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The interaction mechanisms of co-occurrenced engineered nanoparticles and polybrominated diphenyl ethers in environmental waters: A critical review

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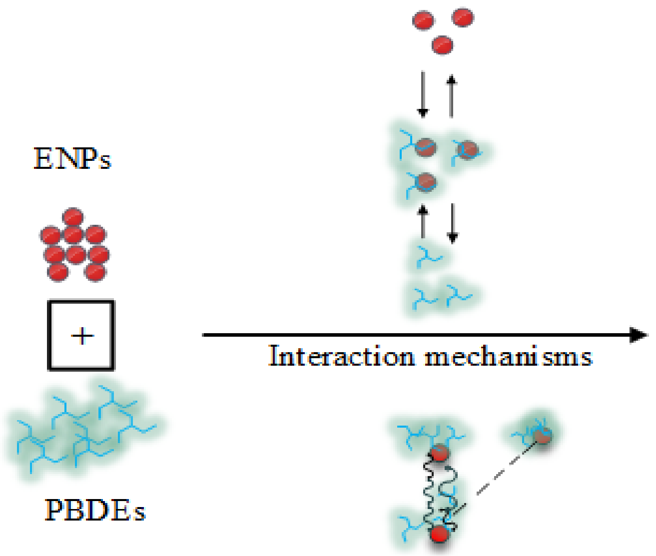
Graphical Abstract



- Cation bridging interaction
- Electrostatic interaction
- Hydrogen bonding interaction
- Hydrophobic interaction
- Ligand exchange interaction
- Molecular bridging linkage
- Steric interaction
- Van der Waals interaction
- π - bonding interaction

Abstract

This review focuses on the occurrence and interactions of engineered nanoparticles (ENPs) and brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) in water systems and the generation of highly complex compounds in the environment. The release of ENPs and BFRs (e.g. PBDEs) to aquatic environments during their usage and disposal are summarised together with their key interaction mechanisms. The major interaction mechanisms were identified including electrostatic, van der Waals, hydrophobic, molecular bridging and steric, hydrogen and π-bonding, cation bridging and ligand exchange. The presence of ENPs could influence the fate and behavior of PBDEs through the interactions as well as induced reactions under certain conditions which increases the formation of complex compounds. The interaction leads to alteration of behavior for PBDEs and their toxic effects to ecological receptors. The intermingled compound (ENPs-BFRs) would show different behaviour from the parental ENPs or BFRs, which are currently lack of investigation in this field. This review provided insights on the interactions of ENPs and BFRs in artificial, environmental water systems and wastewater treatment plants (WWTPs), which are important for a comprehensive risk assessment.

Keywords: Engineered nanoparticles (ENPs), polybrominated diphenyl ethers (PBDEs), wastewater treatment plants (WWTPs), emerging contaminants (ECs), interaction mechanisms.

Contents

1. Introduction

Flame retardants (FRs) additives have been integrated into various consumer products (e.g. textiles, computers) to attain effective fire resistance. Brominated flame retardants (BFRs) are extensively used globally due to their minimal influence on the characteristics of commercial products and cost-effectiveness comparing to other FRs [1]. However, more than 75 BFRs are recognized as persistent, bioaccumulative, and toxic (PBT) to living organisms [2]. For example, BFRs can be toxic to humans and cause cryptorchidism, reproductive problems and alterations in thyroid hormone homeostasis according to one epidemiological study [2]. There are three types of BFRs including additive, reactive and polymeric BFRs. Reactive BFRs show less release into the natural environment as they are covalently bonded to polymer structures, such as tetrabromobisphenol A [3,4]. However, the majority of BFRs can easily leach into environment during the use, disposal, or recycling of consumer products as they are simply used as additives. Both environmental and human health concerns are raised for the released BFR additives due to their persistence and bioaccumulative properties [2,5]. For example, hexabromocyclododecane (HBCD), an additive BFR, is very lipophilic (log K_{ow} = 5.6) and persistent (half-life of 3 days in air and 2025 days in water). Similarly, polybrominated diphenyl ethers (PBDEs), having 209 possible congeners, are environmentally persistent [2,6,7]. Penta-BDE and octa-BDE are particularly persistent, bioaccumulative and toxic, resulting in them being banned and terminated in North America and the European Union since 2004 [8]. However, they can still be found in products manufactured before the completion of the phasing out in these countries due to their persistence. Products containing BFRs (e.g. PBDEs) are still sold in countries where their use is unrestricted [9]. Alternatively, new alternatives to BFRs or “novel” BFRs (NBFRs) have been considered for use as flame retardants [2,10–15]. The estimated total global production of NBFRs has been reported as ranging from 100,000 to 180,000 tonnes per annum [11]. Table S1 lists the possible chemicals used as additive and reactive BFRs, NBFRs and polymeric BFRs with their CAS number, chemical formula, and molecular weight (MW), log K_{ow}, Henry’s law constant, vapor pressure and melting point. BFRs based on polymers (e.g., a copolymer of styrene and butadiene) are recent developments and can achieve fire safety standards in polymeric products, which previously depended on use of HBCD [4]. There is currently a lack of investigations on the environmental fate and behavior of these newly synthesized polymer based flame retardants [16,17].

BFRs are thus frequently detected in sludge and sediment samples from WWTPs throughout the world due to their wide application[18]. For example, Σ_{26}PBDEs concentrations of eight samples collected from four WWTPs ranged between 67-2.5×10^7 ng g^{-1} dry weight (dw) in Turkey, [18]. The presence of PBDEs in sediment samples was also reported from the Nakdong River basin, South Korea, demonstrating a total concentration of 27 PBDEs congeners (including deca-BDE-209) between 0.55-300 ng g^{-1} dw [19]. Once accumulated in WWTPs and released into the environment, BFRs can go through several processes including volatility [20], photodegradation [21–23], thermal degradation [24], adsorption [25–27], bioaccumulation, and persistence [6,28], which will influence their distribution, fate and behavior. These processes can be affected by the physical and chemical characteristics of BFRs and environmental media conditions [29,30]. For instance, various concentrations of BFRs have been identified in the atmosphere of electronic waste and rural sites in China. The measured annual average concentrations in atmosphere were 3260 ± 3370 pg/m^3 (e-waste sites) and 219 ± 192 pg/m^3 (rural sites) for PBDEs and 546 ± 547 pg/m^3 (e-waste sites) and 165 ± 144 (rural sites) for non-PBDEs. Temperature driven evaporation is determined as the controlling factor for the gaseous concentration of less bromine atoms containing BFRs (di- through hexa-BFRs) from contaminated surfaces (e.g., e-waste, soils, and recycled e-waste remains). Moreover, high ambient temperatures facilitate the volatilization of less bromine atoms containing brominated congeners (with relatively high vapor pressures) from contaminated environmental compartments, massive e-waste, and recycled e-waste remains stacked in the fields [31].

Quantum yields of BFRs (e.g BDE-209, TBBPA, TBBPA-DBPE and TBBPA-BAE) were measured in tetrahydrofuran and polystyrene. Higher photo reactivity leading to photodegradation of BFRs was observed in polystyrene. Photodegradation of BFRs induced oxidation and yellowing of polystyrene [32]. Thermal degradation of BFRs (PBDEs) in the presence of a halogenated source and incomplete combustion produces mixed halogenated dibenzo- *p* -dioxins and dibenzofurans (PXDD/Fs) and polybrominated dibenzo- *p* -dioxins and dibenzofurans (PBDD/Fs), respectively [24]. BFRs having higher bromine atoms in the compound are considered as less mobile in the environment due to their low water solubility, low volatility and bioaccumulation and strong adsorption on sediments. Such BFRs tend to end up in sediments, at high residue levels, near their emission sources, rather than in marine organisms or humans. Contrarily, BFRs composed of less bromine atoms are forecasted to be more volatile, water soluble, and bioaccumulative than the higher brominated compounds. Therefore, BDE-209 is generally considered to be less bioaccumulative, possibly because of its large molecular size and strong adsorption to sediment [33].

However, the fate and behavior of BFRs can be influenced by other contaminants, such as increasing reports on ENPs in the environment [34]. It is estimated that the annual production of the most widely employed ENPs is ~ 270,000 metric tons [35]. Post-release of ENPs in the environment may cause them to interact with various environmental components leading to the formation of new complex compounds [34,36]. Many reports have documented the presence of ENPs in the WWTPs and environmental samples [37–40]. For instance, a survey based on WWTPs showed the amounts of ENPs captured by primary sludge particulates were 7.1 kg-ZnO/d and 39.8 kg-TiO_2/d, and were 8.9 kg-ZnO/d and 25.1 kg-TiO_2/d [41] by secondary sludge.

The presence of ENPs can potentially influence the fate and behavior of BFRs. For example, the presence of Fe (III) in water systems could lead to the photochemical synthesis of highly toxic hydroxylated PBDEs (OH-PBDEs) from precursor PBDEs [42]. BDE-47 can be de-brominated to lower congeners (e.g. BDE-28 and BDE-17) in the presence of Au, Cu, Ni, Pd and Pt by utilizing their H_2 in metal-H_2 systems [43]. However, there is still limited information and knowledge about their interaction under environmental conditions. The effects of treatment technologies on the removal of nanoparticles are largely unknown.

Furthermore, intensive and collective efforts are required to evaluate the potential risks of ENPs and their largely unknown interactions with other organic and inorganic species [44]. This review aims to summarize the current research and knowledge gaps about the influential effects of ENPs on the fate and behavior of BFRs (e.g. PBDEs) in the environment, particularly in WWTPs and natural water systems. This critical evaluation aims to provide insights into the interaction between BFRs (e.g. PBDEs) and ENPs as influenced by various parameters and the effects derived from their interactions. The information will be useful for understanding the exposure assessment of BFRs and ENPs.

