Phenols, flame retardants and phthalates in water and wastewater – a global problem

Olushola Sunday Ayanda, Godwin Oladele Olutona, Emmanuel G. Olumayede, Cecilia O. Akintayo and Bhekumusa J. Ximba

ABSTRACT

Organic pollutants in water and wastewater have been causing serious environmental problems. The arbitrary discharge of wastewater by industries, and handling, use, and disposal constitute a means by which phenols, flame retardants (FRs), phthalates (PAEs) and other toxic organic pollutants enter the ecosystem. Moreover, these organic pollutants are not completely removed during treatment processes and might be degraded into highly toxic derivatives, which has led to their occurrence in the environment. Phenols, FRs and PAEs are thus highly toxic, carcinogenic and mutagenic, and are capable of disrupting the endocrine system. Therefore, investigation to understand the sources, pathways, behavior, toxicity and exposure to phenols, FRs and PAEs in the environment is necessary. Formation of different by-products makes it difficult to compare the efficacy of the treatment processes, most especially when other organic matters are present. Hence, high levels of phenols, FRs and PAEs removal could be attained with in-line combined treatment processes.

Key words | flame retardants, organic pollutants, phenols, phthalates, wastewater

INTRODUCTION

Wastewater and water contamination results from industrial activities, rainwater runoff and domestic activities (Ayanda & Akinsoji 2012). Industrial processes involve the production and release of huge quantities of organic pollutants in one form or other into the aquatic and terrestrial environment. Industrial practices produce wastewater that usually contains high concentrations of both the inorganic and organic pollutants such as heavy metals, persistent organic pollutants (POPs), recalcitrant organic contaminants, endocrine disrupting chemicals (EDCs); chemicals that mimic or block the activity of natural hormones in humans and aquatic wildlife, thus disrupting their reproductive systems (Joseph et al. 2011), carboxylic acids, phenols, carbonyls, amines, hydrogen sulphide and other harmful gases, which does not conform to environmental standards and hence requires treatment prior to discharge into the environment. Wastewater generated from coal coking, coal gas purification and byproduct recovery processes of coking contains complex inorganic and organic pollutants which are refractory, toxic, mutagenic and carcinogenic (Zhang et al. 2010). Domestic wastewater contains organic matters and nutrients, and may also contain phthalates (PAEs) (Huang et al. 2010b). Benner et al. (2013) provided a summary of the reported occurrence of micropollutants detected in raw water as well as in treated water. These organic pollutants are not completely removed during water and wastewater treatment processes or might be degraded into other byproducts that are sometimes more toxic than the parent compounds; this has led to their occurrence in the environment after discharge from treatment plants. The increasing use of phenols, flame retardants (FRs) and PAEs worldwide has also raised environmental and health concerns due to their ability to disrupt the endocrine system. Therefore, the total removal of organic pollutants from wastewater is required before discharging the treated wastewater to the environment, while drinking water should be well treated before consumption. This paper will give an overview of recent studies on phenols, FRs and PAEs in water and wastewater.

Phenols

Phenol was discovered in 1834 by Friedlieb Ferdinand Runge, who extracted it (in impure form) from coal tar. Runge called phenol ‘Karbolsäure’ (coal-oil-acid, carbolic...
Coal tar remained the primary source until the development of the petrochemical industry. In 1836, Auguste Laurent coined the name ‘phène’ for benzene; this is the root of the word ‘phenol’ and ‘phenyl’. In 1843, French chemist Charles Gerhardt coined the name ‘phénol’ (Thompson & Welsh 1989). In 1841, the French chemist Auguste Laurent obtained phenol in pure form (Swarts et al. 1998). Phenols or hydroxybenzene, and also referred to as phenolics, are a class of aromatic organic compounds consisting of one or more OH groups bonded directly to an aromatic hydrocarbon. Phenol is a colorless, crystalline substance of characteristic odor, soluble in water and organic solvents (Michałowicz & Duda 2007). Phenols are important raw materials and additives for laboratory, industrial, engineering, wood and plastics processes. Phenols of anthropogenic origin exist in the environment due to the activity of chemicals, petrol, tinctorial or pharmaceutical industries (Michałowicz & Duda 2007). The occurrence of phenols in the environment could further be attributed to the production and use of pesticides, particularly phenoxy herbicides such as 2,4-dichlorophenoxyacetic acid (Rozanski 1998) or 4-chloro-2-methylphenoxyacetic acid and also phenolic biocides such as pentachlorophenol (PCP) (Laine & Jørgensen 1996), disoneb or diaryl-ether pesticides (Schmidt 1998). Phenols and p-cresol could originate naturally through the degradation of humic substances, tannins and lignins or synthesis of chlorinated phenols by fungi and plants (Swarts et al. 1998). Phenols can be obtained in a reaction between chlorobenzene and sodium hydroxide, toluene oxidation and synthesis from benzene and propylene (Michałowicz & Duda 2007). Global industrial usage of phenols includes production of alkylphenols, cresols, xylens, phenolic resins, aniline and other organic compounds (Bobranski 1973), oil, coal processing and metallurgical processes (Bruce et al. 1987), and production of pesticides, explosives, dyes and textiles (Budavari 2001). Phenols are readily absorbed following inhalation, ingestion and skin contact, and are widely distributed in the body (Barlow & Johnson 2007). Certain phenols are endocrine disruptors, carcinogenic and mutagenic. The structures of 11 phenols considered priority pollutants by the United States Environmental Protection Agency (USEPA) are shown in Figure 1. Others include bisphenol A (BPA), 4-chlorophenol, nonylphenol (NP), 4-octylphenol (OP) and 4-nitrophenol.

