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Phthalate pollution and remediation strategies: A review

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ABSTRACT

Phthalate esters (PAEs) are normally used as plasticizers and has potential to leach out from various polymeric materials. Their presence in different environmental matrices has become a significant concern, as they are endocrine disrupting compounds causing various reproductive, genetical, and developmental abnormalities. As a result, it is urgent to develop a robust technology that can mineralize these contaminants from the environment. This review focuses on origin and fate of PAEs in the environment, their exposure routes and health effects, and various remediation strategies from wastewater. The article largely focuses on in-depth understanding of different physicochemical, biological and advanced oxidation processes currently being used for the treatment of PAEs. In addition, based on the physicochemical properties of PAEs molecules, their adsorption interaction mechanisms with adsorbents are introduced. This review also explores the range of materials to be used as an adsorbent and photocatalyst and composite materials can enhance the performance by adsorption followed by mineralization. For large scale PAEs removal, semiconductor photocatalysis and integrated processes seems to be an effective technique for the removal and mineralization of PAEs. Finally, for scaling up the photocatalytic technology, parameters such as, improved reactor design, role of water matrix and economic aspects were discussed and future research directions on catalyst agglomeration, adsorbents design, modification, and synthesis are proposed. Therefore, from the techno-economic perspectives factors like, improving active sites and adsorption rate, self-cleaning catalyst surface, renewable light sources, radical scavenging by organic matter and catalyst recovery need to be addressed for transforming the process form '*lab*' to '*land*'.

1. Introduction

Phthalates or Phthalate esters (PAEs) are diesters of 1, 2-benzenedicarboxylic acid (Phthalic acid). It is one of the useful industrial chemicals and generally used as plasticizer to enhance the softness and workability of polymers by reducing its glass transition temperature (Staples et al., 1997; Jing et al., 2011; Li et al., 2020; Paluselli et al., 2019). Phthalates are also used in the manufacture of polymers, in which it is chemically bonded and do not easily leach out into the environment, but when used as plasticizers, they are physically bonded (Hahladakis et al., 2018; Yuan et al., 2008; Akhbarizadeh et al., 2020) hence, they easily come out into the environment (Chen et al., 2019; Eskandarpour and Sereshti, 2018). The Annual worldwide production of phthalates is about 6–8 million tons (Net et al., 2015; Guo et al., 2011). Moreover, in 2018 the Luo et al. estimated a growth of 1.3% in the global consumption of phthalate esters from 2017 to current year, 2022 (Luo et al., 2018a). Phthalates with high molecular weight, such as di-n-octyl phthalate (DOP) and di-(2-ethylhexyl) phthalate (DEHP) are commonly used in construction materials and furniture whereas phthalates with lower molecular weight such as dimethyl phthalate (DMP), diethyl phthalate (DEP), and dibutyl phthalate (DBP) are largely used in plastic containers, materials packaging, personal care products, solvents, adhesives, lubricants, coatings, and varnishes (Pang et al., 2021; Schettler et al., 2006). Thus, due to their extensive applications phthalate compounds became ubiquitous environmental pollutant. The physical and chemical properties of typical phthalate compounds can varies depending on the different alkyl chains present as represented in Fig. 1 (Johnson et al., 2011; Staples et al., 1997; Net et al., 2015). The physicochemical properties of phthalate esters are enlisted in Table 1. Phthalates are endocrine disrupting compounds as they mimic, compete, and disturb the functioning of hormones within the body (Chen et al., 2011; Huo et al., 2016; Li et al., 2016; Net et al., 2015).

In addition, phthalates show reproductive and genetic abnormalities in different living organisms (Careghini et al., 2015; Benjamin et al., 2017; Swan et al., 2005). Due to these toxicities, United States Environmental Protection Agency (USEPA) has declared six phthalate compounds, namely di-methyl phthalate (DMP), di-ethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di (2-ethylhexyl) phthalate (DEHP), di-

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Table 1
Physicochemical Properties of Phthalate Esters.

PAEs	CAS NO.	Mw (g/mol)	carbon atom per chain	Sw (mg/L)	Vp (Pa)	$logK_{OW}$	$logK_{OA}$	$logK_{AW}$	H ($Pa·m^3/mol$)	K_{oc} (L/kg) (Soil/Sediment)
dimethyl phthalate	131–11–3	194.2	1	5220	0.263	1.61	7.01	−5.40	$9.78 \times 10–3$	55–360
diethyl phthalate	84–66–2	222.2	2	591	6.48×10^{-2}	2.54	7.55	−5.01	$2.44 \times 10–2$	69–1726
diallyl phthalate	131–17–9	246.3	3	165	2.71×10^{-2}	3.11	7.87	−4.76	$4.28 \times 10–2$	
di-n-propyl phthalate	131–16–8	250.3	3	77	1.74×10^{-2}	3.40	8.04	−4.64	$5.69 \times 10–2$	
di-n-butyl phthalate	84–74–2	278.4	4	9.9	4.73×10^{-3}	4.27	8.54	−4.27	0.133	1375–14,900
diisobutyl phthalate	84–69–5	278.4	4	9.9	4.73×10^{-3}	4.27	8.54	−4.27	0.133	
di-n-pentyl phthalate	131–18–0	306.4	5	1.3	1.28×10^{-3}	5.12	9.03	−3.91	0.302	
butyl benzyl phthalate	85–68–7	312.4	4,6	3.8	2.49×10^{-3}	4.70	8.78	−4.08	0.205	9×10^3-17×10^3
di-n-hexyl phthalate	84–75–3	334.4	6	0.159	3.45×10^{-4}	6.00	9.53	−3.53	0.726	52600
butyl 2-ethylhexyl phthalate	85–69–8	334.4	4,8	0.385	5.37×10^{-4}	5.64	9.37	−3.73	0.466	
di-n-heptyl phthalate	41451–28–9	362.5	7	2.00×10^{-2}	9.33×10^{-5}	6.87	10.04	−3.17	1.69	
di (n-hexyl, n-octyl, n-decyl) phthalate	68–648–93–1	557	6,8,10	8.76×10^{-4}	1.31×10^{-5}	8.17	10.78	−2.61	6.05	
di(2-ethylhexyl) phthalate	117–81–7	390.6	8	2.49×10^{-3}	2.52×10^{-5}	7.73	10.53	−2.80	3.95	87420–51×10^4
di-n-octyl phthalate	117–84–0	390.6	8	2.49×10^{-3}	2.52×10^{-5}	7.73	10.53	−2.80	3.95	
diisooctyl phthalate	27554–26–3	390.6	8	2.49×10^{-3}	2.52×10^{-5}	7.73	10.53	−2.80	3.95	
diisononyl phthalate	28553–12–0	418.6	9	3.08×10^{-4}	6.81×10^{-6}	8.60	11.03	−2.43	9.26	
di-n-nonyl phthalate	84–76–4	418.6	9	3.08×10^{-4}	6.81×10^{-6}	8.60	11.03	−2.43	9.26	
di-n-decyl phthalate	84–75–5	446.7	10	3.08×10^{-4}	6.81×10^{-6}	8.60	11.03	−2.43	9.26	
diisodecyl phthalate	26761–40–0	446.7	10	3.08×10^{-4}	1.84×10^{-6}	9.46	11.52	−2.06	21.6	286×10^3
di (heptyl, nonyl, undecyl) phthalate	68515–42–4	557	7,9,11	3.08×10^{-4}	6.81×10^{-6}	8.60	11.03	−2.43	9.26	
diundecyl phthalate	3648–20–2	474.7	11	4.41×10^{-6}	4.97×10^{-7}	10.33	12.02	−1.69	50.5	
ditridecyl phthalate	119–06–2	530.8	13	7.00×10^{-8}	3.63×10^{-8}	12.06	13.01	−0.95	275	1.2×10^6

(CAS NO.: Chemical Abstracts Service Number, MW: Molecular Weight, Sw: Solubility, Vp: Vapour Pressure, K_{OW}: Octanol-water partitioning coefficient, K_{OA}: Octanol-air partitioning coefficient, K_{AW}: Air-water partitioning coefficient, H: Henry's constant, K_{OC}: Organic carbon-water partitioning coefficient).
Source: DOI: 10.1021/es505233b (Net et al., 2015, Environmental Science & Technology, 2015, 49, 4019-4035).

