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REVIEW

Advances in photo-catalysis approach for the removal of toxic personal care product in aqueous environment

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Abstract

Removal of personal care products (PCPs) has become one of the challenging aspects around the globe. From the last few decades, it has been introduced as one of the emerging pollutants to the environment that affects directly or indirectly our ecosystem mainly aqueous environment. From biodegradation to photo-degradation mechanism, there are different categories of treatment methods, while the priority is based upon being cheaper, effective, reliable, environmental and economically friendly that should be compatible to water chemistry. Currently, photo-catalysis is considered as one of the most reliable and efficient non-conservative technologies for the degradation of PCPs industrial effluents from the aqueous environment. A recent development of photo-catalysis technology for the removal of PCPs gives efficient performance by using carbonaceous TiO_2 composites. By using hybrid nature of photo-catalyst, one can achieve suitably high and attractive efficiency with comparable low cost. In this review article, the different photo-catalysis mechanism while moving from non-photo-catalysis to photo-catalysis approach and its practical application for the removal efficiency of various polluting agents have been discussed. A critical evaluation on the various parameters for this approach is highlighted. Future perspective refers to the need for coupling of different semiconducting nano-materials with photo-catalysis that could yield higher efficiency than those of previous one. This facilitates further insight into photo-catalysis approach for the efficient degradation of PCPs to ensure healthy aqueous environment, and some points regarding fate of PCPs should be discussed in future perspective.

Keywords PCPs · Emerging pollutant · Chemical by-products · Aqueous environment · Photo-catalysis · Photo-catalyst

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1 Introduction

Personal care products are being extensively used for the enhancement of personal beauty and to meet the hygiene conditions for cleanliness including cosmetics, sun blocks, hair products, fragrances, body moisturizers, preservatives, nail polishes and various facial products. There are different pathways to degrade PCPs to the aqua environment. The ingredients in PCPs including heavy metals may be toxic for human health such as dysfunctioning of various organs, CNS, respiratory system and also cause cancer cells. Removal of these PCPs in aqueous environment on domestic as well as industrial scales needs proper treatment because these are organic pollutants that persisted in our environment to various ecosystems and thus hazardous to diversity of life (Freyria et al. 2018; Awfa et al. 2018; Siti Zulaikha et al. 2015; Tahir et al. 2019a). These have the potential to accumulate in plants by translocation mechanism (Wu et al. 2016). The major cause of contaminated aqueous environment is due to secondary effluents from wastewater treatment plants (WWTPs) as these plants are not very suitable for the removal of PCPs (Paucar et al. 2019). Studies showed that the contamination of these PCPs in aqueous environment (including surface water and groundwater) may be hazardous to both human and aquatic organisms because they include chemicals such as antibiotics, antiseptics, anti-inflammatory, fragrances, insect repellent, DEET (N,N diethyltoluamide), disinfectants, cosmetics, sun-screens (UV filters) while antiseptics, fragrances, insect repellent detected mainly in surface water and many other organic chemicals in ground water as well as surface water are very first time observed in Italy (Sui et al. 2015; Meffe and de Bustamante 2014). The treatment plants for wastewater (contain largest amount of PCPs) and drinking water are not an efficient one to remove precipitates of PCPs completely from water (Snyder et al. 2003; Montes-Grajales et al. 2017). After consumption, the PCPs are released from manufacturing sites to water surface (either through sewage water, livestock breeding or other means) through which when enters the terrestrial ecosystem through irrigation puts negative impact on the environment. Concentration of PCPs compounds is found larger in surface water (river, lakes) than in ground water (Montes-Grajales et al. 2017; Chen et al. 2018). Emerging contaminants and their contaminants range from ng/L to µg/L of few hundred folds (Ahmed et al. 2017). In 1999, it was pointed out that from all over the polluting reagents infused to the aquatic ecosystem, PPCPs (pharmaceutical and personal care products) were the major ignoring pollutants that may lead to the various diseases and exposure of these PPCPs acts as a chemo-sensitizer for aquatic organisms need to be studied. Although exposure of PCPs to life is overall hazardous, aquatic organisms are more susceptible to PCPs than non-aquatic. From the sensitive chemical analysis, it was shown that PPCPs being persistent organic and polar pollutant could not be easily degraded by conventional methods (Daughton and Ternes 1999). In 2002, traces of PCPs have been detected in natural ecosystem which persists for short to long terms in the environment. Chemicals used in PCPs are bioactive reagents that have particular pathway to interact with the target including humans. From last few years, a critical assessment of prioritized approaches, risk, fate exposure pathways and occurrence of PCPs has been done. Different approaches/models have been mentioned to identify the major issues regarding the PCPs in aqua as well as in terrestrial ecosystem. The several inter-related questions arise regarding, for different organisms, how exposure pathway to PCPs varies from region to region. Effect of availability of ionizable and non-ionizable chemicals in PCPs to the life cycle of organisms (including human) through food chain and food web has been evaluated by many researchers. Identification of the most vulnerable specie due to interaction with the harm of PCPs and its (PCPs) link to various ecological end points that are mortality, growth and reproduction of vertebrates (fishes) and invertebrates have been observed (Boxall et al. 2012). In 2003, US laboratory conducted an experiment to demonstrate the effect of mainly three PPCPs including antibiotic, surfactant and antimicrobial chemicals in stream ecology. The results showed that there exists no effect of treatment process during exponential growth phase of algal community, but increasing the concentration of all these three chemical reagents has a potential impact on the improper functioning of fresh algal bloom that disrupts the capacity of nutrients and natural structure of food web in aqueous medium (Wilson et al. 2003). In 2015, the reported literature suggested that samples from different countries reveal that salicylic acid, carbamazepine and β-blocker are the most obvious compounds in drinking water (Wang et al. 2017).

Recently, it has been revealed that organic compounds in PCPs induce hormonal imbalance, disorderness of reproductive and endocrine system and various physiological effects to human body even at low concentration (Montes-Grajales et al. 2017; Saxe et al. 2018). In 2017, from various analytical methods, ten most prevailing compounds were identified and listed that have a potential to risk for aquatic life in order to discuss the attitude of PCPs and its fate for the aqueous environment. The PCPs may be categorized as persistent and pseudo-persistent bioactive metabolites. Pseudo-persistent compound continuously released into the environment and regulated by biodegradation and photo-degradation thus potentially are more persistent in the environment than persistent one (Pedrouzo et al. 2011). The persistency of PCPs to environment may induce acute or chronic diseases to aquatic life (Saravanan et al. 2017). Toxicity of some pharmaceutical (persistent) bioactive compounds suggested that these are target specific, but their evolutionary study showed that these would activate in non-target specie (particularly fishes), thus leading to interdisciplinary field, ecotoxicology. The study illustrated the calculated bioaccumulation factor for gold fish, beaver tail fairy shrimp (scientific name: *Thamnocephalus platyurus*) for freshwater green micro-alga and for different categories of PCPs in many different organisms. For the detection and quantification of PCPs in wastewater, chromatographic techniques were employed (Pedrouzo et al. 2011). Merely the detection of PCPs in aquatic organisms is not the part of concern, but their cumulative effect in aquatic organisms plays a significant role as these affects the most regulatory system, i.e., endocrine system and homeostasis. The individual effect of PCPs has no importance; rather, their mixture leaves an adverse effect on aquatic organisms. Some chemical compounds transform into daughter products after photo-degradation which induces more toxicity than their parent one (antibiotic and naproxen), while others produce different toxicities at different pH levels. In 2016, carrot cell culture was used as a tool for the tailoring of metabolism of various PPCPs. The study revealed very slow metabolic rate of carbamazepine and only a small portion of carbamazepine metabolized, while $>95\%$ was accumulated in the aqueous culture (Wu et al. 2016). Naproxen and ibuprofen were associated with malfunctioning of central nervous system (CNS) (Hoppmann et al. 1991). Formaldehyde is present in most moisturizing creams and lotions whose toxicity and negative impacts on human health are not defined yet (Siti Zulaikha et al. 2015). Carbamazepine, ibuprofen, diclofenac are included in priority ECs in PPCPs (Archer et al. 2017).

