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Trace organic contaminants in biosolids: impact of conventional wastewater and sludge processing technologies and emerging alternatives

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Trace organic contaminants in biosolids: impact of conventional wastewater and sludge processing technologies and emerging alternatives

Abstract

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Keywords: Trace organic contaminants (TrOC); biosolids; sludge digestion; bioaugmentation; advanced oxidation processes

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1. Introduction

Excess sludge generated by biological wastewater treatment has traditionally been disposed through ocean-dumping, landfilling, or incineration. Due to increasingly stringent environmental regulations, these disposal methods are being phased out and replaced by either aerobic or anaerobic digestion. In these treatment processes, pathogens and volatile solids are removed and sludge is converted to stable “biosolids”. Biosolids are rich in organic matter and nutrients, and can be utilised in various land applications (e.g., as fertilizer, soil conditioner and composting material) depending on its quality. Variables such as pathogenicity, vector attraction, odour, and heavy metals content of biosolids are regulated to protect the environment and public safety. The beneficial use of biosolids is a sustainable option because it has minimal impact on the environment (if the final product is devoid of pollutants), enables the recovery of resources, and

adds economic value to what is conventionally perceived as waste [1, 2]. Nonetheless, significant concern over the occurrence of trace organic contaminants (TrOCs) in biosolids, which can eventually contaminate soil and water and accumulate in plants and grazing animals, has risen in the recent years [3-5]. These TrOCs include pesticides, industrial chemicals, components of consumer products, pharmaceuticals and personal care products, hormones, and other organic pollutants that are ubiquitous in sewage and other environmental samples. Many of these TrOCs have the potential to cause chronic disorders in animals and humans [3]. TrOCs that are present in biosolids are those which are recalcitrant to wastewater and sludge treatment and have high affinity for sludge flocs. Although a few countries have already imposed controls on certain pollutants, e.g. di(2-ethylhexyl)phthalate (DEHP), linear alkylbenzene sulphonates (LASs), nonylphenol (NP) and nonylphenol ethoxylates (NPEs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzo-p-furans (PCDD/Fs), a unified directive addressing TrOCs in biosolids is not yet available [6].

The occurrence of TrOCs in biosolids are influenced by wastewater and sludge treatment operation parameters [4, 7] and could be minimised by the addition of advanced treatment processes including ozonation [8], ultraviolet (UV) oxidation [9], and bioaugmentation [10] in the sludge treatment line. The fate of TrOCs during wastewater treatment is largely determined by their physicochemical properties (e.g. hydrophobicity, charge, and functional group). Thus, their occurrence in biosolids is inherent and unavoidable. Nonetheless, literature suggests that optimisable operation parameters (e.g. pH, sludge retention time (SRT), and temperature) have some degree of influence on TrOC sorption and biodegradation [7, 11]. Further treatment of biosolids can remove TrOCs with high efficiency, but may require additional equipment and resources that drive up the cost of biosolids management.

The aim of this review is to analyse the occurrence and removal of TrOCs in biosolids. The first part of this review will investigate the underlying mechanisms and factors that affect the fate of TrOCs during wastewater treatment. There is a wealth of research about the fate and removal of TrOCs in the conventional activated sludge (CAS) process [12-18]. A few review articles have summarized the effect of various operation parameters on TrOC removal from the aqueous phase [7, 19, 20], but none has systematically collated and scrutinised the available data to identify

operation conditions that are relevant for controlling the occurrence of TrOC in biosolids. The second part will discuss the fate and removal of TrOCs during sludge treatment. Most of the literature available on the fate of TrOCs in the sludge treatment line has focused on conventional aerobic and anaerobic digestion, and much less is known about the behaviour of TrOCs in other sludge treatment processes, e.g. thickening, conditioning and dewatering, and composting. The third part of the review will critically examine the mechanisms and efficiency of the emerging technologies for TrOC removal from biosolids. From these, future research priorities about the management of TrOCs in biosolids will be provided.

2. Fate of TrOCs in conventional wastewater treatment: mechanisms and relevant factors

Upon entry to WWTPs, TrOC may sorb on sludge flocs, undergo biodegradation or abiotic transformation, or remain intact in wastewater. In general, abiotic loss of TrOCs in primary or secondary wastewater treatment and in sludge treatment is limited (Section 2.3). TrOC sorption on sludge largely depends on their physico-chemical properties, e.g. hydrophobic TrOCs are more likely to partition in the organic portion of sludge (Section 2.1). Although sorption separates TrOCs from wastewater, it does not result to their elimination from the sludge and therefore not a means of “TrOC removal.” The sorption of biodegradable compounds on sludge facilitates biodegradation, but sorption of slowly biodegradable compounds lead to contaminant build-up. The liberation of TrOCs from sludge during sludge treatment may increase their bioavailability (i.e., availability for biodegradation). TrOC biodegradation occurs under aerobic, anoxic, and anaerobic conditions (Section 2.2), and may result to complete mineralisation of the compounds. However, formation of metabolites that are potentially more toxic than the parent compounds have been also reported.

2.1 TrOC sorption

Activated sludge has a high sorption capacity for TrOCs due to its large specific surface area [4]. Sorption occurs mostly through hydrophobic interactions between TrOCs and the organic fraction of sludge [21, 22]. Li et al. [21] reported a positive correlation between the sorption of antibiotics and the total organic carbon (TOC) of secondary sludges from different WWTPs (e.g. 7-45% TOC). Similarly, Zhang et al. [22] observed that the sorption of 17α -ethinylestradiol

increased with the TOC of different types of sludge (e.g. 44-47% TOC). A direct relationship between TrOC sorption and TOC is also observed in other environmental matrices, such as soils (e.g. 5-33% TOC) and aquatic sediments (e.g. <1-5% TOC) [23].

Sorption increases with hydrophobicity of TrOCs, which can be quantified using the apparent octanol-water partitioning coefficient $\log D$:

$$\log D = \frac{[HX]_o}{[HX]_w + [X^-]_w} \quad \text{Equation 1}$$

where $[HX]_o$ is the concentration of the un-ionised form of the compound partitioned in octanol and $[HX]_w$ and $[X^-]_w$ are the concentrations of the un-ionised and ionised forms of the compound partitioned in water, respectively, when the octanol-water system is under equilibrium at a given pH and temperature. According to Hai et al. [24], TrOCs with $\log D > 3$ generally have high sorption on sludge. Hydrophobicity depends on the chemical structure of the compound. For example, Niu et al. [25] observed that the sorption of perfluorosulphonate on sludge is significantly higher than that of perfluorocarboxylate because the sulphonate group is more hydrophobic than the carboxylate group. Nonetheless, Taedkaw et al. [26] found that hydrophobic TrOCs that possess electron donating groups (e.g. hydroxyl and amine) do not accumulate in the sludge of an aerobic membrane bioreactor (MBR) due to their high biodegradability.

TrOCs also sorb on sludge by means of electrostatic attraction. The pH at the isoelectric point (pI) of sludge is 2.9 [27], meaning its surface is negatively-charged under typical biological conditions of pH 7. Therefore, TrOCs that predominantly exist in their neutral or positively-charged forms at pH 7 were found to have high sorption in primary and secondary sludge [28-30]. On the other hand, TrOCs that are predominantly negatively-charged at pH 7 did not significantly sorb on sludge due to electrostatic repulsion [31]. Favourable electrostatic conditions also facilitate hydrophobic interactions, as noted by Urase and Kikuta [32] when they found that a linear correlation between hydrophobicity and sorption existed only when TrOCs are predominantly in neutral form. However, exceptions have been reported in literature. Calace

et al. [33] observed that although electrostatic repulsion is expected between negatively-charged chlorophenols and sludge at pH 8, high sorption of the compounds still occurred via hydrophobic binding. Similarly, Stevens-Garmon et al. [28] found that some positively-charged compounds (e.g. trimethoprim and atenolol) that are expected to have high electrostatic attraction with sludge at pH 7 exhibited low sorption due to their hydrophilic nature.

It is also possible that extracellular polymeric products (EPS) can play a significant role in TrOC sorption. EPS are proteins, carbohydrates, humic acids, and other small organic molecules excreted by bacteria that serve as the structural framework of sludge flocs. They are highly hydrophobic, and therefore have greater binding propensity for organic pollutants (e.g. benzene and toluene) than bacterial walls [34]. Thus far, Niu et al. [25] observed a positive correlation between the sorption of perfluoroalkyls and the protein fraction of EPS has been attributed to the linkage of the compounds with the amide group or secondary structure of protein. Likewise, Métivier et al. [35] found that the affinity of erythromycin towards EPS was greater than that of acetaminophen, which may explain why erythromycin has greater sorption on sludge. Khunjar and Love [36] performed TrOC sorption experiments on sludge with and without (i.e., after cation exchange resin extraction) EPS, and observed that 17α -ethinylestradiol have greater affinity towards the protein fraction for EPS, whereas trimethoprim sorbed equally on the protein and polysaccharide fractions. Further investigation is required to confirm the relationship of EPS and TrOC sorption, but this is probably challenging because EPS characteristics are sensitive to many factors including wastewater characteristics, bacterial growth phase, and reactor operation conditions [34].

Notably, the irreversible sorption of organic contaminants and their metabolites has been observed in soils [37]. There is limited information on the irreversible sorption of TrOCs on activated sludge, but it is likely to have impact on TrOC bioavailability and treatment. It may also result in non-extractable residues (i.e. compounds that cannot be liberated from the sludge flocs without significantly altering the sludge matrix) and complicate sample extraction and analysis [38, 39]. The eventual liberation of irreversibly bound TrOCs, e.g. when volatile solids are destroyed or sludge is exposed to soil [40, 41], is also of environmental concern [39]. The

release of TrOCs upon destruction of volatile solids has been observed during anaerobic digestion (Section 3.2.1) and advanced oxidation treatment of sludge (Section 4).

