Emerging contaminant (triclosan) identification and its treatment: a review

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Abstract

Pollutants from personal care products (PCPs), pharmaceuticals, industrial wastes, food additives, pesticides and fertilisers are classified as emerging contaminants (ECs). These ECs have been given much attention due to their deleterious effects on human life, plants and animals. Triclosan (TCS), a broad spectrum antibiotic, is under the category of emerging contaminants; it is shown to have an eco-toxicity. It is a ubiquitous contaminant due to its wide range of applications in PCPs as an antibacterial agent. Inefficacy in the conventional treatment of wastewater which is being discharged into natural streams has led to the bioaccumulation of TCS. Concentrations of TCS have been detected in several wastewater treatment plants and urinary samples of humans and streams. In surface waters, TCS was detected in Korea, USA, Europe, China, Japan and India. In order to overcome the astringent effects of TCS, there is a need for its treatment. This paper addresses studies conducted on methods of treating TCS, and among all the methods, membrane technology (MT) was found to be effective and this is mainly due to hydrophilic nature of TCS, high $\log K_{ow}$ value (4.8), and a removal efficiency > 95% was observed when powdered activated carbon of 100 mg/l was combined with MT.

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Graphical abstract

Keywords Personal care products (PCPs) · Emerging contaminants (ECs) · Triclosan (TCS) · Wastewater treatment plants (WWTP)

1 Introduction

Earlier water contamination was primarily due to the presence of organic matter, bacteria, heavy metals and metal salts. Since the past few decades, a new class of contaminants called as ECs has come into light [1]. These ECs include pharmaceuticals, personal care products (PCPs), insecticides, surfactants, pesticides and industrial waste [2]. Of all the emerging contaminants detected in India, 7% of them constitute PCPs [3, 4]. In studies conducted, it was observed that a number of ECs were detected in many countries like India, UK, Japan, USA, China and Germany; ECs > 70 like estrone, propranolol, codeine, diclofenac belonging to therapeutic classes were found in UK environmental waters, and on the other hand, German municipalities have identified about 32 ECs, and about 70 ECs were detected in tone canal in Japan and also a wide range of emerging contaminants like antibacterial agents, antifungal agents, antimicrobials, personal care products were identified in China [5–9]. These are found in urinary samples of pregnant women [10]; the contaminants enter the fresh water supply through means of various sources like pesticides and PCPs as depicted in Fig. 1 [11]. Over the last few decades, personal care products have emerged as

ECs, and these contaminants have recently shown to occur widely in water resources and identified as being an endocrine disrupting compounds and have potential environmental and public health risk; although PCPs are detected in the freshwater environment at relatively low concentrations, many of them and their metabolites are biologically active and can impact non-target aquatic organisms [5]. A wide range of ECs from PCPs such as cosmetics, of which a wide range of cosmeceuticals like paraformaldehyde, benzalkonium chloride has shown to pose a threat to human health in terms of cytotoxicity, genotoxicity, mutagenicity, neurotoxicity oestrogenicity [12], deodorants, fragrances, toothpastes, have been identified [13].

TCS, a broad spectrum antibiotic depicted in Fig. 2, is one such emerging contaminant. It is a widely found agent in PCPs and antibacterial agents [14]. Properties of TCS are depicted in Table 1 [15]. Concentrations of TCS have been detected in, surface waters in many countries like Korea, USA, Europe, China, Japan and India with reported values varying from 0 to 149 ng/l, 3.5 to 34.9 ng/l, <0.2 to 285 ng/l, 2.5 to 478 ng/l, 11 to 31 ng/l and 139 to 5160 ng/l, respectively [5, 16–21]; its presence has also been identified in tap waters, breast milk and urinary samples [22–26]. Owing to the world scenario, TCS was found to be detected

Fig. 1 Origin and flow of emerging contaminants

Fig. 2 Chemical structure of triclosan

in Germany, USA, Japan, China, India, South Africa, Australia, Korea in surface waters, river sediments, WWTPs, and human bodies; detected concentrations in surface waters, water treatment plants and human bodies are depicted in Tables 2, 3 and 4, respectively. Food and Drug Administration (FDA) has suggested that permissible limits for TCS would be 1% in antiseptic washes and 0.3% in

