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Published online: 01 Aug 2022.

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Occurrence, effects, detection, and photodegradation of triclosan and triclocarban in the environment: a review

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ABSTRACT

Antibacterial agents like triclosan (TCS, 5-chloro-2-(2,4-dichlorophenoxy)phenol) and triclocarban (TCC, 3-(4-chlorophenyl)-1-(3,4-dichlorophenyl)urea) are commonly found in everyday household and personal care products. Both compounds are widely distributed in the environment, acting as potential sources of contamination to ecological safety and human health problems such as algal growth-inhibiting effects; bioaccumulation in algae; endocrine-disrupting effects; development of microbial resistance, and formation of toxic degradable products. Environmentalists are increasingly concerned about the emergence of these micro-organic pollutants in the environment. This review paper focuses on the current state of knowledge, occurrence, effects, detection, and removal techniques for triclosan and triclocarban in the environment. People are exposed to these antibacterial agents when transported from wastewater treatment plants, air, dust, household products, and personal care products. These exposures lead to bioaccumulation in human tissue and biomagnification in the food chain. Surveys have revealed that TCC and TCS under sunlight formed toxic and persistent constituents like chlorinated phenols, methyl triclosan (MTCS), and biphenyl ethers. Different analytical approaches have been used to detect and degrade these compounds to ensure their complete removal in the environment but are found inadequate to effectively eliminate TCS and TCC. Advanced oxidation processes (AOPs) have shown to be promising in successfully breaking down TCS and TCC, considering material and energy consumption and emission of carbon (IV) oxide. Therefore, robust strategies such as electrochemical and nanomaterial methods should be implemented to determine and sequester TCS and TCC in the environment. Furthermore, regulatory bodies and environmental experts should be concerned about the fate and nanocatalyst photodegradation of triclosan and triclocarban in the environment.

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1. Introduction

There is growing production and utilisation with mainly down-the-drain disposal of antimicrobial, antifungal, and antibacterial products both in developing countries and worldwide, implying the continuous release of these compounds in the aquatic environment. Triclosan (TCS) and triclocarban (TCC) are microorganic pollutants continuously released consciously or unconsciously into bodies of water due to inadequate regulatory frameworks, particularly in developing countries [1]. These emerging contaminants are toxic, non-biodegradable, and poorly known. Even at low concentrations, their continued detection in water bodies, breast milk, human urine, and soil vegetation (ng/g to mg/Kg) has raised serious public health concerns [2].

Triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenol) is classified as a crystalline powder, poorly soluble in water but soluble in several organic solvents and exhibits high lipophilicity [3]. Exposure to triclosan and triclocarban in water or other products such as soaps, body washes, toothpaste, and mouthwash is high due to their persistence throughout life [4]. The concentration levels of these pollutants vary from country to country due to the difference in lifestyles, consumption patterns, treatment plant size, population background, and volume of wastewater produced [5]. Han et al. [6] discovered that triclocarban and triclosan were present in 37% and 72% of US human urine samples, respectively. Women in Australia, for example, have triclosan levels that are twice as high as women in Sweden. A Swedish warning statement issued in the year 2000 urging consumers to avoid using antibacterial products containing triclosan may have played a role [7]. Furthermore, the maximum concentration of TCS and TCC allowed in cosmetic products in China is 0.3% and 0.2%, respectively, according to the Hygienic Standard of Cosmetics. In South Africa and European countries, the EU Cosmetics Directive 76/768/ECC permits the maximum allowable concentration of both compounds in any cosmetics to be 0.2–0.3% [8]. The Norwegian Scientific Committee for Food Safety concluded in a risk assessment that widespread use of triclosan and triclocarban, including use in cosmetic products, promotes the development of antimicrobial resistance and may pose a public health risk. As a result, it was recommended that triclosan and triclocarban levels in personal care products be monitored [7].

Wastewater treatment plants and untreated urban wastewater release endocrine-disrupting chemicals into various water sources [9,10]. These compounds mineralise into more toxic and recalcitrant intermediates such as chlorinated phenols, polychlorinated biphenyl ethers, polychlorinated dibenzodioxins, and dichloroaniline. The increased microbial resistance and ecotoxicity to aquatic organisms caused by household biocides have prompted various environmental scientists and regulatory agencies to investigate the fate and behaviour of TCS and TCC in the environment, with a focus on contamination of wastewater, ground, and surface water, and their behaviour during wastewater treatment [11,12].

Numerous techniques for removing TCS and TCC from water with incapacitated antimicrobial activity include activated sludge, adsorption, and membrane filtration. Due to these antimicrobial persistent or pseudo-persistent nature during wastewater treatment, posing a potential risk when discharged in environmental water, it is crucial to improve the physical treatment methods [13]. Studies have, however, proven that adsorption-based systems [14] and membranes [15] trap TCS and TCC; they do not destroy them

completely. For instance, Rosoulzadeh et al. [16] investigated the adsorption of TCS onto magnetic biopolymer bead/diatomite. They found the study to be dependent on the positive effect of pH, time, and dosage, while the effect of TCS concentration was negative on the removal efficiency. The maximum adsorption rate (94.47%) of TCS was achieved at pH 9.18; contact time 58.84 min; initial concentration 3.54 mg/L; and dosage, 0.15 g/L. However, the photocatalyst performance of modified TiO_2 is an alternative and sustainable method for the photodegradation of TCS and TCC [17]. Ferreira et al. [18] identified some intermediate products from TCS by UHPLC-MS/MS, indicating that TCS is completely mineralised using cobalt and nitrogen codoped titania (Co-TiO_2-N). During this study, the photocatalytic activity of as-synthesised catalyst under light irradiation achieved almost 100% TCS degradation and showed antibacterial activity against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* bacteria.