2.2 TrOC biodegradation

Based on a comprehensive review on TrOC biodegradation, Tran et al. [11] contend that due to their low concentration in wastewater, TrOC biodegradation is most likely to occur via co-metabolism. In other words, in many instances, TrOCs do not serve as primary carbon source for microbial growth, and their biodegradation occurs only when other carbon sources are available (e.g. biodegradable COD in wastewater). Co-metabolic pathways may lead to the formation of metabolites that may eventually participate in metabolic reactions resulting in the complete mineralisation of the compounds [11]. Nevertheless, biodegradation of TrOCs by bacterial metabolism, i.e. the utilisation of TrOCs as the primary substrates for bacterial growth, has also been shown in pure bacterial cultures and batch tests using activated sludge [42]. In any case, the biodegradability of TrOCs depends on the chemical structure of the compounds. Those that bear highly branched or short hydrocarbon chains and halogen, sulphonate, methoxy, and nitro moieties are generally recalcitrant [4, 43]. The sorption potential of TrOCs has a dual effect on biodegradation. The sorption of rapidly biodegradable compounds on bacterial surfaces facilitates their reaction with extracellular enzymes and uptake into cells [4], but the sorption of slowly biodegradable compounds on sludge flocs decreases their bioavailability and exacerbates accumulation in sludge [44, 45]. Barret et al. [44] developed a model for TrOC co-metabolism in anaerobic sludge, and showed that compounds partitioned in the aqueous phase undergo biodegradation. Wijekoon et al. [45] reported that hydrophobic and persistent TrOCs significantly accumulate in the MBR. Treatment at higher SRT can enhance biodegradation by increasing reaction time and enabling growth of slow-growing bacteria [4].

TrOC biodegradation can result in toxic metabolites, which may have a greater impact on the environment and human health than the parent compounds [4, 11]. Some metabolic pathways are well-documented. One of the most notable reactions is the aerobic biodegradation of long chain nonylphenol ethoxylates into short chain nonylphenol ethoxylates followed by the anaerobic degradation of the ethoxylate groups that increases the concentration of nonylphenol in sludge [4, 46]. Metabolites from the biodegradation of pharmaceuticals [42, 47], linear alkyl

benzene sulfonates [48], and UV filters [49] in sludge were also identified, as well as products from bioconversion among hormones [50, 51]. However, limited information is available on the biodegradation pathways of TrOCs due to the wide range of compounds in real wastewater, which makes it difficult to relate detected metabolites to the parent compounds [49, 52]. The complexity of the sludge matrix also creates issues in sample extraction and analysis [49, 53]. Therefore, it is beneficial to observe biodegradation of individual compounds by pure cultures to understand potential reaction pathways in sludge. For instance, some biodegradation products of di(2-ethylhexyl)phthalate and bisphenol A exhibit toxicity and/or estrogenicity [53]. It is also useful to perform toxicity or estrogenic activity assays to evaluate the efficiency of treatment procedures and potential hazards of effluent and sludge to be disposed or re-used [52, 54].

Biodegradation occurs under different redox conditions (aerobic, anoxic, and anaerobic), with each condition offering biodegradation pathways that may not be available in others due to its distinct microbial consortia. Aerobic treatment generally results to high biodegradation of TrOC through the action of heterotrophic bacteria and autotrophic ammonia-oxidizing organisms (AOO) in the form of bacteria and archaea [11]. Using 17 α -ethinylestradiol as a model pollutant, several research groups have showed that heterotrophs and AOO utilise the enzymes catechol dioxygenase [55] and ammonia monooxygenase [16] for TrOC degradation, respectively. AOO is necessary for the biodegradation of some pharmaceuticals (e.g. roxithromycin, erythromycin, and iopromide) [13, 17, 56], although cooperative biodegradation of 17 α -ethinylestradiol, trimethoprim, and their metabolites by heterotrophs and AOO has been observed [55]. Interestingly, heterotrophic species belonging to the same group have different TrOC biodegradation capacity. Pure cultures of *Rhodococcus rhodochrous* completely degraded 17 α -ethinylestradiol, whereas pure cultures of *R. equi*, *R. erythropolis*, and *R. zopfii* were only able to degrade about 60% of the same compound [57].

Previous studies generally show that TrOC biodegradation preferentially occurs under aerobic than anoxic conditions [13, 56, 58, 59]. The laboratory-scale reactors of Suarez et al. [13] and Dorival-García et al. [56] demonstrated that compounds such as diclofenac, naproxen and roxithromycin were recalcitrant under anoxic conditions, but had moderate to high removal (e.g. 14.9-60%) under aerobic conditions. Phan et al. [58] investigated the removal of 30 TrOCs by a

pilot MBR consisting of an anoxic/anaerobic and an aerobic compartment. They [58] reported that TrOC biodegradation occurred mostly in the aerobic compartment and only a few TrOCs were readily biodegradable under anoxic/anaerobic conditions. Nonetheless, there are also reports of TrOCs having similar or higher biodegradation in anoxic reactors in comparison with aerobic reactors under specific circumstances such as high SRT or low dissolved oxygen (DO) concentration. Suarez et al. [13] noted that synthetic musks (e.g. tonalide and galaxolide) achieved high biodegradation under anoxic conditions with SRT>20 days. Hai et al. [60] and Stadler et al. [59] observed comparable or higher biodegradation of sulfamethoxazole under near-anoxic conditions (e.g. DO concentration < 0.5 mg/L), probably because both aerobic and anoxic co-metabolic pathways were available under those conditions. Therefore, a systematic combination of aerobic and anoxic treatment can enhance TrOC removal. Phan et al. [58] showed that anoxic conditions promoted the sorption of hydrophobic TrOCs on sludge, which possibly facilitated their biodegradation during sludge recirculation between aerobic and anoxic conditions. Furthermore, Phan et al. [61] observed that a full-scale MBR with a complex configuration involving multiple aerobic and anoxic zones showed higher and more stable removal of TrOCs than a pilot-scale MBR containing only aerobic and anoxic reactors, emphasizing the role of different DO levels in enhancing the sorption-biodegradation process.

Anaerobic treatment is marked by unique biotransformation pathways, such as reductive dehalogenation of chlorinated compounds, conversion of natural hormones, and enantioselective biodegradation [4, 62, 63]. Reductive dehalogenation of six chlorophenols was observed in upflow anaerobic sludge blanket reactors, and the reaction involved either hydrogenolysis, i.e. the substitution of chlorine atoms with hydrogen, or vicinal reduction, i.e. the removal of two halogens from adjacent carbon atoms resulting to the formation of a double bond [4]. Joss et al. [62] reported that estrone is converted to 17 β -estradiol exclusively under anaerobic conditions. This suggests that although anaerobic treatment can result in moderate to high estrogen removal [62, 64], it may have implications on the estrogenicity of sludge. Bioconversion among TrOCs and metabolites was also evident during anaerobic digestion of sludge (Section 3.2.2). Furthermore, the study of Gasser et al. [63] observed that batch anaerobic treatment of the drug *R,S*-venlafaxine and its metabolite *R,S*-O-desmethylvenlafaxine produced degradation products with different enantiomeric distribution than that of aerobic treatment. Wang et al. [65] noted

high removal (e.g. >93%) of five polycyclic musks in a laboratory-scale anaerobic MBR through biodegradation, but did not see enantioselectivity in the reactions.

2.3 Abiotic TrOC transformation

Abiotic TrOC transformation may occur, but there is a consensus in literature that their impact on TrOC removal from the sludge matrix is limited [53]. A small fraction might be removed via abiotic mechanisms such as volatilisation, hydrolysis, thermal degradation, and photolysis.

Volatilisation may occur at ambient temperatures for hydrophilic compounds with relatively low solubility in water and high Henry's law constant (k_H) at liquid-gas interfaces, e.g. surface of aeration tanks [4, 66, 67], or at elevated temperatures, e.g. during composting or thermophilic digestion [46, 68, 69]. Most TrOCs have low k_H and thus TrOC removal by volatilisation in WWTPs has only been observed for a few compounds (e.g. fragrances and polycyclic hydrocarbons) at minimal quantities [46, 67]. Hydrolysis has potential to occur in aqueous environments [4], but thus far negligible TrOCs hydrolysis in sludge matrices has been observed [70, 71]. Thermal degradation of TrOCs has not been substantiated in literature, although the disappearance of pharmaceuticals during sludge drying (e.g. 180° C) has been attributed to this mechanism [40]. Direct or indirect photolysis degrades TrOCs (e.g. pesticides) in aqueous solutions [72], and UV disinfection performed after secondary or tertiary treatment has been observed to remove up to 20% of pharmaceuticals in the effluent [73]. However, overall photolysis has minimal impact on TrOC removal from sludge matrices [53, 70].

2.4 Operation conditions that impact TrOC accumulation in sludge

In this section, the operation parameters of secondary and tertiary wastewater treatment that have potential to impact TrOC accumulation in sludge are investigated.

2.4.1 pH

The interactions of TrOC and sludge at neutral pH have been extensively studied [12, 13].

Nonetheless, secondary treatment may occur at higher or lower pH due to the characteristics of wastewater or addition of chemicals for sludge conditioning [33, 74]. In such cases, the sorption and biodegradation of ionisable compounds is expected to change depending on their pKa and the surface charge of sludge. Urase and Kikuta [32] found that reducing reactor pH from 7 to 5 increased the sorption of TrOCs containing carboxylic acid groups (e.g. fenoprop) because the un-dissociated and neutral form of the compounds predominated at lower pH. Similarly, Hörsing

et al. [75] demonstrated that increasing mixed liquor pH from 6 to 8 caused 10-20% change (decrease or increase) in the sorption of pharmaceuticals containing nitrogen or amine groups. Clara et al. [74] observed in batch experiments that bisphenol A ($pK_a=10.2$) desorbed from sludge when pH was increased from 7 to 9-12. Notably, pH is not expected to influence the sorption behaviour of non-ionisable TrOCs. Tadkaew et al. [76] varied the mixed liquor pH of an MBR from 5-9 and found that the removal of ionisable TrOCs changed with pH, whereas those of non-ionisable TrOCs were independent of pH.