Table 1 Properties of triclosan

Structure of triclosan	
Molecular formulae	$C_{12}H_7Cl_3O_2$
General classification	Non-prescription compound
Possible use	Antimicrobial, antiseptic and disinfectant
Nature	Hydrophobic
Molecular weight	289.54
Dissociation constant (pKa) (20 °C)	8.14
Octanol–water Partition coefficient (log K_{ow})	4.76
Solubility	12 mg L ⁻¹ (25 °C)
Bioconcentration factor	2.7–90 (aquatic organisms)
Vapour pressure	5.2 × 10 ⁻⁶ Pa (mm Hg at 20 °C)
Degradation products	Methyltriclosan, dioxins, chlorophenols, chloroform

Table 2 Detected concentration of TCS in surface waters

S. no.	Country	Detected river	Concentration ($\mu\text{g/l}$)	References
1.	Germany	River Ruhr, Northern Germany	$< 3 \times 10^{-3}$ to 10×10^{-3}	Ebele et al. [5]
2.	USA	Michigan Lake	0.5×10^{-3} to 41×10^{-3}	Blair et al. [18]
		Minnesota River	5.0×10^{-3} to 310×10^{-3}	Lyndall et al. [19]
3.	Japan	Tone Canal	11×10^{-3} to 31×10^{-3}	Nishi et al. [20]
4.	South Korea	Mankyung River	0 to 149×10^{-3}	Lee et al. [17]
5.	Europe	–	$< 0.2 \times 10^{-3}$ to 285×10^{-3}	Lee et al. [17]
6.	India	Vellar Estuary	$(21 \pm 10.5) \times 10^{-3}$	Ramaswamy et al. [16]
		Tamiraparani River	$(16.6 \pm 10) \times 10^{-3}$ to 5160×10^{-3}	
7.	Australia	–	75×10^{-3}	Ying et al. [21]

Table 3 Detected concentrations of TCS in WWTPs

S. no	Country	Detected area	Influent concentration ($\mu\text{g/l}$)	Effluent concentration ($\mu\text{g/l}$)	References
1.	South Africa	Gauteng Province	2.01–17.6	0.99–13	Lehutso et al. [27]
2.	Australia		0.573–0.845	0.023–0.434	Ying et al. [21]
3.	China	Shanghai	0.533–0.744	0.080–0.294	Zhou et al. [28]
4.	Korea	–	0.148–0.785	0–0.127	Lee et al. [17]
5.	USA	–	86.2	0.05–5.037	Lee et al. [17]

Table 4 Detected concentrations of TCS in human bodies

S. no	Country	Samples	No of samples collected/no of samples detected	Concentration	References
1.	Sweden	Blood plasma	26/9	0.0004–0.03838 $\mu\text{g/g}$	Allmyr et al. [25]
		Milk	25/9	0.32–0.95 $\mu\text{g/g}$	
2.	USA	Urine	–	2.4–3790 $\mu\text{g/l}$	Calafat et al. [26]
		Urine	31/31	0.21–819 $\mu\text{g/g}$	Iyer et al. [23]
3.	India	Urine	76/76	0.00022–2.75 $\mu\text{g/ml}$	Xue et al. [24]
		Urine	41/36	0.08–898 $\mu\text{g/g}$	Iyer et al. [23]
4.	China	Urine	47/45	0.08–1600 $\mu\text{g/g}$	Iyer et al. [23]
5.	Japan	Urine	36/31	0.08–287 $\mu\text{g/g}$	Iyer et al. [23]
6.	Korea	Urine	26/21	0.08–558 $\mu\text{g/g}$	Iyer et al. [23]
7.	Kuwait	Urine	40/40	0.26–2.88 $\mu\text{g/g}$	Iyer et al. [23]
8.	Vietnam	Urine	19/15	0.08–27 $\mu\text{g/g}$	Iyer et al. [23]
9.	Saudi Arabia	Urine	30/20	0.08–34.4 $\mu\text{g/g}$	Iyer et al. [23]
10.	Greece	Urine	30/27	0.08–386 $\mu\text{g/g}$	Iyer et al. [23]

soaps, toothpastes and body lotions [15]. There is a need for a protected water supply in today's world and the need to reuse water in order to lead a sustainable life and due to the implications; these contaminants have on human beings, plants and aquatic life and there is a severe need to treat ECs.

TCS was detected in surface waters, WWTPs and human bodies; the highest concentration of 5160 ng/l was detected in Indian surface waters at Tamiraparani River. WWTPs in USA showed the highest concentration

with an influent and effluent concentration of 86.2 $\mu\text{g/l}$ and 0.05–5.037 $\mu\text{g/l}$. The highest detected frequency of TCS was found in Kuwait as reported [23], and the highest concentration detected in human urine sample was found in China which was ranging from 0.08 to 1600 $\mu\text{g/g}$ (Tables 1–3).