Serotonin 5-HT is signaling controlling compound in aquatic organisms, targeted by pharmaceutical bioactive compounds (at low dose), and thus alters the reproduction, metabolism and muscles locomotion. Persistence of ten pharmaceutical compounds was distinguished in a given water samples, from low to high on the basis of their dissipation time (Ebele et al. 2017). Diclofenac—the most obvious compound in surface water—accumulates in tissues of fishes and thus is dangerous to aquatic life (Hashim 2016). Some

PPCPs such as carbamazepine are more persistent in sediments than in wastewater (Ebele et al. 2017). The contamination of PCPs in environment is shown in Fig. 1. There are several pathways through which PCPs persist in our environment such as from dietary intake-when agricultural land is treated with wastewater and solid biowastes, it transported to ground water which then used by the human and animals for drinking purposes. Naproxen, carbamazepine, caffeine and other organic polluting agents were found in wastewater of concentration greater than 80 in South Korea (Kim et al. 2007).

In this review, the various photo-catalytic and non-photo-catalytic approaches for the efficient removal of personal care products from aqueous medium along its efficiency and sensitive contaminants in the form table have been presented in detail. The graph in Fig. 2 indicates it as a hot area to study the removal of PCPs. The graphical presentation of statistical data based upon the removal of PCPs published annually along with significant approaches is mentioned, which is not discussed earlier.

2 Methods for the removal of PCPs in environment

As PCPs became an important part of our life, but emerging contaminants (EC)—effluents of wastewater treatment plant (WWTP)—should be regulated otherwise it may induce an adverse effect severe illness to human as well as aquatic life, is an emerging concern of the modern era (Ahmed et al. 2017). As conventional methods are not an effective one to remove all the contaminants from WWTP because of organic pollutants and suspension of solid materials. Many conventional methods including microbial

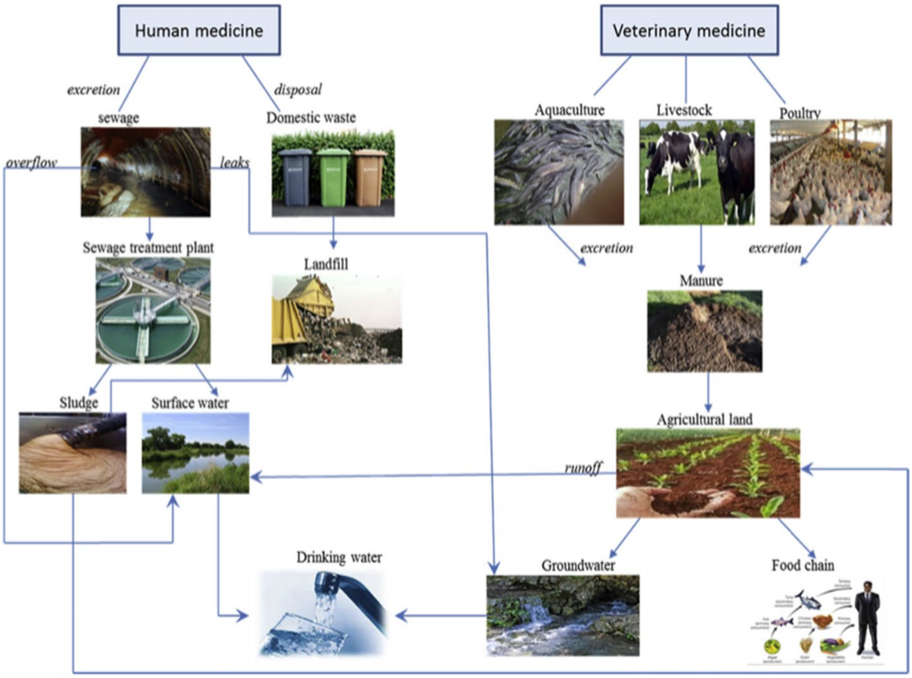

Fig. 1 Contamination of PCPs in the environment including aqueous environment (Ebele et al. 2017)

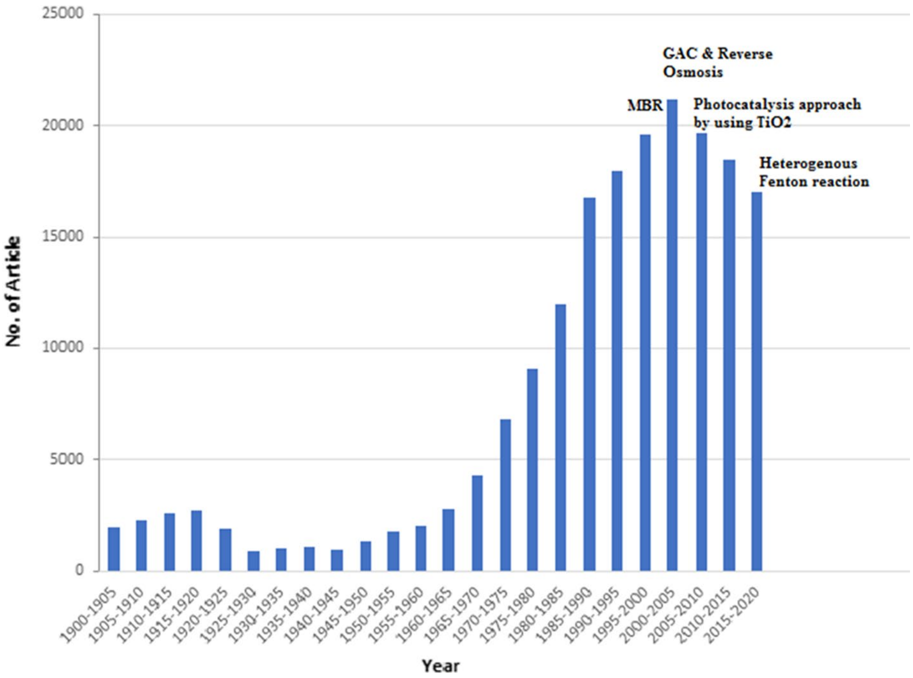

Fig. 2 The number of research articles published yearly based upon "Removal of PCPs." (Data received from https://scholar.google.com.pk/, accessed on December 03, 2018)