2.4.2 Sludge retention time

SRT affects sludge concentration and properties such as EPS composition and hydrophobicity, which may have opposing influence on TrOC sorption [24, 77]. Hence, contradictory results have been reported in literature. For instance, Kim et al. [14] observed that decreasing SRT from 10 to 3 days decreased mixed liquor suspended solids (MLSS) concentration and consequently reduced the sorption of tetracycline by 9%, probably because there were fewer sorption sites at lower sludge concentration. On the other hand, Banihashemi and Droste [78] observed that decreasing SRT from 15 to 5 days increased MLSS concentration due to faster microbial growth rate, and there was no correlation between MLSS concentration and sorption of hormones and pharmaceuticals. These findings imply that MLSS concentration is not the only SRT-dependent factor affecting sludge-TrOC interactions [77]. Lee et al. [79] suggested that increasing SRT may increase EPS concentration, and consequently increase sludge hydrophobicity and affinity towards organic pollutants. The removal efficiencies of TrOC with high sorption (e.g. bisphenol A, estrone, and 17β -estradiol; $\log D > 3$ at pH 8) and moderate sorption (e.g. estriol and bezafibrate; $2 < \log D < 3$ at pH 8) have been found to increase with SRT in different laboratory- (SRT=2 to 68 days) and full-scale (SRT=0.6 to 550 days) conventional activated sludge (CAS) and MBR plants [12]. Nonetheless, various studies have also identified hydrophobic compounds (e.g. 17β -estradiol; $\log D = 4.52$ at pH 7) that are unaffected by SRT [12, 15, 29]. Hyland et al. [29] did not see a correlation between SRT and sorption of various ionisable TrOCs. Stasinakis et al. [15] demonstrated that varying SRT (e.g. 3-20 days) had no impact on the sorption of triclosan and bisphenol A, although nonylphenol exhibited high sorption at 3 days. Further investigation must be performed to elucidate the impact of SRT on other sludge properties, such as floc size and density, and their implications on TrOC sorption.

TrOC biodegradation may increase with SRT due to the (1) increase in sludge biodiversity, and (2) diversification in the metabolic activity of microorganisms due to unavailability of preferred substrate [24]. Clara et al. [12] reported that SRT > 10 days is sufficient to degrade most TrOCs and achieve low effluent TrOC concentrations, although recalcitrant compounds such as carbamazepine are unaffected by operation conditions. Tambosi et al. [80] observed that the biodegradation of TrOCs increased when the SRT of an MBR was increased from 20 to 30 days. However, other researchers found that SRT variation at a low (e.g. 3-20 days) [15] and high (e.g. 10-80 days) [62] range did not have any impact on the biodegradation of TrOCs.

2.4.3 Temperature

As an enthalpy-driven process, the sorption of TrOCs on sludge due to hydrophobic and electrostatic interactions is temperature-dependent [81]. Temperature also affects biodegradation kinetics and microbial communities [82]. Laboratory-scale studies have demonstrated that temperature variation, which occurs in full-scale plants due to seasonal changes [1], may affect TrOC sorption and biodegradation. For instance, Zeng et al. [83] reported that the sorption of 17 α -ethinylestradiol on inactivated aerobic and anaerobic sludge was greater at 10 °C than 30 °C because Gibbs free energy (ΔG° , an indicator of the spontaneity of the process) decreased as temperature decreased. Hai et al. [84] observed that the removal of hydrophobic TrOCs (log D > 3) was stable at 10-30 °C, but was unstable and lower at 45 °C. Moreover, the removal of hydrophilic TrOCs (log D < 3) varied considerably at 10-30 °C probably because of unstable biodegradation.

Thermophilic secondary treatment of high-strength wastewaters such as those from the pharmaceutical industry may show enhanced organic biodegradation along with low sludge yield [82]. However, it may cause a decline in the removal of hydrophobic TrOCs as demonstrated by the study of Hai et al. [84]. Wijekoon et al. [85] reported higher TrOC removal in a thermophilic MBR combined with membrane distillation relative to an MBR alone, but the improvement was attributed to TrOC rejection by membrane distillation rather than enhanced organic biodegradation in the MBR under thermophilic conditions. Thus far, the conceptual

advantage of thermophilic over mesophilic treatment in terms of TrOC removal has not been demonstrated in literature.

2.4.4 Addition of sorbent materials

Addition of chemicals such as coagulants and adsorbents is commonly performed to improve sludge properties such as settling [1]. It can also be used to mitigate membrane fouling (in MBRs) and facilitate the removal of TrOCs from the aqueous phase through sorption [86-91]. For instance, activated carbon-amended activated sludge processes rely on enhanced adsorption of TrOCs on sludge followed potentially by their biodegradation. While the sorption of TrOCs on sorbents such as powdered and granular activated carbon (PAC and GAC, respectively) can help improve effluent quality, the conceptual expectation of 'bioregeneration' of the sorbents is often not accomplished [86-89], consequently necessitating periodic withdrawal of the spent adsorbent and its replenishment. The withdrawn sludge contains high concentrations of resistant TrOCs and needs to be properly treated and disposed. Further investigation is required to determine the impact of sorbent addition on TrOC biodegradability and accumulation in biosolids.

2.4.5 Solids concentration

TrOC sorption has been found to increase with MLSS concentration [14, 92], probably because higher MLSS affords a greater number of sorption sites for hydrophobic compounds. Li et al. [93] found that 17 β -estradiol biodegradation increased with MLSS concentration (0.4 to 1.7 g/L) in batch experiments, and likewise Shariati et al. [94] noted acetaminophen biodegradation was higher at greater MLSS concentration in an MBR (2-15 g/L) [93, 94]. On the other hand, Li et al. [95] did not observe any impact of MLSS (1-15 g/L) on carbamazepine removal of an MBR. Identifying an optimal MLSS value or range for TrOC biodegradation is difficult since only a few studies have focused on the subject, and they assessed removal of different types of TrOCs.

2.4.6 Identification of key operation parameters

Among the operation parameters considered, pH, SRT, and temperature appear to have the most significant impact on TrOC sorption and biodegradation (Figure 1). Changing the mixed liquor

pH for the purpose of sludge conditioning affects TrOC sorption. SRT could be modified to increase the TrOC biodegradation, but further investigation especially on biodegradation of TrOCs at long sludge age is required. Temperature range (e.g. mesophilic or thermophilic) has potential to affect reaction rates and microbial population. The addition of sorbents and solids concentration potentially have impact on TrOC sorption and biodegradation, but due to the lack of literature and/or contradicting reports it is difficult to ascertain their contributions to TrOC accumulation in sludge.

[Figure 1]

3. Fate of TrOCs during sludge treatment for solids reduction and stabilisation

The objective of sludge treatment is to reduce pathogens [96] and volatile solids [2] in sludge, producing biosolids that can be safely disposed or re-used. TrOCs present in the beginning of the sludge treatment line are those that partitioned in the solid phase of the sludge but were not degraded during secondary or tertiary wastewater treatment. Literature suggests that sludge treatment or handling processes that involve aerobic conditions (e.g. air flotation, aerobic digestion, and composting) favour the biodegradation of TrOCs more than those that involve anaerobic conditions (Section 3.1 and 3.2). Although removal of some TrOCs may occur during physical (e.g. thickening and dewatering) or chemical treatment (e.g. conditioning), significant biodegradation and subsequent removal of TrOCs takes place during sludge stabilisation, particularly under aerobic digestion and composting (Section 3.2).

3.1 Thickening

The first step in a typical sludge treatment line is sludge thickening, which is performed to increase the concentration of primary or secondary sludge to 3% total solids (TS) or more using gravity settling, centrifugation, air flotation, rotary drum filtration, or other procedures [1]. A recent investigation by Marti et al. [97] in full-scale plants revealed that thickening under anaerobic conditions (e.g. gravity settling and centrifugation) had no influence on the fate of estrogens in sludge. The same study showed that thickening under aerobic conditions (e.g. dissolved air flotation) decreased estrogen concentration in both liquid and solid phases of sludge due to biodegradation [97]. Thickening under aerobic conditions may contribute to TrOC biodegradation in the sludge treatment line, but may require additional energy for aeration and

water pumping [1]. More systematic study on the impact of thickening on other types of TrOCs is recommended.

3.2 Stabilisation

The key process in producing biosolids is sludge stabilisation, which destroys volatile solids to reduce the pathogenicity, vector attraction, and other undesired qualities and prevent spontaneous biodegradation of sludge [1].

3.2.1 Aerobic digestion

Aerobic digestion involves the treatment of thickened sludge in a completely mixed aerated reactor that is commonly used by small WWTPs (< 22 ML/day) [1] and is notable for greater biodegradation of TrOCs such as nonylphenol/nonylphenol ethoxylates, hormones, and polycyclic hydrocarbons compared to anaerobic digestion [98-101]. Reports to date usually reveal that TrOCs such as nonylphenol have minimal impact on the organic matter and volatile solids removal efficiency of aerobic digestion [100], but the effect of other compounds is yet to be investigated. Studies suggest that TrOC biodegradation in aerobic digestion is strongly dependent on temperature and SRT [97, 101]. Trably and Patureau [101] reported that the biodegradation of polycyclic aromatic hydrocarbons improved from 50 to 80% when the aerobic digester temperature increased from 35 to 55°C, but observed abiotic losses at higher temperatures due to volatilisation. They also noted an increase in polycyclic aromatic hydrocarbon biodegradation by the addition of methanol to sludge, which enhanced the dissolution of TrOCs in the liquid phase. Marti and Batista [97] emphasized that there was appreciable removal of estrogens higher aerobic digester SRT (e.g. 40-60 days) due to longer reaction time.

3.2.2 Anaerobic digestion

The industrial demand for anaerobic digestion has increased considerably due to its relatively low operation cost and potential to generate energy [102-104]. However, the persistence of TrOCs in sludge may pose problems to this process. First, methanogens are susceptible to organic pollutants such as chlorophenols, halogenated aliphatics, and N-substituted aromatics [105]. Second, full-scale anaerobic digesters generally have negligible or poor biodegradation of

TrOCs [97, 99, 106-108], and reports of high TrOC removal are limited to laboratory-scale anaerobic digesters [98, 109]. Third, some anaerobic co-metabolic pathways may produce more potent pollutants, such as the formation of nonylphenol from nonylphenol ethoxylates and 17 β -estradiol from estrone [46, 50, 51], which have serious implications on the toxicity and/or estrogenicity of biosolids. The formation of estrogenic byproducts is consistently observed even in the anaerobic digestion of other materials than sludge (e.g. animal manure) [110-112].

[Figure 2]

It was highlighted in Section 2.1 that TrOC removal efficiency of wastewater treatment can be predicted using the hydrophobicity of TrOC as represented by log D. However, during anaerobic digestion, a relationship between TrOC removal and log D could not be derived from available literature [8, 47, 51, 98, 106, 109, 113-119]. TrOCs with high log D (e.g. 17 α -ethinylestradiol and triclosan) may exhibit lower removal than TrOCs with lower log D (e.g. ketoprofen and diclofenac), and *vice versa* (Figure 2). Narumiya et al. [106] demonstrated that although TrOC sorption on anaerobic digester sludge still depends on its hydrophobicity and/or charge at a given pH, it does not seem to have correlation with biodegradation. Variation in TrOC removal in literature (Figure 2) may be due to varying anaerobic digester conditions and solids destruction efficiency. Studies suggest that TrOC removal in anaerobic digestion could be correlated with solids destruction, which potentially increases the bioavailability of the compounds. For example, Patureau et al. [46] and Trably et al. [120] observed that the removal of nonylphenol ethoxylates and polycyclic aromatic hydrocarbons increased with the TS removal of the anaerobic digester, possibly due to the desorption of the compounds from destroyed flocs and loss of sorption sites. However, Marti and Batista [97] speculated that although estrogen desorbs as sludge flocs are destroyed, it sorbs again on the remaining flocs leading to an increase in estrogen concentration in the solid phase.

