from water.

6.1. pH effect

There are various reports on the effect of pH on the photodegradation of parabens in water. pH is said to have an effect on the formation of hydroxyl radicals, the surface chemistry of the photocatalysts, and the speciation and solubility of the contaminants (Lin et al., 2009; Thakur et al., 2015). Hydroxyl radical can be generated when hydroxide ions and light excited holes (h^+) react with water. The positive holes are the major oxidation species at lower pH while hydroxyl radicals are the major species at neutral or high pH (Lin et al., 2009). Feng et al. (Feng et al., 2014) reported the effect of pH on the photodegradation of parabens in a Fe (III)-citrate system between pH 5.0 and 8.0. The pH order of degradation was observed to be 5.0 > 6.0 > 7.0 > 8.0. However, Ma et al. (2019) conducted the degradation of chlorinated paraben at pH 9.0 using the CdS/rGO/BiOI composite and the degradation of chlorinated paraben were more stable under alkaline condition. Kumar et al. (2017) also reported the effect of pH on the degradation of methylparaben using g-C_3N_4/$FeVO_4$ with highest degradation observed in the pH range of 5.0–7.0. At slightly acidic medium (pH 5.0–6.0), the surface of the g-C_3N_4/$FeVO_4$/Fe@NH_2-Biochar (CIB) was protonated, allowing for improved adsorption of phenoxide form of methylparaben formed at this pH range. In another study more hydroxyl radicals was readily produced on TiO_2 surface at alkaline pH of 9.0, leading to faster degradation of parabens as compared with acidic pH of 3.0 (Lin et al., 2009; Petala et al., 2015). Sheikhmohammadi et al. (2020) opined that the higher removal efficiency of benzylparaben at alkaline pH of 9.0 was as a result of the attractive effect of negatively charged of benzylparaben and the positive surface of ZnO used for the removal of benzylparaben.

pH is an important parameter in ozonation processes, higher pH values (neutral or alkaline) can cause self-decomposition of ozone into hydroxyl radicals which can enhance degradation of contaminants (Kasprzyk-Hordern et al., 2003). On the other hand, some other radical species like ozonide, superoxide radicals can be seen in photocatalytic ozonation, which can favour generation of hydroxyl radicals at lower pH's (acidic) (Mehrjouei et al., 2015; Rodríguez et al., 2013). In terms of the rate of photodegradation, faster degradation of parabens was observed at neutral pH (7) than at acidic pH (Fernandes et al., 2020a; Gomes et al., 2019b) but Gomes et al. (2019b) observed that at lower pH of 3.0, lower amount of transfer ozone dose (TOD) was required for parabens degradation compared with higher pH which required higher TOD. Overall, it is observed that the pH at which photodegradation of parabens is done is dependent on the type of photocatalytic materials employed.

6.2. Water matrix effect

Water matrix plays an important role in the photodegradation of organic contaminants in water. The presence of certain anion and organic matter can affect the rate of photodegradation. Several authors have investigated the effects of different anions, scavengers and organic matters on the removal of parabens in water. The effect of low molecular weight carboxylic acids like formic acid, acetic acid, malonic acid and succinic acid on the photodegradation of methylparaben at pH 6.0 was studied in the Fe (III)-citrate system. The presence of these carboxylic acids inhibited the photodegradation of methylparaben, with almost complete inhibition (99%) at 20 mM in 30 min. The inhibition is a result of the competition of acids for the hydroxyl radical in the photocatalytic system. While formic, malonic, acetic and succinic acid inhibited the photodegradation of methylparaben. However, the reverse was the case with oxalic acid because Ferrioxalate complexes formed were found to be highly photoreactive and generates hydroxyl radicals under irradiation (Zuo and Hoigne, 1992).