Several review papers focused on the monitoring methods, toxic effects of TCC and TCS, and their removal by biotic processes [19–21]. However, a review on the removal of TCC and TCS via an advanced oxidation method using TiO_2 is rare. This review focuses on the occurrence and fate of triclosan and triclocarban, their toxic effect, and analytical methods of detecting and monitoring TCC and TCS. This article also explores TiO_2 nanocatalyst activeness in the photodegradation of TCC and TCS.

2. Properties of triclosan and triclocarban

Triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenyl) and triclocarban, (N-(4-chlorophenyl)-N-(3,4-chlorophenylichlorophenyl)urea) (see Figure 1) are two most commonly used antimicrobial and antifungal common in several household and personal care products such as cosmetics, toothpaste, and detergents at concentrations up to 1.5% [22]. TCC concentrations in antimicrobial soap bars are typically 2% by weight, while TCS concentrations are lower, typically 0.1–0.3% by weight [23]. The different physicochemical properties of TCC and TCS are summarised in Table 1.

3. Occurrence of triclosan and triclocarban in the environment

As stated earlier, the major sources of TCC and TCS are cosmetics, household cleaning, and personal care products. Possible sources of these antibacterial agents in the environment are described in Figure 2. These compounds have been found in treatment plant effluents,
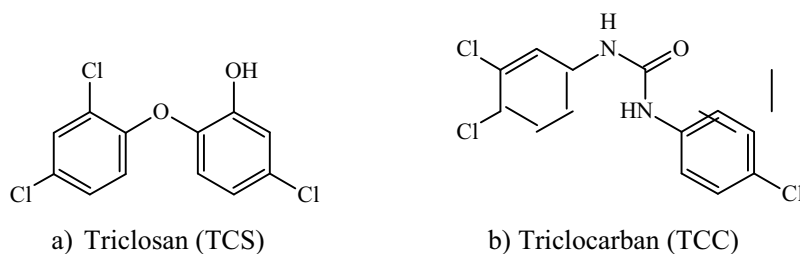

a) Triclosan (TCS)   b) Triclocarban (TCC)

Figure 1. Molecular structure of triclosan and triclocarban [17]. (a) Triclosan (TCS). (b) Triclocarban (TCC).

Table 1. Physicochemical properties of triclosan and triclocarban.

Properties	Triclosan	Triclocarban
IUPAC Name	5-chloro-2-(2, 4 dichlorophenoxy) phenol or 2,4,4-trichloro-2 hydroxydiphenyether	3,4,4'-Trichlorocarbanilide; N-(4-Chlorophenyl)-N'-(3,4 dichlorophenyl)urea;
Possible Uses	Antimicrobial, antifungal, and antibacterial in pharmaceuticals and personal care products (PPCPs)	Antibacterial, antimicrobial, and antifungal in PPCPs
Chemical formula	$C_{12}H_7Cl_3O_2$	$C_{13}H_9Cl_3N_2O$
Chorine content (wt%)	33.7	33.7
Melting point	56℃ −60℃	254–256℃
Boiling point	280℃-290℃	>300℃
Solubility	Non-volatile, insoluble in water (20℃ at 10 mg/L); readily soluble in a wide range of organic solvent or n-Hexane (25℃; 85 g/L); Ethanol and Acetone and Tween 20 are highly soluble (25℃)≥1000 g/L	Water solubility 11 mg/l at 20℃1 g dissolves in 25 ml Acetone; 3 ml Dimethyl formamide
Molecular weight	389.55 g/mol	315.578 g/mol
Specific gravity	1.55×10^3 kg/cm³	
Physical state	White to off-white crystalline powder with a hardly detectable phenolic odour	Fine, White to off-white Powder
octanol-water Partition Coefficient(log K_{ow})	4.76	4.90
Vapour pressure	4×10^{-6} mmHg at 20℃	3.6×10^{-9} mmHg at 25℃
Density	1.49 g/cm³	1.53 g/cm³
pKa value	8.14	Inapplicable under environmental conditions
Degradation Products	Methyl-triclosan, Monochlorphenol, 2,4-dicholorophenol, 2,8-dichlorodibenzo-p-dioxin, dicholrodibenzodioxin	4-chloroaniline and 3,4-dichloroaniline
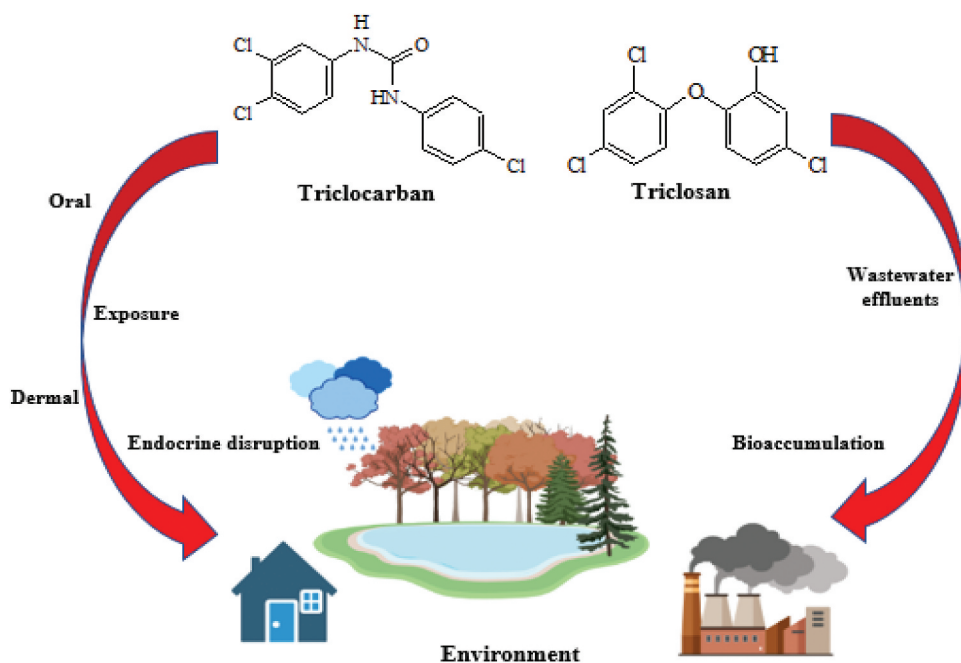
Figure 2. Sources and pathways of environmental exposure to TCC and TCS.

surface water, groundwater, and drinking water. The increased use of TCC and TCS enables several pathways for the compounds to infiltrate the environment. The physicochemical characteristics show that TCC and TCS can bioaccumulate and persist in the environment.