2 Necessity for treatment of triclosan

TCS is found to be used in many PCPs [15]. Concentrations of TCS were detected in natural surface waters, WWTPs and tap waters [3, 16–22, 27, 28], due to its adverse effects on human beings, plants and animals [22, 29, 30], due its ability for causing endocrine disruption and due to its high ecotoxic status, i.e. ($EC_{50} < 1$ mg/l) as reported by [31] and there is a need to treat TCS; this paper discusses the efficiency and suitability of several methods that were employed so far in its removal.

3 Treatment methods

3.1 Biological process

Activated sludge process (ACS), trickling filters (TF), oxidation ditches (OD) and rotating biological contactors (RBC's) are some of the biological treatment methods. The settling time plays an important role in adsorption of TCS in biological method; this could be accounted to its hydrophobic nature as its octanol water partition coefficient, ($\log K_{ow} = 4.8$) [32]. It was observed that persistence of anaerobic conditions led to a lower removal efficiency of TCS, only about (25–30%) of removal was reported by in RBCs [33]. But, the removal efficiency of TCS under anaerobic conditions was found to increase when combined with methanogenic conditions, an efficiency of 87% was found to be obtained, but the removal efficiency was still less as compared to aerobic conditions which is about 95% for a concentration up to 10 mg/l in 5 days [34]. The degradation products generated were found to be similar under both the conditions, and also in a study by it was reported that higher removal efficiency was observed under aerobic conditions than under anaerobic conditions even when coupled with weak magnetic field [35]. With variations in the makeup of the wastewater, feed and change in biomass material can lead to an improved efficiency in [33, 36, 37]. ACS serves as a most promising biological method in removal of TCS. With an increase in the hydraulic retention time (HRT) upto 52 h, it has been observed to an increase in the removal efficiency up to 99.9% [38], the acclimation capacity of bacterial feed to the surroundings and has a major role in removal efficiency [37, 38]. In the literature 80% of TCS removal with ACS is attributed to the mineralisation of compound to CO_2 and therefore concluded that biological degradation is the main removal mechanism for most of the compound and a removal efficiency of 96% has

been observed [39]. Others factors such as temperature, pH, lipid content and protein-to-carbohydrate ratio have shown to influence the removal efficiency because apart from degradation adsorption also contributes in increasing the removal of TCS [40]. Extracellular polymeric substances (EPS) have shown to have a negative impact this may be accounted due to the presence of bound TCS; it was observed that the concentration of TCS in OD was found to be high than that of effluent stream [40], but the removal efficiency was increased to 96% by increasing the (HRT). In case of sewage treatment plants, removal rate is not much efficient as the parent compound which was shown to convert into its metabolites or remains as bounded TCS [41]. Although trickling filters showed a decent removal efficiency of about 92% [40] but are not found to be always promising; as a variable and a less removal efficiency as low as 58% was observed [33].

3.2 Activated carbon

AC used for pollutant treatment can be prepared from a variety of organic materials such as bamboo and agricultural waste [42, 43]. Due to its unique properties such as controlled shape, suitable pore size distribution and high specific area [44], activated carbon (AC) can be used in the removal of wide range of emerging pollutants [43, 45]; moreover, different physical and chemical techniques may be used to improve the surface of the AC accordingly. The reason for which activated carbon could be served as an effective adsorbent for TCS can be attributed to the water–octanol partition coefficient of TCS; compounds having ($\log K_{ow}$ value > 4) can be adsorbed effectively by AC, a removal efficiency of 98% was observed in TCS by [46]. Factors such as characteristics of adsorbent, dosage, pH, agitation time, contact time and temperature have shown to affect the adsorption of TCS, when AC was prepared by using *Cocos nucifera* by [47], it showed a removal efficiency of 80.77% under a dosage of 0.1 g, at 25 °C for a TCS concentration of 90 mg/l, but in the case of charcoal-based granular-activated carbon (GAC), an efficiency of only 31.4% was observed for a dosage of 1 g/l, at 25 °C and for a TCS concentration of 60 mg/l as reported by [43]. Charcoal-based activated carbon with 3 week contact time and 100 mg/l dose had almost same removal efficiency as that of powdered activated carbon with about 4 h contact time with 5 mg/l dose; this may be attributed to the texture of AC [45]. As adsorption of TCS is an exothermic reaction; room temperature of 25 °C is considered to be the most appropriate for carrying out adsorption as studied by [47]. In a study by [48], adsorption of TCS onto activated carbon was observed in the presence of NaCl and $CaCl_2$ salts which is attributed to the salting out effect. Coupling

of adsorption systems with additional treatment processes can lead to an increase in removal efficiency [49]. Using AC as a pre-treatment for membranes has served to be an effective method. > 95% removal was seen which could be attributed to the integrated capacity of AC on membranes and electrostatic and steric stabilisation effects.