2. Occurrence of BFRs and ENPs in the environment

2.1 BFRs contamination

There are currently three most abundantly used BFRs, including hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA) and PBDEs. HBCDs are the most commonly used cyclic aliphatic BFR, widely used as flame retardants in the expended and extruded polystyrene foams and other insulating materials [45]. HBCDs are also considered as PBT compounds and have been detected in all environmental media such as air, sediment, water, human blood and mother’s milk [46]. The concentrations of HBCDs in various soil samples from Ningbo, Zhejiang China were reported, such as farmland soils (7.75 ng g^{-1} dw), industrial area soils (37.9 ng g^{-1} dw), residential areas soils (14.1 ng g^{-1} dw), traffic areas soils (31.8 ng g^{-1} dw), vegetable soils (11.0 ng g^{-1} dw) and waste dumping sites soils (60.74 ng g^{-1} dw) [45]. The HBCDs have also been detected in the aquatic food webs and sediments, e.g. samples from Detroit River and Hunhe River (China) [47–49]. Elevated concentrations of HBCDs were determined in the samples collected from equidistance to the HBCD production company in China, e.g. soils (11,700 ng g^{-1}), sediments (6740 ng g^{-1}) and water (5080 ng L^{-1}) [50].

TBBPA is a reactive brominated flame retardant, and currently, China, Japan, Jordan, Israel and the United States are the leading manufacturing countries of TBBPA. TBBPA is used in resins to produce printed circuit boards, plastics and high impact polystyrene, etc. The higher synthesis and utilization of TBBPA resulted in a widespread occurrence in the environment, which has been detected in air, dust, soils, sediments, sludge and waters. The highest concentrations (1.64–7758 ng g^{-1} dw and <0.5–2900 ng g^{-1} dw) of TBBPA in the soils were identified in BFR production company and electronic waste recycling areas in Shandong, China and Bui Dau, Vietnam, respectively [51]. At the same time, TBBPA concentrations in surface water samples were determined as from non-detectable amounts to 4870 ng L^{-1} in a region of China [52]. Similarly, < 0.4 to 259 ng g^{-1} dry weight of TBBPA in 52 sludge samples were reported from thirty WWTPs in China [53]. Much higher TBBPA concentration in WWTP were determined in Guangzhou (657–732 ng g^{-1} dw [54]) than that reported in South Korea (4.01–618 ng g^{-1} dw) [55]. TBBPA has a short half-life and its concentration decreases with the increase in distance from the source point. Many factors such as sorption, photo/biological and thermal degradation influence the fate and behavior of TBBPA in environmental conditions, hence their concentrations in various environmental samples vary. For example, Fig. 1 depicts the thermal decomposition pathways of TBBPA which results in generation of extremely toxic compound such as polybrominated dibenzodioxins and dibenzofurans (PBDD/Fs) [24].

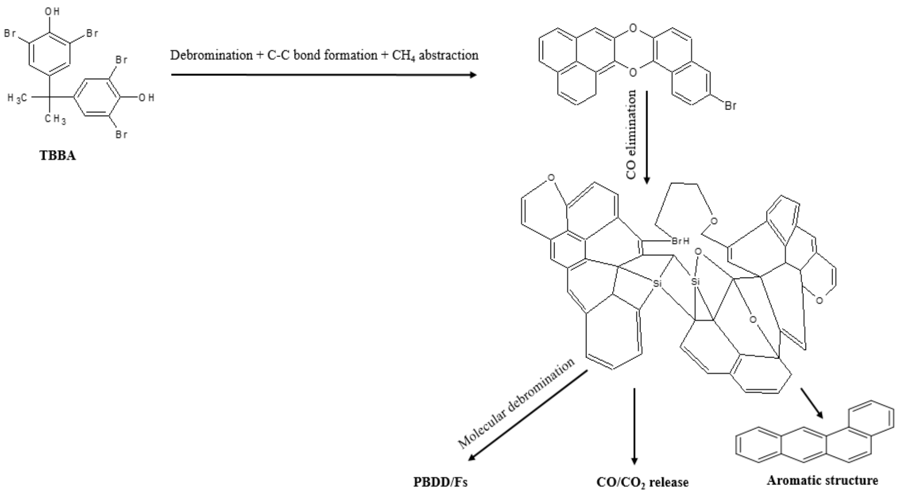


Fig. 1 Decomposition pathways in the thermal breakdown of tetrabromobisphenol A (TBBPA) [24].

PBDEs as another major BFRs have been identified in household dust and food at elevated levels. This could result in their in animal and human tissues [56,57]. The PBDEs were mainly found in non-metallic fractions in waste printed circuit boards apart from other reinforcing materials, thermosetting resins, and additives, which are the residue fraction where valuable metals were extracted from printed circuit boards [58]. Their accumulation in WWTPs have been documented. One of the major source of BFRs including PBDEs entering the WWTPs is during laundry washing of clothes which collects indoor dusts [59,60]. The concentration ranges of Σ_nPBDEs in the WWTPs of different countries are summarized in Table 1 [15,61–68]. The detection of decabromodiphenyl ethane from 42 WWTPs (sewage sludge) in twelve countries has been reported. For example, up to 100 µg kg^{-1} dry weight (dw) of decabromodiphenyl ethane (DBDPE) were found in 25 out of 50 sewage sludge samples from Swedish WWTPs [69]. The highest concentration (216 µg kg^{-1} dw) was found in a sludge sample from the Ruhr area in Germany [70]. Various PBDEs were identified in sewage sludge samples from southern China, including the presence of 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) (1.7 µg kg^{-1} dw), DBDPE (2000 µg kg^{-1} dw and tetrabromobisphenol-A 2,3-dibromopropyl ether (TBBPA-DBPE)(8950 µg kg^{-1} dw) [71]. Concentrations of BTBPE (22 µg kg^{-1} dw), DBDPE (364 µg kg^{-1} dw) and TBBPA-DBPE (2300 µg kg^{-1} dw) were also identified in sediment samples from southern China[71].

Table.1 Concentration ranges of PBDEs in WWTPs of different countries

Country	No. of WWTPs	Σ_nPBDEs	Concentration Range (ng g^{-1} dw)	Reference
Australia	16	8	1.8-2500	[67]
Canada	15	32	415-5967	[64]
China	6	13	278-823	[65]
Germany	11	8	142-2491	[61]
Italy	8	13	158.3-9427	[62]
South Africa	1	7	41.8-558	[66]
South Korea	40	22	298-48000	[15]
USA	4	13	1750-6358	[63]

Apart from the occurrence of three major BFRs in WWTPs and environmental sample, novel NBFRs were also identified in environmental samples. For example, twelve novel NBFRs were found in Western Scheldt seawater samples (up to 25 ng L^{-1}) in the Netherlands. Around 1.96 pg L^{-1} of BTBPE was found in freshwater samples from Lake Winnipeg in Canada, whereas the concentrations of DBDPE were less than the method detection limits (15 pgL^{-1}) [72]. Several NBFRs (e.g., DPTE, PTBX and HBB) were also identified in the Atlantic Ocean and Antarctic waters [73]. Concentration levels of NBFRs including HBCD have also been detected in the sediment samples in South Africa ranged from less than detection to 310 ng g^{-1} with a maximum recorded concentration of 56 ng g^{-1}, 186 ng g^{-1}, 310 ng g^{-1} and 60 ng g^{-1} for EH-TBB, ∑HBCD, BTBPE and BEH-TEBP respectively [74]. Concentration levels of six NBFRs in the urban soils of Melbourne, Australia have been detected. NBFRs such as PBT, PBEB, HBB, EH-TeBB, BTBPE and decabromodiphenyl ethane (DBDPE) were determined in 30 soil samples. NBFRs were detected in 24/30 soil samples with $\sum_5$NBFR concentrations ranging from non-detectable amount to 385 ng g^{-1} dw. HBB was the most frequently detected compound (14/30), while the highest concentrations were observed for DBDPE, followed by BTBPE [75]. Detection of NBFRs has also been reported in the soil samples collected among five Asian countries. Variation in NBFRs concentrations was found in soils ranging from 0.50 ng g^{-1} dw in Vietnam to 540 ng g^{-1} dw in the territory of a BFR producer in China. Concentrations of Σ_{19}NBFRs decreased in the order of Japan > South Korea > China > India > Vietnam in urban, rural, and background locations of the countries [76].

Contamination of soils by PBDEs could be caused by the transformation of effluents discharged from BFRs manufacturing industries [77]. The Σ_8PBDEs in five soil samples collected from an area near Weifang district in China (Deca-BDE manufacturing industry) ranged from 17,000 to 146,000 ng g^{-1} [78]. Similarly, the Σ_8PBDEs in soils from Laizhou Bay area, near two other BFRs manufacturing plants, were from 73,200 to 227,000 ng g^{-1} [79].

Once the BFRs are released into the environment or ultimately reached the WWTPs, several processes are involved in determining their fate and behaivor. Figure 2 illustrates the potential processes for PBDEs, including volatilization, sorption and leaching, photodegradation, thermal degradation, and biodegradation. In WWTPs, their sorption onto the wastewater sludge are more dominant than microbial or biological degradation. High levels of BFRs (e.g PBDEs) have been observed in the biosolids (~2.4 mg kg^{-1} dry weight) compared to WWTP effluent (~26 ng L^{-1}) [80]. The BFRs (e.g PBDEs) in a conventional WWTP do not seem to be degraded extensively and they are removed by applying various techniques such as anoxic, anaerobic and aerobic biological treatments, dissolved air flotation and/or sand-anthracite filtration or aerobic/anaerobic digestion [80]. However, once the BFRs are in the environment, they may form more complex compounds in the presence of other environmental existing organic or inorganic compounds which would influence their fate and behavior under various influencing factors (i.e temperature, pH etc).