The lack of a systematic monitoring programme and the triclosan and triclocarban are present at fluctuating concentrations near analytical method detection limits and have increased their concentrations in various water bodies over time. Also, information on the current levels of TCS and TCC in water systems in the African continent is still very scarce [1]. The occurrence of TCS and TCC in low concentrations (ng/L or below) could explain the reason for the relatively little knowledge of the harmful effects of these compounds and their metabolites. Exposure to these compounds by humans via water or food causes bioaccumulation in living cells. Eventually, it disrupts endocrine glands from functioning correctly, depending on the concentration and duration of exposure [2].

Triclosan and triclocarban are antimicrobial compounds in various household and personal care products such as shampoos, soaps, creams, mouthwash, and toothpaste. Humans have also been exposed to occupational and environmental hazards [24]. Due to their hand-to-mouth activities, dust ingestion is the most likely exposure route for infants, according to the USEPA [25]. TCS in homes is most likely associated with spills of consumer goods such as liquid personal care products, aerosols, and diffusion from textiles treated with this bactericide, according to Geens et al. [24]. TCS levels in household dust range from 25 to 1,828 ng/g (medium = 220 ng/g) in Flanders, Belgium [24], and from 240 to 2,200 ng/g (medium = 702 ng/g) in Santiago de Compostela, Galicia-Spain [26]. Personal care products like toothpaste, soaps and deodorants were major contributors to total exposure to TCS. These results agreed with Lu et al. [27] and Sanidad et al. [28], who observed that TCS and TCC were highest in personal care products. Canadian bio-monitoring study revealed that 4% of TCC was detectable in adult urine, less than 4% in infant urine, and 0% in meconium samples and breast milk. This finding was attributed to the limited use of TCC in Canada [29].

Endocrine disruptors, TCC and TCS, are transformed into hazardous and persistent species such as chlorinated phenols, polychlorinated biphenyl ethers, and polychlorinated dibenzodioxins (mono- and dichloroanilines) [30]. Triclocarban and triclosan are constantly released into surface waters through wastewater discharge. Significant sources of TCS and TCC in the environment are disposal down the drain into wastewater from residential or non-residential sources. These compounds move into wastewater treatment plants (WWTPs) then the effluent water goes into receiving streams where it is used for irrigation on farmlands. The sludge from WWTPs can be applied on land for various uses or disposed of in landfills [31]. In the study of Healey et al. [32], the concentration in runoff post-land application of TCS and TCC was below the detection limit (90 ng/L and 6 ng/L). This indicates that runoff is not a significant route of these compounds into the environments, possibly either as a result of the transformation to other compounds or soil properties of the study site. The study of Yu et al. [33] revealed that sewage sludge composting drastically reduced the ecological threats of TCS and TCC, improving soil characteristics. This showed that sufficient ventilation time during sludge composting enhanced their biodegradations.

TCS concentrations varied from 1.906 to 73.462 µg/L, 1.732 to 6.980 µg/L, and 0.138 to 2.455 µg/kg in influent, effluent, and sludge samples, respectively, while TCC concentrations ranged from 0.320 to 45.261 µg/L, LOQ = 1.103 µg/kg, and 0.107 to 8.827 µg/kg in

influent, effluent, and sludge, respectively [34]. This investigation revealed that significant amounts of TCS and TCC are eliminated throughout the treatment process, which could be a major factor in the drop in TCS and TCC levels observed in effluent samples. Lapen et al. [35] portrayed the migration of various pharmaceuticals and personal care goods from biosolids-added agricultural areas to tile drainage water, and runoff wastewater treatment systems can remove most triclocarban (90–94%) before it is released into rivers and streams. Still, a small amount (about 6%) was not removed during treatment. Due to their hydrophobic nature, a significant amount of TCC and TCS in wastewater streams is partitioned into sludge at a milligram per kilogram [32]. TCS is unstable under environmental conditions with an aqueous photolytic half-life of 41 min [25]; methyl triclosan is very stable and is known not to dissociate in water and is less photodegradable. Although levels discharged from sewage treatment plants are generally low, the chemical properties of TCS could suggest its possible environmental persistence.

TCS and TCC were the most abundant hormone-like personal care items discovered in the dewatered sludge in the Pearl River system, with levels of 5,088 and 1,188 ng/g, respectively, according to Yu et al. [36]. Adsorption of TCS and TCC onto sludge played an important role, while biological degradation was the predominant removal mechanism. Due to higher temperature, the lower detection of TCS in surface water in summer was attributed to higher photodegradation and biodegradation. Lehutso et al. [1] studied the occurrence of TCS and TCC in some selected wastewater treatment plants. The study showed that the TCS level (treated sludge 2.08–7.81 µg/kg) concentration was higher than TCC (treated sludge 1.21–9.19 µg/kg). The levels of TCS were seasonally influenced in the dry and wet seasons, indicating that the degree of TCS was high during the dry season. The reason was attributed to temporal changes. Human exposure to TCS and TCC usually occurs by dermal absorption, ingestion, or other environmental exposures such as inhalation of contaminated indoor or outdoor air [37]. TCS and TCC disrupt intrauterine blastocyst implantation, inhibit oestrogen sulfotransferase, and reduce the thyroxine level. The possible association of TCS and TCC levels in maternal and cord sera blood may be potentially associated with an increased risk for foetal malformations. Zhang et al. [38] hypothesised that there might be a connection between TCS exposure and lowered cognitive performance and caused hypothyroidism. A prospective birth cohort study also discovered a link between decreased levels of maternal urine TCS and maternal and neonatal thyroid hormones, making the thyroid hormone homoeostasis particularly susceptible to EDCs during pregnancy [39]. Efforts to monitor triclosan and triclocarban toxicity at environmental levels are required, according to studies on the adverse health consequences, toxicity, and bacterial resistance. For a healthy ecological status, it is necessary to control the environmental and health concerns linked to TCS and TCC with correct legislation compliance and full dedication to adequate regulation.