degradation, Nano filtration, reverse osmosis, membrane bioreactor (MBR) are no more viable. Ozonation, chlorination, chlramination, GAC biofiltration are all conventional-analytical methods to remove specific target contaminants (Lin et al. 2011; Daghrir et al. 2012). There are many approaches for the degradation of PCPs from the environment such as transformation approach, biodegradation and photo-degradation. Each degradation approach has its own consequences and results that behave differently to the environment, and their efficiency depends upon various sub-parameters mainly temperature, loading rate, aerobic and anaerobic environmental conditions and initial concentration of contaminants. Biodegradation is suitable for the removal of polar organic contaminants (Chen et al. 2018). Biodegradation being less toxic and environmental friendly involves the microbial growth on PCPs substrate and thus leads to the removal of PCPs. The removal efficiency of various biodegradation compounds increases at suitably at high temperature than in low temperature; thus, the seasonal condition affects the biodegradation mechanism. In this mechanism, some compounds are more degradable, while others are refractory (Tahir et al. 2019b). For example, salicylic acid, caffeine, methyl dihydrojasmonate galaxolide and tonalid have high removal efficiency in warm season, while the study reveals that testosterone is more degradable than 17β-estradiol hormone. Some other compounds such as atrazine, carbamazepine cannot be degraded by microbial activity (Bui et al. 2018; Hena and Znad 2018). These microorganisms act as a bioindicator for the envisage of health of the ecosystem. Both aerobic and anaerobic environments have their own characteristic features for the removal of selective organic contaminants; for example, aerobic condition is favorable for the removal of bisphenol A and ibuprofen, and anaerobic environment is suitable for the degradation of naproxen and diclofenac by 93% in dissolved oxygen concentration of 0.5 mg/L. The anaerobic micro-bacteria are more susceptible to carbamazepine than aerobic-organisms. When the concentration of these PPCPs increases, it might inhibit microbial activities and thus limits the biodegradation approach (Bui et al. 2018). In microbial degradation, one cannot tag for the efficiency of this mechanism. This method gives high efficiency of 79–94% for naproxen removal and moderate efficiency for sulphamethoxazole, acetaminophen, antipyrine and crotamiton, while it results in very low removal efficiency for carbamazepine (2–3%). Activated sludge is an environmentally friendly and efficient method for PPCPs with about 85% efficiency. Also it is efficient for PCPs, but it was detected that various pharmaceutical and *β*-blockers are not removed through this process (Ahmed et al. 2017). Adsorption mechanism—whose efficiency depends upon various factors thus having moderate efficiency for the removal of PPCPs—is further proceeded by biodegradation (Bui et al. 2018). Ozonation is the process in which degradation of ionizing and dissociated organic pollutants occurs (Paucar et al. 2019). By ozonation method, one can remove endocrine-disrupting compound—the major consequence of PCPs. Various micro-pollutant organic compounds can be degraded by ozonation (Paucar et al. 2019; Hey et al. 2014). As phthalates, parabens and DEET are majorly concerned with EDCs, estrogenic activities and dermal toxicity, respectively, they are frequently found in aqueous environment. Thus, the ozonation of these chemicals is a viable approach for the removal of selective organic compounds such as aromatic compounds, C=C bond, amino group because they are electron-rich compounds (Paucar et al. 2019). During ozonation of the selected PCPs in water (at pH = 7), O_3 being electrophilic in nature reacts with selected electron-rich compounds, while the decomposition of O_3 occurs in water into hydroxyl radical that reacts with all types of polluting agents and further liberates OH radical in this process (Tay et al. 2011). The kinetic study reveals that transformation of parabens that are electron-rich compound thus occurs by ozone, while transformation of phthalates and DEET occurs by OH radical. The removal of phthalates and DEET is > 92% for 3 mg/L of ozone concentration, whereas the removal of parabens is > 99% for 1 mg/L of ozone concentration (Tay et al. 2011). As O_3 highly reactive for electron-rich functional group, like found in C=C double bond such as carbamazepine and methoxy group such as naproxen, because they undergo electrophilic substitution, while organic compounds with electronegative groups and neutral compounds are not degraded by ozone (shield electrophilic substitution) (Paucar et al. 2019). Thus, it is revealed that carbamazepine is not efficiently degraded by biodegradation technique than being removed efficiently by ozonation. Although ozonation is efficient for the removal of personal care products from water matrices, it faces some limitations due to low mineralization, high energy consumptions and various intermediate oxidants (Gomes et al. 2017; Ahmed et al. 2017). Regeneration economics of granular activated carbon (GAC) tells us about this method which is expensive one. The (GAC) is efficient for the removal of > 99% surfactant from surface water, but the removal of chemical oxygen demand (COD) showed the inefficient removal of selective PCPs from surface water (Sui et al. 2015). Coupling of granular activated carbon (GAC) with slow sand filtration (SSF) gives better performance for the removal of tertiary wastes from wastewater treatment plants and is suitable economically (Freyria et al. 2018; Tahir et al. 2018a; Tahir and Sagir 2019). This GAC sandwiched with SSF is used for the treatment of pesticides. This method provides three operational characteristics: the first layer of sand called biolayer is used to filter biological contaminants; the second layer of GAC is used to purify water, and similarly the third layer removes other contaminants which are not removed by biolayer. This method is the most suitable one for the removal of tricloson, DEET, paracetamol and caffeine. The results showed that removal efficiency for caffeine, tricolson and paracetamol is overall 90%, but removal efficiency of DEET is less than 42%. Thus, this method is not effective for the selective removal of DEET that claimed to be effectively removed by anaerobic membrane bioreactor technique (Li et al. 2018). The GAC and post-chlorination are considered efficient method for the drinking water treatment that removes 100% cocaine but remain persisted to that environment and are not completely removed (Kim et al. 2007; Huerta-Fontela et al. 2008). The calcitrant contaminants that could not be removed by conventional methods can be governed by non-conventional tertiary treatments (Chen et al. 2018). Chlorination method is devoted for the removal of disinfectants and some aromatic PCPs. The removal efficiency ranges from -1.7 to 99% for acetaminophen to triclosan, respectively (Chen et al. 2018). Although aromatic PCPs may be removed by chlorination even in low concentration, but results show the detection of various chlorinated transformation products (TPs) that persist in the aqueous environment and prove to be more fatal. The bioaccumulation of these chlorinated derivatives has been evaluated so far. Chlorination, alphabet and other oxidation method confirm the presence of various transformation products (TPs) in the wastewater, and these TPs seems to be more toxic than their parent one (Chen et al. 2018). The chlorination method is not an effective one, but alphabet, UV, reverse osmosis nanofiltration are all effective and UV dose for disinfectants is not efficient for PPCPs (Paucar et al. 2019). Membrane technology such as nanofiltration, reverse osmosis gives similar results for the removal of organic micro-pollutants; however, reverse osmosis gives 90% results for organic removal from drinking water (Freyria et al. 2018; Abdelmelek et al. 2011), while nanofiltration is efficient only for the removal of macro-molecules (Freyria et al. 2018). Two pilot-scale membrane bioreactor (MBR) proved to be more efficient than conventional activated sludge (CAS) (Radjenović et al. 2009). The MBR is usually associated with WWTPs which is a technique used for the removal of micro-pollutants (range from ng/L to µg/L) from wastewater before entering the aquatic environment. Removal of micro-pollutants by MBR technology provides similar results as obtained by using conventional activated sludge (CAS) however; the former is more efficient as it gives 20–50% results than by using CAS methodology. The MBR technology provides efficient results for most persistent and poorly degraded compound like diclofenac and sulfophenyl carboxylates and not efficient for carbamazepine and EDTA compound (Hena and Znad 2018). Thus, carbamazepine is not removed by conventional treatment (Clara et al. 2005). One of the negative perspectives of MBR technology is the membrane fouling (Freyria et al. 2018). Although MBR is not an expensive one, cleaning process is very costly, and thus, MBR is not a feasible one for the removal of PCPs from aqueous culture (Hena and Znad 2018). Photo-catalysis approach by using UV/TiO_2 as a catalyst is more effective than individual UV approach (Ho et al. 2010). With the assistance of external potential applied to photo-catalytic method, a new photo-electrocatalytic approach was introduced in 2012. Charcoal—the low cost-effective thermal treatment technology—an alternate to conventional methods was introduced in order to remove sediments contamination of polychlorinated dibenzo-p-dioxin (PCDDs) and gas effluents with efficiency equal $>98\%$ (Zhao et al. 2013). Anaerobic biodegradation approach in an up-flow anaerobic sludge blanket reactor (UASB) with total chemical oxidation (total-COD) removal efficiency is 65% (Tawfik and ElBatrawy 2012). Bisphenol AP (BPAP) is endocrine-disrupting chemical can be removed and recovered ($\eta = 95\%$) by multi-walled carbon nano-tube (MWCNT) (Zhang et al. 2013). Anaerobic membrane bioreactor (AnMBR) has been used to remove 38 compounds that are from pharmaceutical, endocrine-disrupting chemicals in PCPs and pesticides. The results indicated that 9/38 removed with > 90% and 23/38 with 50% efficiency (Monsalvo et al. 2014). Carbon nano-tubes (CNTs) have been extensively used to remove both types of EDC and PPCPs of inorganic and organic nature (Jung et al. 2015). Molecular imprinting technology has been used for the analysis and removal of EC (Figueiredo et al. 2016). Selective removal of eleven emerging pollutants was demonstrated by using micellar-enhanced ultrafiltration (MEUF) (Acero et al. 2017). Nano-scale zero-valent iron (NZV) was used for the abatement of chlorinated PPCPs from ground water and wastewater (Freyria et al. 2018). Moving from conservative to non-conservative approach, an advanced oxidation technology so-called Fenton reaction has been introduced with high efficiency for the removal of organic contaminants from WWTP (Cheng et al. 2018). Advanced oxidation process (Fenton reaction) is the process devised to remove organic as well as inorganic compounds (ranging from ppm to ppb) from water by using OH radical (Wang et al. 2017). Fenton reaction is used for the removal of pharmaceuticals in wastewater. But it contains some drawbacks such as H_2O_2 consumption in water that needs to be eliminated before exposure to biodegradation (Freyria et al. 2018). It had been declared as an ineffective method toward all types of polluting agents (Ahmed et al. 2017).