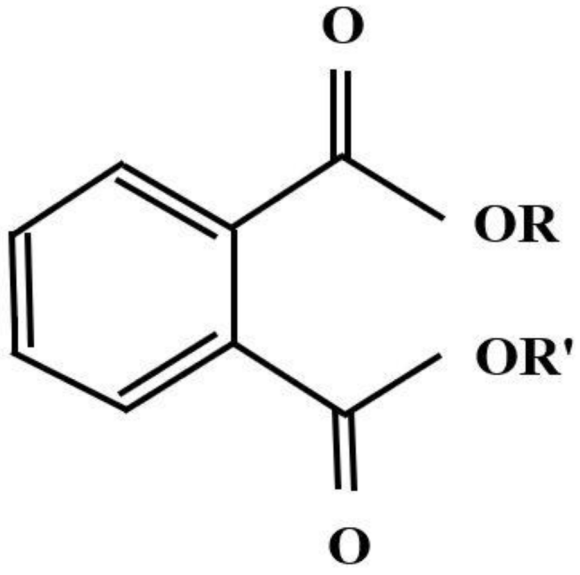

Fig. 1. Chemical structure of phthalate esters. R and R' = C_nH_{2n+1}; n = 4-15.

n-octyl phthalate (DnOP) and butyl-benzyl phthalate (BBP), as priority pollutants and have restricted the production and use of PAEs (Kashyap and Agarwal, 2018; CPSIA, 2008). European Union (EU) have imposed restrictions on five phthalates, namely DBP, DEHP, butyl benzyl phthalate (BBP), di-isononyl phthalate and di-isodecyl phthalate (Ventrice et al., 2013; European Commission, 2005, 2007). Therefore, with this concern, several research papers have been published to resolve the challenges regarding the removal of PAEs. However, the efficient removal strategies based on the inherent properties of phthalates and the technological gaps for the advancement of the technology in a large scale are not properly addressed in the literature. Hence, the objective of this paper is to provide a critical review of the extensive literature data on behaviour, transport, and fate of PAEs in environmental matrices followed by exposure pathways as well as their effects on human health. In addition, this review also summarizes the advancement in various technologies for the removal of PAEs, identified the challenges associated with the methods, and directions are proposed to solve them.

2. Occurrence and fate of phthalate esters in the environment

The demand for phthalates is continuously increasing because of low manufacturing costs and lack of alternatives, leading to piling of phthalate compounds into the environment. Therefore, it is important to study the fate of phthalate compounds in environment as it would help in understanding population exposure risk assessment and also opens the scope for remedial measures. When phthalate compounds enter into the environment they are not confined within a particular compartment of the environment. Depending on their physicochemical characteristics such as, Octanol-air partitioning coefficient, Octanol-water partitioning coefficient, Air-water partitioning coefficient, vapour pressure, water solubility, Henry's constant, they follow various transformations pathways and distributed within the various matrices of the environment (Starling et al., 2019; Pang et al., 2021; Staples et al., 1997; Net et al., 2015). The physicochemical properties of phthalate esters are dependent on alkyl chain length (Net et al., 2015; Gu et al., 2021). In this context, Octanol-air partition coefficient (K_{OA}) is an indicator of partitioning of the compounds between the organic phases and air. Higher is the molecular weight or alkyl chain length of the compound, greater will be its tendency to confine in environmental organic phases (Net et al., 2015; Liang and Xu, 2014). Hence, high values of K_{OA} indicate that phthalate esters present in the atmosphere will be readily adsorbed to suspended particles. Similarly, Octanol-water partition coefficient (K_{OW}) is an indicator of partitioning of a compound between non-polar and polar medium as well as the affinity of an organic compounds with lipid molecules (Cousins & Mackay, 2000; Staples et al., 1997). Hence, K_{OW} indicates the tendency of a molecule to undergo bioconcentration. With increase in alkyl chain length the value of K_{OW} increases so as to hydrophobicity, resulting in higher sorption to soils and sediments. Similarly, volatility from water is expressed in terms of Air-

Table 2
Occurrence of Phthalate Esters in Different Parts of Environment.

Air (Concentration in ng/m^3)							
Location	DMP	DEP	BBP	DnBP	DEHP	DnOP	Reference
Berlin, Germany	919	722.7	26.60	1081.4	155.50	–	Weschler et al., 2008
Home, Sweden	18	1598	28	925	208	–	Bergh et al., 2011
Huachang, China	–	–	–	409.80	13.20	–	Huang et al., 2013
Xinsheng, China	–	–	–	66.30	9.80	–	Huang et al., 2013
Xi'an, China	501	–	–	590	470	–	Wang et al., 2014
Indoor air, Industrialized Area, Delhi, India	18311	12368	11927	13909	14995	11833	Das et al., 2014
Outdoor air, Industrialized Area, Delhi, India	6366	9761	2584	2345	7503	383	Das et al., 2014
Water (Concentration in μg/L)							
Location	**DMP**	**DEP**	**BBP**	**DnBP**	**DEHP**	**DnOP**	**Reference**
Kaveri River, India	0.02	0.24	0.04	0.03	0.51	0.25	Selvaraj et al., 2015
Jukskei River, South Africa	0.04–0.56	0.08–0.39	-	-	0.49–5.58	0.79–3.65	Sibali et al., 2013
Llobregat River, Spain	-	0.22–6.85	N.D.–1.30	-	N.D.–3.09	N.D.–1.30	Pina et al., 2005
Drinking water, Delhi, India	0.38	0.198	0.633	0.317	0.257	0.248	Das et al., 2014
Mopanshan Reservoir, China	N.D.–0.04	N.D.–0.06	N.D.	N.D.–0.45	0.13–6.57	0.05–4.50	Liu et al., 2013
False Creek Harbor, Canada	0.002–0.005	0.05–0.35	0.002–0.006	0.005–0.04	0.17–0.44	0.05–0.244	Mackintosh et al., 2006
Soil and sediments (Concentrations in μg/kg dry Weight)							
Location	**DMP**	**DEP**	**BBP**	**DnBP**	**DEHP**	**DnOP**	**Reference**
Kaveri River, India	1.60	16.50	2.60	2.50	278	35.50	Selvaraj et al., 2015
Jukskei River, South Africa	0.22–12.80	2.48–44.80	-	-	6.54–3660	6.27–57.1	Sibali et al., 2013
Gomti River	N.D.–316	N.D.–137	-	N.D.–155	N.D.–947	N.D.–312	Srivastava et al., 2010
Rivers, Taiwan	-	100–1100	N.D.–1800	-	500–23,900	300–30,300	Yuan et al., 2002
Aquaculture fish ponds sediment, China	1-14	50-160	20-150	160-3670	1310-26600	10-290	Cheng et al., 2019
Kaohsiung Harbor, Taiwan	N.D.	N.D.	N.D.	N.D.–600	400–34,800	13–1310	Chen et al., 2013
Guanting Reservoir, China	N.D.–94.50	0.20–89.5	N.D.–380	6.90–258	N.D.–278	N.D.–571	Zheng et al., 2014

(N.D.: Not Detected, "–": Not Analyzed).

water partitioning coefficient (K_{AW}) and also with Henry's constant. Phthalates with low molecular weight have low K_{AW} values and volatilize slowly from aqueous solution. Whereas, phthalates with higher molecular weight easily gets evaporated from the aqueous medium, unless strongly adsorbed to the organic matters due to having high values of K_{AW} (Cousins et al., 2003; Net et al., 2015; Staples et al., 1997). Thus, the distribution of phthalates in different parts of the environment varies greatly among different phthalate compounds. In fact, phthalates have the tendency to undergo photolysis, volatilisation, hydrolysis, adsorption, and biotransformation (Gao et al., 2018; Pang et al., 2021). And because of these behaviours PAEs are frequently spotted in air, water and soil all over the world, with some key examples illustrated in Table 2.

Studies was conducted on examining the geographical distribution of concentrations and phthalate exposures in Asian countries (Fig. 2) and it was found that, the highest total phthalate metabolite (Σ14 phthalates) concentrations were found in urine samples collected from Kuwait (1050 ng/mL), followed by India (389 ng/mL), China (234 ng/mL), Vietnam (133 ng/mL), Japan (120 ng/mL), Korea (117 ng/mL), and Malaysia (94.9 ng/mL) (Guo et al., 2011). Similarly, the creatinine adjusted median concentration of total phthalates for urine samples from Kuwait, India, China, Vietnam, Japan, Korea, and Malaysia were 692, 506, 289, 119, 103, 104, and 169 μg/g creatinine, respectively (Guo et al., 2011). And, monomethyl phthalate (mMP), monoethyl phthalate (mEP), mono (2-isobutyl phthalate) (miBP), mono-n-butyl phthalate (mBP), and metabolites of di-(2-ethylhexyl) phthalate (DEHP) were the leading molecules, together they cover more than 95% of the total concentration in the samples from the seven countries (Guo et al., 2011).