3.3 Carbon nanotubes

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Their unique properties such as larger specific area, lower weight and better mechanical and electrical properties make them excellent adsorbents [50]. Usually, carbon nanotubes are defined as single-walled nanotubes (SWNT), multi-walled nanotubes (MWNT). Several operational parameters such as dosage, pH, temperature and ionic strength are shown to influence the adsorption capacity of CNTs [51–53]. An increase in ionic strength in MWNTs showed an increase in adsorption up to a permissible limit, thereby decreasing the adsorption capacity due to aggregation of MWNTs [51]. Increase in specific surface area (SSA) of CNTs was shown to increase the adsorption of TCS as studied by [52]; therefore, SWNTs had higher adsorption tendency as compared to MWNTs, and moreover, oxidised multi-walled nanotubes (OMWNT) have shown the lowest adsorption capacity because of higher surface oxygen content. Purified MWNTs were used in the treatment of TCS; these were shown to have improved characteristics than ordinary MWNTs, i.e. increase in SSA was seen [53]. Adsorption capacity of MWNT is a function of its structural and physicochemical properties; molecular weight of the compound also has an impact on the adsorption capacity, TCS has shown to have a removal ratio of 0.93 with pristine MWNT, and this was studied by [54]. The fact that CNTs impart toxicity in the environment was tackled by immobilising them; achieved efficiency of TCS removal was up to 99.7% [55]. When compared to other ECs, TCS showed an increased adsorption onto CNTs; this is attributed to its bigger molecules which have greater affinity to adsorb rather than diffusing into the pores of CNTs [56]. Infusing selected properties in MWNT such as synthesising hydroxylated MWNTs (HMWNTs) could lead to change in characteristics like SSA, thereby increasing adsorption efficiency of TCS [54].

3.4 Clay minerals and zeolites

Clay minerals due to their low cost, high surface area and porosity can be used as an economical method in adsorbing emerging pollutants (EPs) [45]. Various minerals such as montmorillonite (Mt), vermiculite (VER), bentonite (B) and kaolinite (K) are studied in adsorption of TCS. In

a study by [57], it was reported that a significantly high adsorption of TCS was observed in the case of VER, and this is attributed to the low SSA and the hydrophobic nature of VER and TCS; additionally, it was observed that the sorption capacity of VER is independent of pH which determines its usage in treating water bodies of neutral pH and also higher sorption constants were seen in acidic conditions ($K_d = 696$) than under neutral conditions ($K_d = 609$). Treatment of montmorillonite with mineral acids had proven to increase its SSA which will lead to higher adsorption. Moreover, carbonaceous mineral composites of B—(BAIG3%C) had also proven to be promising adsorbent [57]. In a study [58], humic acid (HA) had found to increase the adsorption tendencies of K and M. But, clay minerals as adsorbents are not found to be promising as compared to other adsorbents such as activated carbon. Zeolites were not found to be an effective method in removal of ECs due to their uniform pore size [42]. But, infusing modifications in their properties like synthesising organic zeolites results in hydrophobic nature of surface, thereby causing the hydrophobic TCS to get adsorbed to the surface as studied by [59]; a clays showed a higher removal efficiency of TCS than zeolites.

3.5 Adsorption with biochar

Biochar is one of the charcoal-based materials normally used for soil amendment. Biochar is made by pyrolysis of the biomass [60]. Due to their porous structure and strong affinity for sorption organic compound, biochar has been extensively studied. Studies were conducted by [61] in treatment of ECs using biochar. The removal efficacy of biosolid biochar (BS-B) has shown to be dependent on the flow rate, a low flow rate showed a high removal efficiency, this could be attributed to the longer contact time between the molecules which led to the higher adsorption of TCS; moreover, factors such as techniques for production of feedstock and presence of organic compounds influenced the removal of TCS biochars produced from sewage sludge displayed a high efficacy due to the presence of surface functional groups [62]. In a study was conducted by [63], sludge derived biochar was used in the activation of peroxymonosulphate (PMS) and a removal efficiency of 99.2% was achieved at a pH of 7.2, dosage of 1 g/l and at a PMS concentration of 0.8 mM; this method has found to be highly promising for removal of TCS. Further, studies by [64] were involved in preparation of biochar by using rice straw (RS), corn stalk (CS), coffee grounds (CF) and biosolids (BS) of all BS-biochar had found to be highly promising agent; this may be attributed to the high surface area; moreover, higher pyrolysis temperature of biochar has found to lower the removal efficacy, and this could be accounted for the higher surface

area and aromaticity, and also a pH of 7 has shown to enhance adsorption capacity also and removal of TCS was not affected by ionic strength but was altered with HA, which can question its effectiveness in removing ionisable organic compounds.