Photolytic degradation is favorable for naproxen with 90% efficiency, but for some recalcitrant to some chemicals including 11-sulphamethoxazole (23% removal efficiency), sulfathiozole (44%), sulfamethazine (28%), trimethoprim (8%) and carbamazepine with photolytic degradation efficiency of (57–69)%. The researchers study that photolytic reaction is restricted to some organic matters, such as plant bed media which can be degraded by phyto-degradation or microbial degradation. This organic matter in surface water inhibits the removal of atrazine and testosterone. The studies showed that indirect photolysis when coupled with hydrolysis yields efficient results such as high removal efficiency of carbamazepine and paraxanthine. Similar to biodegradation, photolytic approach is also favorable under high temperature and intensity of light (Bui et al. 2018). Elbele et al. added that several PPCPs suggested that photo-catalysis is a major pathway for the removal of PCPs from surface water. Physiochemical nature of PCPs confirms that they are less volatile, having high polarity, and are hydrophilic compounds that may or may not be metabolized completely (Ebele et al. 2017). The slow mineralization in ozonation that yields intermediate toxic compounds can be speeded up by 85% with toxicity removing efficiency of 90% using photo-catalytic ozonation (Gomes et al. 2017).

3 Heterogeneous photo-catalytic reaction

From last few years, a mechanism that absorbs UV, visible and IR region of spectrum by using photo-catalytic semiconductor materials TiO_2 is known as heterogeneous photo-catalytic reaction (Ibhadon and Fitzpatrick 2013). This approach is suitable for the degradation of biological, organic as well as inorganic compounds. Heterogeneous photo-catalytic reaction undergoes phase transition of PPCPs, followed by absorption on the surface of photo-catalytic material where redox reaction takes place and finally products are removed in bulk fluid from surface (Awfa et al. 2018). The removal efficiency of photo-catalytic material depends upon type of catalyst used, water chemistry, wavelength and the intensity of incident light as well as pH and temperature (Freyria et al. 2018).

3.1 TiO_2-based photo-catalysis approach

TiO_2 as a photo-catalytic material is used widely because of its inertness, low cost, versatility, highly photochemical stability and reducing property (Freyria et al. 2018; Ibhadon and Fitzpatrick 2013; Hashim 2016). Anatase TiO_2 crystal is widely used most efficient catalytic material than other polymorphs with high surface area for efficient diffusion of product (Freyria et al. 2018; Ibhadon and Fitzpatrick 2013). The chemical property of TiO_2 announces that it is a highly oxidizing agent that oxidizes polluting agents and can be used as a homogeneous or heterogeneous catalyst in a given reaction (Ibhadon and Fitzpatrick 2013). The kinetic study of nano-wires of TiO_2 reveals that under UV illumination, oxidation of PPCPs occurs. In addition to TiO_2, ZnO, ZnS and $LeFeO_3$ may also be used as photo-catalytic materials (Ibhadon and Fitzpatrick 2013). ZnO and ZnS nano-materials are used for the removal of various pharmaceuticals with better results at particular time and pH (Freyria et al. 2018; Tahir et al. 2018b).

3.2 Efficiency of TiO_2-based photo-catalysis approach

The efficiency ratio for two different water samples was conducted: one for buffered electrolyte and other for wastewater effluents. The results showed that iopromide, acetaminophen, sulfamethoxazole and carbamazepine are more efficiently degraded in buffered solution than in wastewater, while naproxen is more efficiently removed by photolysis than by using UV/TiO_2 (Wang et al. 2017). The efficiency of photo-catalytic removal approach can be reduced by the presence of organic specie in the aqueous matrices. Thus, in addition to the above-mentioned parameters, the efficiency depends upon nature of the water matrices as well. The efficiency is majorly affected by pH (Freyria et al. 2018). Although the overall efficiency of heterogeneous photo-catalytic reaction is 99%, this approach faces some limitations as well (Awfa et al. 2018).

3.3 Advantages

Photo-catalytic reaction by using semiconductor doped material TiO_2 is highly efficient for the removal of diclofenac. The TiO_2 is highly oxidizing agent for the decomposition of organic PPCPs which are not degraded by conventional processes. The TiO_2 gives 68% removal efficiency for chlorhexidine digluconate (CHD). The reaction proceeds on slowly which ensured that there is no residue left in that aqueous medium. The major benefit of photo-catalysis over conventional treatments is that it does not cause energy consumptions (Freyria et al. 2018; Ibhadon and Fitzpatrick 2013).