[Figure 3]

The operation conditions of anaerobic digesters (e.g. temperature, type of sludge, SRT) could affect sorption, reaction rates, and microbial community, and thus have potential to impact on the

fate of TrOC in anaerobic digestion. The effect of temperature differs with the type of TrOC (Figure 3). Studies concur that thermophilic digestion favours the removal of polycyclic aromatic hydrocarbons [44, 120, 121] especially those with higher molecular weight [120], but different trends are reported for hormones, nonylphenol/nonylphenol ethoxylates, and pharmaceuticals [8, 47, 51, 98, 116, 119]. For instance, Paterakis et al. [119] reported that increasing digester temperature from mesophilic (35 ± 0.2 °C) to thermophilic (55 ± 0.2 °C) enhanced the removal of estrone, but increased the bioconversion among hormones leading to a decrease in the removal of estriol and significant formation of 17β -estradiol. The same study also observed that thermophilic conditions enhanced the biodegradation rate of small nonylphenol ethoxylates (e.g. NP₁E or NP₂E) by nearly 100%, but only increased the removal of large nonyl polyethoxylates (e.g. NP_nE where n=3-12) by 23%. Compared to Paterakis et al. [119], Patureau et al. [46] observed only a 20% increase in nonylphenol and nonylphenol monoethoxylate removal by increasing digestion temperature from mesophilic to thermophilic, probably because of different experimental conditions (e.g. SRT). Since mesophilic and thermophilic digestion each provides unique biodegradation pathways, a temperature-phased anaerobic digestion configuration has potential to improve overall TrOC removal. Samaras et al. [51] found that two-stage thermophilic-mesophilic digestion had higher removal of triclosan, bisphenol A and nonylphenol than either single-stage mesophilic or thermophilic digestion, but did not improve the removal of other compounds such as ibuprofen and naproxen. Notably, Carballea et al. [8] also did not observe changes in the removal of ibuprofen, naproxen, and other pharmaceuticals due to thermophilic digestion, indicating that the biodegradation of such compounds are not dependent on temperature.

Primary and secondary sludge have different composition and floc properties [1]. Paterakis et al. [119] reported that the removal of estrogen and nonylphenol ethoxylates from mixed sludge was 20-80% higher than that of primary sludge, but a clear explanation for this was not provided. SRT has been found to have significant impact on the sorption and biodegradation of TrOCs during wastewater treatment (Section 2.3.2), but so far only a few studies have investigated the effect of SRT on TrOC removal of anaerobic digestion. Carballea et al. [122] covered a range of SRTs under mesophilic (SRT=10, 20, and 30 days) and thermophilic (SRT=6, 10, and 20 days) conditions, but did not see significant difference in the removal of various hormones and

pharmaceuticals due to SRT. On the other hand, Hamid and Eskicioglu [123] found that amount of estrone and androstenedione in the supernatant of a thermophilic anaerobic digester increased by 1.2-1.5 and 2-4 times, respectively, when SRT was increased from 5 to 20 days probably due to bioconversion among hormones or other compounds in sludge (e.g. sterols).

3.2.3 Alkaline stabilisation

Alkaline treatment is a relatively inexpensive process that involves the addition of materials such as lime, fly ash, or cement kiln dust to raise sludge pH to 12 for one day or longer. The drastic change in pH is expected to alter the sorption behaviour of ionisable TrOC. Ivashechkin et al. [124] found that increasing sludge pH to 12.4 using calcium hydroxide caused desorption of BPA ($pK_a=10.3$) from flocs. Likewise, Kim et al. [125] observed that the concentration of polybrominated diphenyl ethers in sludge decreased after alkaline treatment because of dilution. Conceptually, the partitioning of TrOCs in the aqueous phase may enhance their removal from the sludge matrix after dewatering or increase their bioavailability in further sludge treatment (e.g. digestion). Nonetheless, Kouloumbos et al. [41] reported that the removal of radiolabelled nonylphenol ($pK_a=10.7$) from the solid phase of sludge was minimal (e.g. 1.3%) after alkaline stabilisation (e.g. treatment at pH 11 using calcium hydroxide) and centrifugation. The impact of alkaline treatment became apparent when sludge was applied on soil wherein the leaching of nonylphenol increased. Further study is necessary to confirm this trend as the extractability of other non-biodegradable organic components of sludge (e.g. humic acids and lipids) was reported to increase after alkaline stabilisation [126]. Furthermore, Carballa et al. [122] found that alkaline pre-treatment of mixed sludge (70:30 by volume of primary and secondary sludge) at pH 12 for 24 hours did not enhance the pharmaceutical removal efficiency of a laboratory-scale anaerobic digester. On the other hand, alkaline post-treatment of sludge may enhance the transmission of TrOCs from biosolids to receiving soils and have implications on the TrOC biodegradation pathways in the soil matrix [3].

3.2.4 Composting

Composting is an aerobic process that is applied as either a primary or supporting procedure to stabilise dewatered sludge (e.g. $TS>20\%$). In this process, sludge is mixed with one or more types of bulking agents (e.g. wood chips, sawdust, and garden waste) and then incubated in a

vessel or pile with or without aeration for an extended period (e.g. 21 days or more) [1]. Sanz et al. [133] highlighted that spiking high concentrations (e.g. 230 g/kg) of linear alkyl sulphonate, nonylphenol, and bis(2-ethylhexyl) phthalate to a laboratory-scale in-vessel compost did not have negative impact on composting efficiency and TrOC removal, nonetheless further investigation using other types of TrOCs must be performed. Significant TrOC removal (e.g. >60%) of linear alkyl sulphonate [132, 133], nonylphenol [68, 130-132], polycyclic aromatic hydrocarbons [129], and certain pharmaceuticals (e.g. ciprofloxacin and norfloxacin) [40] have been reported depending on composting conditions (Table 1). However, low removal was observed for TrOCs such as polychlorinated dibenzodioxins [69], hormones [128], and other pharmaceuticals (e.g. sulfamethoxazole and fluoxetine) [40, 127, 128], and contradicting trends are reported for the removal of di(2-ethylhexyl) phthalate [68, 132] and polychlorinated biphenyls [68, 69]. Notably, there is similarity in the TrOC removal of composts of different materials, e.g. sludge, manure, and municipal solid waste [40, 112, 131]. For example, the removal of fluoroquinolones and sulfonamides from sludge (e.g. 46-98%) was similar to that observed from manure (e.g. 37-100%) [40, 112]. The study of Moeller and Lee [131] demonstrated that composting sludge (e.g. 50% moisture) and municipal solid waste (e.g. 60% moisture) under the same process temperature results to comparable removals of nonylphenol and nonylphenol ethoxylates. Further investigation is necessary to validate these findings, but results thus far show the versatility and robustness of the composting process in terms of TrOC removal.

[Table 1]

The mechanism of TrOC removal during composting is generally attributed to microbial degradation [68, 69, 133, 135], although volatilisation of compounds with relatively high Henry's constant k_H , (e.g. nonylphenol and polychlorinated biphenyls) has also been observed [68]. Gibson et al. [68] reported that more volatile polychlorinated biphenyls ($k_H=24-40$ Pa·m³/mol) bearing less chlorine atoms have greater removal during composting than less volatile compounds ($k_H=9-15$ Pa·m³/mol) bearing more chlorine atoms. Muñoz et al. [69] observed greater polychlorinated biphenyl removal through biodegradation and volatilisation (e.g. 55%) than that of Gibson et al. [68] (e.g. negligible to 18%) probably due to dissimilar

composting environments (Table 1). Compounds with similar structure may undergo different biodegradation pathways. For instance, Muñoz et al. [69], reported that the concentration of polychlorinated biphenyls in the compost decreased by about 55% after 12 months of incubation probably due to biodegradation, but that of polychlorinated dibenzodioxins (e.g. octachlorodibenzodioxin and 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin) doubled probably due to bioconversion from chloropenols.

The fate of TrOCs during composting depends on the type of bulking agent, sludge-to-bulking agent ratio, type of sludge, temperature, and composting time. Bulking agents are carbon-based materials added to the compost to provide structure and regulate odour, but they can adsorb organic compounds and therefore limit the bioavailability of TrOCs. Oleszczuk [129] found that the addition of 20-30% fly ash to the compost decreased the biodegradation of PAHs from 87.5 to 83% due to the sorption of polycyclic aromatic hydrocarbons on fly ash. On the other hand, the addition of 30% sawdust had minimal impact on polycyclic aromatic hydrocarbon biodegradation probably due to its low sorption capacity. Meanwhile, Das and Xia [135] found that decreasing the ratio of sludge and wood chips from 65:35 to 43:57 significantly decreased the half-life of nonylphenol, probably due to the enrichment of nonylphenol-degrading microorganisms at lower carbon to nitrogen ratio in the compost. The importance of the nutritional makeup of the compost to TrOC removal is also apparent in batch cultures of composted sludge by Sanz et al. [133], which exhibited 10-20% increase in the removal of linear alkylbenzene sulphonates upon supplementation of glucose, tryptone soy broth, yeast extract, or peptone.

Marttinen et al. [134] suggested that the type of sludge may have implications on di(2-ethylhexyl)phthalate biodegradation during composting. There was greater biodegradation of di(2-ethylhexyl)phthalate from raw sludge (58%) than anaerobically digested sludge (34%) after composting, probably because raw sludge had higher moisture content and/or digested sludge already underwent several biological treatment processes and only retained highly persistent fractions. The di(2-ethylhexyl)phthalate removal observed by Gibson et al. (2007) from anaerobically digested sludge was higher than that reported by Marttinen et al. (2004). However,

it is noteworthy that these studies were conducted at different conditions (e.g., temperature profile, bulking agent, and composting period), and thus, a direct comparison is not possible.

