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Chapter 1

Treatment of Organic Recalcitrant Contaminants in Wastewater

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Abstract

Research has shown that a myriad of contaminants enter the environment through industrial and domestic sources on a daily basis. The biodegradable compounds often get degraded or mineralized by various physical, chemical or biological processes, whereas the recalcitrant organic contaminants either are transformed or get dispersed and persist in the receiving environments, and to an extent much greater than was earlier estimated. Many chemical compounds that were not previously included as pollutants can now be detected at much higher concentrations globally. The effect of most of these emerging contaminants on human and environment health is still unknown. Therefore, there is an urgent need to study the fate of these persistent compounds so as to better understand and manage their ecological and health effects.

Keywords: Wastewater, organic contaminants, recalcitrant, biodegradation, sorption

1. Introduction

Water adversely affected in quality by anthropogenic activities is, typically called wastewater. Wastewater is generally collected and treated by various processes at centralized facilities, referred to as wastewater treatment plants (WWTPs). There can be several sources contributing towards wastewater generation, including domestic, industrial and agricultural. As there are various sources of wastewater generation, so are the compounds present in them. Wastewater, thus, is a cocktail of chemicals—the class, structure, biodegradability, toxicity and human and environmental impact of most of which are still unknown.
Some of the wastewater contaminants, including aromatics, pharmaceuticals, pesticides, chlorinated congeners and plasticizers, pose deleterious effects on human and environmental health, even at trace levels [1]. Some of their harmful effects include impairment and/or abnormality in physiological processes, including reproductive impairment, increased risk of cancer in aquatic and terrestrial species, development of antibiotic-resistant bacterial strains and increase in effluent toxicity post-treatment plausibly owing to the synergistic or antagonistic toxic effects of such recalcitrant chemical mixtures. Still unknown are the environmental effects of many emerging contaminants.

While most of the easily degradable wastewater contaminants are removed by conventional treatment methods, compounds that remain even in the treated effluent are recalcitrant and hence persist in the receiving environments, causing environmental and health problems. Low concentrations of such recalcitrants in large volumes of wastewater make their efficient treatment and removal very difficult by the conventional treatment processes including activated carbon, chemical precipitation, ionic exchange resins and membrane filtration [2]. Such processes have other disadvantages such as high plant operation and maintenance cost, accumulation and disposal issues of concentrated sludge, use of excessive chemicals, low sensitivity towards target compounds and accumulation of concentrated sludge and their disposal problems [3]. Removal of some of the organic recalcitrants is not effected even by the traditional biological processes, including activated sludge and trickling filters, employing microorganisms as these biorecalcitrants may result in death of the microbial population, thus reducing the efficiency of or halting the treatment process. Advanced treatment methods such as a pre-separation step or post-treatment of recalcitrants using potent and specialized microbial strains need to be employed for the efficient removal of such persistent organic pollutants from effluent [2].

Hence, there is a need for better understanding of the occurrence, behaviour and fate of organic contaminants during sewage treatment processes. The present paper reviews literature about the fate of some of the recalcitrant organic contaminants during the various treatment processes.

2. Status of wastewater generation

Better management of wastewater at regional and global level requires up-to-date information on the status of sewage generation and treatment. Globally, a complete sewage generation and treatment data are available for only 55 countries, 37% of it being recent (2008–2012) [4]. There is a generation of about 15,644 millions litre per day (MLD) of sewage from 35 metropolitan cities in India, out of which only 8040 MLD (51.4%) is the existing treatment capacity. While 3800 MLD is the municipal sewage generation in the national capital region of Delhi, the city has a treatment capacity of only about 2300 MLD. Rest 31% sewage is discharged into the environment untreated [5].
3. Wastewater treatment processes

Various processes are employed for the removal of wastewater contaminants depending on their type and level in the influent. Municipal wastewater is mostly treated in sewage treatment plants (STPs) which use various treatment processes including physical, chemical and biological. Wastewater treatment and discharge are done according to regional and national regulations and standards. Wastewater treatment is done with the purpose of producing a pollutant- and toxicity-free effluent which can safely be discharged into the environment [6]. Three main stages are involved in wastewater treatment, viz., primary or physic-chemical, secondary or biological and tertiary or advanced treatment.

a. Primary treatment involves physical separation of heavy solid particles gravimetrically and oil and other lighter floating materials mechanically in settling basins called primary-settling tanks or primary clarifiers. The remaining liquid wastewater is pumped to the next treatment tank for secondary treatment.

b. Secondary treatment involves the removal of dissolved and suspended biological component by means of an indigenous microbial population, which is removed prior to release of the treated water into the environment or tertiary treatment stage. It is carried out in secondary treatment chambers such as aeration tanks or bioreactors. In the presence of sufficient oxygen supplied through aeration pumps, the indigenous microflora degrades the soluble organic fractions while segregating the less soluble components into flocs. Secondary treatment may include either fixed-film or attached growth systems such as trickling filters, rotating biological contactors and bio-towers, where the sewage passes over the surface of attached biomass, or suspended-growth systems including activated-sludge process, where sewage is mixed with microbial biomass. While the latter type of secondary treatment system has a lower space requirement for wastewater treatment, requires less space for treatment, the fixed-film systems are better able to acclimatize to sudden microbial changes and have a higher removal rate of organic matter and suspended solids [7–9].

c. Tertiary treatment includes any advanced wastewater treatment methods beyond the primary and secondary treatment, before discharge of wastewater in the receiving environment.