3.6 Other adsorbents (polymeric resins, metal oxides, rubbers)

Studies on several other adsorbents such as metal oxides and polymeric resins were employed in adsorption of TCS. Adsorption of TCS onto manganese oxide (MnO_2) was conducted where an adsorption of 55% was observed; the efficacy of adsorption is attributed to the number of active sites in (MnO_2). The presence of organic salts decreased the efficacy of adsorption [65, 66], 55% of TCS was adsorbed to MnO_2 at pH 5. Using oxides of manganese, a removal efficiency of 3–100% had been achieved under certain conditions as reported by [66]. Tyre crumb rubber (TCR) is economical and ubiquitous in nature; an adsorption efficiency of 89% is observed in TCR at a pH 3 as studied by [67]. Polymeric adsorbents highly promising in adsorption of triclosan; diaion (SP207) had an adsorption efficiency of 98.8%. Moreover, this efficiency is found to increase in case of waters which have undergone biological treatment; this could be attributed to the competitive adsorption effect between TCS and effluent organic matter [68].

3.7 Membrane technology

Membrane technology (MT) possesses a variety of applications in removal of TCS. A number of ECs have been treated using membrane technology in studies conducted by [69]. Ultra-filtration (UF), nanofiltration (NF), microfiltration (MF), reverse osmosis (RO) are types of membrane technologies. UF might not serve to be promising in case of all, but it is highly effective method of treatment in case of TCS, and in a study, an efficiency of over 95% was observed when combined with 100 mg/l of PAC, this was attributed to the hydrophobic nature of TCS [70]. RO filters are effective in removal of EDCs whose molecular weight is ≥ 300 as reported by; this could be suitable for removal of TCS (molecular weight = 289.54) [71]. Modifications in membrane technologies, i.e. use of PAC did not show a significant removal for TCS, UF alone showed the same removal efficiency as that of UF + PAC, i.e. $> 90\%$ [70]. In order to avoid rejection of TCS fouling of membrane layers could be done, in study silica fouled NF, NF270 a loose membrane was developed where adsorption of TCS was predominant in membrane and this could be attributed to polarisation phenomenon but, in case of NF90, a tight membrane rejection was observed due to its dense layer

and steric hindrance. Moreover, increase in pH showed an increase in rejection of TCS [72]. Studies by [73] reported a removal efficiency of 91% and 87% for TCS by NF and UF, respectively. Membrane bioreactors (where membranes are combined with aerobic conditions) had proven to be highly promising for TCS removal with removal efficiency of 99%; this could be accounted to the adsorption tendency of TCS [32]. In another study which combined UF with flocculation (F) and ACS, it was observed that the additional methods did not have an impact in adsorption efficiency, it was same as that of just with UF, but adsorption through sludge mechanism has proven to be predominant as reported by [74].

3.8 Advanced oxidation process (AOPs)

AOPs refers to a set of chemical treatment method for the removal of organic and inorganic contaminants by oxidation through reactions with hydroxyl radicals ($\cdot\text{OH}$) ozonation serves to be a promising method in removal of TCS. It can be combined with other AOPs such as: radiation UV (O_3/UV), catalyst (O_3/CAT) or catalyst and ultraviolet light ($\text{O}_3/\text{UV}/\text{CAT}$) [75]. Incorporating the use of ozone in treatment of water started in the 1960s by Langlais et al. [76]. Treatment of TCS using ozone had proven to be promising in both Milli Q and surface waters, where removal efficiency up to 99% for a dose of 1.22 mg/l of ozone in 45 min was observed [77]. The reaction mechanism of TCS with ozone is explained in Fig. 3 [78], and removal of TCS in surface waters was observed to be comparatively less than Milli Q water; this could be attributed to the matrix effects. Moreover, pH played an important role in removal of TCS; a mildly alkaline pH (7.3) is found to be highly effective as reported by [78], pH is also shown to affect the rate of ozonation [79]. The transformation products of ozonation have been tested for genotoxic and cytotoxic effects by [80] 2,4-dichlorophenol, chlorocatechol, mono-hydroxyl TCS and di-hydroxyl TCS are the most commonly found end products in ozonation of TCS; however, studies have proven to be effective in removal of these products by extended ozonation, [78]. Studies were carried out on coupling ozonation with electrochemical mechanism where efficiency of 67% was achieved [81]. A study conducted by [82] involved combining ozone with UV and the removal efficiency had found to be high at a pH of 12; moreover, in this study, establishing an optimum contact time of 90 min had proven to be promising; Fenton's mechanism is a type of AOP in which OH radicals are the main oxidising agents in removal of TCS. Studies on this showed that the removal efficiency of TCS increased with increase in the concentration of OH radicals; these may be generated by using various mechanisms such as Fe^{+3} when combined with UV-C irradiation as conducted by [83]. In another