The effect of temperature on TrOC biodegradation during composting appears to vary according to the type of TrOC. Xia et al. [130] found that increasing the temperature from 24 °C to 45-65 °C significantly enhanced the biodegradation rate of nonylphenol. However, Moeller and Lee [131] observed thermophilic composting may facilitate the formation of nonylphenol metabolites that increase the toxicity of sludge. Composting at 65-70 °C for 34 days resulted to the accumulation of nonylphenol and formation of nonylphenol ethoxylates, whereas composting at 35-55 °C resulted to the reduction of nonylphenol to below 1 mg/kg. On the other hand, Sanz et al. [133] found that linear alkylbenzene sulphonates were significantly reduced in batch cultures of composted sludge incubated at mesophilic conditions (40-45°C) but not at thermophilic conditions (e.g. >47 °C), probably because only microorganisms that thrive at lower temperature are capable of attacking linear alkylbenzene sulphonates. The findings of Sanz et al. [133] are supported by those of Patureau et al. [136], which showed that the removal of linear alkylbenzene sulphonates from full-scale composts were higher during the fall season (e.g. 30-45 °C) than in spring season (e.g. >45 °C). Interestingly, the disappearance of other TrOCs such as nonylphenol ethoxylates, polychlorinated biphenyls, and organohalogenes during composting and storage of composted sludge varied according to seasonal changes, indicating that biodegradation of such TrOCs is temperature-dependent [136]. Sadeh et al. [137] reported that the removal efficiency of fragrances, antibiotics, and industrial chemicals during composting varied with temperature (e.g. 25 to 70 °C), suggesting that each compound was degraded by a specific type of organism. For example, TrOCs that were optimally removed at 50 °C or more were probably consumed by bacteria, whereas those that were removed at lower temperature were probably consumed by actinomycetes and fungi [137]. An investigation of the microbial diversity during composting is needed to completely elucidate TrOC biodegradation pathways.

3.3 Conditioning and dewatering

During dewatering by physical or thermal treatment, moisture is removed from sludge such that a 'cake' with 20% TS or more is produced to increase the performance of additional sludge stabilisation procedures (e.g. composting) and minimise the cost of final sludge handling and

transport [1]. However, water molecules are tightly bound in sludge flocs due to their biological gel-like structure. Thus, sludge dewatering is commonly preceded by a chemical or thermal sludge conditioning step. In chemical sludge conditioning, materials such as lime, iron salts, and polymer are added into sludge to coagulate small particles into larger aggregates that have greater capacity to release water. In thermal sludge conditioning, sludge is heated to 230 to 290°C to evaporate water that is entrapped in sludge flocs [1].

Thus far, there is inconclusive data on the impact of dewatering on the fate of TrOCs in sludge. Some studies reported that dewatering by centrifugation or filter press increased the concentration of TrOCs in dewatered sludge [97, 116]. Muller et al. [116] suggested that the increase in 17 β -estradiol and 17 α -ethinylestradiol levels after dewatering might be due to the intense treatment conditions of the filter press (200 °C, 2 MPa) that enhanced the extractability of compounds. However, in that study, dewatering had no effect on other hormones such as estrone and estriol. Marti et al. [97] reported that dewatering non-digested thickened sludge by centrifugation increased its total hormone concentration by 41%, but dewatering anaerobically digested sludge by the same procedure did not affect hormone concentration. Other studies demonstrated that dewatering by either centrifugation or filter pressing do not affect estrogen concentration of the solid phase of sludge [54, 138]. The impact of thermal dewatering on other types of TrOC is yet to be investigated in detail, but Lindberg et al. [30] have demonstrated the possibility of thermal degradation of fluoroquinolones when sludge pellets underwent thin layer drying at 180 °C followed by moving belt drying at 105 °C. One could also speculate that high temperature may cause evaporation of relatively volatile compounds such as nonylphenol and polychlorinated biphenyls

As the final or penultimate step in the sludge treatment line, it is interesting to discover the impact of sludge dewatering and conditioning on the mineralisation, degradation, and mobility of TrOCs in biosolids after application on soil. Kouloumbos et al. [41] monitored the biodegradation products, mineralisation products, and mobility of ¹⁴C-labelled nonylphenol in soil amended with dewatered and conditioned anaerobically digested biosolids, and found that centrifuged biosolids was less penetrable to O₂ and have low bioavailability of nonylphenol to microorganisms in the soil. Meanwhile, sludge conditioned by lime had higher leaching potential of nonylphenol due to desorption at high pH, and sludge conditioned by acrylamide-based

cationic polymer potentially have greater toxicity due to the formation of nitrophenol from the reaction of nonylphenol with the biodegradation products of the polymer [41].

3.2.5 Overall abatement of TrOCs in the sludge treatment line

The abatement of TrOCs in the sludge treatment line heavily relies on the type of stabilisation employed. Of the stabilisation types considered in this review, aerobic processes (e.g. aerobic digestion and composting) demonstrate the greatest potential to remove TrOCs and other estrogenic metabolites. Aerobic digestion of thickened sludge achieves high removal of TrOCs such as nonylphenol ethoxylates, hormones, and polycyclic aromatic hydrocarbons depending on reactor temperature and SRT (Section 3.2.1). Similarly, composting of dewatered sludge results to high removal TrOCs such as of nonylphenol ethoxylates, polycyclic aromatic hydrocarbons, linear alkyl sulphonate, and certain pharmaceuticals depending on composting conditions (Section 3.2.4). Although it is interesting to compare the performance of aerobic digestion and composting in terms of TrOC removal, a systematic study on the subject is not yet available. It can be speculated that different reaction pathways arise since they contend with sludge at different levels of treatment and have distinct microbial consortia. In contrast to aerobic digestion or composting, anaerobic digestion appears to achieve lower TrOC removal, and, according to some reports, may exacerbate the estrogenicity of sludge by producing more estrogenic metabolites. Moreover, literature suggests that the sorption of TrOCs on sludge flocs does not necessarily facilitate anaerobic biodegradation (Section 3.2.2). There are only a few studies on the fate of TrOCs during alkaline stabilisation and therefore trends cannot be established. Nonetheless, it has been shown that treatment at elevated pH levels impacts the partition of certain TrOCs in sludge (Section 3.2.3).

Other steps in the sludge treatment line, particularly those that involve aerobic (e.g. thickening by air flotation) or extreme reaction conditions (e.g. thermal conditioning at 230 to 290°C) may contribute to TrOC removal, but to a lesser extent. Physical sludge thickening and dewatering appear to have minimal impact. Penultimate sludge dewatering and conditioning (e.g. by lime or polymer addition) have potential to decrease TrOC partition in the solid phase of sludge [41, 97, 116], but more investigation is necessary to fully understand their implications, especially TrOC fate upon application of biosolids in soil.

4. TrOC removal from biosolids

4.1 Ozonation

The beneficial effect of ozonation on sludge properties, sludge reduction, and TrOC removal from wastewater has been widely studied [20]. Less information is available on the effect of ozonation of sludge or biosolids on TrOC removal, and so far contradicting trends have been reported (Table 2). Bernal-Martinez et al. [139] observed that ozone pre-treatment of sludge at the dosage of 100 mg O₃/g TS increased the removal of polycyclic aromatic hydrocarbons in a laboratory-scale mesophilic anaerobic digester. In contrast, Carballa et al. [8] found that ozone pre-treatment of sludge at 20 mg O₃/g TS had no effect on the capacity of mesophilic and thermophilic anaerobic digesters to remove various TrOCs including musks, antibiotics, and hormones. It can be argued that the ozone dosage utilised by Carballa et al. [8] was too low to impact TrOC removal. In that study, ozone pre-treatment was only beneficial to the removal of carbamazepine because it preferentially partitioned on the aqueous phase of sludge and was amenable to ozone treatment [8]. Qiang et al. [141] observed that ozone treatment of sludge at 0.1 g O₃/g TS resulted to the desorption and complete removal of estrone, estriol, and 17 α -ethinylestradiol, but only to a moderate removal of bisphenol A and nonylphenol due to their strong binding with sludge. This suggests that it is easier for ozone to attack dissolved TrOCs than sorbed TrOCs. Compared to Qiang et al. [141], Lahnsteiner and Vranitzky [140] observed higher removal of nonylphenol because they utilised sludge containing lower concentrations of nonylphenol and nonylphenol ethoxylates. Their study also demonstrated an 18-60% increase in the removal of polycyclic aromatic hydrocarbons from sludge when ozone dosage was increased (0.021-0.081 g O₃/g TS).

[Table 2]

4.2 Fenton treatment

In the Fenton reaction, H₂O₂ is decomposed in the presence of Fe²⁺ to generate a hydroxyl radical (OH·) that serves as the primary oxidizing agent of contaminants. The low environmental impact of hydrogen peroxide and wide availability of ferrous ion sources provide Fenton treatment an economic advantage over other oxidation processes (e.g. ozone and photocatalytic treatment) that have high energy consumption and potential environmental risks. Fenton

treatment has resulted to partial removal of polycyclic aromatic hydrocarbons and hormones from sludge, and demonstrated potential to improve the TrOC removal efficiency of aerobic digestion (Table 2). Flotron et al. [142] reported that only a moderate removal of three polycyclic aromatic hydrocarbons was achieved because natural organic matter in sludge competed with the pollutants for OH· radicals. Zheng et al. [143] found that decreasing the pH of the Fenton reaction mixture from 2 to 4 increased the removal of 11 polycyclic aromatic hydrocarbons from 20 to 30% due to higher stability of the reaction components at lower pH. Li and Zhang [144] observed that Fenton treatment eliminated natural hormones from sludge by 70-98%, resulting to a decrease in sludge estrogenicity as phenolic compounds were converted to cyclohexenone and quinone-like structures. Furthermore, Pham et al. [145] found that Fenton pre-treatment increased the solubilisation of raw sludge (as measured by the ratio of soluble and total chemical oxygen demand) and the desorption of di(2-ethylhexyl)phthalate, and consequently increased the removal of di(2-ethylhexyl)phthalate by aerobic digestion from 72 to 85%.