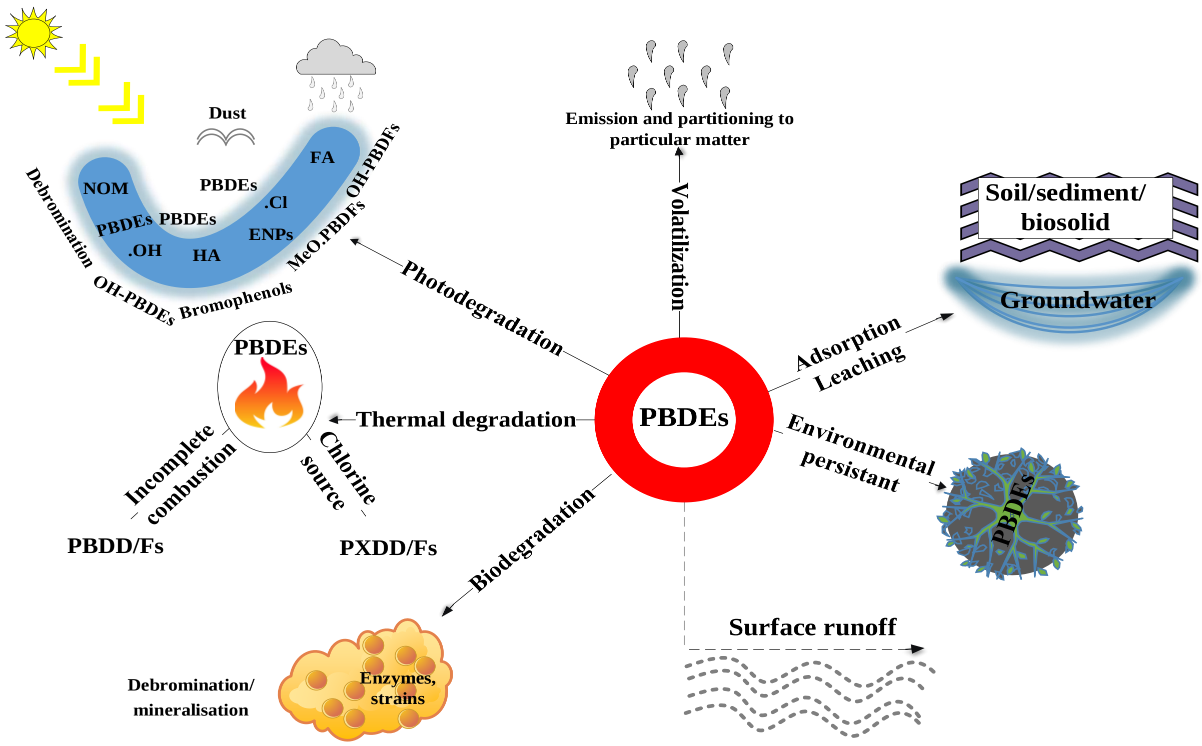


Fig. 2 Fate and behavior of PBDEs in the environment.

2.1.1 Volatilization

There are several modes of transformation of PBDEs into the environment during and after their application in different products. The volatilization of PBDEs from discharged wastewater into Taihu Lake in China has been reported [81]. The air-water gas exchange analysis exhibits an equilibrium in summer and spring while a strong volatilization flux, especially for BDE-28, was identified in autumn and winter, representing a higher wastewater discharge rate of PBDEs into Taihu Lake. PBDEs can bind strongly with soil and sediment particles due to limited dissolution in water. Thus their mobility is reduced as they are accumulated in sediment and soil. However, the strong binding of PBDEs to soil particles enhances their atmospheric mobility as they can attach to airborne particulate matter [82]. The partitioning and fate and behavior of various congeners of PBDEs was analysed based on emission. The lower the congeners number of PBDEs, the more quickly that PBDEs will partition into the air and vice-versa. The higher the number of bromine atoms in the PBDEs congeners, the more easily partitioning for PBDEs to sediments. This in turn will lead to the release of lower number of congeners of PBDEs into the water column [83].

2.1.2 Sorption and leaching

Sorption of PBDEs onto solid materials in water systems plays a significant role in determining their fate and behavior. Around 93% removal of PBDEs in WWTP was due to the sorption onto wastewater sludge [80]. The sorption affinity of BDE-15, and possibly of other PBDEs, is high towards soils. PBDEs could assemble in the topsoil due to irreversible sorption [84]. Increased sorption of PBDEs occur in the presence of organic substances compared to inorganic ones [85], e.g. bio-solids. Low concentrations of PBDEs were found to sorb onto ENPs (TiO_2) surfaces, which could cause organic matter to grow on the surface of ENPs (TiO_2) [9]. Physisorption of PBDEs onto the graphene surface were also confirmed using density functional theory (DFT) and molecular dynamics (MD) studies [86].

Leaching is also one of the major fates and behavior processes of PBDEs[87,88]. The leachability of PBDEs from plastics has been investigated by using different leachants, such as dissolved humic solution, distilled water and 20% methanol solution. The leaching concentration of PBDEs was enhanced in the presence of methanol and dissolved humic solution compared to distilled water. Some complex matters were observed due to interactions between PBDEs and dissolved organic matter [88]. Dissolved humic substance were also found to leach 14,000 to 200,000 ng $L^{-1}\Sigma$PBDEs from waste cathode ray tube plastic housing samples [89].

2.1.3 Photodegradation

The presence of humic materials, halide and metal ions can influence photochemical behavior of PBDEs [21]. The photodegradation of PBDE (e.g., BDE-47) in aqueous media containing ferric and chloride ions in the presence of a Xenon flashlight (500 W, >300 nm) as a radiation source produced lower fractioned PBDEs congeners such as tri-, di-, and mono-BDEs and chlorine containing BDEs as degradation products [90]. A similar study indicated PBDE (e.g., BDE-47) in aqueous media inclosing ferric ions and fulvic acid employing a Xenon flashlight (wavelength >290 nm), transformed to OH-PBDEs as photodegraded products by reacting with $OH^{\cdot}$ [90]. The photodegradation of PBDEs especially PBDEs congeners such as 47, 99, 100, 153 and 154 followed pseudo-first-order kinetics in pure water in the presence of simulated or natural sunlight [21]. Ferric ion (Fe (III)) could be a source of propagation of photo-transformation of PBDEs (BDE-47) and its degradation could increase in the co-presence of Cl^{-1} due to the iron redox cycle [90]. The alteration of Fe^{+3} to Fe^{+2} in water systems under irradiation conditions could generate $OH^{\cdot}$ radicals. The formation of chloride radicals due to the interactions between chloride ion (Cl^{-1}) and hydroxyl ($OH^{\cdot}$) radicals assists the formation of hydroxyl ($OH^{\cdot}$) radicals and stimulates the iron redox cycling (Eqs. 1-9) [21].

$$\mathrm{Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+} \ (1)$$

$$\mathrm{Fe(OH)^{2+} + hv \rightleftharpoons Fe^{2+} + OH^{\cdot}} \ (2)$$

$$\mathrm{Fe^{3+} + Cl^- \rightarrow FeCl^{2+}} \ (3)$$

$$\mathrm{FeCl^{2+} + Cl^- \rightarrow FeCl_2^+} \ (4)$$

$$\mathrm{FeCl^{2+} + hv \rightarrow Fe^{2+} + Cl^{\cdot}} \ (5)$$

$$\mathrm{FeCl_2^+ + hv \rightarrow FeCl^+ + Cl^{\cdot}}\ (6)$$

$$\mathrm{Cl^- + OH^{\cdot} \rightleftharpoons HClO^{\cdot -}}\ (7)$$

$$\mathrm{Cl^- + Cl^{\cdot} \rightleftharpoons Cl_2^{\cdot -}}\ (8)$$

$$\mathrm{HClO^{\cdot -} + H \rightleftharpoons Cl^{\cdot} + H_2O}\ (9)$$

Where, hv represents sunlight. Lower brominated PBDEs and small amounts of polybrominated dibenzofurans (PBDFs) can be generated under photodegradation as by-products or photo-products in the presence of pure water and surfactant solutions. For instance, in the presence of acetonitrile, BDE-153 undergoes photodegradation (1st route) and produces PBDFs by intramolecular elimination of HBr, the 2nd route describes the photo-Fries rearrangement, and the 3rd route describes the actual transformation pathway from brominated-2-hydroxybiphenyl to PBDFs [21,91]. Similarly photodegradation of PBDE (BDE-209) in the presence of methanol occurred with the formation of lower BDEs (LBDEs), synthesis of methoxylated-PBDFs (MeO-PBDFs) and hydroxylated-PBDEs (OH-PBDFs), and formation of bromophenols and bromobenzenes by cleavage of ether bonds [21,90]. It was also reported that the photochemical formation of OH-PBDEs has been observed in the presence of $\mathrm{Fe^{+3}}$ and/or fulvic acid solutions using BDE-47 [21,42].

2.1.4 Thermal degradation

Several factors can influence the behavior of BFRs during thermal treatment, for instance, polymer matrix, temperature, residence time, bromine and oxygen concentration. In the presence of heat, brominated flame retardants degrade and generate brominated products of incomplete combustion and subsequent emissions of polybrominated dibenzo- *p* -dioxins and dibenzofurans (PBDD/Fs). The release of intense concentrations of the mixed halogenated dibenzo- *p* -dioxins and dibenzofurans (i.e. PXDD/Fs) result in co-ignition of BFRs-containing substances with a chlorine source [24]. The thermal degradation of PBDEs could occur at 300 °C using micro/nano $\mathrm{Fe_3O_4}$ materials. It is reported that PBDEs were degraded from higher congeners to lower congeners such as BDE-209 to -207, -197, -183 → (-144*, -154) →, -103, →

unknown compounds (X=0,1,2,3,4), → unknown compounds (X=0, 1, 2, 3) and BDE-7 [92]. It could be assumed that the thermal degradation of PBDEs shifts from higher congeners to lower ones.