3. Human exposure and health impacts

The major routes for direct phthalates exposure in humans are inhalation and dermal contacts from the cosmetics, perfumes, scents, textiles, sanitary napkins, etc. (Hahladakis et al., 2018; Heudorf et al., 2007; Schettler et al., 2006; Pang et al., 2021; Eichler et al., 2019). Similarly, the major routes for indirect phthalates exposure are from consuming contaminated food stuffs such as, edible plants, vegetables, etc. Naturally, plants may take up and accumulate PAEs from soil, potentially imposing human health risks through dietary intake. In this regard, cultivation study was carried out using lettuce, strawberry, and carrot plants to evaluate the potential of plant uptake, translocation, and metabolism of di-n-butyl phthalate (DnBP) and di(2-ethylhexyl) phthalate (DEHP) and their primary metabolites mono-n-butyl phthalate (MnBP) and mono(2-ethylhexyl) phthalate (MEHP). And they reported that all four compounds were detected in the plant tissues, with the bioconcentration factors (BCFs) ranging from 0.16 ± 0.01 to 4.78 ± 0.59 (Sun et al., 2015). Several studies have also reported that the major sources of phthalate consumption are from various food items like, packed food items, processed meat, carbonated drinks and alcoholic beverages, pharmaceuticals, and packed drinking water (Akhbarizadeh et al., 2020; Benjamin et al., 2015; Clark et al., 2003a, 2003b; Fierens et al., 2012; Tsumura et al., 2002). It was reported that phthalate compounds have been reported in amniotic fluid of a pregnant women (Silva et al., 2004) and breast milk of a lactating mother (Filardi et al., 2020), which acts as a potential source for secondary exposure for foetus and breast-feeding infants. Several studies have reported that indoor contaminated dust is the potential source of phthalate exposures and DEHP is the most abundant among various phthalate exposures around the world (Net et al., 2015; Becker et al., 2004; Das et al., 2014; Otake et al., 2004). Some studies have also reported that medical treatment facilities like, dialysis, grafting and extracorporeal membrane oxygenation (ECMO) therapy are the dominant sources for the intravenous phthalate exposures (Kaestner et al., 2020; Calafat et al., 2004). All these potential sources constitute towards total phthalate exposure of an individual. Based on various exposure mechanisms and urinary phthalate concentrations of mEP, miBP, mBP, mEHHP, and mEOHP phthalates exposure (DEP, DBP

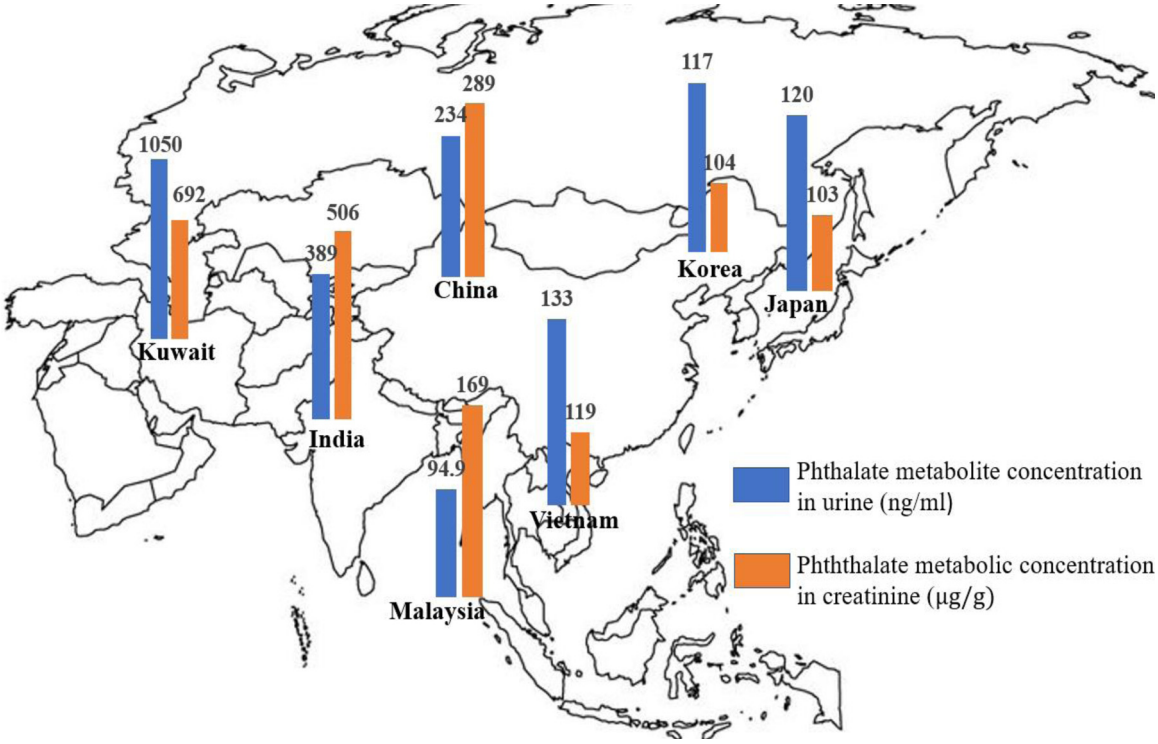

Fig. 2. Concentrations of urinary phthalate metabolites (Σ14 phthalates) in samples from seven Asian countries (ng/mL of urine and μg/g of creatinine) (Guo et al., 2011).

Table 3
Estimated Daily Exposure to Phthalates in Seven Asian Countries (μg/day).

PAEs	Reference dose		China	India	Japan	Korea	Malaysia	Kuwait	Vietnam
DEP	800[a]	16000[b]	285	1228	181	177	693	3900 (2)[c]	64.0
DBP	100	2000	580 (2)	178	140	110	124	822 (5)	173
DEHP[d]	20	400	182 (2)	339 (7)	92.5	102	97.7 (1)	435 (21)	112

Source: dx.doi.org/10.1021/es103879m (Guo et al., 2011, Environmental Science & Technology, 45, 3138-3144).
[a] Reference doses of U.S. EPA (μg/kg body weight/day).
[b] Estimated reference doses from U.S. EPA (μg/day, the body weight assumed as 20 kg).
[c] Number of samples exceeded the estimated reference doses.
[d] Average values calculated from urinary mEHHP and mEOHP.

and DEHP) were calculated for the seven Asian countries using a simple steady-state exposure model, as shown in equation

$$DI = CV \times \frac{M_1}{M_2} \times \frac{1}{f}$$

Where, DI is the total daily intake of phthalate (μg/day), C is the urinary phthalate metabolite concentration (μg/L), V is human daily excretion volume of urine (L/day), M_1 and M_2 are the respective molecular weights of parent phthalate and its metabolite (g/mol), and f is the molar fraction of the urinary monoester metabolite excreted in relation to the ingested amount of phthalate (Guo et al., 2011). The approximated daily exposure to different phthalate compounds in the seven Asian countries are represented in Table 3.

Phthalates are mainly endocrine disrupting compounds and have the potential to hamper the functions of hormones by hampering its synthesis and mimicking its activities (Benjamin et al., 2017; McLachlan et al., 2006; Careghini et al., 2015). PAEs are lipophilic compounds and they have the tendency to absorb to human body fluids and gets converted into respective primary and secondary metabolites by the processes of oxidation, hydroxylation and carboxylation. And, before excretion, some of these metabolites would interact with the cellular signaling system as ligands (agonist or antagonist or co-activator) of transcription factors residing in the nucleus and creates several molecular disorders (Benjamin et al., 2017). These phthalate metabolites undergo glucuronide conjugation by the help of enzyme Glucuronyl transferase and finally excreted through urine, sweat and fecal matter (Genius et al., 2012; Benjamin et al., 2017). Phthalates and its metabolites also have the tendency to bind with the histone protein of DNA and brings abnormalities in the gene expression by methylation, demethylation and alteration of chromatin (Wu et al., 2010; Manikkam et al., 2013). It also effects primordial germ cells which are precursors of gamete formation (Benjamin et al., 2017; Swan et al., 2005). Other than hormonal and genetic abnormalities, phthalates also have the tendency to cause respiratory trouble, kidney failure, tumors, pregnancy related complications, improper cognitive development of children, hampers thyroid functioning, skeletal malformation, insulin resistance, etc. (Benjamin et al., 2017; Bollinga et al., 2020). Potential health effects of different phthalate compounds are enlisted in Table 4.