The most important aerobic treatment system is the activated-sludge process, based on the maintenance and recirculation of a complex biomass composed by micro-organisms able to absorb and adsorb the organic matter carried in the wastewater. Other biological treatment processes such as expanded granular sludge bed (EGBS) reactor and upflow anaerobic sludge blanket (UASB) are also employed for wastewater treatment. Synthetic membranes and micro-filtration are now commonly being used as tertiary treatment technologies.
4. Fate of organic recalcitrant contaminants in wastewater treatment

4.1. Pathways of contaminant removal

There has been a radical increase in the occurrence and concentration of organic contaminants in wastewater and sludge as a result of an increase in the demand and industrial production of synthetic organic chemicals. Point discharge sources including discharges from industrial users or manufacturers and diffuse discharge sources such as commercial and domestic premises or run-off after aerial deposition are some of the major contributors to the loading of organic contaminant in sewage. The following are some of the pathways (Figure 1) through which organic contaminants may be transformed or degraded during sewage treatment:

- Air stripping
- Biodegradation
- Chemical degradation
- Sorption
- Volatilization

![Figure 1. Some of the pathways involved in transformation of organic contaminant in wastewater treatment.](image-url)
While some compounds may get completely degraded or mineralized in the process of treatment, some others are partially degraded and form breakdown products and a few other recalcitrant compounds may remain unaffected and persist in the effluent even after treatment. The occurrence of these synthetic organic contaminants in wastewater may be either in solution or sorbed onto solids. The hydrophobic or lipophilic nature of many organic contaminants result into their getting adsorbed on solid particles during wastewater treatment, eventually resulting in their accumulation in the sludge solids, sometimes at concentrations much higher than in the untreated wastewater [10, 11].

Structural composition of the organic residues may also provide information about their biodegradation pathways. For instance, biodegradation of unbranched and long-chained hydrocarbons is easier as compared to the short-chained or highly branched molecules. Biodegradation of unsaturated aliphatic compounds is generally more favoured than their saturated analogues. Molecules having highly polar groups and linkages tend to react by nucleophilic displacement (such as hydrolysis) [12]. Petrasek et al. [13] reported the association of recalcitrant and toxic chloro-organic pentachlorophenol (PCP) with the sludge solids, and considerable degradation of phenolic compounds having polar groups.

4.2. Processes involved in contaminant removal

Several researches have been made to study the removal efficiency of various contaminants by different wastewater treatment processes. Partitioning of hydrophobic contaminants of influent onto settled primary sludge solids may take place during the primary sedimentation process in the primary clarifiers. Bulk organic components of wastewater such as cellulose, proteins and carbohydrates get biodegraded during the secondary treatment involving aerobic processes such as trickling filters, activated-sludge process, oxidation ponds or anaerobic processes resulting in sludge digestion. Transformation or loss of some of the synthetic recalcitrant organic contaminants may also take place during the secondary treatment processes. Polysaccharides, proteins and fats occur in two phases during the anaerobic digestion process. First phase (acid phase) involves hydrolysis of polysaccharides to form mono- and disaccharides, of proteins to form amino acids, and of fats resulting in the formation of long-chain fatty acids, and volatile acids such as formic, acetic and butyric acid. Second phase (methanogenic phase) results in the reduction of the volatile acids to methane and carbon dioxide [12, 14]. In one study involving a generalized model for the presentation of fate of organic compounds in an activated-sludge process, it was demonstrated that the phase distribution of xenobiotic chemicals depended quantitatively upon their physico-chemical properties and the operating conditions of wastewater treatment. The study also showed the removal of hydrophobic chemicals of wastewater, mostly by the process of sorption onto sludge particles followed by their transfer to the sludge-processing units. Meanwhile, advective transport into the final effluent and biodegradation was shown to be the common mechanism for the removal of hydrophilic compounds of wastewater. The model also predicted an increase in the effluent concentration of complex organics such as substituted phthalates, high molecular weight (HMW) polycyclic aromatic hydrocarbons (PAHs) and
dioxins with increasing solids retention time (SRT) during the operation of wastewater treatment plant [15].