3.4 Disadvantages/challenges

Barely TiO_2 photo-catalytic reaction may face many difficulties regarding poor recovering from water treatment due to its low adsorption capability (Awfa et al. 2018). Limitation of TiO_2 lies in the broad band gap that requires efficient energy for electron to move toward conduction band (Hashim 2016). The efficiency of doped semiconductor TiO_2 slows down in the visible part of the spectrum which turns the researchers to other hybrid techniques. Photo-catalysis approach may be limited to UV spectrum for wavelength greater than 400 nm. As sunlight consists of 5–8% UV spectrum, the remaining requirement is looking for artificial UV generator that needs high energy. This need can be fulfilled by using further catalytic approach. To overcome the difficulty faced by TiO_2 photo-catalysis approach, researchers found the new carbonaceous TiO_2 photo-catalytic material that exhibits improved efficient performance. By introducing carbonaceous material, one can enhance the optical property of TiO_2 photo-catalytic treatment. Moreover, carbonaceous material with bonding interaction shows better absorbing capability for wide range of spectrum. The carbonaceous photo-catalytic materials are introduced, namely activated carbon, carbon nano-tubes and graphene-based TiO_2 for the superior and most promising approach for the efficient removal of pharmaceutical and personal care products from aqueous environment. By using AC-TiO_2, one can reach the complete removal of pharmaceuticals (due to different functional groups attached on the surface of AC-TiO_2) by merely 180-min sunlight exposure that could not be achieved by using barely TiO_2. One of the main perspectives of AC-TiO_2 is the absorption in the long range of visible-light wavelength with efficiency remains constant in the whole treatment process. Although AC-TiO_2 is considered to be costly effective for the efficient removal of pharmaceutical and personal care products, there is no significant difference in the cost of both AC-TiO_2 and barely TiO_2. Moreover, due to inappropriate interaction between AC and TiO_2, there is no significant improvement in the diffusion reflectance spectrum by using AC-TiO_2 and barely TiO_2. So the emerging of most efficient, superior photo-catalytic material is the carbon nano-tubes (CNTs) TiO_2 that ensures the best hydrophobic photo-catalytic material and suitable interaction between TiO_2 and CNTs further reveals to be the most promising photo-catalytic material as compared to AC-TiO_2. The CNTs TiO_2 shows better efficiency for the removal of diclofenac photo-degradation whose efficiency can be further enhanced by using H_2O_2 and dissolved oxygen (Awfa et al. 2018; Ibhadon and Fitzpatrick 2013). A highly engineered approach, i.e., hybrid UV/TiO_2/O_3 technique, is reported in the literature for the removal of recalcitrant compounds which are not decomposed by biodegradation (Freyria et al. 2018). Nano-composites of CNTs TiO_2–SiO_2 are used for the proper interaction of CNTs and TiO_2 for the discouragement of the toxicity of treated water. The CNTs being electron-scavenger is declared to be superior for the photo-degradation of PPCPs for secondary wastewater effluents (Freyria et al. 2018; Awfa et al. 2018). The CNTs TiO_2-N is used for the efficient degradation of ibuprofen with the illumination of sunlight. The graphene-based CNTs with different functional groups attached on the surface have potentially higher adsorption capacity than CNTs. Graphene oxide (GO) (Tahir et al. 2018c) and reduced graphene oxide (rGO) (Tahir et al. 2019c) both are used efficiently for the treatment of water. The rGO is declared to be more stable than GO because of higher photo-catalytic activity and better electrical conductivity. There are various techniques for the synthesis of different composites of graphene-based photo-catalytic material. Each method reflects different photo-catalytic properties for its materials (Awfa et al. 2018; Ibhadon and Fitzpatrick 2013). Recently, an advanced photo-catalysis treatment has been introduced for the improved removal of diclofenac (DCF) from water surface. A density functional theory (DFT) modulation of carbon quantum dots (CQDs) anchored in graphite–carbon nitride (g-C_3N_4) with controlled band gap that showed obvious results than barely g-C_3N_4 (Liu et al. 2002).

Photo-catalysis by using TiO_2 is more stable and cost effective that should be hybrid with other semiconductor nano-material for the sake of efficient results (Hashim 2016). Different composites of carbonaceous material with TiO_2 focus majorly on two important factors: one is the adsorption capability, and other is the available sites for the suitable interaction between carbonaceous material and TiO_2 surface (Awfa et al. 2018).

The higher the contact between them, the more will be the photo-catalytic activity/ degradation. Meanwhile, both are the essential perspective for the efficient removal of about all types of PPCPs in aqueous matrices. Economically, AC-TiO_2 has superiority over other composites because it is cost effective, whereas having less number of interacting sites limits its value, while graphene-based TiO_2 having most effective number of interacting sites on its surface gives more adsorption to visible spectrum than other TiO_2 composites. But it is an expensive one and prone to more aggregate than CNTs and AC (Awfa et al. 2018).

Although WWTPs is responsible for the removal of contaminated agents from wastewater and drinking water, still there exists no designed treatment method to remove all the contaminated agents from aqueous environment. It is revealed from various studies that the removal approaches mentioned above are all selective. Some contaminants can be removed by one method, while other contaminants could be removed by any other approach. There are plenty of factors upon which various removal mechanisms depend such as operational loading rate, initial concentration, nature and structure of chemical, hydraulic retention time (HRT), effect of various system parameters, such as mass–volume ratio of the material used, pH and temperature. Some approaches are suitable to environmental conditions such as weather, climate and physical parameters. From the above-mentioned various degradation processes, the most recalcitrant compound is the carbamazepine that can only be efficiently removed by photo-degradation (Baena-Nogueras et al. 2017). Moreover, tricloson is also susceptible to photodegradation (Baena-Nogueras et al. 2017). One of the significant problems faced by researchers is that after degradation of polluting agents the material used for the degradation may itself become persistent; for example, H_2O_2 used in photo-catalysis is poisonous to environment. Photo-catalysis approach is a highly promising tertiary treatment which is being used as a non-conservative approach to remove PCPs effluents from an aqueous environment. The effect and efficiency of different removal techniques used by several researchers are given in Table 1. It is pointed that endocrine-disrupting compounds can be efficiently removed by MBR technology, GAC, hybrid ozonation and UV photo-catalysis approach (Ahmed et al. 2017). By using hybrid mechanism, one can achieve highly refining, viable, visible, reliable and suitable approach to water chemistry that is feasible in the case of environmental (biotic and abiotic factors) and economic perspective under some operational conditions.

4 Category of personal care products

4.1 Nail polishes (phthalates)

Phthalates are used in wine, spirits, cosmetics, paints, synthetic coating, plastics. There are highly toxic at low concentration and very low soluble in water and can easily be transformed into ethanol containing products. They provide mechanical property, flexibility in plastics and resistance to corrosion to various substrates. The DBP and DEHP are found in high concentration in spirit (Chatonnet et al. 2014). Phthalates including, diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), diethyl hexyl phthalate are most commonly occurring into the environment (Chatonnet et al. 2014). The chemical structure of some common phthalates is shown in Fig. 3.

Table 1 The effects and efficiencies of different removal techniques reported in the literature

Removal techniques	Effective (for polluting agent)	Non-effective (for polluting agent including PPCPs)	Efficiency	References
Microbial degradation	Naproxen Triclosan	Carbamazepine	79–94% for naproxen 2–3% for carbamazepine, triclosan (95% in 5 days)	Bui et al. (2018), Baena-Nogueras et al. (2017)
Activated sludge	PPCPs mainly PCPs	Various pharmaceutical and β -blockers	Overall 85% efficiency	Ahmed et al. (2017)
Ozonation	Electron-rich functional group (C=C bond, methoxy group, naproxen, carbamazepine, etc.)	Electronegative groups (fluoro, nitro, carboxyl groups, etc.)	> 92% efficiency for phthalates and DEET for 3 mg/L ozone doses and > 99% efficiency for parabens for 1 mg/L ozone doses	Tay et al. (2011)
GAC sandwiched with SSF	Tricolson, paracetamol, caffeine	DEET	90% overall efficiency for triclo-son, paracetamol and caffeine and 42% for DEET	Li et al. (2018)
Chlorination	Disinfectants and aromatic PCPs	Acetaminophen and chlorinated derivatives TPs	− 1.7% for acetaminophen to 99% for tricloson	Chen et al. (2018)
MBR	Diclofenac and sulfophenyl carboxylates	Carbamazepine and EDTA compound	20–50% overall whereas 28% for the removal of carbamazepine	Hena and Znad (2018)
Charcoal absorbent	For contaminated gas effluents, PCDDs/FF	Not to others	99.7% efficiency	Zhao et al. (2013)
Photolysis	Naproxen removal UV photolysis for β-blocker (Ahmed et al. 2017) diclofenac	Carbamazepine, sulfamethoxazole, sulfathiozole, sulfamethazine, trimethoprim and other organic carbon compounds	90% for naproxen, diclofenac (80%) 57–69% for carbamazepine, 23% for sulfamethoxazole, sulfathiozole (44%), sulfamethazine (28%), trimethoprim (8%)	Bui et al. (2018), Ahmed et al. (2017)
Photo-catalysis	Bisphenol A and progesterone		Overall 99% efficiency, bisphenol A and progesterone (with 100%)	Awfa et al. (2018), Ahmed et al. (2017)