![Figure 1](https://iwaponline.com/wst/article-pdf/74/5/1025/459101/wst074051025.pdf)

*Figure 1* | Structures of 11 phenolic compounds considered priority pollutants by USEPA (Santana et al. 2009).
BPA

BPA is an EDC of xenobiotic origin that has been widely used for the production of polycarbonate (PC) and epoxy resins used as coatings in food containers (Staples et al. 1998; Mahata et al. 2006) and beverage cans. Brominated bisphenols, like tetrachlorobisphenol, in considerable concentrations are present in ashes produced during aluminum processing (Stachei et al. 2005). Consequently, there is great concern regarding the harmful effect that results from BPA leaching into foods and beverages from packaging or storage containers (Cooper et al. 2011). For instance, a high concentration of BPA and F (2.0–35.5 mg/kg) found in honey was attributed to its packaging with rubber products and plastic stretch film materials (Brede et al. 2003). High concentrations of BPA were also found in fluids that were in contact with PC bottles intended for infants. Moreover, patients on kidney dialysis may receive elevated exposures to BPA as a result of the use of PC components in the equipment (Ritu et al. 1999). BPA is also used in powder paints, as additives in thermal paper, in dental fillings, as an inert ingredient in pesticides, as FRs, as rubber and plastic stretch materials (Brede et al. 2003). BPA enters the environment through leaching from final products and during manufacturing processes, and the release of BPA into streams and rivers occurs mainly via discharges of sewage treatment plants (Rodríguez-Mozaz et al. 2005). BPA is also present in the atmosphere through respiration by living organisms and the release of BPA into the environment through treated wastewater effluents. BPA is also found in the food chain, where it can be transferred from food to organisms (Rodriguez-Mozaz et al. 2005). BPA is a ubiquitous compound that exhibits the potential to contribute to global endocrine disruption.

NP, OP and 4-chlorophenol

NP and OP are emerging EDCs; they are the precursors in the production of non-ionic surfactants used in detergents emulsifiers, wetting agents, dispersants or solubilizers (Selvaraj et al. 2014). The degradation of alkylphenol polyethoxylates in the environment results in NP and OP; these two are therefore more toxic than alkylphenol polyethoxylates (Selvaraj et al. 2014). NP is used as precursors in the manufacture of antioxidant and lubricating oil additives and it is the major degraded metabolite of nonylphenol ethoxylates (Lee et al. 2015). The structure of NP is similar to estradiol (E2); hence, it is also able to imitate E2 by competing for the binding site of the estrogen receptor (Lee & Lee 1996; Lee et al. 2013). NP and OP can enter the environment via treated wastewater effluents and direct discharge from pesticide applications, while human exposure to NP and OP can occur via drinking water and food consumptions (Chen et al. 2013). 4-Chlorophenol is generated as a by-product in plastic, paper making, insecticidal and petrochemical industries. It is carcinogenic and mutagenic to aquatic life and mammals, including human beings.

Toxicity of phenol

Phenol and its vapors are corrosive to the eyes, the skin, and the respiratory tract. Its corrosive effect on skin and mucous membranes is due to a protein-degenerating effect (Michałowicz & Duda 2007). Repeated or prolonged skin contact with phenol may cause dermatitis, or even second- and third-degree burns. Inhalation of phenol vapor may cause lung edema. The substance may cause harmful effects on the central nervous system and heart, resulting in dysrhythmia, seizures, and coma. The kidneys may be affected as well. Long-term or repeated exposure of the substance may have harmful effects on the liver and kidneys. There is no evidence that phenol causes cancer in humans. Besides its hydrophobic effects, another mechanism for the toxicity of phenol may be the formation of phenoxyl radicals (IARC 1999).

Since phenol is absorbed through the skin relatively quickly, systemic poisoning can occur in addition to the local caustic burns. Resorptive poisoning by a large quantity of phenol can occur even with only a small area of skin, rapidly leading to paralysis of the central nervous system and a severe drop in body temperature. The LD₅₀ for oral toxicity is 500–500 mg/kg for dogs, rabbits, or mice; the minimum lethal human dose was cited as 140 mg/kg.

Toxic influence of organic compounds such as phenols depends on several factors. The ability of phenol to penetrate organisms depends on diffusion of the compounds across a cell membrane. Hydrophobicity is a factor that strongly affects diffusion – the higher the hydrophobicity the more effective penetration of a cell’s membrane by phenol – and thus enhances the toxicity of xenobiotics. The pKₐ (acid dissociation constant) is a strong parameter in the toxic effects of phenol. The increase of hydrophobicity and the value of log P (partition coefficient), and the decrease of pKₐ value
result in more effective membrane penetration by xenobiotics and thus enhance their toxicity (Moridani et al. 2004). Moreover, another factor that determines toxicity of phenol is the reactivity of the compound with a cell’s biomolecules, which is related to easiness of donation of free electrons by phenols from oxidized substrate.

### PAEs

PAEs or phthalate esters are esters of phthalic acid. PAEs are hazardous pollutants due to their mutagenicity and carcinogenicity and have been classified as EDCs. Higher molecular weight PAEs are mainly used as additives and plasticizers (Barreca et al. 2014) to soften PVC, rubber, cellulose and styrene products while the lower molecular weight PAEs are used as components of industrial solvents, adhesives, wax, ink, pharmaceutical products, insecticide materials, and cosmetics (Koniecki et al. 2011). PAE esters are poorly water-soluble but are readily sequestered or absorbed by organic residues and solid surfaces in environmental water systems. Moreover, PAE esters are colorless liquids, have low volatility, and are poorly soluble in water but soluble in organic solvents and oils (Autian 1973). The general chemical structure of PAEs is presented in Figure 2.