3.1. *Effects on male reproductive health*

Several studies have reported that reproductive health of adult males is affected by exposure to various phthalate compounds. In this context, toxicological studies have showed that urinary phthalate metabolites are responsible for the reduction in sperm motility (Pant et al., 2011; Duty et al., 2003; Hauser et al., 2006; Tranfo et al., 2013), testosterone

Table 4
Health Effects Associated with Phthalate Esters.

Health Effects	Phthalates/ metabolites tested	Matrix assessed	Reference
Neurodevelopment, ADHD	DEHP, DBP and metabolites	Urine	Kim et al., 2011
Obesity	High MW: MECPP, MEHHP, MEOHP, MEHP and MBzP	Urine	Teitelbaum et al., 2012
Asthma and Allergy	DEP, DnBP, DiBP, BBzP and DEHP	Urine and dust	Bekö et al., 2013
Insulin resistance	MEP, MBP, DEHP and their metabolites	Urine and blood	Trasande et al., 2013a
Higher cystolic BP	MEP, MBP, DEHP and their metabolites	Urine and lipid profile	Trasande et al., 2013b
Decreased cognitive function	MMP, MEP, MBP, MBzP, MEHP, 5-oxo-MEHP and 5-OH-MEHP	Urine and IQ test	Huang et al., 2015
Austin Spectrum Disorders	DEHP and its metabolites (MEHP, 5-oxo-MEHP and 5-OH-MEHP)	Urine	Testa et al., 2012
Endometriosis	DEHP and MEHP	Peritoneal fluid	Cobellis et al., 2003
Affects gestational period	DEHP and MEHP	Cord blood	Latini et al., 2003
Delayed pubarche in girls	MEP, DBP, DBzP, DEHP and DINP	Urine and Blood	Frederiksen et al., 2012
Spermatotoxicity	Phthalate metabolites of MEP, MMP, MEHP, MBP, MBzP, MOP, MINP and MCHP	Urine and semen parameters	Duty et al., 2003
Sperm DNA damage	MEP, DEHP and metabolites of DEHP	Urine	Hauser et al., 2007
Gynecomastia	DEHP and MEHP	Blood	Durmaz et al., 2010
Prenatal exposure	MMP, MEP, MnBP, MBzP, MEHP, MEHHP and MEOHP	Urine	Suzuki et al., 2012
Reduced anogenital distance	MEP, MBP, MBzP and MiBP	Urine	Swan et al., 2005
Obesity and insulin resistance	MBP, MEP, MEHP, MBzP, MEHHP and MEOHP	Blood and urine	Stahlhut et al., 2007
Functioning of thyroid hormones.	MBP, MEP and MEHP	Blood and Urine	Huang et al., 2007
Diabetes and obesity in the elderly	MMP, MiBP, MEP, MMP and metabolites	Blood and serum	Lind et al., 2012b
Insulin resistance	MMP, MCPP, MEP, 5Cx-MEPP, 5Cx-MEPP, 5HO MEHP, MiBP, 5Oxo-MEHP, MnBP, MBzP and MEHP	Blood and urine	Huang et al., 2014

levels (Pan et al., 2006), anogenital distance, and increase in sperm aneuploidy (Benjamin et al., 2017). It was also proved that phthalate esters mimic the androgen hormones which resulting into “Testicular Dysgenesis Syndrome” or “phthalate syndrome” which was characterized by cryptorchidism, undescended testes, reduction in sperm count and its quality, and testicular cancer (Caporossi et al., 2020; Sharpe et al., 2008). All these findings established a strong correlation between phthalate exposures and male sterility.

3.2. Effects on female reproductive health

The effects of phthalate esters on a pregnant woman would directly affect foetus in addition to her own health, so pregnant women need special attention. It was reported that phthalates have been detected in amniotic fluid (Huang et al., 2009), peritoneal fluid (Cobellis et al., 2003), breast milk (Hines et al., 2009; Lin et al., 2011). From the general biomonitoring studies, it was revealed that DEHP, DEP, DnBP, BBzP, MnBP, and MBzP could cross the placental barrier in their unconjugated form (Tranfo et al., 2014). In some studies, it was found that DEHP has the tendency to lowering gestation period resulting into premature birth and also affects foetal development (Latini et al., 2003; Whyatt et al., 2009). Few case studies informed that there is a high correlation between developing breast cancer with phthalate exposures (López-Carrillo et al., 2010). Toxicological studies have revealed that monomethyl phthalate (MMP) and mono-2-ethylhexyl phthalate (MEHP) were responsible for premature birth (Song et al., 2014). And, these problems were more critical for male babies, with testicular development and growth of Leydig cell are affected by phthalates (Main et al., 2006). Researchers have also reported that the presence of phthalate are linked with delayed puberty in girls, low yield of oocytes, endometriosis and infertility (Upson et al., 2013; Frederiksen et al., 2012; Masuyama et al., 2003; Hauser et al., 2015; Du et al., 2016). Hence, phthalate esters are capable of creating various health effects in females due to their endocrine disrupting potential and lipophilicity.

3.3. Effects on growth and development

Multiple studies have reported that exposure to phthalates to the foetus from the pregnant mother and also in early childhood has tremendous effects in the growth and development of children. It was reported that neonates born from phthalate exposure have the tendency to suffer from developmental problems resulting into poor IQ and attention deficit hyperactivity disorders (ADHD) Olesen et al., (2018). proved that high phthalate exposure in uterus impairs the language development in early childhood. Austin Spectrum Disorders (ASD) or pervasive developmental disorder was found associated with the exposure of DEHP secondary metabolites (5-OH- and 5-oxo MEHPs); particularly, 5-oxo-MEHP exhibited 91% specificity in identifying patients with ASDs (Testa et al., 2012). In a study on Korean Mother-Infant pairs (N=460), it was found that phthalates exposure specifically DEHP and DBP hampers psychomotor development of infants, particularly males (Kim et al., 2011) Trasnade et al., (2013a)., (2013b) reported that phthalate metabolites of MEP, MBP and DEHP are responsible for insulin resistance and higher systolic blood pressure among U.S. children and adolescents. Phthalate exposure is also associated with allergic response in infants and children resulting into asthma, eczema, wheezing, respiratory trouble, and itchy rashes Wang et al., (2015). reported a strong correlation between MEHP level and onset of asthma in children due to hypomethylation of the promoter region of *TNF-α*. Multiple studies have reported that high molecular weight phthalates and their monoesters (DEHP, BBP, DBP and DEP) are responsible for generating oxidative stress and changes the secretion of numerous cytokines which resulted into allergic responses in infants.

4. Treatment processes for the removal of phthalate esters

It is essential to develop robust strategies that can effectively achieve complete removal and mineralization of PAEs as these are spreading in different environmental matrices at a rapid rate, coupled with the significant health risk they pose to human beings. In this aspects, various technologies and treatment methodologies have been employed by many researchers however, each methodology has its own challenges. Therefore, this review considers the limitations of various processes that have been studied and discuss the strategies to overcome, by developing an efficient method with a view of future pilot scale and potential industrial deployment. And, it can be achieved by analysing technological gaps and the operational cost of the processes as parameters to recognize and evaluate the key features which could enable the transition of the process from ‘*lab*’ to ‘*land*’.

4.1. Physical/chemical treatments

Physical and chemical treatment includes processes like coagulation/flocculation, and adsorption which are commonly used to reduce the load of suspended solids, ions, colloid particles, floating materials, oil and grease, colour, heavy metals and toxic compounds (Metcalf and Eddy, 2003). However, these processes suffer from certain limitations such as generates sludge, releases metal ions, difficulty in regenerating

adsorbents, non-availability of effective low-cost adsorbents, and not effectively mineralizing the toxic organic compounds into harmless by-products (Flores et al., 2020; Gu et al., 2021). These are basically traditional methods and are not efficient for the separation of contaminants that are present in ppb levels and also not effective to mineralize the phthalates due to their complex structures (An et al., 2014).

4.1.1. Coagulation/Flocculation

Coagulation is basically performed by the addition of various types of coagulants/floc-forming chemical reagents to the wastewater to facilitate destabilization of the colloidal dispersion and agglomeration of the individual colloidal particles by neutralization of charge and finally removed by sedimentation. It is an effective and commonly used process, particularly for heavy metals, though it can be expensive because of the quantity of chemicals needed (Fu and Wang, 2011). Coagulation is not generally used with organic pollutants, though it is a potential removal option for dyes present in wastewater (Daneshvar et al., 2003). Removal of PAEs from landfill leachate through a coagulation-flocculation process was studied by using three coagulants viz., ferric chloride, aluminum sulfate and poly aluminum chloride. The results concluded that compounds with log K_{OW} more than 4 and dissolved organic matter can be removed at the same time through the coagulation-flocculation process and the removal rate is greater than 50% (Zhang and Wang, 2009). And, among three coagulants poly aluminium chloride was most efficient for phthalate removal (Zhang and Wang, 2009). Similarly, 30% removal of PAEs was reported from fresh landfill leachate by coagulation and flocculation process using aluminium chloride as coagulants (Zheng et al., 2009). The most important limitation to coagulation is, it generates ample amounts of sludge, that is typically hazardous due to the removal of heavy metals and additional cost was needed to handle (Bhatnagar and Sillanpaa, 2011).