Even with the introduction of inorganic species like nitrate, bicarbonate, chloride, sulphate, calcium, magnesium, iron, zinc, copper and dissolved organic matter into the photocatalytic system does negatively influence the process since these species can be adsorbed on catalytic sites on the photocatalyst surface or even act as radical scavengers and form their respective radicals, whose potentials are lower than that of hydroxyl radicals (Zacharakis et al., 2013). For instance, the effect of bicarbonate (250–500 mg/L) on photodegradation of parabens was found to be negative due to the formation of carbonate radicals (Eq. (37)) which is a weaker but a more selective oxidant than hydroxyl radical.

$$HCO_3^- + HO^\bullet \rightarrow CO_3^{\bullet -} + H_2O \tag{37}$$

Similar trend was observed with chloride but only above 125 mg/L. The chloride ion is known to scavenge hydroxyl radicals and photogenerated holes to form chloride radicals which is less reactive than hydroxyl radicals (Eqs. (38)–(40)).

$$Cl^- + HO^\bullet \rightarrow HOCl^{\bullet -} \tag{38}$$

$$HOCl^{\bullet -} + H^+ \rightarrow Cl^\bullet + H_2O \tag{39}$$

$$Cl^- + h^+ \rightarrow Cl^\bullet \tag{40}$$

Greater inhibition of degradation by chloride is said to be dependent on solution pH and concentration of chloride, with higher effects observed at acidic pH rather than at near-neutral pH (Boutiti et al., 2017).

Petala et al. (2019) observed that the addition of anions like bicarbonate and chloride (dominant ions in natural waters) at 250–500 mg/L to ultrapure water had no considerable effect on the photodegradation of propylparaben compared with secondary treated wastewater (WW) sample which lowered the photodegradation rate. The negative impact of the WW was attributed to the presence and scavenging action of some unidentified constituents present in it. Similar result was reported by Arvaniti et al. (2020). However, the influence of organic matters such as humic acid (HA) had a good effect on degradation rate. Kotzamanidi et al. (2018) reported the effect of HA on the degradation of propylparaben, it was observed that 1.25 mg/L of HA decrease the rate of photodegradation by 65% while with 10 mg/L of HA, an almost total photodegradation inhibition was observed. This is contrary to findings by Petala et al. (2015) who reported a negative effect with the rate of photodegradation of parabens decreasing with increasing concentration of HA. Antonopoulou et al. (2015) attributed this effect to i) the light shielding effect of HA which reduces the amount of incident light entering the solution, thereby reducing the number of catalytic sites that can be activated on the photocatalyst ii) the competing effect of HA for the active sites on the photocatalyst and iii) the scavenging effect of HA through its reactive functional groups that could interact with the photogenerated holes and hydroxyl radicals. Arvaniti et al. in their study also found that the addition of persulfate ions ($S_2O_8^{2-}$) in the reaction mixture enhanced the performance the photocatalytic system (Arvaniti et al., 2020).

7. Perspectives for the future

In view of the forgoing, it is obvious that parabens in our environment, especially in drinking water, is a future threat to the health of man. It therefore demands that action is taken now to reduce or remove completely, these chemicals from potable water. There are very few researches focused on the occurrence of halogenated parabens (chlorinated and brominated parabens) in water samples. It is evident from the studies carried out that both chlorinated and brominated parabens show strong estrogenic activity, brominated parabens being more active than their parent compounds. More studies need to be carried out to investigate the occurrence of halogenated parabens in water bodies, their impact on human health and how best to remove them from water.