4.3 UV oxidation

UV treatment of sludge in various configurations (e.g. UV only, UV/H₂O₂, and UV/TiO₂) can result to the removal of TrOCs through oxidative degradation [9, 150], and also through the evaporation of volatile or semi-volatile TrOCs when temperature rises during UV irradiation [146, 150]. It also has potential to enhance biodegradation by oxidising persistent TrOCs into smaller, more biodegradable products [147]. Varying TrOC removal has been observed depending on UV treatment conditions (Table 2) [9, 146, 147]. Salihoglu et al. [146] found that UV treatment caused only 15-21% removal of polycyclic aromatic hydrocarbons from sludge through volatilisation. On the other hand, UV/TiO₂ treatment with 0.5 and 20% by weight TiO₂ (Degussa P25) resulted to 77 and 63% removal of polycyclic aromatic hydrocarbons, respectively. TiO₂ particles absorb UV light and produce numerous electron-hole pairs that react with oxygen and water molecules to generate hydroxyl radicals. The addition of TiO₂ can enhance TrOC removal, but an excessive addition of the particles causes UV scattering in the suspension and decreases treatment efficiency [146]. UV/TiO₂ has high potential to treat polycyclic aromatic hydrocarbons in particular because it results to minimal evaporation of the compound into air since photodegradation is faster than evaporation [150]. Meanwhile, UV/H₂O₂

treatment of sludge achieved high removal of natural hormones and bisphenol A (e.g. 89-97%) and a moderate removal of nonylphenols (e.g. 67%) [9]. The observed degradation rate constants of the TrOCs under UV/H₂O₂ treatment were 45–197 and 11–53 times greater than those under UV treatment alone and H₂O₂ treatment alone, respectively. Keen et al. [147] found that ¹⁴C-labelled carbamazepine was photodegraded into smaller products containing hydroxyl and carbonyl moieties through UV/H₂O₂ treatment. Furthermore, UV-treatment of wastewater increased the mineralisation of carbamazepine by 45% in batch tests, indicating that UV/H₂O₂ is a potential pre-treatment process targeting highly recalcitrant TrOCs.

4.4 Ultrasonication

Ultrasonic treatment degrades TrOCs in aqueous media by inducing the implosion of cavitation bubbles that generates hydroxyl radicals capable of oxidizing organic matter. Ultrasonic treatment also promotes the desorption of TrOCs from sludge by destroying sludge flocs [50, 121], which generally enhances TrOC removal from sludge (Table 2). Chawla et al. [50] observed that ultrasonic pre-treatment of sludge at 3,000 kJ/L increased the aqueous concentration of estrone in an anaerobic digester. TrOC desorption may increase their bioavailability during sludge stabilisation [121, 148]. Benabdallah El-Hadj et al. [121] found that the ultrasonic pre-treatment of mixed primary and secondary sludge at 11,000 kJ/kg TS increased the naphthalene removal efficiency of a mesophilic digester from 34 to 54% and that of a thermophilic digester from 50 to 65% due to the solubilisation of the compound. However, ultrasonication did not improve the removal of pyrene due to its strong binding to organic fractions of sludge. Chang et al. [148] observed that ultrasonic pre-treatment of phthalate esters decreased the half-lives in aerobic sludge by 33-68%. There is also evidence that ultrasonic treatment can stimulate microbial activity and further enhance phthalate ester degradation. The findings of Chang et al. [148] are supported by those of Pham et al. [145], which reported that ultrasonic pre-treatment of raw sludge increased the di(2-ethylhexyl)phthalate removal efficiency of an aerobic digester from 72 to 89%. This enhancement is possibly owed to the solubilisation of sludge, which caused greater mass and oxygen transfer during aerobic degradation.

4.5 Thermal treatment

Exposure of sludge to heat has been reported to induce degradation and evaporation of TrOCs [30, 146], but thus far thermal treatment has been found to have varying impact on TrOC removal from sludge (Table 2). Mcnamara [149] reported that thermal hydrolysis of raw sludge at 150°C and 5.1 bar for 2 hours deteriorated the biodegradation of nonylphenol ethoxylates in a laboratory-scale mesophilic anaerobic digester, probably due to an increase in volatile fatty acids that inhibited nonylphenol ethoxylate-degrading microorganisms or competed with nonylphenol ethoxylates as substrate [149]. Hamid and Eskicioglu [123] showed that the treatment of dewatered sludge cake in a microwave reactor operating at constant wavelength of 2.45 GHz, 1200 W, and 35 bars and varying temperature (80, 120, and 160°C) decreased the total concentration of 16 hormones by up to 69% due to auto-oxidation and/or denaturation of the compounds under extreme conditions. Moreover, microwave pre-treatment of sludge at 80, 120 or 160°C increased the hormone removal of an aerobic digester by 42, 52, and 78%, respectively. Carballa et al. [122] found that thermal pre-treatment of mixed sludge by autoclaving at 130°C for 1 hour had no impact on the removal of various pharmaceuticals, musks, and hormones, but a clear reason was not provided.

4.6 Bioaugmentation

Bioaugmentation is a treatment procedure that involves the addition of exogenous microorganisms to enhance the biodegradation of contaminants. So far, only a few studies have investigated TrOC removal from sludge by bioaugmentation with different organisms such as bacteria, yeast, and fungi (Table 3). Larsen et al. [151] augmented digested sludge with *Proteiniphilum acetatigenes*, a bacteria that degrades polycyclic aromatic hydrocarbons in synthetic media under anaerobic methanogenic conditions, and found improvement in the removal of low and high molecular weight polycyclic aromatic hydrocarbons. Boon et al. [152] inoculated the bacteria *Comamonas testosteroni* to activated sludge and observed a 50% removal of 3-chloroaniline from the aqueous phase. Hesham et al. [153] observed that the augmentation of a mixture of five strains of yeast (*Pichia anomala*, *Sporidiobolus salmonicolor*, *Pichia guilliermondii*, *Rhodotorula dairenensis*, and a *Candida maltosa*-like strain) to an aerated bioreactor increased the removal of chrysene and benzo(a)pyrene from zero to 90.7% and 80.7%,

respectively. An enrichment of the yeast strains in activated sludge was observed, as well as an abundance of catechol 2,3-dioxygenase that is responsible for benzene ring cleavage.

[Table 3]

White-rot fungi (WRF) are well-known for their ability to co-metabolically degrade a wide range of TrOCs from wastewater and soils through enzymatic action [158]. Mixed cultures of bacteria and WRF have been found to remove TrOCs from wastewater via biodegradation and biosorption [158, 159]. There is also evidence that WRF can eliminate TrOCs from biosolids. The research group of Rodríguez-Rodríguez found that the augmentation of *Trametes versicolor* to sterilised dewatered sludge caused 40% to complete removal of a wide spectrum of TrOCs and significant reduction in sludge toxicity [10, 154-157]. However, treatment of non-sterilised sludge resulted in less efficient TrOC removal (e.g. fewer TrOCs underwent biodegradation) and decline of fungal activity after 21 days [155]. In this context, it is interesting to note the population of the exogenous organism tends to eventually decline due to microbial competition, and therefore a continuous re-inoculation is necessary to maintain appreciable TrOC treatment efficiency. Larsen et al. [151] observed that the re-inoculation of *P. acetatigenes* to digested sludge every two days enabled the reduction of both low and high molecular weight polycyclic aromatic hydrocarbons, whereas single inoculation of the bacteria during start-up only led to the removal of low molecular weight polycyclic aromatic hydrocarbons. Rodríguez-Rodríguez et al. [157] reported that the re-inoculation of *T. versicolor* to dewatered sludge in the middle of 42 days of treatment caused 80-86% removal of TrOCs, whereas only 22-69% removal can be achieved without the re-inoculation step. On the other hand, Hesham et al. [153] was able to maintain stable TrOC removal from an aerated bioreactor co-habited by activated sludge and yeast for 56 days, with yeast being the dominant species in the system.

4.7 Future research priorities in TrOC removal from biosolids

The use of advanced oxidation processes has high potential to eliminate TrOCs from biosolids. Among the advanced oxidation processes discussed, ozonation and ultrasonication appear to demonstrate the greatest potential. Literature suggests that ozonation at 0.1 g O₃/g TS or more could result to more than 60% removal of TrOCs [139-141], and has the potential to provide an

additional 30-60% removal of TrOCs in the sludge treatment line if used as pre-treatment for anaerobic digestion [110]. Ultrasonication can increase the bioavailability of TrOCs by liberating them from sludge flocs [50, 145]. Thus far, ultrasonication has been demonstrated to provide an additional 13% removal of di(2-ethylhexyl)phthalate in anaerobic digestion [115]. Therefore, future research could focus on optimising treatment conditions (e.g. ozonation time and ultrasonic frequency) for TrOC removal and determining by-product formation. Notably, advanced oxidation processes generally achieve high treatment efficiency but have high maintenance cost and energy consumption, and their practical implementation will depend on the cost-effectiveness of the formats introduced to the market. Bioaugmentation using exogenous organisms, being a biological process, is potentially more environmentally friendly and cost effective than advanced oxidation processes [10]. Among the organisms that have been studied (e.g. bacteria, yeasts, and fungi), WRF emerges as a promising option because it removes a wide range of TrOCs that bacteria are typically unable to degrade [157, 160]. Indeed small-scale studies demonstrate that WRF can significantly remove TrOCs from digested or dewatered sludge [10, 56, 154, 155, 157]. However, a major limitation impeding its application is that WRF enzymatic activity is prone to disruption due to bacterial contamination [157]. Future research should focus in using WRF as pre-treatment to sludge stabilisation and implementing WRF treatment of biosolids in pilot-scale.

5. Concluding remarks

Implementing significant changes to conventional wastewater treatment to minimise the occurrence of TrOCs in sludge is impractical. In particular, it is difficult to pinpoint specific conditions that will mitigate the TrOC accumulation in sludge due to the wide range of TrOC characteristics. However, literature generally shows that aerobic condition results to higher TrOC biodegradation compared to either anoxic or anaerobic conditions, and anoxic condition may promote the sorption of TrOC on sludge. A combination of different redox conditions and careful control of DO levels has potential to facilitate the TrOC sorption-biodegradation process. Operation at SRT of more than 10 days could facilitate the biodegradation of hydrophobic and persistent TrOCs. The impact of the use of adsorbents on TrOC accumulation in sludge should be examined in more detail, as it may have ramifications on the treatability of TrOCs during sludge stabilisation.