4.1.2. Adsorption

Adsorption is a surface phenomenon in which adsorbate accumulates at the surface rather than in the bulk of a solid or liquid. The dominant parameters that regulates the adsorption process is the availability of surface area or the active sites of the adsorbent. Other important variables that regulates the adsorption process are pH of the medium as it determines the surface charge of adsorbents then, temperature because it governs the thermodynamics of the process (Gao et al., 2017). Moreover, the adsorption of organic substances is determined by the chemical structure and polarity of that molecule. And the role of chemical structure is depending upon the availability of different functional groups. Thus, pH of the medium determines the extent of the adsorption onto different surfaces. And the partitioning coefficient K_{OW} determines the hydrophobicity (lipophilicity) of a particular compound in reference of octanol-water system which is a quantitative measure of polarity. Hence, the tendency of the substance to adsorb is dependent on the value of Log K_{OW}.

Possible adsorption mechanisms of PAEs. Phthalate compound comprised of ester group, benzene ring, and alkyl chain of different lengths. Depending on this structure, phthalate compounds are able to perform various interactions for their adsorption onto the surface, which are as follows:

I Hydrophobicity: PAEs are generally hydrophobic in nature. The hydrophobic effect increases with increase in the alkyl chain as illustrated in Table 1 and is measured by Octanol-water partition coefficient (K_{OW}). Therefore, PAEs with high alkyl chain length are adsorbed more easily from aqueous medium because of their hydrophobic effect with the adsorbents (Ye et al., 2021; Julinová and Slavík, 2012).

II Interaction based on ester group of phthalates: Ester groups act as electron acceptors, and interacts with π-electron donor from the adsorbent, leading to π-π electron-donor-acceptor (EDA) interaction. The ester group also has the capability to form hydrogen bond with some functional groups which promotes the adsorption process (Lu et al., 2017; Ye et al., 2021).

III Interaction based on benzene ring: Aromatic ring can bring π-π stacking with π electron clouds of adsorbent. These interactions are comparatively weaker than hydrophobic and π-π electron-donor-acceptor interaction (Ye et al., 2021; Gao et al., 2017; Julinová & Slavík, 2012).

IV Electrostatic interactions: The pKa values of two carboxylic acid groups of phthalic acid (H_2-PA) are 2.9 and 5.4, respectively. Thus, the PAEs could exist in H_2-PA/H-PA^-/PA^{2-} forms depending on the pH of the medium. Therefore, phthalates have the electrostatic attraction or repulsion interactions with the charged adsorbents depending on pH (Ye et al., 2021; Qureshi et al., 2013; Julinová and Slavík, 2012).

These are the dominant mechanisms that govern the adsorption behaviour of phthalate compounds as illustrated in Fig. 3. And these interactions may occur independently, but it can co-exist in one adsorption system. There are various types of phthalate esters present in water and each PAEs has different adsorption mechanism which possess a challenge in structural design of adsorbents. Similarly, in municipal sewage or real wastewater, PAEs usually coexist with other contaminants (e.g. inorganic ions, organic matter, pesticides, dyes, PPCPs, EDCs, etc.). Hence, developing an efficient adsorbent surface which shows a specific adsorption capacity towards target pollutants and also having high surface area, is urgently required.

Adsorption of phthalates by different adsorbent materials. Several studies have reported that carbonaceous materials are the promising candidate for adsorption, because they contain interstitial space and grooves, which acts as a high adsorption site for various kinds of pollutants. And, the typical surface area of some carbonaceous materials were approximately 2600 m^2/g, 900–1200 m^2/g, 400–900 m^2/g and 200–400 m^2/g for graphene, activated carbon, SWCNT, and MWCNT, respectively (Leary and Westwood, 2011) Venkata Mohan et al., (2007). studied DEP sorption on activated carbon having surface area 500 m^2/g and geometric mean size of 70 mm from the aqueous phase. Basically, they investigated the effect of various factors such as initial concentration, contact time, carbon dosage, and operational pH. The experimental outcomes revealed rapid removal of DEP, and then slowly reducing over time until it reached equilibrium. The author concluded that the initial high rate of removal is due to having active surface sites. Also, the rate of adsorption was different for different concentrations of DEP tested. In addition, adsorption equilibrium was studied by the author using adsorption isotherm models to quantify the whole process. And Langmuir's isotherm seems to fit better for the adsorption of DEP onto an activated carbon Fang and Huang (2009). investigated the adsorption of DBP onto activated carbon synthesized from nutshell having surface area of 1224 m^2/g. They observed that adsorption capacity increases from 40.1 mg/g to 104.7 mg/g with a rise in temperature from 25 to 55 °C, which revealed that it is an endothermic process. Thus, it suggests with a rise in temperature, diffusion of DBP molecules increases and also increasing the adsorption capacity of adsorbent. Also, the experimental data proved that the isotherms was most suited with the Freundlich model. It was reported that copper and tetrabutylammonium iodide (TBA) modified activated carbon was studied for phthalate esters removal from actual industrial streams containing di-isopropyl phthalate (Adhoum and Monser, 2004). And from the experimental data, it was found that activated carbon adsorbs substantial quantity of phthalates (55 mg/g) but, it is less than simulated wastewater (93.5 mg/g). This might be due to the competitive adsorption of co-contaminants present in industrial effluents. It was found that amount of phthalate adsorbed on activated carbon modified with Cu and TBA was 117 mg/g and 92 mg/g, respectively (Adhoum and Monser, 2004). And in terms of adsorption capacity, Cu-modified activated carbon is around 2.12 times greater than pure activated carbon. Similarly, adsorption capacity

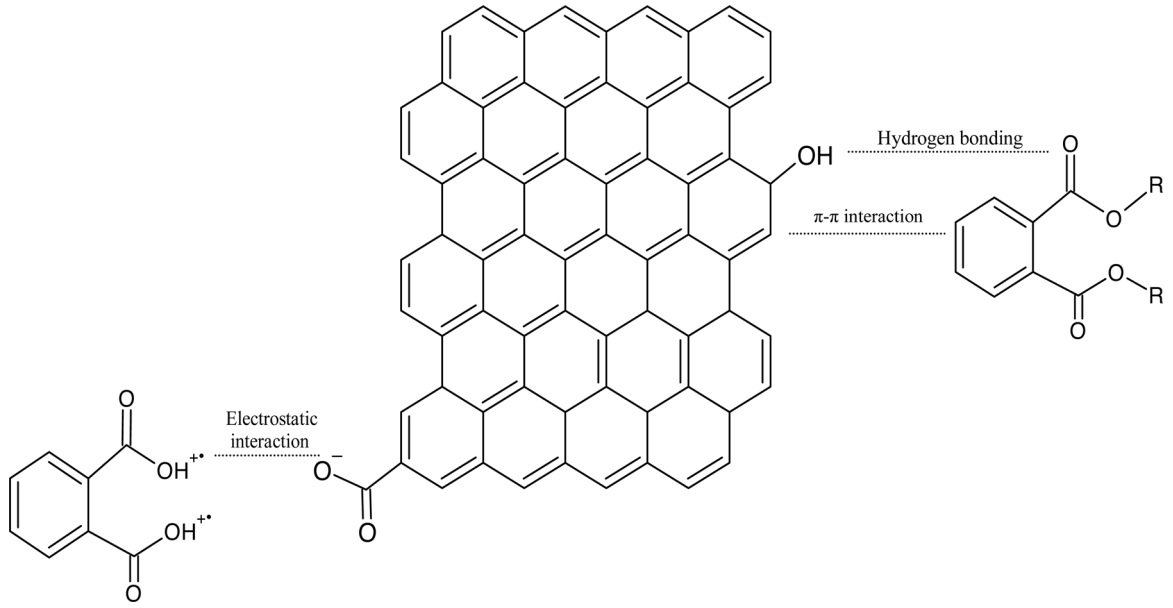

Fig. 3. Possible adsorption mechanisms of PAEs.