PAEs are physically bound to the matrices and may be leached into the environment; they are universally found in environmental matrices (Orecchio et al. 2014). Since one of the starting materials for the manufacture of PAE esters is phthalic anhydride, it is important to recognize the toxic nature of the agent. Phthalic anhydride is a solid crystalline and is slightly soluble in water (Autian 1973). It has been reported that PAEs may be involved in reprotoxicity, carcinogenesis, cardiotoxicity, hepatotoxicity and nephrotoxicity and may influence immune and allergic responses in animals (Gimeno et al. 2014).

### PBDEs

PBDEs are organobromine compounds that are used as FRs and have been used in building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, textiles and other materials. The chemical structure of PBDEs is presented in Figure 3. PBDEs are lipophilic, toxic, resistant to chemical and biological metabolism, bioaccumulative and persist in the environment.

PBDEs have been detected in water, soil, air, sediments, marine organisms, birds that feed on fish, human blood, adipose tissue and breast milk (Vrkoslavova et al. 2010; Jiang et al. 2013). Human exposure to PBDEs can be through ingestion of food with high content of fat, inhalation of PBDEs in the gas phase or dust particles, and direct dermal exposure to FR products. Mueller et al. (2006), Huang et al. (2005), Vrkoslavova et al. (2010) suggested that the absorption, accumulation and translocation of PBDEs by plants and their transfer to the food chain could represent a possible risk for human exposure. Several PBDE congeners have been associated with endocrine disruption, reproductive and developmental toxicity, reduced human fertility, neurotoxicity and potential carcinogens (Quinete et al. 2011; Zhang et al. 2014). Hydroxylated PBDEs and their metabolites have been shown to bind to the thyroid receptor and interfere with thyroxin transport in blood. The production of pentaBDEs and octaBDEs was stopped around 2004; the production of decaBDE still continues. The tetraBDE, pentaBDE, hexaBDE and...
heptaBDE congeners have also been listed as POPs in the Stockholm Convention on Persistent Organic Pollutants in 2009 (Cai et al. 2012; Moon et al. 2012).

Organophosphorus FRs

Tris(1,3-dichloro-2-propyl)phosphate (TDCPP), triphenyl phosphate and tris(2-chloro-isopropyl) phosphate are common examples of organophosphorus FRs that have been increasingly used as a result of the ban on common PBDEs. Organophosphorus FRs accounted for 14% of the global production volume of FRs, compared to 21% for BFRs in 2004 (Brandsma et al. 2015). They have been known to be persistent, carcinogenic, mutagenic, neurotoxic, or reproductive toxicants and skin irritants.

Chlorinated FRs in wastewater.

Chlorinated phosphate esters belong to the group of organophosphorus compounds, which had a market share of 58,000 metric tons in the United States in 2001 with a worldwide consumption of 186,000 tons (ERFA 2006). Commonly used aliphatic chlorinated trisphosphates are tris(2-chloroethyl)-phosphate (TCEP), tris(1-chloro-2-propyl)phosphate (TCPB), and TDCPP. The occurrence of TCPB in raw sewage has been reported to show great day-to-day variation, with lower concentrations during weekends (Meyer & Bester 2004). Several studies showed that chlorinated alkyl-phosphates were poorly eliminated during wastewater treatment and tend to pass through the biological processes unaffected (Meyer & Bester 2004). The TCEP, TCPB and TDCPP chlorinated FRs exhibit modest hydrophobicity with log Kow (octanol–water partition coefficient) below 2 and are expected to remain in the water phase (Drewes et al. 2012). Due to the fact that the mode of the discharge pattern of FRs to wastewater is site specific, concentrations of chlorinated alkyl-phosphates reported to occur in secondary treated wastewater effluents vary significantly.

SOURCES, DETECTION AND QUANTIFICATION OF PHENOLS, FRS AND PAES

All PAEs found in environmental matrices can be attributed to human activities. They are released from painted surfaces, a long time after the paint has been applied, and, because of improper disposal of waste, they are usually found in air, water, soils, and sediments (Li et al. 2006). PAEs can also gas out in the atmosphere or enter directly into human body fluids through medical products (Zia et al. 2013). The arbitrary discharge of wastewater from chemical, dyeing, mining and pharmaceutical industries would cause a serious environmental problem, due to the presence of complicated and considerable amounts of inorganic and organic pollutants. Zero release in wastewater discharge is not regularly practiced by most industries due to technical and economic limitations. These incompletely treated industrial effluents contain trace amounts of organic and inorganic pollutants that are discharged into nearest water bodies. Other sources of pollution by PBDEs, FRs, PAEs, etc. are the treatment plants, through the discharge of wastewater effluents and sludge, and contamination also results from manufacture, handling, use, and disposal of these chemicals. The presence of EDCs in seawater could be attributed to the transport of contaminated wastewater effluent by rivers into oceans and seas (Joseph et al. 2011). The government policies on environmental management have therefore mandated all industries to properly manage their waste. These policies include the treatment of wastewater generated by these industries before it comes in contact with natural water streams.

Many analytical methodologies have been applied for the detection and quantitation of organic pollutants in water and wastewater; the majority of these methods involve an extraction procedure followed by instrumental analysis. The type of extraction, volume of water used, and type of analytical equipment used depend on the compounds to be analyzed and the source of the water (Snyder et al. 2005). Analytical techniques commonly used in the determination of phenols are ultraviolet (UV) detection, high-performance liquid chromatography (HPLC) and capillary electrophoresis in combination with UV, electrochemical detection or mass spectrometry (MS) detection (Lewis 1993). Liquid chromatography of phenols is generally carried out with the addition of acids or buffers to the mobile phase. Their function is to suppress the ionization of both the analytes and the residual silanols of the stationary phase base material, which otherwise would either decrease retention on the analytical column or lead to interactions of the analytes and the stationary phase, resulting in lower separation efficiencies (Swarts et al. 1998).