3.1. Fate, transport, and behaviour of triclosan and triclocarban in the environment

To comprehend their possible environmental concern, TCS and TCC must be investigated for their concentration levels, behaviour, and fate in wastewater treatment plants (WWTPs) and their environmental exposure to the environment. TCS, TCC, and other antibacterial agents and their breakdown byproducts are present in wastewater, surface

waters, soil, fish tissue, and human breast milk, among other places [6]. Wastewater treatment plant effluent, urban stormwater, rural stormwater, and agricultural runoff are possible sources of triclosan and triclocarban in the environment [40]. When people use antibacterial soap or items containing triclosan to wash their hands, teeth, dishes, clothes, and bathe or shower, triclosan and triclocarban are transported to wastewater treatment plants. Unlike wastewater, most untreated stormwater runoff runs directly into streams, rivers, and seas. TCS concentrations in effluents can vary from 35 to 2700 ng/L [41].

Physical, chemical, and biological activities reduce the concentrations of TCS and TCC in the environment [42]. The kind of organic carbon present and solubility characteristics influence the extent and kinetics of TCS and TCC sorption and desorption in natural systems. The availability of a substance to biota is reduced as the amount of organic matter in the system increases. Half-lives are measured in hours, years, or decades depending on the environmental compartment and prevailing conditions [43].

When exposed to sunlight, researchers believe that one to twelve percent of the triclosan is transformed into dioxin [44]. Furthermore, highly chlorinated byproducts were purportedly converted into methyl triclosan, which was used to boost microbial activity [45]. TCS and its hydrophobic metabolites, such as methyl triclosan (MTCS), are absorbed into sewage sludge (activated sludge and biosolids) and present in higher concentrations than in the aquatic effluent medium [46]. When triclosan is exposed to sunlight in its solid-state, dioxin is formed at more negligible levels than in aqueous solutions. The aryl hydrocarbon receptor is impacted by dioxin-like compounds (DLC), resulting in several gene deregulations. DLC is also linked to cancers, developmental and reproductive abnormalities, and immunotoxicity. The synthesis of dioxins from TCS breakdown or metabolism in human skin/tissues or other eukaryotic organisms is still going on even when TCS is photodegraded into dioxins by UV light [3]. Chlorinated TCS derivative CTDs are exposed to solar radiation, which causes the formation of chlorinated dioxins, which are the source of TCS-derived dioxins. When chemical byproducts from the photochemical degradation of TCS are exposed to UV light after the reaction of TCS with chlorinated water, 2,8-DCDD, and 2,4-dichlorophenol (2,4-DCP) is produced [47].

3.2. Ecotoxicity of triclosan

Triclosan is relatively non-toxic to people and mammals; however, one of its metabolites, dioxin, has been found. Dioxin is a highly carcinogenic substance that can damage the immune system, cause infertility, altered sex hormones, cause miscarriages, congenital defects, and cancer [48]. With 10 nM MTCS treatment, changes in thyroid hormone-response gene transcripts and stress markers in amphibian and human cells were found [49]. Because TCS is degraded into MTCS, which is more persistent in the environment, these data reveal the impacts of MTCS at low concentrations and raise the question of the method of action of TCS in organisms [50]. The toxicity of TCS has been shown in various cells, including human life and cancer cells [51,52]. Triclosan has also been associated with multiple health and environmental impacts, including skin irritation, allergy susceptibility, bacterial and compounded antibiotic resistance, and the degradation of sensitive aquatic ecosystems, according to studies [3]. The structure and function of algal communities in

stream ecosystems are affected by triclosan effluents [53]. Because algae are the first-step producers in aquatic ecosystems, significant levels of triclosan released into the environment could jeopardise the ecosystem balance, causing harm to aquatic habitats [54]. Amphibians have been found to affect thyroid function at doses as low as 0.15 g/L [55]. Lin et al. [55] investigated the toxicity of TCS on Eisenia fetida (earthworm). Their findings demonstrated that after a 2-day treatment, catalase (CAT) and glutathione-S-transferase (GST) activity may be enhanced at the maximum studied level, reaching 148% and 123% with sustained exposure, respectively. The action of CAT and GST, on the other hand, was suppressed at the highest tested dose, decreasing to 47% and 33% of the control, respectively.

3.3. Ecotoxicity of triclocarban

Li et al. [56] have shown that TCC disrupts the gut microbiome in animals and humans, which can affect health. Human exposure to TCC at high concentrations can disrupt the human reproductive organs, thus, enhancing the action of progesterone, testosterone, and other steroids [29]. Analysis of human urine shows that after triclocarban has undergone glucuronidation (xenobiotic metabolism of organic pollutants), their oxidative metabolites are less readily excreted than triclocarban. This proves that TCC does remain in the human system.

James et al. [57] reported the anti-oestrogenic effect of TCS in sheep and its anti-androgenicity in albino rats which was also demonstrated by Kumara et al. [58]. Triclocarban is highly toxic to fish and other aquatic organisms. Laboratory studies have suggested that the levels of triclocarban being found in the environment could negatively impact the reproductive organs of these animals [59]. Triclocarban may bioaccumulate in animals and plants that live in water. It may also affect wildlife behaviour. Studies have shown that TCC bioaccumulates in aquatic organisms such as water algae, snails, and plants are treated with water containing triclocarban [60]. TCS perturbs thyroid homoeostasis [61]. In exposed animals, it lowers hormone levels in the blood (hypothyroxinaemia). The chemical disrupts the thyroid-mediated developmental processes in tadpoles to frogs [62]. TCC also impacts the transcription of genes in frog and rat cells that respond to thyroid hormone [49].