Fig. 3 Reaction mechanism of triclosan with ozone **Fig. 4** Photolysis and photocatalysis of triclosan

study where photon–Fenton oxidation was employed, the increase in concentration of OH radicals and catalysts had led to an increase in the concentration of intermediate products, a removal efficiency of 99.5% was achieved at an optimum dosage of $H_2O_2/Fe(II)/TCS = 50/0.1/10$. Cokay and Oztamer [84], however, this did not hinder the generation of intermediate products, In a study using H_2O_2 as an

oxidant and $BiFeO_3$ magnetic nanoparticles ($BiFeO_3$ MNPs) as catalysts has proven to solve the issue of accumulation of intermediate products by modifying the particle surface with EDTA ligands [85], also this facilitated in reducing removal time and increasing removal efficiency of TCS. In a study conducted by [86], photocatalysis was found to be a promising method for abatement of TCS than photolysis,

Table 5 Efficiencies of different methods employed in removal of TCS

S.no	Treatment method	Efficiency/rate constant (R^2)	Removal mechanism	External conditions	References
1.	Biological method				
1.1	Membrane bioreactors	99%	Sorption onto sludge	Influent con (10^3-10^4) ng/L	[32]
1.2	Rotating biological contactors	81%	Sorption	Influent conc: 494–4945 ng/L, effluent conc, 75–322, pH $\ll$ 8.1, lipid conc 327–670 μ g per g dm	[40]
	Oxidation ditches	96%	Sorption	Influent conc 710–5115, Effluent conc 4–104, pH $\ll$ 8.1 lipid conc, 483–783 μ g per g dm	
1.3	Rotating biological contactors	58–96%	Sorption	Dissolved oxygen levels < 0.3 mg/L	[33]
	Trickling filters	86–97%	Sorption	Influent conc: 3.7 μ g/L, effluent conc: 0.13 μ g/L removal of 96.5%	
	Activated sludge	95–98%	Sorption	Influent conc 1.1 μ g/L, effluent conc 0.027 μ g/L, removal of 97.5%: dissolved oxygen levels 1.5–2.0 mg/L	
1.4	Degradation under: aerobic conditions	95 $\pm$ 1.2%	Degradation in mineral broth and agar media	10 mg/L of TCS degraded in 5 days, phenol, catechol, and 2,4-dichlorophenol are intermediate products	[34]
	Anaerobic conditions	87%	Degradation	Methanogenic conditions for 10 days with acetate as co substrate	
1.5	Using bacteria	$> 60\%$	Degradation	<i>N. europaea</i> has degraded TCS $> 60\%$ for an initial conc of 0.5–2 mg/L	[36]
1.6	Activated sludge	99.9%	Sorption	Dissolved oxygen = 5000 mg/L, SRT = 2–4 days, HRT = 52 h, removal efficiency varied 92.5%, 95.4%, 99.1%, 99.9% for 18, 24, 48, 52 h	[38]
1.7	Activated sludge	90%	Sorption	Influent conc: 1.1–1.3 μ g/L	[41]
1.8	Activated sludge	96%	Sorption	Influent conc: 3.8–16.6 μ g/L, effluent conc 0.2–2.7 μ g/L, 6 h on aeration basin, HRT = 18 h, TSS < 15 mg/L	[39]
2.	Activated carbon				
2.1	Charcoal-based GAC	31.4%	Sorption	TCS conc 60 mg/L, AC dosage 1 g/L, temperature = 25 degrees, pH = 3–10	[43]
2.2	Powdered activated carbon	98%	Sorption	5 mg/L dose of carbon with a contact time of 4 h	[46]
2.3	Carbon derived from biomass	80.77%	Sorption	0.1 g of AC for $C_0 = 5$ mg/L at acidic pH, time of 20 min, at 25 degrees	[47]
2.4	Activated carbon	0.979	Sorption	pH < 7	[48]
3.	Carbon nanotubes				
3.1	Multi-walled carbon nanotubes	0.97 for first order and 0.99 for second order	Sorption	At 298 K and at pH $< pK_a$, $C_0 = 12$ mg/L, sorbent dose = 0.05 g/L for MWNTs	[51]
3.2	Single-walled carbon nanotubes	0.99	Sorption	At pH = 7, and 20 degrees, $C_0 = 50-2500$ μ g/L	[52]
	Multi-walled carbon nanotubes	0.99	Sorption		