Xie et al. (2012) reported the use of a UV–visible (UV-vis) Unico spectrophotometer (model UV-2102PCS) for the determination of phenol at a wavelength of 270 nm, p-chlorophenol at 280 nm, and BPA at 276 nm wavelengths, while Yüksel et al. (2013) determined the concentration of BPA in water samples by the use of UV-vis (Shimadzu UV-1800 model) at a wavelength of 276 nm. The concentrations of BPA were quantified by Joseph et al. (2011) with the use of HPLC. Detection was carried out using a fluorescence detector at an excitation wavelength of 280 nm. The concentration of 2-chlorophenol was measured by Hu et al. (2014)
using HPLC with an eclipse XDB-C18 column. An ATVP HPLC with a C18 column was used by Nawawi & Nawi (2014) for the detection of phenol; the UV detector was set at 220 nm with 60:40 methanol: water mixture as the mobile phase. The determination of PAEs (butylbenzylphthalate and di-(2-ethylhexyl)phthalate) in water samples by polystyrene solid-phase extraction and quantification by gradient elution reversed-phase liquid chromatography (LC) with UV detection at 280 nm was reported by Jara et al. (2000). Qiu et al. (2011) identified the intermediates and products formed during the degradation of BPA by LC/MS and LC/MS/MS. Lee et al. (2013) also measured the concentrations of NP and BPA by the use of LC-ESI-MS/MS (ESI: electrospray ionization) while Choi et al. (2012) evaluated the level of BPA in ultrapure water by the use of an offline solid-phase extraction coupled with LC/MS. Choi et al. (2012) mentioned that the evaluation was conducted without chemical derivatization. The authors used an Agilent 1200 series LC equipped with an Agilent C18 column, a UV detector and an API 2000 mass spectrometer (electrospray ionization). The mass spectrometer was operated at the anionic mode in the m/z range 50–500 for LC/MS and 50–500 for LC/MS/MS. The concentration of phenol during electrochemical degradation was monitored by HPLC (HPLC 2200-2, Ful) at a wavelength of 254 nm, using an Ultimate TMAQ-C18 (4.6 mm × 100 mm, 5 μm) column (Wang et al. 2013). The methanol and deionized water at a ratio of 50:50 was used as the mobile phase at a flow rate of 1 mL/min.

The intermediates formed during Fe₂O₃/TiO₂ photocatalytic degradation of 4-chlorophenol were analyzed by gas chromatography–mass spectrometry (GC-MS) (PerkinElmer Clarus 500) using helium as the carrier gas (Palanisamy et al. 2013). The analysis of PBDEs by GC-MS in electron capture negative ionization mode and operated in selected ion monitoring mode has been reported by Quinete et al. (2011). The determination was conducted after saponification of fat present in the biological tissues, extraction into organic solvent and clean-up. Santhi et al. (2012) assessed the level of BPA in surface water used as potable water, drinking water and human plasma in the Langat River basin, Malaysia, by the use of GC-MS. The BPA was derivatized with 20 μL of N,O-bis(trimethylsilyl)trifluoroacetamide + 1% trimethylchlorosilane at 75 °C for 40 min, dried under nitrogen and reconstituted with 100 μL dichloromethane:ethyl acetate, prior to analysis. Selvaraj et al. (2014) determined the concentration of BPA, NP and OP in river water from India by the use of GC-MS; N-methyl-N-(trimethylsilyl)trifluoroacetamide was used as the derivatizing reagent. The determination of dimethyl, diethyl, diallyl, dibutyl and diisooctyl PAE esters in water samples using polyaniline-based solid-phase microextraction coupled with GC with flame ionization detection was developed by Li et al. (2006). Cao (2008) determined PAEs in bottled water by headspace solid-phase microextraction and GC-MS. Cai et al. (2012) utilized gas chromatography-ion trap-mass spectrometry for the determination of PBDEs and decabromodiphenylethane (a replacement for decaBDEs in the 1990s). Keresztes et al. (2013) determined PAEs in polyethylene terephthalate bottled water by GC-MS, and Orecchio et al. (2014) and Barreca et al. (2014) evaluated the PAEs content of mural paintings by GC-MS. The use of GC-MS for the analysis of phenols, PAEs, etc. in coal gasification wastewater before and after treatment with an anoxic moving bed biofilm reactor–biological aerated filter system was reported by Zhuang et al. (2014).

**REMOVAL OF PHENOLS, FRs AND PAES FROM WATER AND WASTEWATER**

Phenols, FRs and PAEs treatment techniques frequently reported include adsorption, chlorination, ultrafiltration (UF), reverse osmosis (RO), microbial and advanced oxidation processes (AOPs).

Adsorption is a very promising method for removing many micropollutants from water and wastewater systems. Xie et al. (2012) examined the adsorption capability and mechanism of hexadecytrimethylammonium-modified zeolite (synthesized from coal fly ash) for the removal of ionizable phenolic compounds (phenol, p-chlorophenol and BPA). Qureshi et al. (2012) and Qureshi et al. (2013) utilized ionic liquid modified resin (XAD-4) and pine nutshell carbon, respectively, for the removal of PAEs from aqueous system. The adsorption of BPA from seawater and brackish water by single walled carbon nanotubes was investigated by Joseph et al. (2011) while Zhang et al. (2010) investigated the adsorption of organic pollutants from coking wastewater by activated coke. The sorption of phenol and 4-nitrophenol onto composite geomaterials based on montmorillonite, activated carbon and cement was investigated by Houari et al. (2014), while the removal of dibutyl PAE from aqueous solution by adsorption using vanillin-modified chitosan beads was reported by Li et al. (2014).