of TBA-modified activated carbon is 1.67 times higher than pure activated carbon (Adhoum and Monser, 2004). In all these cases the driving force for the adsorption is chemisorption. Consequently, the regeneration of the modified adsorbent is difficult Den (2006)., studied adsorption of DEP onto multi-walled carbon nanotubes (MWCNTs). The results revealed that nanotubes having outer diameter of 10–20 nm takes 120 min, while for outer diameter of 40–60 nm, it takes 180 min for achieving equilibrium. However, the time required for achieving equilibrium is 300 min for granular activated carbon which is significantly higher comparing to carbon nanotubes (Den, 2006). The adsorption was best fitted with Langmuir isotherm (monolayer adsorption) with adsorption capacities for DEP were 8.5 mg/g and 4.8 mg/g for 10–20 nm and 40–60 nm, respectively. The adsorption capacity of carbon nanotubes is significantly higher than activated carbon, because of π-π stacking and π-π electron-donor acceptor interactions between the benzene ring of the phthalates and the graphite surface of the carbon nanotubes. Similarly, Wang et al., (2010) demonstrated the adsorption of three phthalate compounds (DMP, DEP, DBP) onto single-walled CNTs (SWCNTs) with outer diameter 1–2 nm and MWCNTs (MWCNT10: outer diameters <10 nm, MWCNT20: outer diameters 10–20 nm, MWCNT40: outer diameters 10–40 nm) as an adsorbent. And, they found that adsorption capacity was depends on the hydrophobicity of individual DEPs as follows: DMP < DEP < DBP. In addition, the efficacy of adsorption reduced with increases in the external diameter of CNTs as follows: SWCNT > MWCNT10 > MWCNT20 > MWCNT40 (Wang et al., 2010).

Multiple studies reported that the adsorption on CNTs or any graphitic surface was possible by various interactions such as hydrophobicity, π-π EDA interactions, π-π stacking, electrostatic interactions, etc. (Julinová and Salvik, 2012; Ye et al., 2021). Moreover, for the industrial effluents which having high concentration of phthalate compounds, suitable adsorbent is needed and that should have high surface area, efficient in bringing all kinds of interactions which promotes the adsorption of target molecules and should be cost friendly. Table 5 lists various adsorbents, representing the cost of new generation nanomaterials such as graphene oxide (GO) is much higher comparing to traditional adsorbents like, activated carbon, biochar, zeolite and clay.

In aqueous medium, the pH plays a critical role in adsorption because it determines the charge density of the adsorbent (Radovic et al., 2001; Moreno-Castilla, 2004; Tüzün et al., 2005) and the chemical form of compounds (e.g., PAEs) (Rivera-Utrilla et al., 2009) Venkata-Mohan et al., (2007). investigated the adsorption of DEP from aqueous solution onto commercial activated carbon and revealed that adsorption of DEP is strongly regulated by the solution pH and diminishing from 80% to 50% as the pH of the solution was increased from 2.0 to 10. The same trend was reported for the adsorption of PAEs on activated carbon cloth (Ayranci and Bayram, 2005). The sorption inhibition detected might be due to an increase in the hydroxyl ion, leading to development of aqua-complexes which thereby reduces the performance (Venkata Mohan et al., 2007). Hence, solution pH was one of the important variables in the adsorption of PAEs due to ionization. A summary of key studies on the removal of PAEs by adsorption was enlisted in Table 6.

Table 5
Cost of Different Adsorbents.

Adsorbent	Cost (US $/kg)	Reference
Activated Carbon	20-22	Lin and Juang, 2009
Biochar	0.5	Marousek, 2014
Natural zeolite	0.03-0.12	Lin and Juang, 2009
Clay	0.04-0.12	Lin and Juang, 2009
Chitosan	15.43	Babel and Kurniawan, 2003
ZIF-8	14,900	https://www.sigmaaldrich.com
SWCNT	29,800	https://www.sigmaaldrich.com
GO (powder, 15–20 sheets, 4–10% edge-oxidized)	129,000	https://www.sigmaaldrich.com

Source: https://doi.org/10.1016/j.cej.2020.128127 (Ye et al., 2021, Chemical Engineering Journal 409, 128127).

It was also found that temperature plays a vital role in adsorption of phthalates and the effect is clearly identified where the adsorption controlled by intra particle diffusion (Gani and Kazmi, 2016). Because as the temperature rises the rate of diffusion of phthalate molecules into the pores of adsorbent increases Fang and Huang, (2009). established that the adsorption capacity of NAC increased from 40.1 mg/g to 104.7 mg/g when temperature was increased from 25–55 °C. It was also reported that adsorption of DEP onto multi-walled carbon nanotubes (MWCNTs) having diameter 10–20 nm was endothermic (i.e., increases with temperature) in nature (6 mg/g at 288 K to 10 mg/g at 308 K) (Dan, 2006). Moreover, it was found that with increase in rate of surface diffusion with temperature, decrease in surface tension of DEP was detected as potential reason for more adsorption (Gani and Kazmi, 2016). In last few years, several researchers have studied the potential of metal organic frameworks for the adsorption of phthalate

Table 6
Adsorption of Phthalate Compounds by Different Adsorbents.

Adsorbent	PAEs	Experimental Condition					Adsorption capacity (mg/g)	Mechanisms	Reference
		Feed (mg/l)	pH_{pzc}	pH	Contact time	T (°C)			
BC from wheat straw	DMP DEP	80			2-3 d	35	2027.41 2047.15	$\pi-\pi$ EDA interaction, H-bonding and pore filling	Jing et al., 2018
BC from peanut hall	DMP DEP	80			2-3 d	35	1,071.85 1,293.79		
AC from *Albizzia julibrissin* pods	DEP DBP	150	2.9	3.8	30 min	20	438 977	Electrostatic interactions, dipole–dipole and H-bonding	Bouhamidi et al., 2016
BC derived from the pine nutshell	DBP DAP DEP DMP	5	1.5	2.0	60 min	25	5.65 3.64 2.87 2.48	Electrostatic attraction, hydrophobicity and $\pi-\pi$ EDA interaction	Qureshi et al., 2013
Nano-scale BC	DEP	60	1.5	9.0	4 d	25	34	Pore filling	Ma et al., 2019
BC-MnO_2 composite	DBP	6 (0.0215 mmol/L)			240 min	25	10.2 (3.639×10^{-2} mmol g^{-1})	$\pi-\pi$ EDA interaction and chemical reaction	Gao et al., 2017
BC-graphene composite	DMP DEP DBP	10 10 4		7	48 h	25	30.78 23.86 21.98	$\pi-\pi$ EDA interaction, hydrophobicity and pore filling	Abdul et al., 2017
Graphene	DBP DEHP	10 5		6.4	24 h	25	27.03 39.22	Hydrophobicity	Yang & Tang, 2016
GO	DMP DEP DBP	3–200 5–120 1–8.5		7	3 h	25	62.26 58.9 84.13	$\pi-\pi$ EDA interaction, H-bonding, and hydrophobicity	Lu et al., 2017
GO-functionalized magnetic nanoparticle	DEP	80		3-10	10 min	25	8.71	$\pi-\pi$ EDA interaction and H-bonding	Yin et al., 2014
SWCNT	DMP DEP DBP	0–4			30 min	25	148 145 324	Hydrophobicity, $\pi-\pi$ EDA interaction	Wang et al., 2010

(AC: Activated carbon, BC: Biochar, SWCNT: Single Walled Carbon Nanotube).

esters Li et al., (2018). found that copper-based metal organic frameworks effectively adsorbs DBP and also acts as a heterogeneous catalyst in the presence of persulfate over a wide range of pH. However, this system suffers from certain limitations such as, the molecular size of activated copper-based metal organic frameworks has a smaller microporous cage diameter (Approximately 9 x 9 Å) comparing to molecular size of DBP (15.84 x 11.00 x 7.56 Å). Hence, persulfate can enter inside the pore spaces but DBP is blocked outside. Therefore, radical scavenging happens in activated copper-based metal organic framework (Cu-BTC) system; which need to be addressed by modifying the material and improving the free radical utilization efficiency. Similarly, Khan et al., (2014) found that the ZIF-8 (zinc-methyl imidazolate framework-8) has the tremendous potential for the adsorption of phthalic acids from aqueous solutions. They suggested that the adsorption capacity of the ZIF-8 for phthalic acid was much higher comparing to commercial activated carbon or other typical metal-organic frameworks (MOFs). Electrostatic interaction between the positively charged surface of ZIF-8 and the negatively charged phthalate anions is the dominant interaction for promoting adsorption on ZIF-8 surface and the surface area and pore volume of the adsorbents have not indicated any positive effect on the adsorption (Khan et al., 2014). In addition, the layered double hydroxides (LDHs) with flaky structure can effectively adsorbs phthalates into its surface. It was reported that TiO_2 particles distributed on the surface of the interconnecting organic LDHs nanoflakes could effectively adsorbs DMP molecules and ultimately leads to photodegradation. The external hydroxyl groups of the composite show a synergistic effect leading to enhancement of the photocatalytic efficiency for the mineralization of DMP (Huang et al., 2013).