At low doses, toxicity caused by complex combinations of PPCPs could result in synergistic interactions. Individual PPCPs may be present at low concentrations with no major harmful effects when acting alone, but PPCP combinations can have a significant environmental impact [63]. TCC, TCS, and their biodegradation products are currently attracting a lot of interest due to the possible damage they pose to the environment and human health. As a result, it is also critical to develop a simple, sensitive, and repeatable analytical approach for detecting and degrading these chemicals in various environmental water samples to ensure their safety.

4. Analytical methods for detecting triclosan and triclocarban

Because of the negative health consequences of triclosan and triclocarban exposure, highly efficient technology is required to protect public health and ecosystem stability [64,65]. The instrument and detection method used to measure the organic pollutants in

wastewater is determined by the type of target compound. TCS and TCC have been classified as pollutants and endocrine-disrupting substances by the USEPA (the United States Environmental Protection Agency). The rise of TCS and TCC in the environment, already widely discovered in wastewaters, is causing rising concern. As a result, several analytical techniques have been developed for detecting and quantifying persistent organic pollutants such as triclosan and triclocarban in wastewater and cosmetics at low levels that are not harmful to the environment [66]. GC/MS [60,67], GC/MS/MS [68], LC/MS [69,70] and LC/MS/MS [68] have all been demonstrated as sensitive and selective methods for determining TCC and TCS [71]. Because TCC, TCS, and MTCS are polar molecules with complex derivatisation procedures and possible interferences from other chemicals, HPLC-ESI-MS was chosen for sensitive determination [72]. As shown in Table 2, these devices were used to identify triclosan and triclocarban in effluents. Before determining TCS, most researchers have addressed sample preparation. Instrumental analysis in the mass-based analytical approach follows pre-treatment or extraction processes. Reversed-phase solid-phase disk extraction (SPDE), SPE-UHPLC-MS [72], super-critical fluid extraction (SFE), and stir sorptive bar extraction (SBSE) are examples of sample pre-treatment for TCC and TCS enrichment [73].

Liu and Wu [81] concluded that using a high–performance liquid chromatographic (HPLC) method to determine triclosan and triclocarban in 168 cosmetic products is a reliable and efficient method. Yinan et al. [72] demonstrated the detection and quantification of triclocarban (TCC), triclosan (TCS), and Methyl-triclosan (MTCS) in environmental water using silicon dioxide/polystyrene composite microspheres solid-phase extraction and detection with HPLC-ESI-MS. TCC, TCS, and MTCS spiked recoveries in water samples ranging from 89.5% to 96.8%, with an RSD of less than 5.7%. Several operational parameters were explored and optimised, including the eluant and its volume, the flow rate, and the acidity of the water sample. The detection limits for TCC, TCS, and MTCS were 1.0 ng/L, 2.5 ng/L, and 4.5 ng/L under ideal conditions. The proposed method has successfully tested actual water samples with positive results.

Noelia et al. [82] used two ultrasound-assisted emulsification-microextraction (USAEME) techniques to assess triclosan in cosmetics and wastewater. A micellar ionic liquid was used as an extractant in the design. The novel method provides for a precise and quick determination of triclosan. In a study conducted by Bai and Acharaya [83], triclosan was measured at 8.0 ng/L in Las Vegas, Wash. Using liquid chromatography-tandem mass spectrometry (LC-MS-MS) with negative ion multimode ionisation, Cha and Cupples [84] studied the presence of triclocarban (TCC) and triclosan (TCS) in agricultural soils following land application of biosolids. The detection limits for the approach were 0.58 ng TCC/g soil, 3.08 ng TCC/g biosolids, 0.05 ng TCS/g soil, and 0.11 ng TCS/g biosolids, with an average recovery of > 95% from all sample matrices.

The combination of USAEME and DLLME in detecting triclosan in wastewater and cosmetics appears promising. Wang et al. [85] used gas chromatography and the hazardous chemical ionisation technique to assess the concentrations of phenolic chemicals such as 4-tert-octylphenol, 4-nonylphenol, bisphenol-A, oestrone, oestradiol, and triclosan in several rivers. The target chemicals were discovered at trace or low

Table 2. Triclosan and triclocarban mean concentrations in wastewater.

Matrix	Measured Environmental concentration	Compound Quantification Method	Method of Extraction	LOD	LOQ	Reference
River water	TCS = <MDL-5.4 ng/LTCC = NA	Ultra-performance liquid chromatography	SPE			Sharma et al. [74]
Wastewater treatment plants	TCS = 165 ng/L-872 ng/L	Ultra-performance liquid chromatography	LLE			Bai and Acharya [75]
Dust	TCS = 390 ng/gTCC = 270 ng/g	LC-MS/MS	d-SPE		TCS = 17.5 ng/ gTCC = 8.6 ng/g	Chen et al. [76]
Effluent	TCS = 0.99–13.0 µg/ LTCC = <LOD-1.89 µg/L	Liquid chromatography tandem mass spectrometry	LLE-SPE			Lehutso et al. [1]
Wastewater treatment plants (#16WWTPs)	TCS = 0.61 µg/gTCC = 0.08 µg/ g	HPLC-MS/MS	SPE		TCs = 0.01 µg/L	Healy et al. [32]
Wastewater	TCS = 0.5–1000 µg/LTCC = 0.2–1000 µg/L	LC-UV	Mini-bar µ-SPE	TCS = 0.07 µg/ LTCC = 0.04 µg/L	TCS = 0.22 µg/ LTCC = 0.13 µg/L	Alshishani et al. [73]
Urine (Adolescent)	TCS = 25.4 ng/mLTCC = 8.7 ng/ mL	ID-µPLC-MS/MS	SLE	TCS = 0.1 ng/ LTCC = 0.1 ng/mL	TCS = 0.3 ng/ mLTCC = 0.3 ng/mL	Chen et al. [77]
Urine	TCS = 8.37 ng/ mLTCC = 10.46 ng/mL	µHPLC/ESI-MS/MS	SPE	0.001–0.3 ng/mL		Luo et al. [78]
Water	TCS = 3.25×10^{-6}	ES	Ion selective membrane	9.86×10^{-10}		Safwat et al. [79]
Water	TCS = 3–200 µg/L	UV	UA-DLLME	0.8 µg/L	2.7 µg/L	Shahvalinia et al. [80]