Bourgin et al. (2013) investigated the chlorination of BPA and reported that chlorination is effective at removing BPA in drinking water within 10 min; however, several chlorination byproducts of BPA were revealed. Bourgin et al. (2013) affirmed therefore that the generated compounds
have significantly lower estrogenic activity after 120 min of chlorination. Chen et al. (2013) reported that chlorination is effective in the degradation of NP in raw water while conventional coagulation and rapid filtration processes were less effective in the reduction of phenolic compounds in water.

UF is a membrane water treatment technique in which pressure or concentration gradients leads to a separation of contaminants and water through a semipermeable membrane. Low-pressure hollow-fiber UF has gained increasing importance in water treatment technology, as a pretreatment for RO systems in the preparation of drinking or process waters (Zupančič et al. 2014). In UF, large molecular weight polymers, e.g. poly(vinyl alcohol), sulfonated poly (vinyl alcohol), poly(ammonium acrylate), poly(acrylic acid) and polyethylenimine, are linked with heavy metal ions to form macromolecular complexes. These metal complexes are therefore retained and concentrated by the UF membranes (Emnigrou et al. 2014), such that no metal ions or polymer passes through the membrane during the filtration. Mierzwia et al. (2008) investigated the direct treatment of drinking water by spiral-wound UF membranes and stated that their results provide substantial evidence of the technical feasibility of spiral-wound UF membranes for direct drinking water treatment. UF has been reported to be effective in the separation of dispersed or dissolved materials 2 to 200 nm (>1 nm) in size (Kawada et al. 2014) and the removal of turbidity, microorganism, a variety of water-borne viruses, and a certain amount of the dissolved organic matter (Song et al. 2014). However, fouling is a major problem in the UF process. Pretreatment before UF, especially by coagulation, is therefore an effective way to control membrane fouling and improve water quality (Yu et al. 2014). The application of amphiphilic polymer nano-particle-enhanced UF process for the removal of phenol, 4-nitrophenol, etc. was reported by Noh et al. (2008). The combination of UF and activated carbon adsorption has been reported to be effective in the removal of toxic organic pollutants (Mozia & Tomaszewska 2004; Ivancev-Tumbas et al. 2008).

RO is presently the most commonly used method of converting naturally available non-potable water (Srivathsan et al. 2014) and is now the leading desalination process used worldwide (Mezher et al. 2011). RO can separate particles or molecules of dimensions higher than 0.1 nm (Qi et al. 2011) and it has replaced some of the thermal desalination technologies such as the multi-effect distillation, multi-stage flash distillation and vapor compression distillation due to its lower cost-intensiveness, higher quality of purified water, reduced plant size and simpler water treatment processes (Bae et al. 2014). Nonetheless, RO, despite having numerous advantages over contemporary techniques, faces a major challenge of membrane fouling. Membrane fouling lead to increase in operation and maintenance costs due to the need for applying higher pressures as well as frequent membrane cleaning and replacement (Xu et al. 2013; Matin et al. 2014), and membrane surface modification (via surface coating and grafting (Cheng et al. 2015)) is therefore required to control and/or prevent fouling. Although, municipal wastewater effluent treated by RO produces highly purified water that can be used for landscape irrigation, industrial process water, and aquifer recharge, the RO method also produces a concentrated form of the wastewater effluent, which may contain high concentrations of contaminants such as trace organic pollutants, biological oxygen demand, chemical oxygen demand and pathogens that are not fully removed by the preceding biological treatment process (Hurwitz et al. 2014). The removal of BPA from model solutions by selected nanofiltration and RO membranes was studied by Yüksel et al. (2013); they reported that the polyamide-based membranes exhibited much better performance than cellulose acetate membrane for BPA removal.

Yeast wastewater treatment processes have attracted a great deal of attention worldwide. They have been applied for the treatment of acidic, high-carbohydrate, oil-rich, high-salinity, and ammonia- or sulfate-ridden high-organic-strength industrial wastewater. A yeast-based process has been used for the biodegradation of phenols present in industrial wastewater (Yang & Zheng 2014). Cryptococcus terricola (Bergauer et al. 2005) is one of the yeasts reported in literature for the degradation of phenols and chlorophenols. Loffredo et al. (2012) reported the use of ligninolytic fungi (Trametes versicolor, Stereum hirsutum and Pleurotus ostreatus) for the removal of BPA. Phanerochaete chrysosporium has been reported to have strong ability to degrade phenol and chlorophenols (Lu et al. 2009).

The AOPs which oxidize complex organic pollutants into simpler end products or degrade them to CO2 and H2O (Shannon et al. 2008) may be classified as photochemical or non-photochemical processes. Non-photochemical processes are ozonation in basic media (O3/HO−), O3/H2O2, O3/ultrasound, H2O2/ultrasound process, Fenton (Fe3+/H2O2) processes etc., while photochemical processes are O2/UV, H2O2/UV, O3/H2O2/UV, photo-Fenton (Fe2+/H2O2/UV) processes etc. The Fenton oxidation process has been successfully applied for the treatment of highly polluted industrial wastewaters (Munoz et al. 2014).
degradation of BPA by the use of zero-valent iron/polygors-kite composite materials via AOPs was reported by Xi et al. (2014). It has been noted that the photochemical degradation (pyrolysis) of PBDEs might convert PBDEs to highly toxic byproducts, such as polybrominated dibenzo-furans and polybrominated dibenzodioxins (Jiang et al. 2013).