4.3. Common classes of contaminants found in wastewaters

Although wastewaters contain a multitude of contaminants, yet they can be broadly grouped under different classes on the basis of their chemical structure. A total of 129 specific pollutants including heavy metals and specific organic chemicals have been defined by the US Clean Water Act as “Priority Pollutants”. Municipal Environmental Research Laboratory (MERL), US EPA, conducted a comprehensive research programmes on the occurrence and fate of priority pollutants present in wastewater and sludge. The study assessed the fate and behaviour of 22 harmful organics including phenols, pesticides, poly aromatic hydrocarbons and phthalates in the conventional water treatment systems and demonstrated up to 95–98% removal of organic compounds from the liquid phase. Many such organic compounds were found to have been partitioned onto the solid phases of primary and return activated sludges. Similar results were reported in other studies as well [16, 17]. In one study, the highest degree of enrichment of PAHs was observed in the primary sludge and phthalates such as bis-(ethylhexyl) and di-n-octyl phthalate were found to be among the most recalcitrant compounds present in wastewaters [13]. Wild and Jones [18] reported the occurrence of volatile chemicals, such as benzene, in sewage sludge, possibly as a result of their sorption over organic substances present in the sludge. Based on the reported literature, the following description discusses the fate of some common classes of organic compounds occurring in wastewaters (Figure 2).

![Contaminant classes](Image)

**Figure 2.** Classes of organic contaminants commonly found in wastewater.
4.3.1. Phthalic acid esters

Phthalates have a high environmental significance owing to their high production volumes as well as their eco-toxicological effects especially on aquatic fauna including molluscs, crustaceans and amphibians. They have been reported to cause biological effects even at very low levels of exposure, varying in the range of ng L\(^{-1}\) to μg L\(^{-1}\) [19, 20]. Microbial degradation of phthalates under aerobic and anaerobic conditions has been previously reported [21]. The difference in the biodegradability of various phthalates could possibly be due to the steric effect of their side ester chains that hinders the binding of hydrolytic enzymes to the phthalates thus inhibiting their hydrolysis [22]. In a previous study on the occurrence of phthalates in raw and treated wastewater of WWTPs, it was found that most of the studied phthalates were present in post-treated water samples, bis(2-ethylbenzyl) phthalate (DEHP) being the most abundant. Also, biotransformation and adsorption onto sludge solids (that directly depend on the molecular weight and lipophilic nature of the compound) were shown to be the possible pathways of phthalate removal from liquid phase during wastewater treatment [23]. Roslev et al. [24] studied the degradation of four different phthalic acid esters in an activated-sludge process, and showed an almost 96% association of DEHP (showing the least biodegradation among the four phthalates) with the wastewater suspended solids. The study also revealed a 7–9% recovery of the influent phthalate esters in the effluent. Also, aerobic and anoxic-denitrifying conditions were found to be less favourable for biodegradation of phthalate esters as compared to the alternating aerobic-anoxic conditions.

4.3.2. Polycyclic aromatic hydrocarbons

PAHs are among the most mutagenic, carcinogenic and toxic class of organic contaminants some of which have also been included in the US-EPA and EU list of priority pollutants [25]. The presence of PAHs in the environment is commonly attributed to various anthropogenic activities such as petroleum refining, power and heat generation from coal production, and chemical manufacturing [26]. A study on the fate of PAHs and other volatile organic compounds (VOCs) during wastewater treatment by the conventional activated-sludge process (CASP) and the membrane bioreactors (MBRs) concluded that aromatic VOCs were removed mainly by volatilization and with comparable removal efficiencies for both treatment processes, that is, CASP and MBRs. On the other hand, removal efficiency for PAHs was found to be enhanced in case of MBRs [27]. In another study conducted by Zhang et al. [28], the occurrence, behaviour and fate of 18 PAHs in a coking wastewater treatment plant was investigated and it was found that mostly high molecular weight PAHs were present in the raw coking wastewater, while 3–6 ring PAHs were the predominant PAHs detected in the effluent. There was detection of PAHs such as pyrene, phenanthrene and fluoranthene in the gas samples and pyrene, fluoranthen, chrysene and benzo[k]fluoranthen in sludge. While there was almost 97% removal for all the PAHs during treatment, the percent removal of PAHs from the liquid phase varied in a range of 47–92% in the biological stage. It was also observed that low molecular weight (LMW) PAHs were mostly removed in the aerobic tanks and following the mechanism of transformation, whereas their HMW counterparts were mainly removed in anaerobic tank. While transformation was observed to be the most common
mechanism of removal of LMW PAHs from wastewaters, adsorption onto sludge solids was mainly responsible for the removal of HMW PAHs from the liquid phase.