Table 1 (continued)

Removal techniques	Effective (for polluting agent)	Non-effective (for polluting agent including PPCPs)	Efficiency	References
Photo-catalysis barely (UV/TiO_2)	Carbamazepine		Carbamazepine 98% removal efficiency	Awfa et al. (2018)
Photo-catalysis AC-TiO_2	Carbamazepine, Salicylic acid, diclofenac	Metoprolol	Carbamazepine (98% for 60 min) salicylic acid (60–80% for 180 min), metoprolol (50% for 120 min) metoprolol (20–60% for 300 min) diclofenac (40–85% for 180 min)	Awfa et al. (2018)
Photo-catalysis CNTs-TiO_2	Diclofenac, carbamazepine, caffeine	Bisphenol A	Bisphenol A (> 50% for 60-min irradiation), carbamazepine (> 95% for 60-min irradiation), caffeine (100% for 120/180-min irradiation)	Awfa et al. (2018)
Photo-catalysis GO-TiO_2	2-4-dichlorophenol	Nitrophenol	2-4-dichlorophenol (> 99% for 60 min exposure), nitrophenol (7–85% for 90 min)	Awfa et al. (2018)
Photo-catalysis rGO-TiO_2	Carbamazepine, sodium pentachloro-phenol	Carbamazepine	Carbamazepine,(99% for 90 min), carbamazepine,(10–54% for 180 min), sodium pentachlorophenol (> 99% for 60 min)	Awfa et al. (2018)

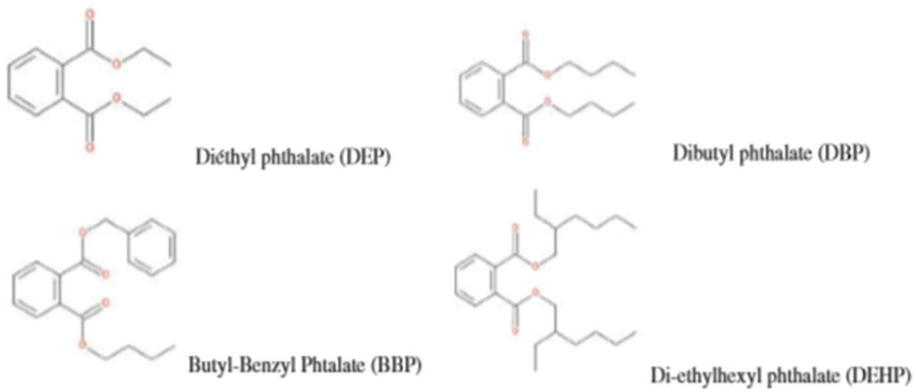

Fig. 3 Chemical structure of some common phthalates (Chatonnet et al. 2014)

4.1.1 Harmful effect on the environment

Phthalate, being the most obvious chemical in personal care products, has primarily highest concentration in nail polishes in the form of dibutyl phthalates (DBP) of about 90%. Dibutyl phthalates are forbidden currently by legislation (Guo and Kannan 2013; Huang et al. 2018; Sikka and Bartolome 2018). In 2018, a survey was conducted for the detection of different concentration of different phthalates compounds in different categories of nail polishes, and results suggested that those samples who are labeled as 3-free have low concentration of DEHP and those which are labeled as 5–13 free have high concentration of DEHP (Young et al. 2018). Probably, phthalates are known to be the most endocrine-disrupting chemical in human body that may harm fetus through placenta (Machtinger et al. 2018; Huang et al. 2018; Chatonnet et al. 2014). A research had been conducted to detect the concentration of phthalates metabolites and found to be in urine and placental samples (Machtinger et al. 2018). A recent research on different urine samples with $n=108$ also points out that the contamination of phthalates metabolites by comparing for different pre- and post-shift levels further analyzed the exposure and risk of phthalates. Risk of exposure to different compounds of phthalates (such as DEP, DBP, BBP and DEHP) for cosmetics and perfumes is higher in women than in men. Phthalates exposure doses (ED) and their risk are investigated for those sales women working in cosmetics and clothing stores. It was assumed that exposure of phthalates for women is primarily concerned with inhalation and men by the usage of PCPs. Results from different questionnaire approaches showed that sales clerks working in cosmetics department are more susceptible to ED; thus, accumulation of DEHP concentration is observed higher in them, whereas MEP and MEHP metabolized rapidly so did not accumulate in human body (Huang et al. 2018).

Risk summarized for phthalates considerably associated with hormones and regulatory systems such as homeostasis, thyroid system and reproductive system thus affects both mother and fetus as well (Huang et al. 2018; Sikka and Bartolome 2018). Phthalates affect reproductive system of both humans and animals especially to the rodents. Animal study of DEHP showed carcinogenic activity toward human (Chatonnet et al. 2014). Different routes for phthalates and its compounds exposure include inhalation and dermal contact (Huang et al. 2018; Sikka and Bartolome 2018). In the very recent study, it is found that phthalates have an adverse effect on marine ecosystem by conducting a 7-day-based experiment. Results showed that *pacificum* is more sensitive to these phthalates-based contaminants than phytoplankton having effect on photo-synthetic activity as well. It had been demonstrated that phthalates-based ester perturbs the endocrine system in human and also identified in ecosystem as well (M'Rabet et al. 2018; Paluselli et al. 2018). In 2013, a comprehensive research was conducted for 170 types of personal care products which are categorized as rinse-off leave-on and baby care products. The statistical data for the concentration (in µg/g of the product) of phthalates and parabens were carried out for these three categories of products. These chemicals, phthalates and parabens (about 60%), were found more in leave-on PCPs that include perfumes, skin tones and mainly in nail polishes. The frequent concentration of different classes of phthalates and parabens was found to be 1000 µg/g of the PCP. The exposure of daily intake of different groups of phthalates (DEP diethyl-phthalates, and DBP dibutyl phthalates) in different categories of PCPs to human skin was found more susceptible to adult female (Guo and Kannan 2013).