Abbreviations: d-SPE (Dispersive Solid Phase Extraction); SLE (Supported Liquid Extraction); ID-µPLC-MS/MS (Isotopic dilution–Ultra Performance Liquid Chromatography-Tandem Mass Spectrometry); LC-UV (Liquid Chromatography – Ultra Violet); µSPE (Ultra Solid Phase Extraction); µHPLC/ESI-MS/MS (Ultra-High-Performance Liquid Chromatography Electrospray Ionisation Tandem Mass Spectrometry); LOD (Limit of Detection); LOQ (Limit of Quantification); UV-vis (Ultra-Violet Visible); UA-DLLME (Ultrasonic Assisted–Dispersion Liquid-Liquid Microextraction); LLE (Liquid-Liquid Extraction)

levels in water samples from the Liao Rivers. In wastewater effluent samples from the Great Lakes and upper Mississippi River regions, triclosan levels ranged from 100 to 140 ng/L [86].

The majority of these pieces of equipment are too complicated to use for sample analysis. Despite the extensive pre-treatment sample, the technology can only detect or identify a limited number of comparable contaminants in the matrices at any moment. Apart from that, long pre-concentration operations, the inability to process and detect a sample quickly, the lack of portability and sustainability during fieldwork, and time-consuming analysis make these analytical instruments unsuitable for long-term usage [87]. Not only that, but the sophisticated nature of the equipment, their labour-intensive nature, and the requirement for derivatisation of samples prior to analysis forms the foundation for the development of more simple and robust instrumental techniques that are affordable, durable, and easy to maintain. Sensors and biosensors have recently been employed to replace those devices due to their ease of use, shorter consumption time, higher sensitivity, fast responses, and ability to determine contaminants in a variety of media without requiring extensive sample preparation [88].

4.1. Removal of triclosan and triclocarban – an overview

Environmental pollution has sparked substantial scientific interest worldwide in the last decade due to the unregulated disposal of triclosan and triclocarban. TCS and TCC harm organisms and their functions in the formation, maintenance, transfer, and dissemination of antibiotic-resistant genes. Due to their complicated molecular structure and low concentration in the aqueous matrix, current water and wastewater treatment plants are not intended to adequately break down new pollutants. Efforts are still being made to stop this dreadful trend of removing or reducing refractory pharmaceuticals and endocrine-disrupting substances from water and wastewater. So far, several traditional wastewater treatment systems have been reported to regulate triclosan and triclocarban concentrations in wastewater, such as activated carbon adsorption [89,90, 91], chlorination oxidation [91], ozonation [92], coagulation/flocculation [93], membrane filtration [94] and reverse osmosis [95]. There have been studies reported on the elimination of TCS and TCC. Despite this, there is little or no comprehensive collection of studies on integrated advanced oxidation technologies for triclosan and triclocarban degradation in wastewater.

Chlorine oxidation efficiently removed several endocrine-disrupting chemicals (EDCs) and PPCPs such as acetaminophen, oestradiol, oestriol, oestrone, ethynylestradiol, oxybenzone, and triclosan in a bench-scale drinking water treatment research (> 95% in 24 h). Other compounds, such as N, N-diethyl-m-toluamide, meprobamate, tri(2-chloroethyl) phosphate, and heptachlor epoxide (30%), were resistant to chlorination [96]. These treatment procedures were proven ineffective at removing EDCs from wastewater, incomplete removal, sludge production, and hazardous disinfection byproducts (DBP) that are genotoxic, mutagenic, and carcinogenic to human health were frequently discovered.

Table 3. Comparative studies of degradation performance of TiO_2 – based Heterostructures for the removal of TCC and TCS.