Table 5 (continued)

S. no	Treatment method	Efficiency/rate constant (R^2)	Removal mechanism	External conditions	References
3.3	Purified multi-walled carbon nanotubes	> 85%	Sorption	0.1 g of MWNTs, at 293 K, pH = 7, 15 g/L of Na_2SO_4	[53]
3.4	Pristine multi-walled carbon nanotubes	0.93	Sorption	1.0 mg/L of feed conc, TCS conc = 3–120 ng/L	[48]
3.5	Designer carbon nanotubes	99.7%	Sorption	85.6%-enzyme catalysed degradation, 14.1%-adsorption	[55]
4	Clay minerals				
4.1	Vermiculite	Sorption constant $K_d = 92.9 \pm 12.8$	Sorption	pH = 3.1	[57]
	Acidic modified montmorillonite K10	$K_d = 696.6 \pm 52$	Sorption	pH = 3.9	
4.2	Kaolinite	0.99 for Freundlich isotherm and 0.96 for Langmuir isotherm	Sorption	$C_0 = 60$ mg/L, Sorbent dose = 1 g/L, pH at 6 and 9, Humic acid conc = 200 mg C/L	[58]
	Montmorillonite	0.99 for Freundlich isotherm and 0.97 for Langmuir isotherm	Sorption	$C_0 = 60$ mg/L, Sorbent dose = 1 g/L, pH at 7, Humic acid conc = 200 mg C/L	
5.	Zeolites				
5.1	Organic zeolites	0.992 for Langmuir isotherms and 0.984 for Freundlich isotherm	Sorption	For OZ 2.5 zeolite at 298 K, pH = 6.14	[59]
6.	Biochar				
6.1	Biosolids derived biochar	0.8	Sorption	At 10.3 gpm/ft ² , mass breakthrough bed volume = 450, mass of TCS removed after 2000 bed volumes = 500 µg/g	[62]
6.2	Sludge derived biochar	99.2%	Sorption	pH = 7.2, biochar dosage = 1.0 g/L, PMS conc = 0.8 mM, temperature = 25 degrees, 32.5% removal in 240 min	[62]
6.3	Biosolid biochar		Sorption	Sorption was high under humic acid and at pH = 7	[64]
7.	Other adsorbents				
7.1	Manganese oxides	55%	Sorption	pH = 5	[65]
7.2	Mn(IV)	3–99%	Sorption	–	[66]
7.3	Tyre crumb rubber	89%	Adsorption	pH = 3	[67]
	Carbon black	95%	Adsorption	–	
	Styrene butadiene polymer	92%	Adsorption	–	
7.4	Polymeric adsorbents	98.4%	Adsorption	Adsorbent dosage of 1.2 g/L	[68]
8	Membrane technology				
8.1	Ultra-filtration + PAC	> 98%	Adsorption	Influent conc = 2.4 µg/L, conc after UF = 0.03 µg/L, conc after PAC = < 0.025 µg/L, 100 mg/L of PAC	[70]
8.2	Nanofiltration	Adsorption > 15 µg/cm ²	Adsorption	pH = 5, polyamide and polysulphone layers	[72]
8.3	Ultra-filtration	87%	Adsorption		[46]
	Nanofiltration	91%	Adsorption		

Table 5 (continued)