4.2. Biological treatments

Biological treatment refers to the aerobic and anaerobic processes that converts organic pollutants into carbon dioxide, nitrates, and sulphates in aerobic conditions. Similarly, in anaerobic conditions it transformed organic pollutants into ammonia, methane and hydrogen sulfide (Metcalf and Eddy, 2003). Several studies have reported that microbial breakdown are the dominant mechanisms for their natural degradation in various regions of the environment (Xu et al., 2008; Jianlong et al., 2000; Johnson et al., 1984; Pujar and Ribbons, 1985). Few of the microorganisms responsible for phthalate degradation are reported and tabulated in Table 7. Various studies show that microbial remediation of PAEs are depends upon the water solubility of the molecule, alkyl chain length, sludge retention time, hydraulic retention time and the enzymatic machinery of the organisms (Chang et al., 2007; He et al., 2015; Huang et al., 2008). However, biodegradation is not effective for long chain phthalate esters (e.g., DEHP, DOP, etc.) due to their complexity in the structure, such that microorganisms are not able to break the bonds within the molecule. Although biological treatment not able to degrade long chain PAEs, but coupling biological treatment with AOPs has the potential to overcome such limitations. In this regard, Chen et al., (2009) studied the potential of photo-biological system for the treatment of wastewater containing DEHP. They performed pre-treatment of the DEHP containing wastewater by the photo-Fenton process and finally treated biologically. They concluded that pre-treatment system (i.e., photo-Fenton process) was able to remove 54% of the DEHP at a concentration of 30mg/l but, the photo-biological coupled system had a removal efficiency of more than 80%. Hence, these results clearly indicate that photo-biological reactions have a tremendous potential for the treatment of wastewater containing DEHP. However, the technical aspects for implementation of engineered bioremediation processes under environmental conditions are still lacking.

4.3. Advanced oxidation processes

Advanced oxidation processes (AOPs) are used in wastewater treatment to oxidize complex organic pollutants that are difficult to degrade into simpler by-products in a conventional treatment processes (Metcalf and Eddy, 2003). AOPs are characterized by the generation of hydroxyl radicals (·OH) as potential oxidising agent and other free radicals to improve the mineralization process and the complete conversion

Table 7
Phthalate Degrading Microorganisms.

Organisms	Isolated from	PAEsmetabolized	Biodegradationefficiency	Reference
Bacteria				
Agromyces sp. MT-O	Landfill soil	DEHP (200 mg/L)	90 % within 96 h.	Zhao et al., 2016b
*Bacillus megaterium*YJB3	*Canna indica* root tissue	DBP (1000 mg/L)	82.5 % within 120 h.	Feng et al., 2018
Bacillus thuringiensis	Agricultural soil	DBP (400 mg/L)	88 % after 80 h.	Surhio et al., 2017
Mycobacterium sp. YCRL4	Petroleum contaminated soil	DMP, DEP, DBP, DEHP, DCHP (50 mg/L)	Above 85% within 120h.	Ren et al., 2016
Providencia sp. 2D	Compost soil	DBP (500 mg/L)	89% within 72 h.	Zhao et al., 2016a
Pseudomonas sp. W1	Activated sludge	DBP (1000 mg/L)	99.88% within 192 h.	Wang et al., 2020
Fungi				
Fusarium culmorum	Paper wastes recycling facility	DEHP (1000 mg/L)	92% within 36 h.	González-Márquez et al., 2019
Pleurotus ostreatus Po50	College of Post graduates (COLPOS Puebla, Mexico) culture collection	DEHP (1000 mg/L)	100% within 504 h.	Ahuactzin-Pérez et al., 2018
Aspergillus japonicus BP *Penicillium brocae* BP6 *Purpureocillium lilacinum* BP12	Plastics contaminated soil	DEHP bound to PCV blood storage bags (BB)	33.3% w/w DEHP were utilized in two weeks in a two-stage cultivation Process.	Pradeep et al., 2013
Algae				
Cylindrotheca Closterium, *Chaetoceros muelleri*	Strains from the Institute of Oceanology, Chinese Academy of Sciences.	DEP, DBP (0.1 mg/L)	Above 90% within 96 h.	Chi et al., 2019; Gao & Chi, 2015

of the model pollutant into CO_2, H_2O, and mineral acids (Joseph et al., 2009; Pang et al., 2021). Thus, AOPs has the ability to transform pollutants into less harmful products within a short span of time, hence they have been considered as a potential alternative for the treatment of persistent organic pollutants (Chen et al., 2009; Flores et al., 2020). AOPs include processes like, ozonation, sonolysis, Fenton processes and photocatalysis.

4.3.1. Ozonation

Several studies have reported that the interaction of ozone with contaminants is direct or through the formation of secondary oxidants (·OH) (Sevimli & Sarikaya, 2002; Jabesa and Ghosh, 2016). Medellin-Castillo et al. (2013) found ozonation removes 65% of DEP after 60 min of exposure but when the reaction was carried out in the presence of t-BuOH (0.1M) which is a radical scavenger, only 5% degradation was achieved. Thus, ozone had a very low reactivity to degrade DEP, and the DEP degradation mainly occurred by the oxidative pathway through the decomposition reaction with the ·OH radicals. Similarly, a study was conducted with 2.5, 5 and 10 mol/m^3 t-BuOH at the ozone generation rate of 1.94 mg/s at pH 7, and it was found that in the absence of t-BuOH, almost all of the DEP was removed within 1.8 ks reaction time whereas, only 9% removal was achieved in the presence of 10 mol/m^3 t-BuOH. This clearly indicates that the reaction involving ·OH dominated (Jabesa and Ghosh, 2016). It was reported that in ozonation, significant energy input is required (Summerfelt and Hochheimer, 1997) and it also generates toxic oxidation by-products (Ike et al., 2019; Huber et al., 2003) like, chlorate (ClO^{3-}), bromate (BrO^{3-}), low molecular weight carbonyls and organic halogenated oxidation by-products.

4.3.2. Fenton processes

The photo-Fenton process ($UV/H_2O_2/Fe^{2+}$) effectively degrades Diethyl phthalate (DEP) with an efficiency of 75.8% after 120 min at pH 3, DEP concentration of 10 mg/L, H_2O_2 of 5.44 x 10^{-4} mol/L, and Fe^{2+} of 1.67 x 10^{-4} mol/L (Yang et al., 2005). Similarly, electro-Fenton process with sacrificial anode can effectively removes 93% of Di-isobutyl phthalate (DiBP) under optimum conditions of 1A initial current, 5cm plate spacing, pH 5, 40μL H_2O_2 and 2g/l of Na_2SO_4 as electrolyte (Yang et al., 2020). Fenton processes works under acidic conditions and large amount of iron sludge is generated (Yang et al., 2016). Hence, there is a need for developing energy efficient treatment technologies that can treat with high efficiency without generating harmful by products.

4.3.3. Sonolysis

Among various AOPs, high-frequency ultrasound (US) has attracted considerable interest in recent years by virtue of its particular advantages, such as safer, cleaner and requires less chemical dosing. Although US can achieve the degradation of refractory compounds, one of its shortcomings is its relatively low efficiency, mostly due to the inevitable recombination of generated radicals to form more stable molecules ($H\cdot + OH\cdot \rightarrow H_2O$, $2OH\cdot \rightarrow H_2O_2$, etc.), which reduces the effective contact between radicals and target contaminants (Pirsaheb and Moradi, 2020) Xu et al., (2013). demonstrated the efficiency of degradation of dimethyl phthalate (DMP) by catalyst-free ultraviolet irradiation, high-frequency ultrasound and their combination. And they observed that by using only UV light the degradation of DMP was 16.6% in 120 min with 6 lamps as compared to 57.4% in 120 min by using only ultrasound. But, when they used combination of ultrasound and UV light (i.e., sonophotolysis) the degradation of DMP was increased to 98.4% in 120 min with 6 lamps. Thus, the effectiveness of the three processes could be summarized as: UV (6 lamps) < US < UV (6 lamps)/US. Similarly, Na et al., (2012) studied the degradation of DEP by sonolysis (US: 283 kHz), photocatalysis (UVC + TiO_2 (0.45 g/L)) and sonophotocatalytic process. And, they revealed that the degradation of DEP under photocatalysis was 60% after 80min of contact time but, under sonophotocatalysis almost 80% removal achieved with same contact time at a frequency of 283 KHz. However, not a significant removal happens in sonolytic process. Hence, integrated process like sonophotocatalysis might be an effective technology to bring complete mineralization of phthalate compounds. The coupling of ultrasound with photocatalysis helps in preventing the agglomeration of catalyst particles in aqueous solutions by the physical effects of acoustic cavitation (i.e., generation of