Heterostructure component	Organic pollutants removed	Removal efficiency (%)	Findings/Result/Comments	Reference
S-Ag/TiO_2@g-$C_3$$N_4$	Triclosan	92	The TCS removal rate increased with increased pH and catalyst dosage up to optimum values (pH6.5 and 0.2 g/L). The degradation products of TCS were identified by liquid chromatography-tandem mass spectrometry analysis.	Xie et al. [98]
TiO_2/UV.	Triclosan	100	TCS degradation efficiency (92.3%) was achieved under optimised conditions. Optimum degradation of TCS was achieved at optimum condition; pH (10), TiO_2 dosage (40 mg/l), irradiation time (120 min).	Anupama and Shrihari, [99]
TiO_2/UV	Triclosan	99	The Langmuir – Hinshelwood kinetic model was used. The TCS degradation rate increased with prolonged irradiation but decreased with increased pH and pollutant concentration.	Constantin et al. [100]
Ag/TiO_2	Triclosan	80	Fast degradation follows the pseudo-first-order kinetics. The rate of TCS degradation decreased significantly with increased pollutant concentration (0.5–15.0 mg/L) and pH (4.0–10.0).	Tiwari et al. [101]
TiO_2/UV	Triclosan	82	Triclosan mineralisation by photocatalytic degradation (82%)> TCS degradation by TiO_2 only (75%). Hydroxyl radicals during photolysis and photocatalysis were the key factors responsible for preventing the production of dioxin-type intermediates.	Son et al. [102]
DBD/TiO_2/ACFs	Triclocarban	99	Degradation efficiency of TCC was in the following order; DBD/TiO_2/ACFs > DBD/TiO_2 > DBD/ACFs > DBD. The reaction rate increased with increasing output power, initial concentration, and radius of catalyst.	Wang et al. [90]
TiO_2/Solar irradiation	Triclosan	97.6	Increase in pH, catalyst loading and TCS concentration has a negative effect on the degradation efficiency of TCS. Highest degradation % was achieved at optimum conditions ($C_{triclosan}$ = 1 mgL^{-1}, C_{TiO2} = 550mgL^{-1}, I = 700Wm^{-2}). TCS degradation followed a pseudo-first-order kinetics.	Stamatis et al. [103]
TiO_2/UV	Triclosan	Almost complete	Degradation by TiO_2/UV presented typical first-order kinetics. The irradiation time necessary for TiO_2 to achieve degradation below the limits of quantification (LOQ) is around 113 min for triclosan at an initial pollutant concentration of 0.1mg/L with TiO_2 at 5 mg/L.	Klamerth et al. [104]
TiO_2 nanotubes	Triclosan	78.7	Photoelectrocatalytic (PEC 78.7%) degradation of TCS by TiO_2 nanotubes arrays was much better than photocatalytic (PC 67.2%) and electrolysis (EC) degradation processes (50%) at 30 min illumination. 2,7-dichlorodibenzodioxin was a major intermediate. The highest degradation rate of PEC was achieved at 0 V.	Liu et al. [105]
TiO_2/UV	Triclosan	90	Intermediates include dichlorophenols, 2,8- dibenzo-p-dioxin, tetrachlorinated diphenyl ether (tetraclosan), and hydroxylated triclosan were produced by photoreaction. TCS was hardly decomposed with only TiO_2, while approximately 90% of the initial TCS concentrations were decomposed within 120 min of UV irradiation.	Sankoda et al. [106]
TiO_2/UV	Triclocarban	80	The photodegradation rate of TCC via direct photolysis was greater than TiO_2 photocatalysis. TCC photocatalytic degradation rate was enhanced with increasing pH. The reaction followed pseudo-first-order kinetics.	Ding et al. [107]

As a result, there is a pressing need to find and implement highly efficient and long-term water treatment strategies for degrading EDCs to less hazardous chemicals or total mineralisation. Advanced oxidation processes (AOPs) use heterogeneous photocatalysis to develop better and environmentally friendly technology. In situ generation of highly potent chemical oxidants such as the hydroxyl radical (OH•) has recently emerged as a sustainable technology for speeding the oxidation and destruction of a broad spectrum of EDCs in polluted water [19]. Heterogeneous photocatalysis involving TiO_2-based photocatalyst has received scientific interest [97], and it has proven more effective in decomposing recalcitrant complex organic pollutants than other semiconductor metal oxides catalysts.

The formation of highly reactive hydroxyl radicals is the fundamental mechanism of advanced oxidation processes (AOP). Compared to known oxidising agents like potassium permanganate, these hydroxyl radicals are unstable, non-selective, and potent oxidants. Organic contaminants are quickly decomposed by the hydroxyl radical into CO_2 and H_2O, considered harmless end products. Organic pollutants were targeted by the hydroxyl radical by hydrogen abstraction, electron transfer, and establishing a double bond with the organic molecules [2]. UV/TiO_2, UV/O_3, UV/H_2O_2, Fe^{2+}/H_2O_2, TiO_2/H_2O_2, and a variety of other processes might produce very efficient hydroxyl radicals. These techniques have been successfully applied individually and combined with other conventional methods to degrade triclosan and triclocarban. The oxidation power and functions of the contaminant structure and oxidant dose are often proportional to the removal efficiency. Table 3 highlights the degradation of TCC and TSC under the influence of TiO_2-based materials.

Figures 3 and 4 show the photodecomposition schemes for TCS and TCC, respectively. The photodegradation of TCS depicted in Figure 3 involves molecule cleavage, chlorination, and dechlorination reactions. The formation pathways of dichlorodiben-p-dioxin and
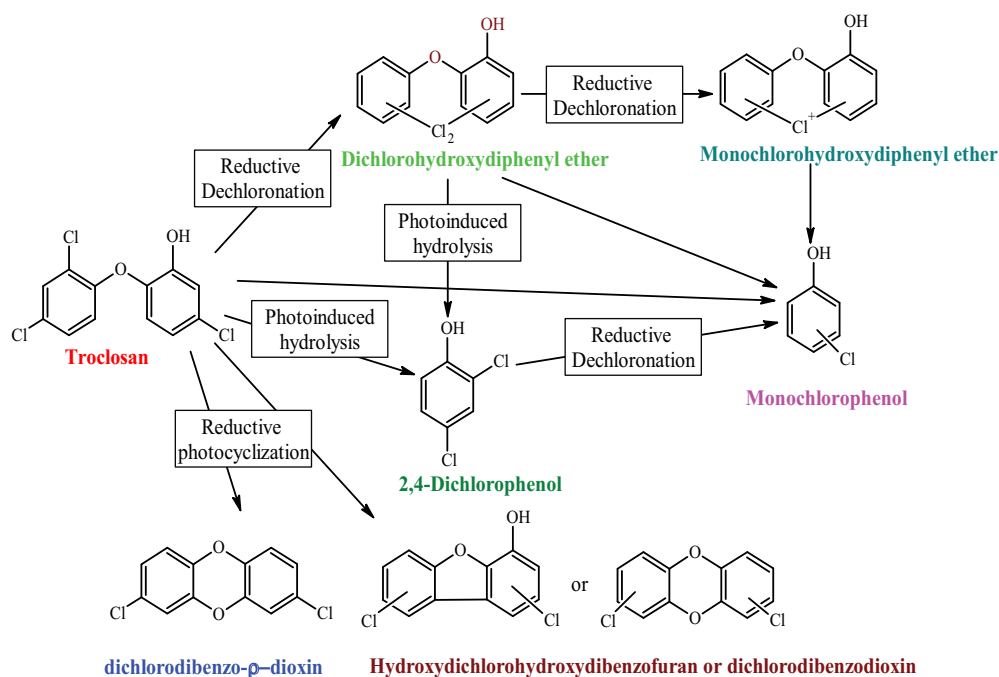