S. no	Treatment method	Efficiency/rate constant (R^2)	Removal mechanism	External conditions	References
9.	Advanced oxidation process				
9.1	Ozonation of: Milli Q water	99%	Oxidation	Spiked with 100–1600 µg/L at PAC dose of 1.25 g/L, contact time of 5 min	[77]
	Aerobically treated grey water	> 87%	Oxidation	Ozone dose of 15 mg/L	
9.2	Biological treatment + ozonation	Concentrations found to be detected at (340 mM)	Oxidation		[79]
9.3	Ozonation in surface waters	99.7%	Oxidation	Ozone dose = 5 mg/L, TCS conc = 3 mg/L	[78]
	Ozonation in Milli Q waters	88.1%	Oxidation	Ozone dose = 5 mg/L, pH = 7.3	
9.4	Ozonation	99.9%	Oxidation	Molar ratio of 1:5 for TCS: ozone, TCS conc = 1.4 mg/L, residual TCS conc = 0.001 mg/L	[37]
9.5	Ozonation with electrochemical mechanism	67%	Degradation		[83]
9.6	TiO ₂ /UV and O ₃ /UV Processes	> 90% in O ₃ /UV	Degradation	pH = 12, molar ratio of ozone: TCS = 5 Contact time > 480 min in TiO ₂ /UV	[82]
9.7	Fenton's process Fe ³⁺ combined with UV-C irradiation	> 95% within	Degradation	Contact time of 120 min	[84]
9.8	Photo-fenton oxidation	99.5%	Degradation	Ratio of H ₂ O ₂ /Fe(II)/TCS ratio of 50/2/0.1	[84]
9.9	Enhanced fenton like process	82.7%	Oxidative degradation	Initial conc of TCS = 34.5 µmol/L, H ₂ O ₂ conc = 10 mmol/L, EDTA conc = 0.5 mmol/L, BiFeO ₃ load = 0.5 g/L, pH = 6	[85]
9.10	TiO ₂ only	30%	Degradation	30% removal occurred in 20 min, in dark condition, pH = neutral	[86]
	Photolysis	75%	Degradation	UV irradiation is done, light source 245 nm, pH = neutral, TCS conc = 5 mg/L	
	TiO ₂ photocatalysis	82%	Degradation	Light source used is UV A range, 365 nm, pH = neutral, TCS conc = 5 mg/L	
9.11	Photocatalysis under UV	90%	Degradation	TCS initial conc = 1 mg/L, 90% was removed in 2 h	[87]
	Photolysis	78%	Degradation	300–450 nm light, 4–11 mg/L of TCS, 1 g/L of TiO ₂ , 8% removal in 60 min	
	Photocatalysis	95%	Degradation	245–365 nm light, 9 mg/L of TCS, 95% removal in 6 h	
	Photocatalysis of TiO ₂ with LED's	53%	Degradation	At pH = 7, 53% of removal has occurred in 8 h	

an efficiency up to 82% was achieved; moreover, using OH radical has proven to be effective in eliminating dioxin intermediate, and the mechanism of photolysis and photocatalysis is shown in Fig. 4 [86]. In a study on the types of light sources for photochemical degradation of triclosan, Photon–Fenton reaction serves as the most promising mechanism where removal efficiency up to 100% was achieved and photo catalysis of (TiO₂) by LED's displayed a least efficiency of 53% [87].

4 Suggested treatment methods

Nanotechnology serves to be a promising technique in removal of ECs [88]. Due to its unique properties, nanozerovalent iron (nZVI) can be applied for removal of wide range of emerging contaminants [89]; moreover, it has proven to be effective in removal of halogenated hydrocarbons [90], TCS being a halogenated hydrocarbon can, therefore, be treated using (nZVI). A wide range of methods can be employed in the synthesis of nZVI [91]. Due to the limitations of many conventional methods, an environmentally benign method can be implemented in its synthesis. This could be achieved by the tendency of plants extracts to act as natural reducing agents; this can be attributed to the polyphenols present in plants which help them in functioning as reducing agents [92]. Although plant extracts may undergo degradation and prove to be unstable as reducing agents, these extracts may be stabilised in the presence of certain pH and temperature conditions. Cocoa seed extracts and tea leaf extracts have shown to be stable under certain conditions [93, 94]. Therefore, this method could also be implemented for removal of TCS (Table 5).

5 Conclusions

Although high removal efficiency could be achieved in biological treatment, some constraints could be observed such as EPS, and these have shown to give a negative impact on removal rate. Further, in the case of ACS, a high removal could be achieved only under extended hydraulic retention time (HRT). A consistent removal was not observed in the case of AC and it varied from 31 to 97%, but the removal efficiency was found to improve when it was combined with MT. MT serves to be an extremely promising method for removal of TCS as compared to other ECs due to its hydrophobic nature ($\log K_{ow}$ 4.8), for contaminants whose ($\log K_{ow}$) value is (< 2.6) are unlikely to get adsorbed over the surface due to high hydrophilicity. Moreover, the issue of rejection of TCS in MT could be avoided by fouling of membranes.

Unlike AOP, MT does not generate harmful intermediate products. Moreover, unlike CNTs, MT does not impart toxic effects on the environment and is found to be economical as compared to polymeric resins. Therefore, due to the hydrophobic nature of TCS and due to unique properties of membranes, MT could serve as an ideal method for its treatment.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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