2.1.5 Biodegradation

Biodegradation of BFRs, especially PBDEs, is considered to be a serious environmental issue because their debromination results in the release of smaller but toxic PBDEs [1,93]. The debromination of BFRs from BFR-contaminated sediments were reported in the presence of microorganisms under anaerobic conditions [1,94,95]. The biodegradation of $\sum_{11}$PBDEs in wastewater sewage sludge (polluted by indigenous microflora) were reported under aerobic conditions. The presence of 4-bromobiphenyl and yeast extract eventually enhanced the aerobic degradation of $\sum_{11}$ PBDEs congeners in this study[96].

It is stated that the conversion of PBDEs into water and carbon dioxide occurs through a tricarboxylic acid cycle, during which various enzymes function to catalyze and mineralize the PBDEs. The conversion of BDE-3 into 4-bromophenol and 4-bromocatechol is evident by Sphingomonas sp. SS3 and Cupriavidus sp [97]. Similarly, Sphingomonas sp. PH-07 can induce the degradation of BDE-3 into 2-hydroxymuconic acid. 2,4-dibromophenol formed from the aerobic degradation of BDE-7 and BDE-28 [98]. Hydroxylation of BDE-15 by 2,3-dioxygenase into 2′,3′-dihydroxy-4,4′-dibromodiphenyl ether occurred in the presence of Sphingomonas sp. PH-07 [93,98] and debromination into 4-bromophenol and 4-bromocatechol by Sphingomonas sp. occurred [93,99]. Smaller PBDEs such as BDE-154, BDE-28 and BDE-15 were detected from the aerobic degradation of BDE-209 by strain JP12 [100]. Aerobic transformation of BDE-209 into smaller PBDEs were also reported by Pseudomonas aeruginosa [101]. Samples of Burkholderia xenovorans were employed to transform mono-PBDEs into OH-mono-PBDEs [102]. The conversion of BDE-209 into hydroxylated PBDEs (OH-PBDEs) were identified by employing extracted crude enzyme from Pseudomonas aeruginosa [103].

2.2 ENPs contamination

Engineered nanoparticles (ENPs) are chemically synthesized NPs and generally found in the 1 to 100 nm size range [104], which are also commonly found in consumer products [105,106], agricultural chemicals, the environmental and many industrial applications. ENPs can be made from metals (Ag, Cu, Au, Zn, Ni, and Fe), non-metals (carbon nanotubes, fullerenes, quantum dots, carbon dots and graphene oxides), metal oxides (SiO_2, CeO_2, Al_2O_3, ZnO, TiO_2, MnO_2 and Fe_2O_3), metal sulfides (FeS_2, AgS, CuS and ZnS), polymers (chitosan, aliginate and hydroxymethyl cellulose), and lipids (soybean, steric acid and lecithin). The exponentially growing use of ENPs has led to their ubiquitous occurrence in the environment through natural or incidental processes [106,107].

For example, TiO_2 and ZnO are commonly used as inorganic UV-active ingredients with nano-size particles being employed recently due to properties like transparency, wider UV absorption and being very difficult to irritate or sensitize the body skin [108,109]. In 2017, 524 Australian available sunscreen products were composed of 9.7% nTiO_2 and 14.1% nZnO [109]. The survey on the use of sunscreen by 87 Australian school-going children in the 5-12 age range in 2012 reveled different application of sunscreen for different application methods. Comparatively more sunscreen was applied when it was disbursed via a pump (0.75 mg cm^{-2}) and squeeze bottle (0.57 mg cm^{-2}) compared to a roll-on (0.22 mg cm^{-2}) [110]. This gives indication of exposure of nanoparticles of school-age children. Besides large application in sunscreen, nano TiO_2 and ZnO have many other applications, e.g. TiO_2 nanoparticles are used in paints, pigments, food, fabric coatings, catalysts, solar cells, papers. Meanwhile, ZnO nanoparticles are used in sensors, photovoltaic cells, catalysts and dye-sensitized solar cells [107,111].

The application of ENPs has led to increasing detection of ENPs in water systems such as surface water, raw and treated drinking water, industrial wastewater and municipal wastewater [112,113]. The concentration ranges, detection techniques and recovery of various ENPs in WWTPs are listed in Table 2. It was reported that TiO_2 ENPs concentration from the effluents of ten municipal amenities in the United States varied from <2 to 20 μg L^{-1} [40]. The TiO_2 ENPs concentrations were estimated as 3.47 and 1.75 μg L^{-1} in the effluent of urban wastewater in Europe and the United States, respectively [114]. The mass concentrations of TiO_2 (95 ng L^{-1}) and Ag (2.1 ng L^{-1}) in WWTP effluents were estimated using single-particle inductively coupled plasma mass spectrometry (sp-ICP-MS) [115]. Predicted environmental concentrations of the most abundant ENPs such as Ag (0.3 µg $kg^{-1}y^{-1}$), TiO_2 (0.7 µg $kg^{-1}y^{-1}$) and CNTs (0.0005 µg $kg^{-1}y^{-1}$) in freshwater; TiO_2 (13.4 µg $kg^{-1}y^{-1}$) in runoff water, (17.9 µg $kg^{-1}y^{-1}$) in river water (1.21 µg $kg^{-1}y^{-1}$) in drinking water and (16 µg $kg^{-1}y^{-1}$) in surface water, have also been reported [107].

Table 2. ENPs identification and quantification in WWTPs.

ENPs	Wastewater	Detection	Concentration	Recovery	Reference
$nTiO_2$	Field	ICP-OES, SEM, EDX	10µg L^{-1}–10 mg L^{-1a}	N/A	[116]
nAg	Field	GFAAS[c]	<30 µg $L^{-1a,b}$	Mill Q water: 100%	[117]
nAg nAu nC_{60}	Field	Ag, Au: ICP-OES; nC_{60}: HPLC	>0.1 mg L^{-1b}	N/A	[118]
nAg	Laboratory scale reactor	ICP-MS; DLS; TEM	1.5 µg L^{-1}–3 mg L^{-1b}	N/A	[119]
nAg $nTiO_2$ $nSiO_2$	Laboratory scale reactor	ICP-MS, ICP-OES, TEM	0.1 mg L^{-1}–10 mg L^{-1b}	N/A	[120]
nZnO	Laboratory scale reactor	ICP-MS	0.1 mg L^{-1}–2 mg L^{-1a}	N/A	[121]
nAg $nTiO_2$ nC_{60}	Laboratory scale reactor	ICP-OES; UV/VIS; HPLC; LC/MS; SEM; TEM; EDS; PALS[d]; XRD	nC60: 10 µg L^{-1}–0.5 mg L^{-1} nAg: 10 µg L^{-1}–1 mg L^{-1} nTiO2: 10 µg L^{-1}–2 mg L^{-1b}	N/A	[122]
$nCeO_2$	Laboratory scale	ICP-OES	0.5 mg L^{-1}–10 mg L^{-1b}	N/A	[123]

	reactor				
nAg	Laboratory scale reactor	ICP-MS	100 μg L^{-1}–400 μg L^{-1b}	N/A	124
nZnO nAg	Laboratory scale reactor	ICP-MS	10 μg L^{-1}–40 mg L^{-1b}	N/A	125
$nTiO_2$ nZnO	Field	ICP-OES; SEM	Ti: 0.1–1 mg L^{-1} Zn: 0.1–1 mg L$^{-1a,b}$	Ti: 63–100% Zn: 86–100%	126

[a] Measured sample.
[b] Spiked sample.

[c] Graphite furnace atomic absorption spectrometry

[d] Phase analysis scattering technique.

It is likely that elevated concentrations of ENPs in wastewaters will occur in the future due to increases in their synthesis and utilization. The presence of ENPs can impact the performance of conventional WWTPs in the alteration of physicochemical properties of the water[37]. The nano-sized characteristic of ENPs and their correspondingly enhanced reactivity increases their interaction opportunities with other natural organic matters, organic and/or inorganic compounds through hydrophobicity, electrostatics, ligand exchange, flocculation, and hydrogen bonding. These processes may generate more or less persistent, bio-accumulative, toxic and complex species recognized as emerging contaminants (ECs), which would pose potential environmental and human health hazards [30,127,128].

The properties of ENPs such as their size, shape, surface morphology, crystallinity, pore size, hydrophilicity, hydrophobicity and surface area may play a significant role in their interaction and fate in WWTPs. ENPs are present as a suspension or an emulsion in water systems and the presence of surfactants and other chemical agents may alter their surface and interfacial characteristics as well. Various chemical agents such as coagulants and polyelectrolytes used in WWTPs could indirectly stabilize against coagulation or aggregation by conserving particles charge and by modifying the outmost layer of the particles leading to the formation of very complex compositions. Carbon based ENPs could adsorb to the commonly employed materials in WWTPs. For instance, fullerenes can adsorb to natural organic matter. The natural organic matter caused disaggregation of nC60 crystals and aggregates under typical solution conditions of natural water, leading to significant changes in particle size and morphology. Such effects magnified with increasing natural organic matter concentration and it may act as a carrier in the transport and toxicity of C60 in waste streams. The ENPs (e.g. fullerenes) in WWTPs could sorb to organic contaminants, such as naphthalene and other contaminants, which if not removed during wastewater treatment, could be discharged with the effluent into the environment [129].