Sludge thickening and dewatering by physical methods (e.g. centrifugation) do not affect the sorption of TrOCs in sludge. However, the introduction of air or heat during these steps could facilitate the removal of TrOCs from sludge via biodegradation, thermal degradation, volatilisation, or evaporation. Significant biodegradation of sorbed and dissolved TrOCs occur during sludge stabilisation by aerobic digestion and composting. Anaerobic digestion can also remove TrOCs, but has poor removal of metabolites that may increase the toxicity and estrogenicity of biosolids irrespective of operation conditions (e.g. temperature and SRT). To further improve TrOC removal, pre- or post-treatment of sludge by advanced oxidation or bioaugmentation of sludge using exogenous organisms could be considered. These technologies increase the removal of TrOCs from biosolids by increasing the bioavailability of the compounds and/or converting the compounds into inert or more biodegradable products.

6. References

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Figure 1 Schematic diagram depicting the key operation conditions impacting the accumulation of TrOCs on activated sludge

Figure 2 TrOC removal by anaerobic digestion superimposed with log D at pH 7. Error bars represent variation in removal efficiencies reported by different independent studies (n = number of samples): 17 α -ethinylestradiol (3), bisoprolol (1), bisphenol A (2), carbamazepine (4), clofibric acid (1), diazepam (2), diclofenac (4), estriol (4), estrone (4), galaxolide (2), ibuprofen (2), iopromide (2), ketoprofen (3), naproxen (3), roxithromycin (2), sulfamethoxazole (2), triclocarban (2), triclosan (4). Data source: [8, 47, 51, 98, 106, 109, 113-119]

Figure 3 TrOC removal by mesophilic and thermophilic anaerobic digestion. Error bars represent variation in removal efficiencies reported by different independent studies ((n, m) = number of samples in m mesophilic and, n thermophilic condition, respectively): 17 β -estradiol (4, 2), estriol (4, 2), estrone (4, 2), ibuprofen (2, 2), naproxen (3, 2), nonylphenol (3, 3), nonylphenol monoethoxylate (3, 3). Data source: [8, 47, 51, 98, 116, 119]

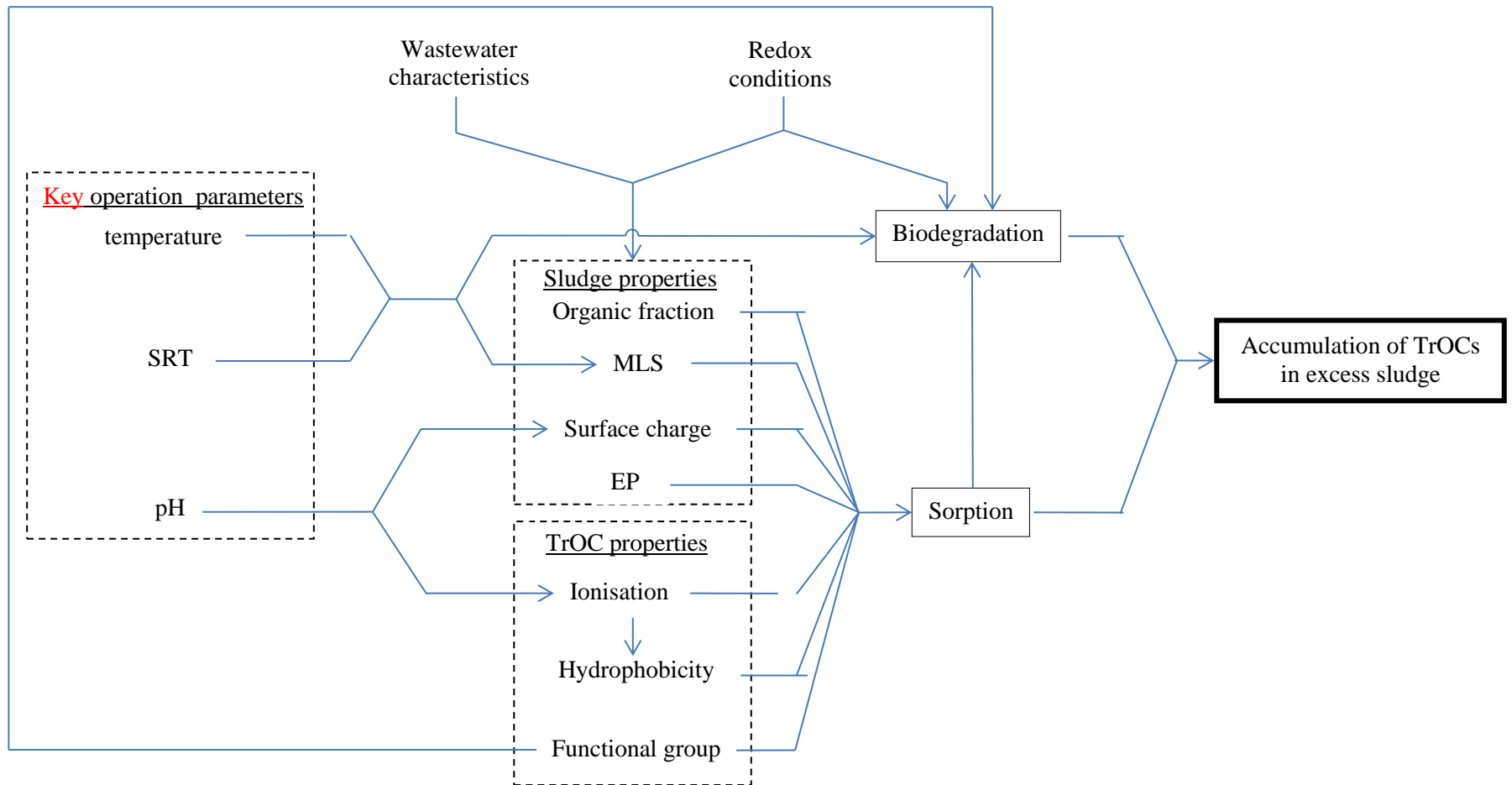


Figure 1 Schematic diagram depicting the key operation conditions impacting the accumulation of TrOCs on activated sludge

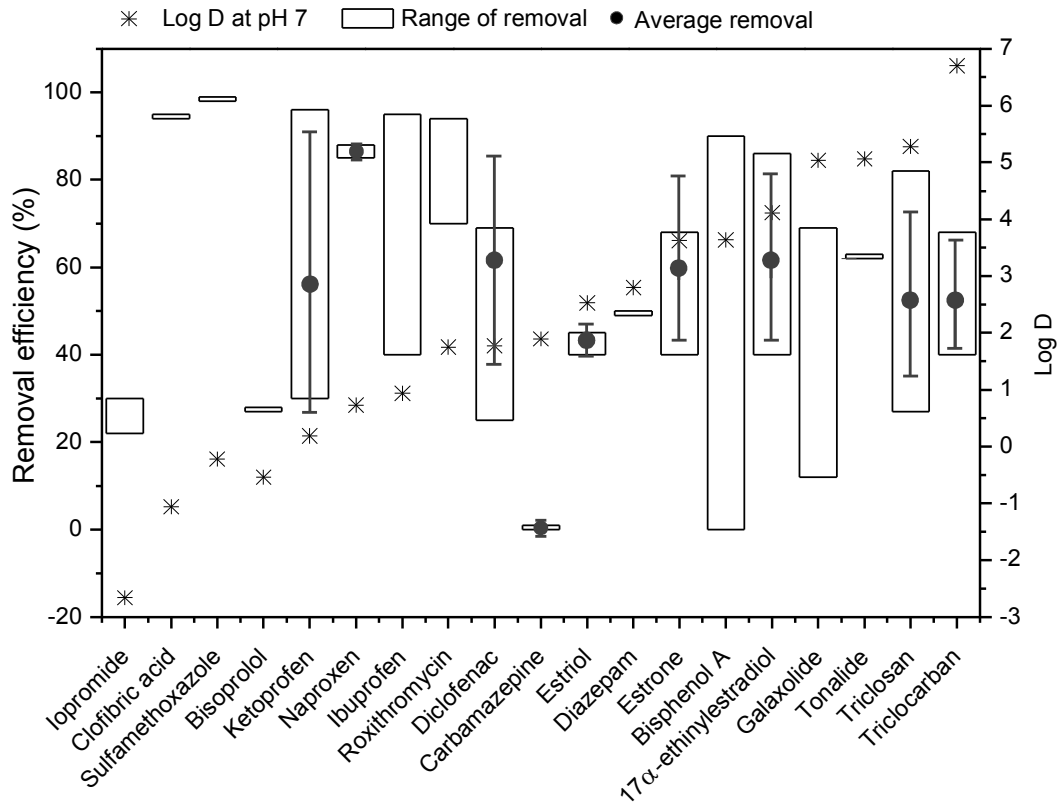


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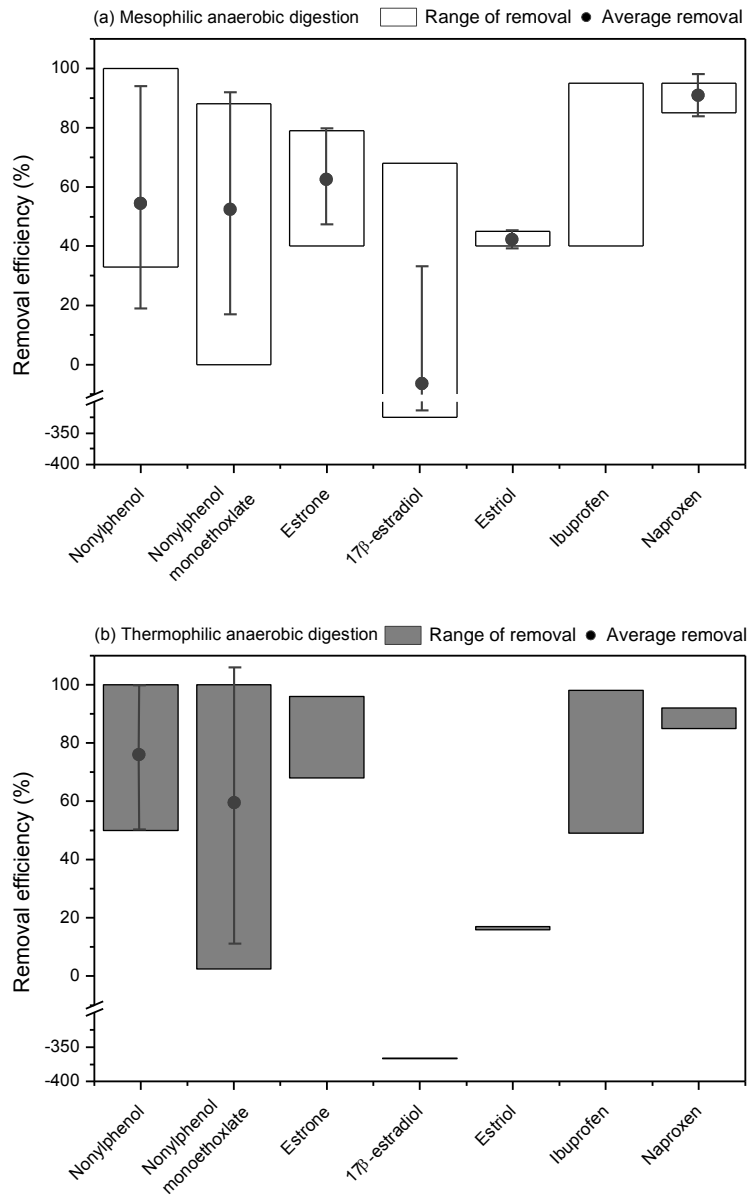


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Table 1 TrOC removal efficiency at different composting conditions.