4.2 Deodorants (parabens)

The maximum exposure of human to parabens is through personal care products which are the ester of 4-hydroxybenzoic acid (Dornath et al. 2015; Giordano et al. 1999). Parabens are found in different categories of PCPs because these contain antimicrobial preservatives and define the shelf-life (period of validity) of the product (Guo and Kannan 2013; Tay et al. 2011; Dornath et al. 2015). These are extensively used in personal care products due to low cost, long chain of carbon that reveal effective antimicrobial activity, longevity, inertness toward active ingredients in products and high stability toward varying temperature and pH (Dornath et al. 2015). These are found in powder, foundation,

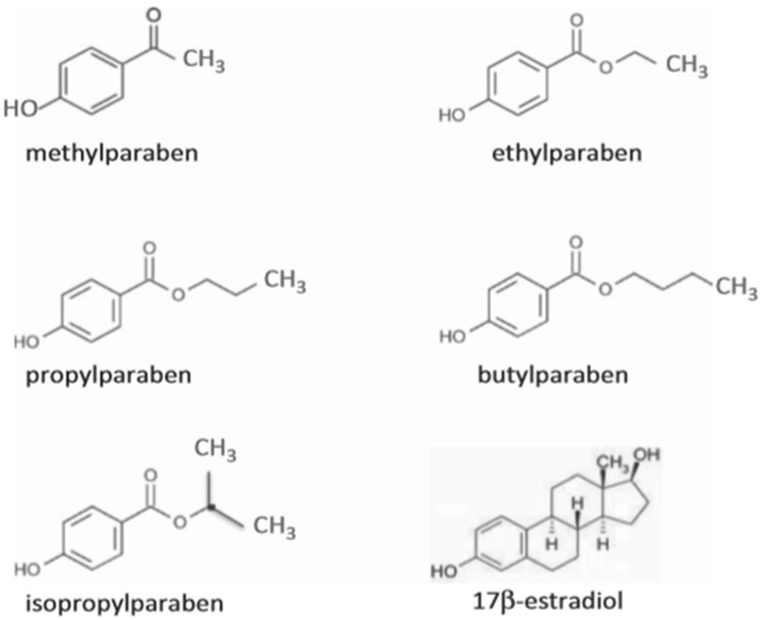

Fig. 4 Structure of parabens (with different functional groups attached) and estrogen (Karpuzoglu et al. 2013)

mascaras, lotions, sun blockers, deodorants, hair dyes and various hair products. (Dornath et al. 2015). Different chemical structure of parabens is similar to that of phthalates that depends upon the different functional groups attached and carbon catenation as presented in Fig. 4 (Dornath et al. 2015). Butyl-parabens (in hair conditioner), ethyl parabens (in make-up), benzyl parabens (in creams), isobutyl-parabens (shower gel), methyl parabens (in wet tissues) and many other including propyl parabens are the common ingredients in personal care products (Siti Zulaikha et al. 2015).

4.2.1 Harmful effects

In the USA, from different surveys it was concluded that more than 90% of the population is under the influence of phthalates and parabens (Guo and Kannan 2013). Researches showed that phthalates and parabens both are cost effective and less toxic that can be metabolized rapidly in hours whose constant exposure to human body tailored in breast milk, breast tissues, urine and in plasma. Exposure rate told that several reproductive disorders associated with malfunctioning of human sperm, endocrine disruption. Parabens are also cause of allergic reaction reported by authors (Guo and Kannan 2013; Karpuzoglu et al. 2013). Infants and toddlers are more susceptible to phthalates. The risk of susceptibility of infants and toddlers to parabens is calculated three times more than the susceptibility found for adult female to phthalates (Guo and Kannan 2013). Through various investigations, the studies showed that parabens alone are found to be in 17,000 different types of products whose exposure frequency to environment is high enough to cause adverse effect not only on the people with using parabens in their products but on those who do not use parabens in their product (Dornath et al. 2015). The exposure frequency to parabens resulting in estrogen level imbalance, improper functioning of endocrine system and prolong accumulation in body may affect healthy brain cells, emotional intelligence, immune system and various other social behaviors as well (Dornath et al. 2015; Karpuzoglu et al. 2013).

Results showed that parabens can cross the placenta and affect male-fetus sex organ in the womb of mother (Dornath et al. 2015). Parabens show estrogen-like function but not remarkably similar activity to 17β-estradiol and associated with the estrogen metabolism that may lead to breast cancer. Products applied on underarms may interact with estrogenic activity in the breast tissues and trigger breast cancer (Dornath et al. 2015), while breast cancer due to parabens is not recorded yet (Tay et al. 2011; Siti Zulaikha et al. 2015; Karpuzoglu et al. 2013). Parabens are safe to use up to 25% (Siti Zulaikha et al. 2015). Daily exposure doses (DEP) for these three PCPs are calculated by using two approaches: environmental monitoring approach and biomonitoring approach. The later one shows discrepancies for the estimation of DEP. The DEP is calculated by using the formula (Guo and Kannan 2013):

$$\mathrm{DED} = \frac{C_{\mathrm{PCPs}}M}{\mathrm{BW}} f1f2.$$

Methyl parabens are deeply absorbed into the body, while butyl-parabens are associated with reduction in the sperm production in male (Dornath et al. 2015). The chemical composition of personal care products showed that there are some other compounds that are coupled with the parabens activity, the most remarkable are alcohol and phthalates/tricolson inhibits the parabens metabolism and avails deep penetration of parabens into the skin, respectively (Dornath et al. 2015). In aquatic life, parabens cause the same adverse effect as in terrestrial life to human and wild life. Their hydrophobic nature makes them accumulate in sediments in aquatic ecosystem where they come into contact with bottom dwelling organisms, large fishes, male rainbow trout, daphnia and algae, etc. Small fishes are more susceptible to parabens due to their hydrophobic nature where the small concentration causes the similar results as high concentration in large fishes in aquatic matrices. Parabens are also responsible for the endocrine disruption in fishes and responsible for chronic toxicity (Dornath et al. 2015; Karpuzoglu et al. 2013; Lee et al. 2017). Methyl parabens are detected in surface water and sediments in India (Dornath et al. 2015; Karpuzoglu et al. 2013). MeP has been detected in marine ecosystem, especially in invertebrates and fishes (Xue et al. 2017). Acute and chronic effect of MeP on sexual specie has been analyzed (Comeche et al. 2017). Chemicals used in fragrances and in most preservatives usually induce skin allergic reactions of 30–40% (by fragrance) that affect immune system (Siti Zulaikha et al. 2015).

4.3 Oral care products (triclosan)

Triclosan is a halogenated aromatic hydrocarbon, with two different functional groups attached namely phenol and di-phenyl ether as given structure in Fig. 5. Similar to parabens, triclosan is regarded as one of the active ingredients used as an antimicrobial and disinfectant in various PCPs (Dornath et al. 2015; Ma et al. 2013; Hontela and Habibi 2013). It is most commonly used in rinse-off product such as orally products, in deodorants, hair care products, as well as in plastics. They are hydrophobic in nature and perform the same activity as thyroid gland of the human body (Dornath et al. 2015; Hontela and Habibi 2013; Park et al. 2016).

4.3.1 Harmful effect on the environment

Triclosan is usually used in leave-on products such as deodorants but remains to penetrate into the skin and causes allergic reactions. As found in rinse-off product, thus it usually remains in wastewater effluents, through which it contaminates the terrestrial ecosystem. These are found in 700 anti-bacterial products (Dornath et al. 2015; Hontela and Habibi 2013). Due to hydrophobic interactions, the triclosan interacts with fatty tissues of breast and passes to babies from breast milk. The study revealed that these are not regarded as toxic compounds, but their intermediate products may persist to the environment. It is recorded that triclosan can be degraded by WWTPs by 100% efficiency, but their daughter compounds such as methyl triclosan, dioxin, furans and polychlorinated biphenyl in wastewater as well as in aquatic system have been detected (Dornath et al. 2015). These intermediate compounds are more toxic than their parent one (Dornath et al. 2015). They can affect hormonal system such as thyroid, endocrine system, estrogen and testosterone (Hussien and Hamdi 2017; Wang and Tian 2015).