An advanced O3 membrane reactor that uses membranes for O3 distribution, reaction contact and selective water separation has been used for the treatment of PAEs in water (Ho et al. 2012), while the sorption onto a cyclodextrin-based material as well as in combination with advanced oxidation using a UV-O3 process as pretreatment was applied for the removal of chlorophenols and alkylphenols from industrial effluents by Charles et al. (2014). They reported that high levels of pollutant removal were attained with the combined use of oxidation and sorption when compared with single treatment process. The application of O3 for the removal of BPA from water and wastewater was reviewed by Umar et al. (2013). Umar et al. (2013) opined that the degradation of BPA by O3 leads to the formation of different by-products which makes it difficult to compare the efficacy of the treatment processes reported in literature and that the situation is complicated when other organic matter are present. The use of Fe3O4 magnetic nanoparticles for the catalytic oxidation of phenolic compounds from aqueous solution was investigated by Zhang et al. (2009); they reported that the nanoparticles have good stability and reusability, and could be separated from solution by an external magnetic field. The preparation of nitrogen-doped K2Nb4O11 for the photocatalytic degradation of BPA by P2O5 and PCP was reported by Qiu et al. (2011) while the application of mesoporous mixed Fe2O3/TiO2 photocatalyst for the degradation of 4-chlorophenol has been reported by Palanisamy et al. (2013). Anchieta et al. (2014) investigated the photodegradation of phenol molecules by the use of synthesized ternary zinc spinel oxides (Zn2SnO4, ZnAl2O4 and ZnFe2O4); they reported that Zn2SnO4 oxide was the only ternary zinc spinel oxide that showed activity in the degradation of phenol molecules under solar irradiation, reaching removal of 100% at 240 min of reaction. However, ZnFe2O4 also presented activity for the degradation of phenol under artificial UV–light (Valenzuela et al. 2002). The use of silver-based oxides for photocatalytic applications has also received much attention (Kato et al. 2002; Konta et al. 2003; Tang et al. 2003). Hu et al. (2014) reported the photocatalytic activity of Cu2O-Ag/AgBr/Al2O3 for the degradation of 2-chlorophenol under visible light irradiation.

The photoelectrochemical treatment of organic pollutants from wastewater has been reported (Shaw et al. 1996; Zanoni et al. 2004; Catano et al. 2006). Xue et al. (2011) investigated the electrochemical oxidation of BPA on Ti/SnO2-Sb2O5/PbO2 electrode, and their results showed that BPA could be oxidized directly on the surface of the electrode at a pH of 4. Wang et al. (2013) studied the electrocatalytic degradation of phenols by TiO2 nanotubes-based Sb-doped SnO2 anode. The combination of photochemical (UV) and electrochemical processes for the enhancement of the degradation of dissolved organics in RO concentrate produced from municipal wastewater was reported by Hurwitz et al. (2014). Hurwitz et al. (2014) thus reported that the treatment of municipal wastewater RO concentrate by UV and electrochemical process alone resulted in 25% and 35% removal of dissolved organics after 5 h, respectively; however, the photo-assisted electrochemical treatment degraded more than 80% of dissolved organics after the same treatment time.

Westerhoff et al. (2005) reported the fate of chlorinated FRs during a drinking water treatment process. Drewes et al. (2012) in their studies of the occurrence of chlorinated FRs in wastewater-impacted stream and ground water under the impact of surface water reported that no removal of TCEP was observed during coagulation or softening; less than 10% removal of TCEP was observed during chlorination and ozonation of water samples, while activated carbon adsorption represented the most efficient process with removal exceeding 90% after addition of 20 mg/L powdered activated carbon and contact time of 4 h.

Electrical discharge methods of degradation include the pulsed corona discharge, barrier discharge, DC discharge and gliding arc discharge. The energy supplied into the discharge is used preferentially to create free electrons, which are used to produce ionization and excitation of the gas mixture components. Therefore, the generated gas phase radicals which are consumed in chemical reactions promote the desired conversion of pollutants (Cormier et al. 2008). A corona system is a process by which a current, perhaps sustained, develops between two high potential electrodes in a neutral fluid (Samanta et al. 2006). The gliding arc discharge has a dual character of thermal and non-thermal plasma, and can involve relatively high electric powers compared with the corona discharge (Zhang et al. 2009). It is a simple way to generate non-thermal plasma. The dielectric barrier discharge (DBD), also known as silent discharge or atmospheric pressure glow discharge, is a typical non-equilibrium high pressure gas discharge. The history, discharge physics, and industrial applications of DBD were detailed by Kogelschatz (2003). For a 2D simulation of micro-discharge (DBD) development reported by Kogelschatz (2003), a rotational symmetry was assumed and two
equation sets were used to describe the evolution of a microdischarge. The continuity equations for the charged species $n_i$ (electrons, positive and negative ions) with source and sink terms $S_i$ (describing ionization and attachment) were presented as follows:

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (\mu n_i D_i \nabla n_i) = S_i$$  (1)

$v = \mu E$ is the drift velocity, defined as mobility $\mu$ times electric field strength $E$, $D_i$ is the diffusion coefficient. $E$ is also defined as the gradient of the potential $\phi$, $E = -\nabla \phi$. It is related to the charge density $\rho$ by the Poisson equation:

$$\nabla^2 \phi = \frac{\rho}{\varepsilon}$$  (2)

where $\varepsilon$ is permittivity.

Kogelschatz (2003) stated that the equations are to be solved simultaneously in the discharge gap and inside the dielectric with appropriate boundary conditions at the interface.