Coagulation ("sweep flocs") process is used to remove ENPs in conventional WWTPs while the efficiency of this process is reduced due to the interaction (binding) of ENPs with other contaminants. Unfortunately, it remains unclear to understand the behavior of interacted ENPs. Further studies are required to determine whether ENPs are stabilized or degraded with surfactants and organic matters and/or can be removed sufficiently during the treatment process in WWTPs [37]. The removal of ENPs based on their size distribution is also challenging especially after they interact with other contaminants i.e BFRs. Some WWTPs are advanced enough to eradicate the ENPs in wastewater through bio-sorption, aggregation, precipitation or other biomass mediated procedures. However, the increasing trend of nanoparticles being concentrated in sewage sludge should also be taken into consideration [130].

Studies based on the nature and behaviors of ENPs (carbon-based, metal and metal oxide and others) in WWTPs, have been investigated [130–132]. These studies shed light on the processes such as dissolution, sedimentation, adsorption, oxidation and transformations associated with the transport and toxicity of ENPs. ENPs released into the environment are subjected to transformations including many physicochemical and biological processes, for instance agglomeration, deposition, sulfidation, mineralization, adsorption, photo-oxidation and reduction, distribution among organisms, bioturbation, and ingestion-egestion transformations [30], which can be altered after their interaction with other organic contaminants, e.g. BFRs.

3. Interaction between ENPs and PBDEs

Once the ENPs and BFRs end up in the natural environment from various sources and pathways as described in section 2, their co-existence and interactions with each other and other compounds could generate some complex compounds. These increase the complexity for their removal by conventionally designed WWTPs. The understanding on their interaction mechanisms would benefit in development of removal strategies. Thus, the following section summarizes the possible interaction mechanisms between ENPs and BFRs (e.g. PBDEs), their interfacial properties, surrounding environmental conditions, types of formulated complex compounds, and their fate and behavior.

3.1 Interaction mechanisms

3.1.1 Electrostatic and van der Waals interaction

Classical DLVO (Derjaguin–Landau–Verwey–Overbeek) theory [133], the net interaction of van der Waals and electrostatic forces, is involved in the interactions between almost all nanoparticles (NPs) and the PBDEs (Fig. 3). DLVO theory is defined in equation 10, where F_{tot} is the net interactive force.

$$F_{\mathrm{tot}} = F_{\mathrm{van\ der\ waals}} + F_{\mathrm{electrostatic}} \qquad (10)$$

It is reported that the van der Waals force is a non-directional force that subsists in the molecules and also impacts on the physicochemical characteristics of the molecules. Van der Waals forces exhibit little sensitivity to chemical changes [134]. Electrostatic forces are mostly employed to elucidate the adsorption behavior of the ENPs, depending on their geometry, surface charge and potential [135,136].

The electrostatic interaction is a significant mechanism for sorption on ENPs that have points of zero charge (PZC) beyond the environmental condition (pH), such as metal ENPs and some metal oxide ENPs. For instance, Al_2O_3, ZnO, CeO_2 and magnetite, usually carry a positive charge [136,137], which would react with delocalized negatively charged hydroxylated and methoxylated PBDEs by electrostatic attraction. On the other hand, CuO, SiO_2 and carbon-family ENPs usually carry a negative charge [136] and would have electrostatic repulsion with hydroxylated and methoxylated PBDEs (delocalized negatively charged). Zeta potential of ENPs, for instance TiO_2 and MnO_2, varies with pH [136]. There are several influencing factors (e.g., electrolyte, pH and temperature, etc.) that could influence the electrostatic interactions between PBDEs and ENPs. For instance, the surface charge of TiO_2 decreased from -35 mV in distilled water at 7 pH to -14.8 mV in the presence of 1 mM NaCl due to electrostatic interaction with 10 mg L^{-1} BDE-47, while it decreased to -12.3 mV in the presence of 0.1 mM $CaCl_2$ [9]. Similar results have been reported by Khan et al. [138]. It is revealed that the presence of different electrolytes such as (0–0.1 mM) $Al_2(SO_4)_3$), (0-20 mM) KCl and (0–0.5 mM) $MgCl_2$ significantly enhanced the surface charge of ZnO NPs in PBDEs (BDE-47 and BDE-209) at 7 pH [138].

The pH could also be considered as one of the key factors affecting the electrostatic interactions between ENPs and the organic pollutants (PBDEs) in water bodies. For instance, the slower agglomeration of sulfide/silica mutated nZVI in the maximum days of cultured media (11-d) was reported due to high pH value. ENPs typically have more negative charge at higher pH and their stability could be improved due to an increase in electrostatic repulsion. Once they interact with organic pollutants, electrostatic interaction could alter their stability as well [139]. Change in temperature could also affect the performance of the electrostatic forces in the ENPs in environmental media [34]. For example, the increase in the agglomeration of gold nanoparticles with rising temperature (20-60 °C) has been reported due to an increase in the collusion frequency of the nanoparticles [140]. In the carbon-based materials, the presence of monovalent (Na^+ and K^+) and divalent (Ca^{2+}) cations with a temperature increase from 6 to 40 °C promoted the agglomeration of graphene oxide (GO). This was mainly due to enhanced cation dehydration and reduced electrostatic repulsion [141].

The interactions between PBDEs and TiO_2 nanoparticles in water systems are listed in Table 3 [9]. According to DLVO theory, enhancing the ionic strength decreases the electrostatic energy obstacle and escalates the secondary minimum well, which induces agglomeration due to a rise in attachment efficiency. Consequently, the behavior of TiO_2 NPs in the presence of an electrolyte (NaCl) followed DLVO theory.

The interactions between PBDEs and graphene by employing density functional theory (DFT) and molecular dynamics (MD) methods have been reported [86] (Table 3). Both the local density approximation (LDA) and generalized gradient approximation (GGA) were used to define the biomolecules' adsorption behavior on inert surfaces where van der Waals interaction plays a major role.

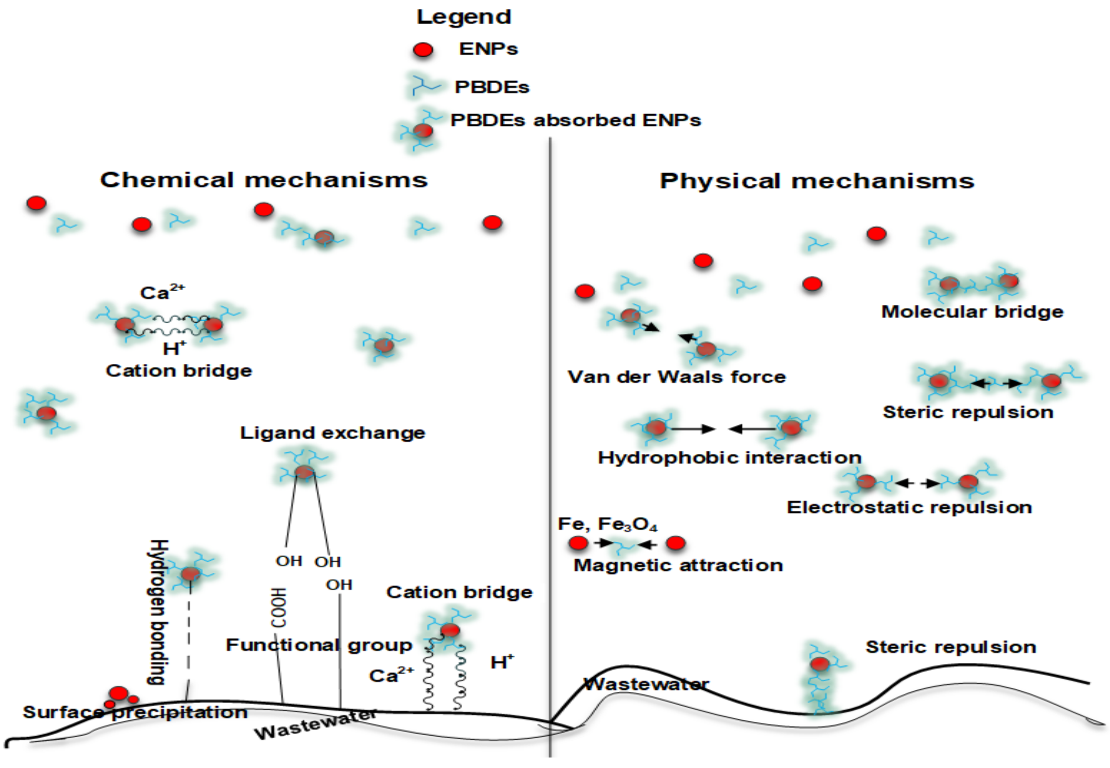


Fig. 3 Chemical and physical interaction mechanisms involved between ENPs and PBDEs [136].

Tan et al. [142] reported interaction of PBDEs with human serum albumin (HSA) (Table 3). They employed a molecular docking technique to calculate the binding force, energy and sites of typical PBDEs, such as BDE-47, BDE-99, BDE-100, BDE-153 and BDE-209, with an HSA macromolecule. It was found that PBDEs with a higher molecular weight exhibited higher binding energy with HSA. On the other hand, BDE-209 without hydrogen atoms revealed the lowest binding energy i.e. ($-\Delta G_{\text{binding}}$, 17.99 J mol^{-1}) compared with other PBDEs ($-\Delta G_{\text{binding}}$, 33.18–35.23 J mol^{-1}). The reason for this pattern could be the position of Br atoms on their benzene rings which affects the binding free energy of PBDEs. BDE-209 has no hydrogen atoms for the potential formation of hydrogen bonding, and steric hindrance may also explain the lower binding energy. The binding site depth (Å) was also calculated by the molecular docking modeling which revealed that the higher the hydrophobicity (log K_{ow}) of PBDEs induce interaction with deeper binding sites within the central channel of HSA.