TrOC	Removal efficiency (%)	Composting material	Temperature (°C)	Time (days)	Reference
Pharmaceuticals	80–98 (ciprofloxacin, norfloxacin, and ofloxacin)	2:3 v/v anaerobically digested sludge and tree bark 4:3 v/v anaerobically digested sludge and peat	Not specified	30, 180, and 360	[40]
	46–95 (sulfadimethoxine and sulfamethoxazole)				
	26–48 (fluoxetine, paroxetine, sertraline, and citalopram)	10:1:0.2 v/v/v sewage sludge, spruce bark and coarse garden waste, and mature sludge compost	10–55	21	[127]
	Negligible to 83% (various pharmaceuticals)	Anaerobically digested sludge only	Not specified	Not specified	[128]
Hormones	Negligible (various hormones)	Anaerobically digested sludge only	Not specified	Not specified	[128]
Polycyclic aromatic hydrocarbons	83–88	Anaerobically digested sludge with and without 20–30% fly ash or 30% saw dust	21–27	353	[129]
Nonylphenol	88	10:1 w/w Anaerobically digested sludge and dry wheat	10–55	143	[68]
	50–80	43:57, 65:35, and 84:16 v/v anaerobically digested sludge and wood shavings	24, 45, and 65		[130]
	75–95	1:1:1 v/v/v sewage sludge, straw, and garden park waste	35–55	34	[131]
	60	2:1 w/w raw sludge and secondary sludge with 10% sheep manure	25–60	30	[132]

Linear alkylbenzene sulphonates	77-91	2:1 w/w raw sludge and secondary sludge with 10% sheep manure	25-60	30	[132]
	62-99	Batch cultures inoculated with sludge composted at 1:1 w/w sewage sludge and sawdust/straw mixture	40-45	40	[133]
Di(2-ethylhexyl)phthalate	60-97	2:1 w/w raw sludge and secondary sludge with 10% sheep manure	25-60	30	[132]
	60	10:1 w/w anaerobically digested sludge and dry wheat	10-55	143	[68]
	34-58	2:2 v/v raw or anaerobically digested sludge with chipped bark and peat	Not specified	85	[134]
Polychlorinated biphenyls	11	10:1 w/w anaerobically digested sludge and dry wheat	10-55	143	[68]
	55	Not specified	Not specified	21 (fresh) and 720 (mature)	[69]
Polychlorinated dibenzodioxins	Negligible	Not specified	Not specified	21 (fresh) and 720 (mature)	[69]

Table 2 TrOC removal efficiency of advanced oxidation treatment of sludge.

Treatment	Treatment configuration	Treatment conditions	TrOC/s	Effect on TrOC removal	Reference
Ozonation	Pre-treatment to anaerobic digester	Ozone dosage = 0.1 g O ₃ /g/total solids (TS)	Polycyclic aromatic hydrocarbons	Pre-ozonation increased the TrOC removal by anaerobic digestion from about 25 to 50%	[139]
	Sludge treatment	Ozone dosage=0.021-0.081 g O ₃ /g TS	Polycyclic aromatic hydrocarbons	Resulted to 18-60% polycyclic hydrocarbon removal from sludge	[140]
	Sludge treatment	Ozone dosage = 0.1 g O ₃ /g/TS	Estrone, estradiol, estriol, 17 α -ethinylestradiol, bisphenol A, and nonylphenol	a) Significantly enhanced the desorption and removal of estrone, estriol, and 17 α -ethinylestradiol b) Less impact on bisphenol A and nonylphenol removal due their high sorption on sludge	[141]
	Pre-treatment to anaerobic digester	Ozone dosage=0.02 g O ₃ /g TS	Various pharmaceuticals and hormones	a) Only carbamazepine was amenable to ozonation b) The removal of other pharmaceuticals and	[8]

				hormones in anaerobic digestion were not affected by ozonation	
	Sludge treatment	4.9 mol/L H ₂ O ₂ and 0.1 mol/L Fe ²⁺	Polycyclic aromatic hydrocarbons	Resulted to 38-67% removal from sludge	[142]
Fenton treatment	Sludge treatment	3% by volume H ₂ O ₂ and 11% by weight Fe ²⁺ adjusted to pH 2 or 4	Polycyclic aromatic hydrocarbons	Decreasing pH from 4 to 2 increased polycyclic aromatic hydrocarbon removal from sludge from 20 to 30%	[143]
	Sludge treatment	15.62 mmol g ⁻¹ H ₂ O ₂ , 0.167 Fe ²⁺ -to- H ₂ O ₂ molar ratio, adjusted to pH 3	Various hormones	Resulted to 70- 98% removal of various hormones	[144]
	Pre-treatment to aerobic digestion	0.01 mL H ₂ O ₂ /g SS and 150 [H ₂ O ₂] ₀ /[Fe ²⁺] ₀ at 36 °C	Di(2-ethylhexyl)phthalate	Increased di(2-ethylhexyl)phthalate removal of aerobic digestion from 72 to 85%	[145]
	UV oxidation	Sludge treated under three 24-W UV lamps (λ=254 nm) at 36 °C	Polycyclic aromatic hydrocarbons	Resulted to 15% polycyclic aromatic hydrocarbon removal	[146]
UV/TiO ₂ oxidation	Sludge with 0.5 and 20% by weight TiO ₂ (Degussa P25) treated under three 24-W UV lamps (λ=254 nm) at 36 °C	Polycyclic aromatic hydrocarbons	Resulted to 21-63% polycyclic aromatic hydrocarbon removal	[146]	
UV/H ₂ O ₂ oxidation	Sludge treated under UV (λ=253.7 nm) at the rate of 0.069 mW/cm ² and 0.5 mol/L H ₂ O ₂	Estrone, estradiol, estriol, 17α-ethinylestradiol, and bisphenol A	Resulted to 67-97% removal of bisphenol A and various hormones	[9]	

	Sludge treatment	UV treatment ($\lambda=254$ nm) at the rate of 3.0 mW/cm ² and 0.5 mol/L H ₂ O ₂	Carbamazepine	Increased batch carbamazepine removal by 45%	[147]
Ultrasonication	Pre-treatment to anaerobic digestion	Ultrasonication at 11,000 kJ/kg TS	Napthalene	Increased naphthalene removal of anaerobic digestion from 34-50 to 54-65%	[121]
	Pre-treatment to anaerobic digestion	Ultrasonication at 3,000 kJ/L	Estrone	Increased the aqueous concentration of estrone in the anaerobic digester	[50]
	Pre-treatment to a batch aerobic reactor	Ultrasonication at 20 kHz and 0.1-0.2 W/ml for 10-40 min	Phthalate esters	Decreased half-lives of phthalate esters by 33-68% in aerobic treatment	[148]
	Pre-treatment to aerobic digestion	Ultrasonication at 20 kHz and 0.75 W/cm ³ for 60 min	Di(2-ethylhexyl)phthalate	Increased di(2-ethylhexyl)phthalate removal of aerobic digestion from 72 to 89%	[145]
	Pre-treatment to anaerobic digestion	Autoclaving at 130°C for 1 hour	Various pharmaceuticals, musks, and hormones	No effect on TrOC removal of anaerobic digestion	[122]
Thermal treatment	Pre-treatment to anaerobic digestion	Thermal hydrolysis at 150°C and 5.1 bar for 2 hours	Nonylphenol	No effect on TrOC removal of anaerobic digestion	[149]
	Pre-treatment to anaerobic digestion	Microwave treatment at 2.45 GHz, 1200 W, and 35 bars at 80, 120, or 160°C	Various hormones	Decreased hormones in the effluent of anaerobic digester by 42-78%	[123]

Table 3 Sludge treatment by bioaugmentation with different microorganisms

Organism	TrOC	Result	Reference
<i>Proteiniphilum acetatigenes</i> (bacteria)	Polycyclic aromatic hydrocarbons	Improved the removal of low and high molecular weight polycyclic aromatic hydrocarbons	[151]
<i>Comamonas testosterone</i> (bacteria)	3-chloroaniline	Increased the removal of 3-chloroaniline from zero to 15%	[152]
<i>Pichia anomala</i> , <i>Sporidiobolus salmonicolor</i> , <i>Pichia guilliermondii</i> , <i>Rhodotorula dairenensis</i> , and a <i>Candida maltosa</i> -like strain (yeasts)	chrysene and benzo(a)pyrene	Improved removals of chrysene and benzo(a)pyrene from negligible to 81 and 91%, respectively	[153]
<i>Trametes versicolor</i> (fungi)	Various pharmaceuticals and polycyclic aromatic hydrocarbons	a) Resulted to 40-100% and 3-100% removal of various pharmaceuticals and polycyclic aromatic hydrocarbons, respectively, from sterilised sludge b) Decreased sludge toxicity (compared to sterilised sludge)	[10]
	Sulfamethazine	Resulted to the complete removal of sulfamethazine from sterilised sludge	[154]
	Various pharmaceuticals	a) Resulted to 60-100% removal of various pharmaceuticals from non-sterilised sludge b) Loss of <i>T. versicolor</i> activity after 21 days of treatment	[155]
	3-(4'-methylbenzylidene) camphor and benzophenone-3	Resulted to 87-100% removal of 3-(4'-methylbenzylidene), camphor, benzophenone-3, and their metabolites from sterilised sludge	[156]
	Various pharmaceuticals, brominated flame retardants, and UV filters	Re-inoculation of <i>T. versicolor</i> at the 22 nd day of treatment caused > 80% of the trace organic compounds from non-sterilised sludge	[157]