Cormier et al. (2008) described the plasma of a stationary arc reactor (used for the conversion of methane) by the energy equation in which transport properties are polynomial fitted as a function of plasma temperature (Equation (3)). Furthermore, the kinetics was described by Equation (4) in which the rate constant is a function of temperature.

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-\lambda \nabla T + \rho C_p T \mathbf{\hat{u}}_s) = \sigma E^2$$  (3)

$$\nabla (-D \nabla y + y \mathbf{\hat{u}}_s) = k([CH_4]_0 - y)([H_2O]_0 - y)$$  (4)

The energy yield of degradation by an electrical discharge created in a parallel plane coaxial non-thermal plasma-DBD reactor is represented by Equation (5) (Reddy et al. 2013).

$$Y \left( \frac{g}{kWh} \right) = \frac{C(g/L)xV(L)x100}{P(kW)xI(h)}$$  (5)

$C(g/L)$ is the concentration of the pollutant, $V(L)$ is the volume of the solution, $P(kW)$ is the power and $I$ is the time.

According to Stryczewska et al. (1998), the arc discharge dynamic theory was worked out by Mayr and Cassie; likewise, the dynamic behaviour of the arc discharge is described by the voltage – current relationship (Equation (6)).

$$u_{arc} = f(i_{arc})$$  (6)

And in 1902, the first relation for dynamic voltage-current characteristic of the arc was given by H. Ayrton (Equation (7)); however, the Ayrton relation has been modified taking into account the geometry of the reactor’s electrodes as well as the forced gas flow (Stryczewska et al. 1998).

$$u_{arc}(t) = A + B i_{arc} + \frac{C + D i_{arc}}{i_{arc}}$$  (7)

where $u_{arc}$ is arc voltage; $A$, $B$, $C$ and $D$ are experimentally determined constants; $i_{arc}$ is the arc discharge length and $i_{arc}$ is the instantaneous value of the arc current.

DBD has been found to be effective for the degradation of phenols. The removal of phenol in water by pulsed high voltage discharge was reported by Kunitomo & Sun (2001). The degradation of 2-chlorophenol, 4-chlorophenol and 2,6-dichlorophenol by a plasma reactor based on a coaxial DBD has been reported by Dojcinovic et al. (2008). It was reported that the initial chlorophenols concentration of 20 mg/L diminished by up to 95% after one pass through the reactor. Gliding arc discharge assisted catalytic degradation of BPA in solution with ferrous ions was reported by Abdelmalek et al. (2008). Zhang et al. reported that the degradation rate of 100 mg/L phenol solution reached 98.4% after 15 min treatment with 170 V voltage, 0.5 mA current, and 5 mm dielectric distance. The mechanism of degradation was attributed to oxidation by hydroxyl radicals (Zhang et al. undated). A critical review of the removal of phenolic compounds in water by low-temperature plasma was presented by Zhang et al. (2009). At present, there are very few reported works on the degradation of FRs and PAEs by electrical discharge methods.

CONCLUSION

Phenols, FRs, PAEs, PBDEs, etc. are frequently detected in wastewater discharged from municipal and industrial sources. The molecular structure of PBDEs is similar to polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and furans; hence, the physicochemical properties of these organics are similar, and result in their persistence, widespread distribution, bioaccumulation, toxicity and
long-range transport. There is the need to reduce pollutant release by industrial and domestic activities, and lower the burden on natural water bodies through strict discharge standards and regulations. The stringent regulations will make industries find better treatment and/or reduce the quantity of effluent released. Excellent treatment performance at acceptable costs of the treatment plants should also be encouraged. AOPs such as ozonation, photolysis, catalytic ozonation, electrochemical oxidation and photocatalysis have been effectively used as advanced treatments to remove phenols, FRs, and PAEs in water and wastewater. However, transformation products might be formed that could sometimes be more toxic than the original pollutants. AOPs can also not be used to treat large volume of wastewater. The separation of photocatalyst particles from treated water and the aggregation of the suspended particles are major obstacles in photocatalysis. These problems could be overcome by mobilization of the photocatalyst upon suitable support. For the electric discharge methods, chemical mechanisms in high voltage transient discharges (DBD) and in non-thermal arc discharges (gliding, rotating and stationary discharges) lead to the production of active species needed for the degradation of pollutants. The presence of energetic electrons that excite, dissociate and ionize water molecules to form active species in non-thermal plasma drives degradation and mineralization. Lastly, additional data are needed to understand the relevance of phenols, FRs, PAEs, and other contaminant of emerging concerns in water and wastewater.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

REFERENCES


Bobranski, B. 1975 Organic Chemistry. PWN, Warsaw, Poland.


Catanho, M., Malpass, G. R. P. & Motheo, A. J. 2006
Photoelectrochemical treatment of the dye reactive red 198

Charles, J., Crini, G., Morin-Crini, N., Badot, P. M., Trunfo, G.,
Saney, B., de Carvalho, M., Bradu, C., Avramescu, S.,
Winterton, P., Gavoille, S. & Torri, G. 2014 Advanced
oxidation (UV-ozone) and cyclodextrin sorption: effects of
individual and combined action on the chemical
abatement of organic pollutants in industrial effluents.
Journal of the Taiwan Institute of Chemical Engineers 45,
603–608.

Chiang, P. C. & Wang, G. S. 2015 Occurrence and
treatment efficiency of nonylphenol, octylphenol and
bisphenol-A in drinking water in Taiwan. Science of the Total

M. & Gao, C. 2015 Surface modification of a commercial thin-
film composite polyamide reverse osmosis membrane
through graft polymerization of N-isopropylacrylamide
followed by acrylic acid. Journal of Membrane Science 447,
236–245.