Table 3. Interactions of typical ENPs with PBDEs

Interacting Species	Interaction mechanisms with PBDEs	Comments	References
TiO_2	Electrostatic attraction, van der Waals, hydrophobic and steric interactions, hydrogen bonding	Addition of electrolytes decreased the magnitude of the surface charge of TiO_2 ENPs with or without BDE-47 and BDE-209, due to the addition of the positively charged ions around the electric double layer of the particle, screening the surface charge of the ENPs. The interactions between TiO_2 ENPs and PBDEs may occur by electrostatic forces due to their respective surface charges, physical interactions. Coating of TiO_2 by organic pollutants may cause steric hindrance as well.	[9]
Graphene	Van der Waals, electrostatic, hydrophobic interactions, π-π stacking, steric hindrance.	Density functional theory (DFT) and molecular dynamics (MD) methods were used to study the interaction mechanisms between PBDEs and graphene surface. Aromatic ring favors adsorption on graphene with a corresponding alignment to the graphene surface and the interaction energy rises with the increase in bromination. Ortho-position substitution of bromine in BDE-183 and -209 causes steric hindrance.	[86]
Dissolved organic	π-π interaction	Substituent positions (ortho and non-ortho) exerted an important influence on the binding affinities of organic pollutants, such as PBDEs and PCBs with DOM, such as leonardite humic acid (LHA) derived from the brown coal, and the natural organic matter derived from surface water (SW)	[143]

matter (DOM)			
Human serum albumin (HSA)	Hydrogen bonding, electrostatic and hydrophobic interactions,	Molecular docking technique was employed to calculate the binding force, energy and site of typical PBDEs (BDE- 47, 99, 100, 153 and 209) with HSA macromolecule. PBDEs with higher MW showed higher binding energy with has. However, without hydrogen atoms in BDE 209, it showed the lowest binding energy ($-\Delta G_{binding}$: 17.99 J mol^{-1}) compared with other PBDEs ($-\Delta G_{binding}$: 33.18–35.23 J mol^{-1}). The higher the hydrophobicity (log K_{ow}) the deeper the binding site within the central channel of HSA.	[142]

3.1.2 Hydrophobic interaction

The presence of hydrophobic interactions between two hydrophobic surfaces has been proven by several studies and the interaction can be stronger than van der Waals attraction [136,144–147]. Water molecules move from hydrophobic surfaces into bulk water ($\Delta S > 0$) where they have abundant binding opportunities resulting in the theory of nanobubbles as the origin of hydrophobic forces [134]. Hydrophobic interactions could even form from a long distance. A schematic diagram elaborating hydrophobic interaction is shown in Fig. 4.

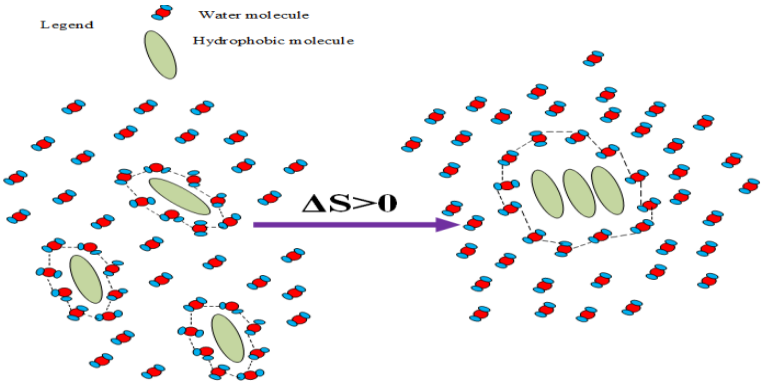


Fig. 4 Schematic diagram of hydrophobic interaction, where ΔS represents the change in entropy.

The hydrophobic interaction between PBDEs and TiO_2 ENPs was reported in water systems[9]. The $\log k_{ow}$, as a measure of the hydrophobicity of a compound indicates higher values of $\log k_{ow}$ corresponding to stronger hydrophobicity. PBDEs' adsorption on graphene is not only regulated by the hydrophobicity of the adsorbates but also influenced by π - π interaction (Table 3) [86]. The degree of hydrophic interaction between PBDEs and ENPs can vary according the properties of ENPs as some ENPs are hydrophilic by nature while others are hydrophobic. For instance, nanoparticles belonging to the carbon family exhibit hydrophobic properties but metal oxide-based ENPs (alumina, zeolite, TiO_2) are mostly hydrophilic [148–150]. In addition, the hydrophobic interaction between ENPs and PBDEs could be also affected by the presence of surface coating and/or existence of functional groups. For instance, the hydrophobic interaction with graphene oxide is muted compared to graphene because of the presence of oxygen-containing groups at the boundaries of graphene oxide [151,152]. The modification of ENPs with surfactants or polymers can also influence the hydrophobic interaction between PBDEs and the ENPs [153]. It is reported that carboxymethylcellulose, a surfactant, increased the colloidal stability of metal (Fe) ENPs, altered their surface properties and also played a significant role by affecting their interaction with contaminants (PBDEs) by manipulating the sorption-desorption. The water solubility of hydrophobic non-ionic organic composites could be enhanced by using surfactants due to micellization of the heterogeneous monomer species [153,154].

The presence of humic acids and fulvic acids inhibit the photodegradation of PBDEs (e.g. BDE-209) in water systems, due to the screening of light by the humic substances and the hydrophobic interaction of the target compound (e.g. BDE-209) with hydrophobic sites of the humic substance [155]. The interaction between PBDEs and dissolved organic matter based on the substituent position by molecular docking calculations and quantum chemistry, has been reported by Nuerla et al. [143]. The hydrophobicity and volumes of non-ortho-substituted isomers are revealed to be higher compared to that of ortho-substituted ones, while the interaction of non-ortho-substituted isomers with dissolved organic matter tends to favor hydrophobic partition [143,156,157]. Biosolids of WWTPs contain a large number of PBDEs (99% of BDE-209) due to their higher hydrophobicity and interaction (adsorption) with solid matter in wastewaters [67,158–160]. Similar outcomes have also been reported where sludge from WWTPs contained a larger amount of PBDEs [161–163]. The reaction mechanisms between deca-BDE and zerovalent iron nanoparticles (nZVI) has been reported by Shih and Tai [164]. It emerged that the adsorption of deca-BDE with zerovalent iron nanoparticles was high in acidic environments due to hydrophobic interaction based on its high hydrophobicity [164]. The particle-particle surface interaction could also occur due to hydrophobic forces and these forces are dominant in improving adsorption and aggregation of engineered nanoparticles compared to van der Waals forces [136].

3.1.3 Steric effect

Steric effects or nonbonding interactions are the repulsive forces which occur between overlapping electron clouds. They can influence the shape and reactivity of molecules and ions. An interaction between two coated surfaces takes place if the distance of separation between the surfaces is less than twice the thickness of the adsorbed layer. Steric interactions involve the forces resulting from interactions between adsorbed chains and/or chain elements, which can be defined quantitatively in terms of the energy change occurring upon the interaction of the adsorbed layers. Steric interactions can be attractive or repulsive [165]. A similar concept reported by H. Wang et al. [166] states that when the ENPs are coated by an organic compound, their nature and behavior cannot be explained entirely by classical DLVO theory because of steric repulsion.

Ding et al. [86] explained the steric interaction between PBDEs and graphene surfaces (Table 3) and reported the affinity of aromatic ring (its configuration with number of bromine molecules in benzene ring) in-terms of adsorption on graphene surface. For instance, the interaction energy between tri-BDE (BDE-28) and graphene is -9.99×10^4 J mol^{-1} while that between penta-BDE (BDE-99) and graphene is -1.27×10^5 J mol^{-1}. However, the interaction energy between diphenyl ether (DE) and a graphene surface was the smallest, i.e.-7.41×10^4 J mol^{-1} by GGA+DFT-D, reflecting the comparatively weak bonding between graphene and diphenyl ether. This trend was not followed by hepta-BDE (BDE-183) and deca-BDE (BDE-209) congeners, although they have more bromine atoms compared to hexa-BDE (BDE-153). Steric hindrance is the reason behind the reduction in interaction energies. The ortho-position substitution of bromine in BDE-183 and -209 plays a significant role by providing steric hindrance effects which block their co-planar alignment with the graphene surface [86].

The interaction between ZnO nanoparticles and brominated diphenyl ether,-47 and -209 in water systems was investigated by Khan et al. [138]. The results indicated that the presence of both brominated flame retardants enhanced the colloidal stability of nanoparticles and their adsorption diminished the van der Waals effects between particles due to the increase in steric hindrance effect [138,167,168]. The surface coating and surface potential of ZnO nanoparticles coated by BDE-47 is more effective compared to BDE-209 and the aggregation rate of ZnO nanoparticles has been concealed due to electrostatic hindrance even when mono and polyvalent cations exist [138]. The debromination of PBDEs occurs in metallic systems follows the pattern of para > meta > ortho-position (Fig.5). Steric hindrance could be the main explanation for such a pattern by deterring the formation of any complex between PBDEs and H-atom where ortho-position (bromines) are the most hindered by adjoining oxygen and the para-position (bromines) carry the least hindrance [23,169,170]. A similar finding has been described by Mylon et al. [171]. The debromination of PBDE (e.g.BDE-209) using TiO_2 nanoparticles in the water system has been found. The one possible reason could be due to the stronger interaction of PBDEs with TiO_2 nanoparticles leading to weakening of the arylbromine bond energy at the meta position compared to the ortho position. This is due to steric hindrance or the following mechanisms (Eqs. 11-12) based on arylbromine bond breakage:

$$\mathrm{R-X+e^- \rightarrow R-X^{\circ-} \rightarrow R^{\circ}+X^-} \quad (11)$$

In concerted form the equation is written as:

$$\mathrm{R-X+e^- \rightarrow [R\ldots X\ldots e^-] \rightarrow R^{\circ}+X^-} \quad (12)$$

This could occur because of polarization of the C-Br bond by titanium trapped electrons and acceptance of the leaving bromine atom by the Ti site of TiO_2 (acting as strong Lewis acid) [23,171]. Steric hindrance also plays a significant role in the stabilization of colloidal particles of humic substances in the presence of monovalent salts but does not follow the same trend when divalent cations are present (e.g. Ca^{2+}, Cu^{2+}, and Pb^{2+}). It is most probably due to cation complexation with humic substances [172–175].