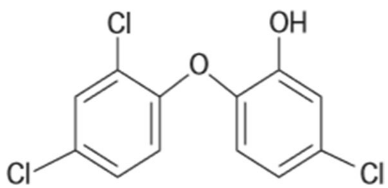

Fig. 5 Chemical structure of tricloson (Hontela and Habibi 2013)

Dioxin (toxic) can be formed by the photolysis of triclosan (non-toxic). Polychlorinated biphenyl is reportedly formed during the chlorination and photochemical reactions which is detected in wastewater and aquatic environment, respectively. Methyl triclosan occurs commonly in wastewater during WWTP that cannot be degraded by photo-degradation. Triclosan-being disinfectant used in rinse-off product such as detergents, soaps etc. when react with Cl-free radical present in tap-water hence chloroform formed which is however itself non-toxic but when interact with the active ingredients of chlorinated by-products may induce adverse physiological effect to human health. These are responsible for waterborne diseases (Dornath et al. 2015; Hontela and Habibi 2013). A study reported that it induces neurological effects in rats and apoptotic cell division (Park et al. 2016; Hill et al. 2018). In vitro and in vivo study on animals showed that they could cause biological (reproductive) adverse effect on human health (Yueh and Tukey 2016; Weatherly and Gosse 2017). Triclosan has potential negative impact on aquatic life (Hill et al. 2018). In aquatic matrices, fishes (fresh water/marine), snails, rainbow trout, mammals, amphibians, reptiles and especially algae and mosquito fish are markedly more susceptible to triclosan and methyl triclosan. Bioaccumulation of triclosan in marine mammals has been detected so far. The study shows fresh water organisms and invertebrates are less sensitive to triclosan than marine organisms and algae. The abnormality has a main concern to growth, reproduction, metabolism, regulatory system. The reduction in the sperm production occurs in mosquito fish. The adverse effect of triclosan depends upon type of specie, water chemistry, exposure frequency and concentration of contaminants (Horie et al. 2018; Hontela and Habibi 2013).

4.4 Fragrances

Fragrances are used in daily life such as in the form of perfumes, hair care products, baby care products, lotions, essential oils, air fresheners, detergents and as a flavor in bakery items. These are volatile and the organic chemical dispersed in the air (Siti Zulaikha et al. 2015; Steinemann 2018). From individual to industrial level, 27.8% of population are daily exposed to fragrances (Steinemann 2018). Allergy-causing chemical in fragrances include α-pinene, β-pinene, limonene, benzaldehyde, benzyl-alcohol, salicyl aldehyde, terpinolene,

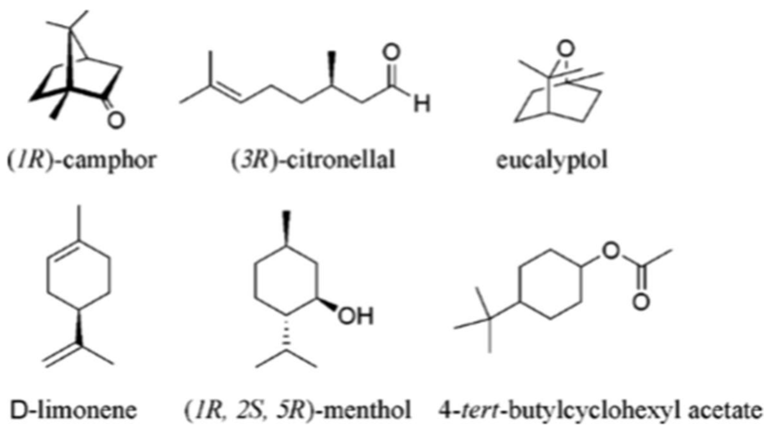

Fig. 6 Chemical structure of some common fragrances (Sansukchareampon et al. 2010)

linalool, menthol, α-terpinol, γ-terpineol, methyl salicylate and methyl 2-octynoate, etc. (Abedi et al. 2018). Some chemical (IR)-camphor, (3R)-citronellal, eucalyptol, D-limonene, (IR, 2S, 5R)-menthol and 4-tert-butylcyclohexyl acetate are mentioned with their chemical structure as shown in Fig. 6 (Sansukcharearnpon et al. 2010; Steinemann 2018).

4.4.1 Harmful effect on the environment

Chemical agents in fragrances are responsible for 30–45% of all the dermatological allergic reactions. The studies showed that these harmful chemicals may penetrate deep inside the skin by dermal contact and release into the blood stream. As a component of food, it might be taken in through ingestion and affects immune system and causes acute skin diseases, neurotic problems, memory losses, joint infections, heart variability, asthma problem, stomach diseases, headache and migraine (Siti Zulaikha et al. 2015; Sansukcharearnpon et al. 2010; Steinemann 2018). It is well reported that females are more exposed to adverse nature of chemical reagent used in fragrances, than male. In comparison, 34.7% US while 33% Australians are exposed to its adverse effects (Steinemann 2018). It is investigated that chemicals used in fragrances have negative impact on both male and female hormones that are testosterone and estrogen, respectively. It is studied that these may cause reduction of sperms in male, thus leading to infertility (Zellner et al. 2007; Sikka and Bartolome 2018). Various essential oils and their effect are associated with fertility, sperm production, testes morphology, reproduction system, etc. The synthetic musk such as nitro-musk is detected in breast milk which contains negative impact to reproduction (Sikka and Bartolome 2018). Various techniques have been used to remove fragrances musk from wastewater such as by ozonation and advanced oxidation, but no efficient results are founded (Ternes et al. 2003).

5 Conclusion and future perspective

Effluents from WWTPs to aquatic environment are hazardous to both human and aquatic life. These chemicals interact with the reproductive or growth hormone and are responsible for the endocrine disruption and abnormal attitude of the specie. Although there are many methods for the treatment of wastewater, significant results are not achieved yet. Some methods are efficient for some typical organic or inorganic contaminants, while others are devised for the removal of all types of contaminants of organic or inorganic nature.

1. There are many reviews for the removal of pharmaceutical, but for the degradation of mainly personal care products there is still a lot of space for researchers to work. Photo-catalysis approach considered as efficient, comprehensively focuses on the degradation of pharmaceutical.
2. There should be awareness on public level for the negative impacts of PCPs in our aquatic system. Various conservative approaches are cheap but not efficient one, so researcher should move toward non-conservative for economic support and environmental sustainability.
3. Photo-catalysis by using TiO_2 is more stable, but it needs further modification in its fabrication to activate at low-energy solar spectrum for the abatement of toxicity of personal care products.

4. Hybrid nature of photo-catalysis with various nano-materials is an efficient for the removal of all types of contaminants to some extent and their nano-particles after treatment are removed efficiently from aquatic system with no declaration of toxicological issues.
5. Various reagents used in PCPs and their by-products have no previous record for their individual as well as cumulative (to some extent) impact on marine ecosystem. Photo-catalysis approach for the removal of various PCPs such as fragrances is not recorded yet. There is no significant method for the removal of fragrances from wastewater.
6. Researchers should focus on the comprehensive report for the chemistry of these nano-particles (such as used in photo-catalysis) to water matrices after treatment process—a major research gap. Efficiency for the removal of various personal care products by different photo-catalysis approaches should be declared.
7. As gamma radiation is under the score of researcher to get efficient degradation of PPCPs, it is regarded as the combination of gamma rays with photo-catalysis that could be the promising and efficient one for all types of ECs, EDCs and mainly traces of PCPs in wastewater, fresh water and marine ecosystem as well.

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