Choi, Y. S., Cho, S., Lee, C., Luu, H. M. D. & Guo, J. 2013
Contamination of ultrapure water with bisphenol A leached

Cooper, J. E., Kendig, E. L. & Belcher, S. M. 2011 Assessment of
bisphenol A released from reusable plastic, aluminium and

Cormier, J. M., Aubry, O. & Khacef, A. 2008 Degradation of
Organic Compounds and Production of Activated Species in
Dielectric Barrier Discharges and Glidarc Reactors. GREMIPolytech’Orleans, Orleans, France.

Dojcinovic, B. P., Manojlovic, D., Roglic, G. M., Obradovic, B. M.,
Belgrade No. 84, 391–395.

Drewes, J. E., Hoppe, C., Bellona, C. L. & Wang, G. 2002 Fate of
Chlorinated Flame Retardants in the Environment and Water
Treatment. Colorado School of Mines, Environmental
Science and Engineering Division, Golden, CO, USA,
pp. 1–11.

Ennigrou, D. J., Ali, M. B. S. & Dhabhi, M. 2014 Copper and zinc
removal from aqueous solutions by polyacrylic acid assisted-
ultrafiltration. Desalination 343, 82–87.

European Flame Retardant Association (ERFA) 2006 Flame

Gimeno, P., Thomas, S., Bouquet, C., Maggio, A. F., Civade, C.,
Brenier, C. & Bonnet, P. A. 2014 Identification and
quantification of 14 phthalates and 5 non-phthalate
plasticizers in PVC medical devices by GC–MS. Journal of

Ho, H. L., Chan, W. K., Blondy, A., Yeung, K. L. & Schrotter, J. C.
2012 Experiment and modeling of advanced ozone
membrane reactor for treatment of organic endocrine

Houari, M., Hamdi, B., Boursa, O., Bollinger, J. C. & Baudu, M.
2014 Static sorption of phenol and 4-nitrophenol onto
composite geomaterials based on montmorillonite, activated
carbon and cement. Chemical Engineering Journal 255,
506–512.

photostability of CuO–Ag–AgBr/Al2O3 for the
degradation of toxic pollutants with visible-light irradiation.
Applied Catalysis B: Environmental 154–155, 44–50.

Behaviour of decabromodiphenyl ether (BDE-209) in the
soil–plant system: uptake, translocation, and metabolism in
plants and dissipation in soil. Environmental Science and
Technology 44, 663–667.

Huang, M. H., Li, Y. M. & Gu, G. W. 2010b Chemical composition of
organic matters in domestic wastewater. Desalination 262
(1–3), 36–42.

Photo-assisted electrochemical treatment of municipal
wastewater reverse osmosis concentrate. Chemical
Engineering Journal 249, 180–188.

IARC 1999 IARC Monographs on the Evaluation of Carcinogenic

Ivancev-Tumbas, I., Hobby, R., Kuchle, B., Panglisch, S. &
Gimbel, R. 2008 p-Nitrophenol removal by combination of
powdered activated carbon adsorption and ultrafiltration–
comparison of different operational modes. Water Research
42 (15), 4117–4124.

Jara, S., Lysebo, C., Greibrokk, T. & Lundanes, E. 2000
Determination of phthalates in water samples using
polystyrene solid-phase extraction and liquid
chromatography quantification. Analytica Chimica Acta 407,
165–171.

Jiang, X., Lai, Y., Wang, W., Jiang, W. & Zhan, J. 2013 Surface-
enhanced Raman spectroscopy detection of polybrominated
diphenylethers using a portable Raman spectrometer.
Talanta 116, 14–17.

Adsorption of bisphenol A and 17α-ethinyl estradiol on single
walled carbon nanotubes from seawater and brackish water.
Desalination 281, 68–74.

Kato, H., Kobayashi, H. & Kudo, A. 2002 Role of Ag+ in the
band structures and photocatalytic properties of AgMO3 (M: Ta
and Nb) with the Perovskite structure. Journal of Physical
Chemistry B 106, 12441–12447.

Kawada, S., Saeki, D. & Matsuuma, H. 2014 Development of
ultrafiltration membrane by stacking of silver nanoparticles
stabilized with oppositely charged polyelectrolytes. Colloids
and Surfaces A: Physicochemical and Engineering Aspects

Keresztes, S., Tatár, E., Czégény, Z., Záray, G. & Mihucz, V. G.
2013 Study on the leaching of phthalates from polyethylene
terephthalate bottles into mineral water. Science of the Total

Kogelschatz, U. 2005 Dielectric-barrier discharges: their history,
discharge physics, and industrial applications. Plasma
Chemistry and Plasma Processing 23 (1), 1–46.

cosmetic and personal care products: concentrations and
Quinet, N., Lavandier, R., Dias, P., Taniguchi, S., Montone, R. & Moreira, I. 2011 Specific profiles of polybrominated diphenylethers (PBDEs) and polychlorinated biphenyls
(PCBs) in fish and tucuxi dolphins from the estuary of Paraíba do Sul River, Southeastern Brazil. Marine Pollution Bulletin 62, 440–446.


Rozanski, I. 1998 The Transformation of Pesticides in Living Organisms and the Environment, Agra-Enviro Lab, Poznan, Poland.


Xi, Y., Sun, Z., Hreid, T., Ayoko, G. A. & Frost, R. L. 2014 Bisphenol A degradation enhanced by air bubbles via advanced oxidation using in situ generated ferrous ions from...


First received 2 March 2016; accepted in revised form 8 June 2016. Available online 23 June 2016.