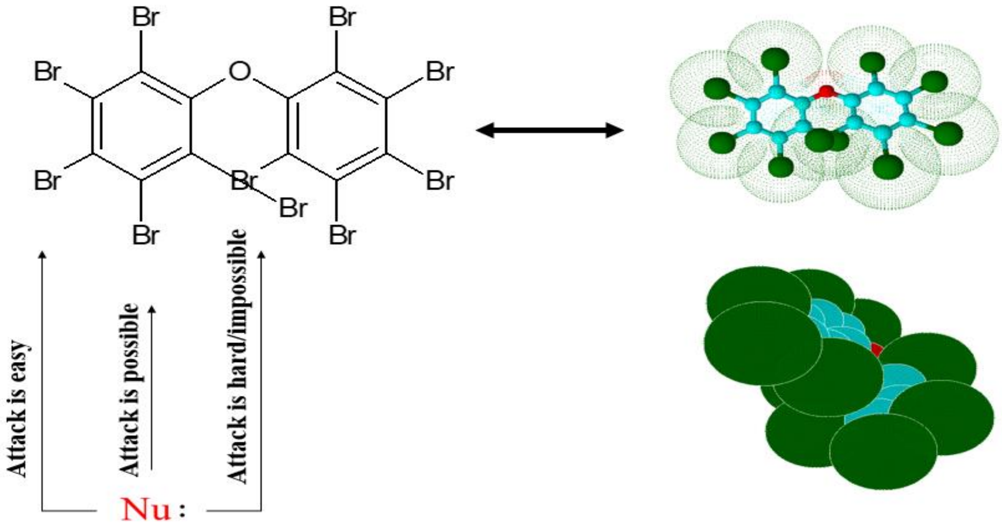


Fig. 5 Steric hindrance phenomena for BDE-209, Nu: nucleophile.

It has been reported that a stabilizer (polyanionic cellulose) could play a significant role in the prevention of aggregation and oxidation of Pd/Fe nanoparticles, employed to degrade PBDEs, by steric hindrance and finally could boost the reactivity of the nanoparticles [176–178]. The influence of steric hindrance is very high at the ortho-bromine position in the debromination reaction mechanism of PBDEs (e.g. BDE-47) by using Pd/Fe nanoparticles and is much less at the para-bromine position [178,179].

3.1.4 Molecular bridging linkage head-on coagulation-flocculation

Molecular bridging linkage is a type of molecular connection including nanoparticles to nanoparticles interaction and the nanoparticles to organic compounds (e.g. PBDE molecules) interaction. Furthermore it is directed towards aggregates in aqueous systems. Once the molecules start adsorbing at the surface on the ENPs, the bridging effect could occur due to molecular linkage with each other and with the adsorbed one (Fig. 3) [136]. Once the protrusion distance of the absorbed molecules is greater than the electrical double layer, the molecular bridging interaction would occur between two similarly charged engineered nanoparticles [136]. Huang et al. [177] reported the molecular bridging mechanism using FTIR spectra of virgin Pd/Fe NPs and polyanionic cellulose modified Pd/Fe nanoparticles for the debromination of PBDE (e.g. BDE-47). Stretching frequencies ($\Delta v = v$as- vs) were employed to interpret the bonding mechanism between metal nanoparticles and the carboxylate polymer. Three types of bonding bridging interactions were reported based on the frequency ranges, such as monodentate bridging interaction ($200 < \Delta v < 320$ cm^{-1}), bidentate bridging interaction ($140 < \Delta v < 190$ cm^{-1}) and bidentate chelating interaction ($\Delta v < 110$ cm^{-1}) [177,180,181]. The higher the ionic strength, the lower the Debye length, leading to lower electrostatic repulsion and ultimately stronger bridging interaction and vice versa [182183]. Different types of composites based on clay and polymer have been reported as usable for removing organic pollutants (e.g. PBDEs), principally by employing them in various removal techniques. These include membranes, bridging linkage by using as coagulation /flocculation agents and in columns/barriers [184–187].

3.1.5 Hydrogen bonding

Hydrogen bonding may occur when the organic adsorbate and ENPs consist of -OH, -COOH and -NH_2 moieties [137136], especially in carbon NPs [188]. Hydrogen bonding between PBDEs and TiO_2 ENPs in natural waters occurs (Table 3), where surface Ti-OH groups of the ENPs act as an electron donor and the ether groups present in the structure of PBDEs act as an acceptor, and/or an induced dipole may be responsible for reaction between PBDEs and TiO_2 ENPs [9,189,190]. Tan et al. [142] reported hydrogen bonding interactions between PBDEs (BDE- 47, -99, -100, -153 & -209) and human serum albumin (HSA) using a molecular docking calculation (Table 3). It was found that only one congener (BDE-47) among all those selected, formed hydrogen bonding with SER202.A (the residue of human serum albumin) due to a large number of hydrogen atoms when compared to others.

It is reported that bio-mineralization of PBDE (e.g. BDE-47) occurred in a nano-bio-integrated system. Hydrogen bonding including other interactions could occur by reacting the nZVI/Pd ENPs with dissolved oxygen in the water system. This reaction also generates $OH^{\cdot}$ radicals and leads to damage the bacteria [191]. Sorption behavior of PBDEs to natural and artificial fabrics has also been reported. It is revealed that hydrogen bonding play a significant role in the sorption in natural fabrics (e.g. cotton and linen),composed of cellulose with –OH functional groups on glucose monomer, compared to artificial fabrics (e.g. polyester) composed of terephthalic acid monomers [192–194]. X. Li et al. [195] synthesized a nanocomposite named PVP@CNTs-Cu_2O for the removal of persistent organic pollutants through adsorption. The adsorption of TBBPA on the nanocomposite could be due to hydrogen bonding under acidic conditions [196,197]. T. Wang et al. [198] in their research documented the adsorption of PBDEs onto the surficial surfactant components (e.g. Fe oxides, Mn oxides, organic matter and residues). The hydrogen bonding interaction was found to be one of the major interactions which occurred in the synergy of iron oxides with organic matter in the adsorption of PBDEs. The sorption mechanism of PBDEs by micro-plastics including salinity (NaCl) suggested that the sorption of PBDEs (e.g. BDE-47) is unaffected (not significantly affected) by salinity due to the presence of hydrogen bonding in the molecules of organic compounds [199–201].

3.1.6 π - bonding interaction

π bonding interactions comprising π - π, cation - π, anion - π and n - π bonding are normally exist in the interactions between graphene family nanoparticles and other organic pollutants (Table 3). The attractive interaction between the π - clouds of the aromatic moieties in parallel or face-to-face orientation is known as a π -π interaction [136,188,202]. The occurrence of pi - pi bonding usually happens between benzene rings present on the surface of graphene family nanoparticles and the double bonds between carbon atoms or existing benzene rings in the molecules of organic matter. Carbon atoms in carbon nanotubes have a π electron orbit directed perpendicularly to the surface of carbon nanotubes [203]. However, there could be π – π interactions between carbon nanotubes and those organic compounds (e.g. PBDEs) containing π electrons and benzene rings or $C = C$ double bonds. They have been identified by experimental data [204–206], Raman band [207], NMRS (nuclear magnetic resonance spectra) [208], MDS (molecular dynamic simulations) [209–211] and FTIR (Fourier transform infrared spectra) [211].

For instance, the π - π interaction plays a significant role in PBDEs' adsorption on graphene surface [86]. Nuerla et al. [143] reported the effects of substituent position on the interactions between PBDEs/PCBs and DOM (Table 3) by an equilibrium dialysis experiment, and quantum chemical and molecular docking calculations. It was observed that substituent positions (ortho and non-ortho substitutes) had a significant role in the π - π binding affinities of organic pollutants with DOM. Also, n - π bonding takes place between graphene family nanoparticles electron depleted sites and n - electron donors of the organic composites comprising nitrogen or oxygen atoms through lone electron pairs [212]. Graphene family nanoparticles aid as an e^- acceptor for the adsorption of anions, such as Cl^- and F^-, which can lead to the foundation of anion - π interactions [213]. Graphene family nanoparticles π electrons and easily protonated amino acid groups may establish cation - π bonding [25]. X. Li et al. [195] synthesized a nanocomposite called PVP@CNTs-Cu_2O for the removal of persistent organic pollutants through adsorption. It has been reported that the adsorption of TBBPA on the nanocomposite could be due to π - π bonding interaction under acidic conditions [196,197].

A sigmatropic shift of bromine atoms has been reported in the degradation process of PBDEs without representing the reshuffle of π system arrangements [214,215]. Debromination of PBDEs has also been studied. The size of one of the C-Br bonds in the anionic BDE congeners at a specific position is longer (0.6-0.9 Å) than the corresponding neutral BDE compounds. It shows weakening of the bond strength which is broken or cleaved when electrons are added from the zerovalent iron nanoparticles in the reductive system. This behavior of bond cleavage indicates the sign of π*–σ* orbital mixing [216–218]. Sheng et al. [219] reported photo-reduction of PBDEs (e.g. BDE-209) on graphene in aqueous media. It has been reported that the π–π interactions between π orbital of the graphene and the aromatic ring of PBDEs (e.g.

BDE-209) are responsible for the photo-induced electron transfer in the water system and lead to the degradation of PBDEs (e.g. BDE-209).