In seeking for efficient techniques for removal of parabens from water, the sustainability of such techniques, nature of transformation products (in case of AOP techniques), environmental friendliness of materials and methods used in developing the technique or materials, scalability and cost of technology, should all be crucial factors to consider. Adsorption, heterogeneous photocatalysis, biodegradation and membrane filtration are very efficient technologies deployed for the removal of parabens from aqueous matrices. Adsorption and heterogeneous photocatalysis are relatively cheaper compared to membrane technology. High cost of maintenance is the main bane of the membrane technology and this is due to frequent fowling of the membrane and cost associated with the development of the membrane itself. Besides, with biodegradation there is the possibility that complete degradation may not be due in a few hours and with recent scientific findings, parabens are only transformed from one form to another during biodegradation in the presence an alcohol. This obviously does not appear to be the much needed solution for the removal of parabens from aqueous matrices. The adsorption technique on the other hand, is limited in its efficiency and in the volume of contaminated water that could be treated per weight of an active adsorbent. This is because other polar organic molecules like parabens, if present together with parabens, will certainly compete for the active sites on adsorbents and thereby lead to reduction in the efficiency of the adsorbent for parabens. Similarly, other ions present in water could also compete for these active sites on the adsorbents and reduce the efficiency of the adsorbent. Furthermore, it will be difficult to scale up adsorption technique without any significant increase in the cost of the treatment process as this will involve the inclusion of pressure systems and temperature controllers.

Although, adsorption and heterogeneous photocatalysis offer the advantage of regeneration and reuse of materials, the use of photocatalysts appears more favoured because there is the possibility of mineralizing parabens to CO_2, H_2O and other less harmful organic and inorganic by-product which are desirable. Besides, new photocatalysts are now developed that can utilized the UV and visible spectrum of sunlight. This further reduces the cost of applying the technology in real water treatment. This review shows evidently that the use of advanced oxidation techniques for paraben removal from water has gained wide acceptance. Unfortunately, approximately 90% of exciting reports of the success of heterogeneous photocatalysis still reside on the work bench of scientists in the laboratory. It is therefore crucial, that for its future to become a reality, more research is focused on how the technology can be scaled up and properly utilized in the treatment of large volumes of contaminated water. Furthermore, it is important that green starting materials for the development of efficient photocatalysts and green design processes are encouraged. Likewise, the treated water from AOPs should be subjected to toxicity test and analysis with Liquid Chromatography-Time-of-Flight-Mass Spectrometer (LC-TOF-MS) to ascertain that by-products of the process are not relatively harmful to humans.

The future of heterogeneous photocatalysis for environmental remediation demands that the photocatalyst have long shelf-life, high mineralization rate and capacity, and are stable over several reuse cycles.

As for sustainability, the use of renewable or abundant natural resources would be worth considering. For example, developing solar active photocatalyst from clay and/or agrowaste materials could provide new, low-cost and efficient materials for parabens removal from water. In addition, it will be useful for scientists to develop broad spectrum photocatalysts that have the ability to operate between the UV to visible region of the electromagnetic spectrum of light.

Water remains one of the most valued natural resource that is vital to life here on earth. Currently in several developing countries, there are little or no researches focused on monitoring of parabens and their removal from the environment. To the best of our knowledge, all scientific reports on the fate, occurrence and behaviour of these parabens have been focused on surface water. Sadly and to the best of our knowledge, there is no report on their presence in groundwater which serves as a major source of drinking water in most developing countries especially Africa. For these countries to meet the United Nations Sustainable Development Goals #3 (Good health and wellbeing for people) and #6 (Clean water and sanitation) in 2030, there is need to urgently provide more scientific data on the presence and amount of these parabens in their major sources of drinking water, their toxicity, their transformation products in such drinking water sources (as influenced by the physical and chemical nature of the surrounding environment) and the most efficient but cost-effective technique for their removal in water. Toxicity study of parabens (analytical measured concentration in the environment) using human cell lines to investigate the impact of these parabens on growth, reproduction of human and also on the human immune system should be carried out. Furthermore, it is crucial for scientists to look into the relationship between parabens in our environment, especially in water bodies that serves as drinking water sources, and antimicrobial resistance. In addition, a critical investigation into gene expressions induced by biocides like parabens and the specific genes responsible for these expressions will be one right step in the fight against antimicrobial resistance in humans.

All of these findings should drive a policy shift towards the delivery of cleaner potable water for healthy life here on earth.

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.

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