4.3.3. Chlorinated congeners

Chlorinated congeners including polychlorinated biphenyls and polychlorinated pesticides are very toxic to human and environment health and are mostly added into the environment by industrial and domestic sources. Their presence has commonly been reported in wastewater, surface water bodies as well as in sediments. Biologically mediated reductive dehalogenation process is one of the common pathways of degradation of these chlorinated contaminants during wastewater treatment. The less investigated reductive dechlorination process has also been identified as one of the possible pathways for the transformation of specific contaminants during anaerobic digestion of sludge. Previous studies have reported the formation of intermediates such as 1, 2, 4-trichlorobenzene and pentachlorobenzene, 1, 2, 4, 5-tetrachlorobenzene and final products such as dichlorobenzene isomers and 1, 3, 5-trichlorobenzene during the reductive dechlorination of hexachlorobenzene. The formation of 2, 4-dichlorophenol and 4-chlorophenol as intermediates and phenol as the end product during reductive dechlorination of 2, 4-dichlorophenoxy acetate has similarly been reported [29].

While some of the chlorinated congeners such as polychlorinated biphenyls, have been known for long [30], some others have recently been documented as toxic contaminants including pharmaceuticals such as diclofenac and pesticides 4-hydroxychlorothalonil and clomazone [31, 32]. The detection of such chlorinated contaminants, some of which are also endocrine-disrupting and toxic to biota, in effluent and receiving water bodies is a matter of concern [33]. The concentrations of chlorinated congeners in effluent have been reported to be much lower than in the influent, indicating their efficient removal by various physical, chemical or biological processes operational during the treatment of wastewater [34]. Nevertheless, there have been reports indicating the presence of chlorinated contaminants such as triclosan and triclocarban in effluent of STPs, and eventually in the downstream water bodies and sediments [35, 36], thus pointing towards a need for upgradation of treatment mechanisms for their efficient removal. In a study conducted on the efficiency of aerobic and anaerobic processes in organic contaminant removal during treatment processes, it was concluded that a sequential system using a combination of both oxidative and reductive processes was probably the most efficient for the removal of recalcitrant organics. Highly chlorinated and volatile organohalogen compounds were found to degrade appreciably only under anaerobic conditions, while being resistant to oxidative degradation under aerobic conditions [37].

4.3.4. Pharmaceutical compounds

Pharmaceutical compounds are another class of emerging contaminants that have gained growing concerns in the past two decades mostly because of their less known health and environmental effects and ever-increasing usage and unchecked release into the environment. Metabolic excretion post consumption and improper disposal techniques are the main sources of these compounds in the environment. In a study conducted to investigate the presence of some common pharmaceutical compounds and fluoroquinolones (one of the “priority
pollutants” having potential hazardous effects on the aquatic life) in two wastewater treatment plants in Spain, frequent detection of pharmaceuticals such as analgesics, anti-inflammatory and lipid regulators in effluent and incomplete elimination of most of the fluoroquinolones posttreatment was observed. The results also demonstrated higher efficiency of membrane bioreactor technique in removing pharmaceutical compounds as compared to the activated-sludge process [38]. Similar findings have been reported by other workers as well [39, 40].

4.3.5. Personal care products

There has been a recent concern over the toxic and ecological impact of personal care products (PCPs). Although there have been several reports on the assessment of concentrations of these chemicals in the environment [41–43], less work has been done to know their fate in the environment. In one assessment of the efficiency of various treatment processes for the removal of pharmaceuticals and personal care products, it was concluded that membrane bioreactor and activated-sludge process with nitrogen treatment were the most efficient processes for the treatment of such compounds [44].

5. Conclusion

Wastewater treatment facilities such as wastewater treatment plants, or domestic septic systems, which have been operating on the conventional technologies, are often inefficient in treating such a cocktail of compounds ranging from simple to complex and recalcitrant organic compounds. Thus, these centralized facilities, discharging treated effluent, which may still be contaminated with household chemicals, pharmaceuticals and biogenic hormones, into the environment end up being a source of pollutants for the receiving water bodies. Also, the sewage sludge generated at the STPs, often having a high accumulation of recalcitrant and hydrophobic contaminants, acts as a sink of such contaminants in the treatment facilities but a major source of organic recalcitrants when directly used as manure.

Such unchecked disposal and use of sewage and sludge into the environment or their direct application for domestic or agriculture purposes could lead to exposure of toxic contaminants to biological systems, possibly resulting in adverse metabolic responses. Advanced treatment technologies such as membrane bioreactors and sequential system using a combination of both oxidative and reductive processes were found to be more effective in the removal of various organic recalcitrant compounds. Therefore, implementation of such treatment technologies and addition of tertiary treatment techniques to the conventional methods, for the removal of such persistent contaminants, have become quintessential.

Thus, the occurrence of persistence organic contaminants in the effluent and sludge posttreatment and ambiguity about their fate pose a serious environmental challenge. Therefore, much research is still needed to identify the source, behaviour and sink as well as their ecological and health effects.
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