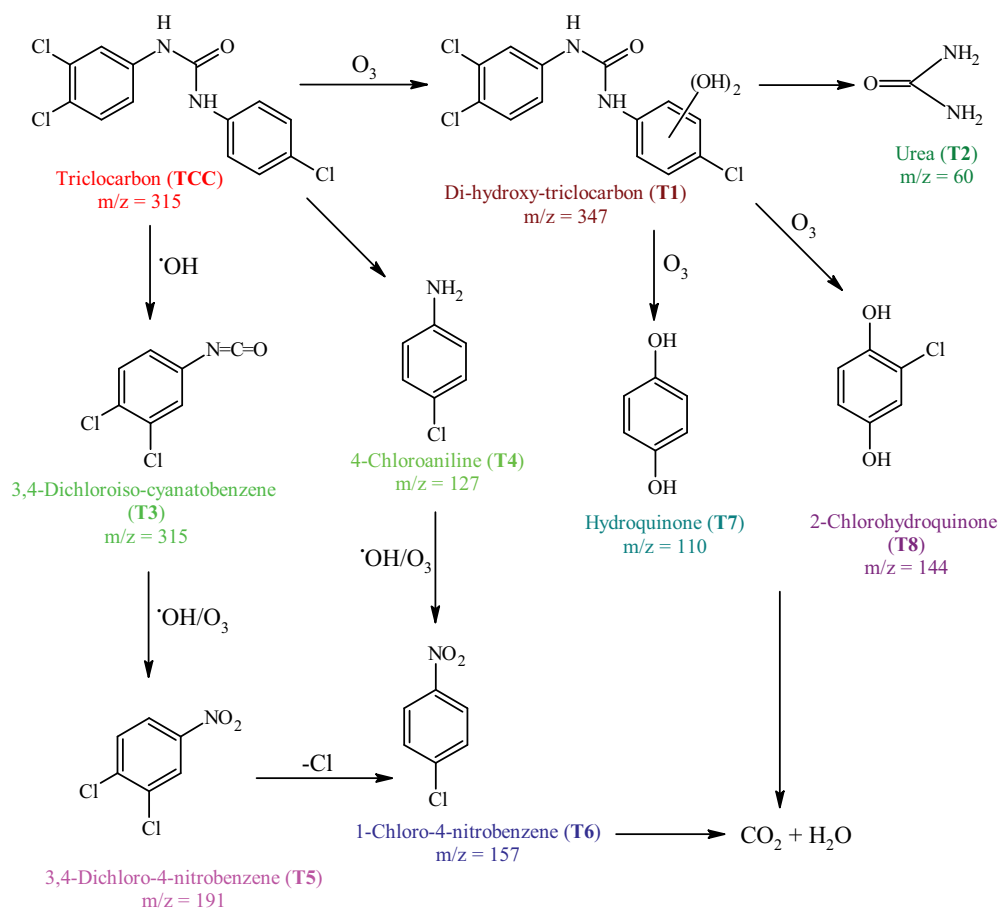**Figure 3.** Photodecomposition pathway of TCS [108].

Figure 4. Photodecomposition pathway of TCC [103].

2,4-dichlorophenol may be attributed to photo-induced hydrolysis or the action of hydroxyl radicals which leads to homolytic scission of the carbon-oxygen bond. The formation of chlorophenol from 2,4-dichlorophenol is due to a dechlorination reaction, and further dechlorination reaction of chlorophenol could lead to phenol formation.

In Figure 4, di-hydroxy-triclocarban formation resulted from the direct attack of ozone and hydroxylation on the aromatic ring on the TCC. The cleavage of the C-N bond yielded hydroquinone and 2-chlorohydroquinone. The reaction between TCC with hydroxyl radicals led to the formation of 3,4-dichloroiso-cyanato-benzene and 4-chloroaniline. The attack of N-atom of aniline by active oxygen species generated 1,2-dichloro-4-nitrobenzene, and further dechlorination led to the formation of 1-chloro-4-benzene. This formed product oxidised and mineralised to carbon (IV) oxide and water.

5. Conclusion and recommendations

The two common antimicrobial agents associated with personal care products are triclosan and triclocarban, which are toxic, persistent, and bioaccumulative. These compounds and their derivatives are present in measurable amounts, thus affecting water quality and

human health. The determination of triclosan and triclocarban has predominantly been performed by the chromatography-based method. These methods are sensitive and selective but are complicated, time-consuming, and low detection of TCC and TCS in matrices. Several techniques have shown to be somewhat effective in the degradation of TCS and TCC, but an advanced oxidation process using TiO_2 is found to oxidise and mineralise the compounds. Thus, integrating electrochemical sensors and the nanomaterial approach will be a robust alternative for detecting and removing TCS and TCC in the environment.

As a result, TCS and TCC in personal care products must be strictly regulated and monitored. There is also a requirement to generate meaningful data on the health hazard effects of TCS and TCC. To meet these goals, a collaborative effort involving research institutions, relevant government departments, and regional and local councils will be needed to determine the sources, levels, environmental consequences, and treatment solutions for triclosan and triclocarban. Thus, further research should include large-scale monitoring networks are required to better understand their environmental impacts, fate, and transit pathways. Furthermore, a systematic review of the photodegradation of TCC and TCS using nanomaterials such as silver, ferromanganese, zinc oxide, tungsten oxide, and their nanocomposites could aid in future research.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Authors' contribution

All authors read and approved the manuscript

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