3.1.7 Cation bridging

The adsorption of similarly charged surfactants is unusual. However, the presence of multivalent ions of opposite charge at the surface and surfactants could enhance adsorption, attributed to the so-called “bridging” effect. Simply, the bridging effect or cation bridging is the bridging of an anionic surfactant onto the anionic surfaces by addition of divalent cations [220]. Once the released ENPs get entered into the water systems containing organic pollutants (e.g PBDEs), they can be coated with PBDEs. This could lead to the occurrence of cation bridging of layered ENPs or between ENPs and PBDEs with the assistance of metal ions present in wastewaters. Di-valent or multi-valent metal ions (Ca^{2+} and Ba^{2+} etc) or other cations have reportedly bridged oxygen-comprising functional groups ($-\mathrm{COOH}$ and $-\mathrm{OH}$) [136,221,222].

Cation bridging is associated with cations concentration [223]. Heavier divalent cations, such as Ca^{2+}, Ba^{2+} and Sr^{2+}could participate in bridging, but on the other hand, some multivalent cations like Fe^{3+}, $\mathrm{Al}^{3+}$and Mg^{2+} have not shown bridging behavior [136,223,224]. Nonetheless it is quite possible that heavier divalent ions (Ca^{2+}, Ba^{2+} and Sr^{2+}) could bind to hydroxylated ($-\mathrm{OH}$) and methoxylated ($-\mathrm{OMe}$) PBDEs and other PBDEs in wastewaters and sediments [225], resulting in cation bridging. Similar cation bridging could occur between silanol groups [226] and Ca^{2+} and Mg^{2+} in wastewaters. The bridging efficacy is also exaggerated by the extent and orientation of oxygen-containing functional groups present in surfactants. Overall, cation bridging increases adsorption and aggregation by attractive forces [136,137,223]. T. Wang et al. [198] documented PBDEs’ adsorption in the surficial surfactant components (e.g. Fe oxides, Mn oxides organic matter and residues). It was revealed that the cation exchange could occur in the alliance of iron oxides with organic matter in the adsorption of PBDEs.

3.1.8 Ligand exchanging

Ligand exchange can take place between hydroxylated ($-\mathrm{OH}$) and methoxylated ($-\mathrm{OMe}$) PBDEs and hydroxyl groups on ENPs surfaces in wastewaters and sediments [136,137,223,225,227]. Ligand exchange should also be considered as a portion of the Lewis acid base-base concept, such as metal ion interchange [188]. Generally, there are three basic steps involved in adsorption that end up as ligand exchange: firstly, protonation of surface -OH groups of engineered nanoparticles allows them to remain more readily interchangeable; secondly, the complication of protonated surface -OH groups; and thirdly, the ligand exchange, e.g., existence of condensation reactions [228]. It was reported that sorption instigated by the ligand exchange is frequently irreparable because of large extent of binding energy, and it could also cause some degree of corrosion of Cu NPs through the release of copper ions into solution [136,137]. However, the interaction mechanisms of PBDEs with ENPs would be influenced by many variables, for instance, molecules' size, steric hindrance, surface area and surface properties of ENPs, presence of other organic-inorganic contaminants, pH, ionic strength, presence of anions and cations, aggregation, disaggregation, sedimentation and deposition of ENPs. Wei et al. [22] reported the ligand assisted debromination of PBDE (e.g. BDE-47) based on a metallic Ni catalytic system. Triethylamine was used as a hydrogen transfer source (surface ligand of Ni) in the debromination process.

3.2 Effect of ENPs on the toxicity of BFRs (PBDEs) and human health

Abiotic and biotic processes can alter the properties of parental BFR compounds after their release and interactions with other compounds especially ENPs in terms of their fate and behavior, mobility and toxicity. Subsequently, the environmental modified compounds could be more or less toxic to human, plants, wild and marine lives compared to their original compounds. For instance, different concentrations of PBDEs (i.e. BDE-209) alone and with the co-occurrence of the TiO_2-NPs were exposed to the zebrafish larvae in their developing stage. The results revealed that both the bioavailability and metabolism of BDE-209 were enhanced in the presence of TiO_2-NPs (co-exposure) compared to alone and also increased the rate of disruption of thyroid endocrine system [229]. Reductive debromination of TBBP-A in the presence of microbes and Pd/Fe NPs has revealed an absolute potential for the detoxification of TBBP-A. The presence of Pd/Fe NPs further improved the respiratory metabolic ventures [230].

3.2.1 Epigenetic and mitochondrial effects

According to epidemiological studies, human health is being affected by the sustained brominated flame retardants inside the treated water from conventional WWTPs [6,7,231]. Alterations in thyroid hormone homeostasis, reduced children growth, PBDEs-produced epigenetic effects (DNA methylation), cryptorchidism and neuro developmental disorders are the major effects on human health [2,28,232–235]. On the other hand, studies have also reported that oxidative stress in the cells could occur due to ENPs (e.g. Ag, Cd-Se, Fe, QDs, TiO2, ZnO and ZnS) [235–239]. PBDEs could impact on the biological mechanisms such as calcium signalling (Ca^{2+} to communicate and drive intracellular processes) disruption, intrusion with thyroid hormone homeostasis and cellular toxicity due to mitochondrial disruption and the generation of reactive oxygen species (ROS) and DNA damage in some cases as well [240–242]. The release of intracellular calcium (an oxidative stress response) could affect mitochondrial anxiety and perturbation [243]. Studies revealed that the released ENPs ions such as, Fe^{2+} and Ag^{+} could react with produced H_2O_2 in the mitochondria or could interact with dissolved oxygen to generate reactive oxygen species (e.g.OH°, $O_2^{-\cdot}$ or FeO^{2+})[239244]. Meerts et al [245] reported the potent interactions of BFRs (e.g. PBDEs, PBP, TBBPA) with human transthyretin in Vitro and revealed that BFRs are very potent competitors for T_4 (thyroid hormone thyroxine) binding and may influence the thyroid hormones functions.

3.2.2 Endocytosis

Once the engineered nanoparticles alone or coated with PBDEs passed through the extracellular fluid and come into contact with the internal cells, the cells could be internalized by the ENPs. Endocytosis and penetration are internalization mechanisms [136,246]. It is reported that the small graphene-family nanoparticles agglomerates ($\leq 500\ nm$) mostly internalized via endocytosis and on the other hand, large aggregates ($\geq 5\mu m$) are internalized through phagocytosis [247]. The intrinsic characteristics of ENPs, such as hydrophobicity, cationic charge and the surface roughness, generate non-specific binding forces on the surface of ENPs and ultimately assist them to penetrate directly into the cell membrane [248]. This process differs from endocytosis and causes direct physical damage which comes from a particular receptor-ligand interaction [136,248]. There could be a strong binding of ENPs with receptors or Y-shaped molecules on a cell membrane due to surface ligands and could urge to receptor-mediated endocytosis, known as a particular biological mechanism for cellular uptake [136,248,249]. Membrane surface could be wrapped by contacted ENPs lead to endocytosis by neighbouring vesicles. Some cationic nanoparticles could flow into an acidified lysosomal compartment, and the unsaturated amino groups would entirely cut off from the protons given by the v-ATPase (proton pump), which prevents the pump effect and results in the retention of one chlorine ion and one water molecule per proton. Consequently, the nanoparticles are deposited in the cytoplasm, and the lysosomal content spills owing to lysosomal swelling and rupture [136,248].

4. Conclusions and outlook

Brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs), have been detected in various environmental samples globally. Understanding their fate and behavior is crucial for risk assessments for ecological receptors and human health, which are also influenced by the presence of engineered nanoparticles (ENPs). The co-presence of ENPs and BFRs has been reported in water from wastewater treatment plants (WWTPs) and in natural systems, but there is a lack of solid data on their interactions that may influence their fate and behavior. In this review, the mechanisms of interactions of typical ENPs with major BFRs of concern (e.g. PBDEs) are summarized, considering the dissolution, adsorption, aggregation, sedimentation and transformation processes. The major mechanisms include physical and chemical interactions.

There are knowledge gaps that need to be addressed so that we fully understand the reaction mechanisms between ENPs and BFRs (e.g., PBDEs). It is important for addressing the relevant risk assessment and modifying the conventional WWTPs to achieve appropriate safety guidelines. Further research is required to explore the complex mechanisms when ENPs and BFRs interact with each other and their diverse environmental impacts by considering the following issues:

1) The surface of the ENPs is being coated by the BFRs compounds present in the environment by various interactions. The modified surface chemistry of the BFRs-coated ENPs assists the slowdown of aggregation or even possibly induces the disaggregation and ultimately hinders their (ENPs) sedimentation and deposition. In turn it encourages their mobility in the surface of porous media. More studies are required to examine the surface coating phenomena of various ENPs (especially nAg, CeO_2, nC_{60} and ZnO) with BFRs and their transformation pathways, fate and behavior, bio-uptake and toxicity.
2) Identification and quantification of functional groups are required in environmental conditions by considering environmental parameters, once ENPs and BFRs interact in miscellaneous contamination. This is also important to understand the surface and structural morphology of ENPs aggregates and BFRs coating thickness in environmental media.
3) The role of BFRs in the colloid aging of ENPs at environmental conditions requires further investigations.
4) There is lack of investigations on the interaction mechanisms between “novel” BFRs and the emerging ENPs such as quantum dots, carbon dots and CNTs by applying advanced analytical techniques.

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Author contributions

Anwar Ul Haq Khan: Methodology, Writing - original draft. **Yanju Liu:** Conceptualization, Visualization, Writing - review & editing. **Ravi Naidu:** Supervision, Funding acquisition, Writing - review & editing. **Raja Dharmarajan:** Writing - review & editing. **Cheng Fang:** Writing - review & editing. **Hokyong Shon:** Writing - review & editing.

Conflicts of interest

There is no financial and/or personal conflicts of interest among the authors.

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