shock waves), the catalyst surface is continuously cleaned, increases the mass transport of the pollutants to the catalyst surface and finally, the rate of chemical reaction gets increases as these physical forces increases the collision frequency within the molecules. Thus, ultrasound has the capability to improve the photocatalytic performance in a synergistic manner. From the extensive literature data, it is clear that achieving desirable removal of PAEs with a single process is difficult. In this context, the combination of ultrasound with other processes such as electrocoagulation, electro-Fenton, and electro-oxidation is beneficial to achieve effective removal of organic pollutants from wastewater (Hassani et al., 2022). The combination of ultrasound and electrochemical AOPs as well as AOPs generates synergistic effects by inducing physical as well as chemical processes by acoustic cavitation: the formation, growth and adiabatically implosive collapse of bubbles in the aqueous medium and overcomes the limitations of individual processes (Hassani et al., 2022). The major advantage of integrating ultrasound with electrochemical processes is the enhancement in the electrode performance by preventing passivation, leading to increase in the generation of radical species and improvement in the degradation performance (Hassani et al., 2022).

4.3.4. Photocatalysis

Although, AOPs are effective in degrading organic pollutants but, these processes are relatively costly because of expensive reagents like H_2O_2 and O_3 and high electrical energy is required for the generation of ultrasound and ultraviolet radiation. In this context, the most promising and effective solution is to use semiconductor photocatalysis for mineralizing persistent organic pollutants in water as it is capable of completely mineralizing complex pollutants and leaves no toxic reagents into the system after treatment (Chen et al., 2005; Jing et al., 2011; Zhang et al., 2019). Wastewater contains variety of pollutants; therefore, it is highly desirable to have some treatment technology which is capable of removing more than just one pollutant.

As per the literature, a variety of photo-active materials are reported and studied as photocatalyst. And among them TiO_2 is one of the common choices among researchers because of its several advantages such as, chemically stability and suitable band position (Fujishima et al., 2000). The TiO_2 has a suitable band position comparing to other photocatalyst and can be activated by sunlight by tuning its band gap. In TiO_2, the potential of conduction band minimum (CBM) and valence band maximum (VBM) was about -0.37 V (vs. NHE) and +2.83 V (vs. NHE), respectively (Yan et al., 2013). To achieve degradation of pollutants, reduction capacity of e^- must be able to produce superoxide anion radicals ($\cdot O_2^-$), while oxidation capacity of the photogenerated holes (h^+) must be able to oxidize OH^- to produce reactive hydroxyl radicals ($\cdot OH$). Hence, CBM for semiconductor photocatalyst should have a band potential lower than $(O_2+H^+)/HO_2$ (vs. NHE = -0.13 V) simultaneously, VBM should rise to narrow band gap and maintain oxidation capacity for h^+ (electrode potential of valence band will still lower than O_2/ H_2O (vs. NHE = +1.23 V)) so that they can able to generate free radicals ($\cdot OH$ and $\cdot O_2^-$). These free radicals will oxidize various organic pollutants to produce dioxide, water and other non-toxic small organic molecules. Therefore, using TiO_2 for the removal of phthalate esters is a promising technology compared to other photocatalyst which don't have a suitable band position for the synthesis of both the radicals ($\cdot OH$ and $\cdot O_2^-$). The TiO_2 photocatalyst upon excitation by light of suitable wavelength, produces holes (h^+) in the valence band and the electrons (e^-) moves to conduction band. This e^- and h^+ are capable of reducing and oxidizing adsorbed O_2 and H_2O molecules into superoxide anion ($\cdot O_2^-$) and hydroxyl radicals ($\cdot OH$) as illustrated in Fig. 4. PAEs in wastewater can be degraded by using TiO_2 (Huang and Chen, 2010), forming $\cdot OH$ and $\cdot O_2^-$ having capability of degrading DMP by 91.9% and 78.1%, respectively (Wang et al., 2018b).

However, TiO_2 shows reactivity under UV region due to wide bandgap (E_{bg} of 3.2 eV for anatase and 3.0 eV for rutile), also it has high recombination rate of electron-hole pairs that in turn lead to low quantum yield, and it also has limited surface area for the adsorption of pollutants. Therefore, to improve the degradation performance, co-catalyst could be added either on the surface or by doping into the matrix of the catalyst. In fact, doping with the metals and non-metals would reduce the energy band gap of photocatalyst and promote the absorption to longer wavelengths, as dopants are capable of creating intermediate energy levels (Hassan et al., 2016). Also, the addition of co-catalysts can significantly suppress recombination of electron-hole pairs by providing alternative charge transfer pathways and also improves the surface area for the adsorption of pollutants, which subsequently can enhance the degradation of PAEs Kaur et al., (2018). studied the performance of transition metals (Ni, Mn and Co) doping on TiO_2 for the degradation of DEP. And they found higher DEP degradation in doped TiO_2 over that of undoped TiO_2 and Mn-doped TiO_2 showed the lowest optical band gap at 2.47 eV, which would be suitable for visible light activation. In addition to TiO_2 based catalysts, degradation of DBP by Fe, Ag co-doped ZnO and visible LEDs was reported (Akbari-Adergani et al., 2018). And the experimental outcomes revealed that almost 90% degradation achieved under optimum conditions of pH = 3, photocatalyst concentration of 150 mg/L and initial DBP concentration was 15 mg/L. In recent years, Z-scheme photocatalyst gained tremendous interest among researchers due to their redox ability, can separate the charge carriers, ability to get excited under visible light and bi-functional catalytic property. These photocatalyst system can follows both oxidative and reductive pathways at a time and resistance to photo-corrosion. Hence, Z-scheme photocatalyst are stable and can be reusable. The efficiency of Z-scheme systems depends on various factors such as, morphology, defect engineering, surface modification, etc. It was also found that recycling and anticorrosion properties of z-scheme systems can be improved by non-metallic electron mediators (e.g., carbon dots, graphene, etc.) compared to individual catalysts (e.g., CdS). All these factors need to be taken into consideration for its practical application. One of the limitations of the Z-scheme system is the backward reactions which reduces the visible light activity of the heterojunction (Hassani et al., 2021).

Carbonaceous materials are promising candidates to be used for the preparation of nanocomposites with TiO_2, as they have large surface area and helps in electron transfer from the CB of TiO_2 nanoparticles to the carbon surface due to their lower Fermi level, so that the recombination of charged pairs reduces and photocatalytic performance increases (Chen et al., 2011). Studies have reported that carbon aerogels (Cui et al., 2016) and multiwall carbon nanotubes (MWCNTs) (Tan et al., 2018) have higher potential when combined with TiO_2 than pure TiO_2 for the degradation of DMP. Other than charge separation, visible light response and pollutant adsorption, nanocomposites help in catalyst recovery by acting as support structure in which the catalysts are impregnated. In this context, studies have reported the use of hollow glass microspheres (HGM) (Jiang et al., 2013) and magnetic poly (methyl methacrylate) (mPMMA) (Chen et al., 2019), as a support structures to enhance the catalyst recovery after degrading DMP. Similarly, TiO_2 immobilised onto hydrophobic layered double hydroxides (LDHs) showed high adsorption capacity for DMP due to hydrophobic flaky structure of LDHs followed by photocatalytic removal by TiO_2 and the double layered hydroxides acts as s good support structure for catalyst recovery (Huang et al., 2013). LDHs are extensively used as catalysts or catalyst precursors in AOPs due to their high surface area, high anion exchange capacities, and flexible inner space (Karim et al., 2022). Modifying the LDHs materials with other materials can improve the surface properties of the composite and enhance the adsorption capacity (Karim et al., 2022). Also, LDHs materials with transition metals on their crystalline structure have gained considerable interest due to their higher redox chemistry and structural characteristics. It was reported that LDHs has the potential to overcome limitations like, low specific surface area, low visible light absorbance and high recombination rate of charge carriers. In this regard, the photocatalytic properties of LDHs could be enhanced by coupling them with semiconductor materials or metal oxides. This will help in improving the structural properties by forming hydroxylated

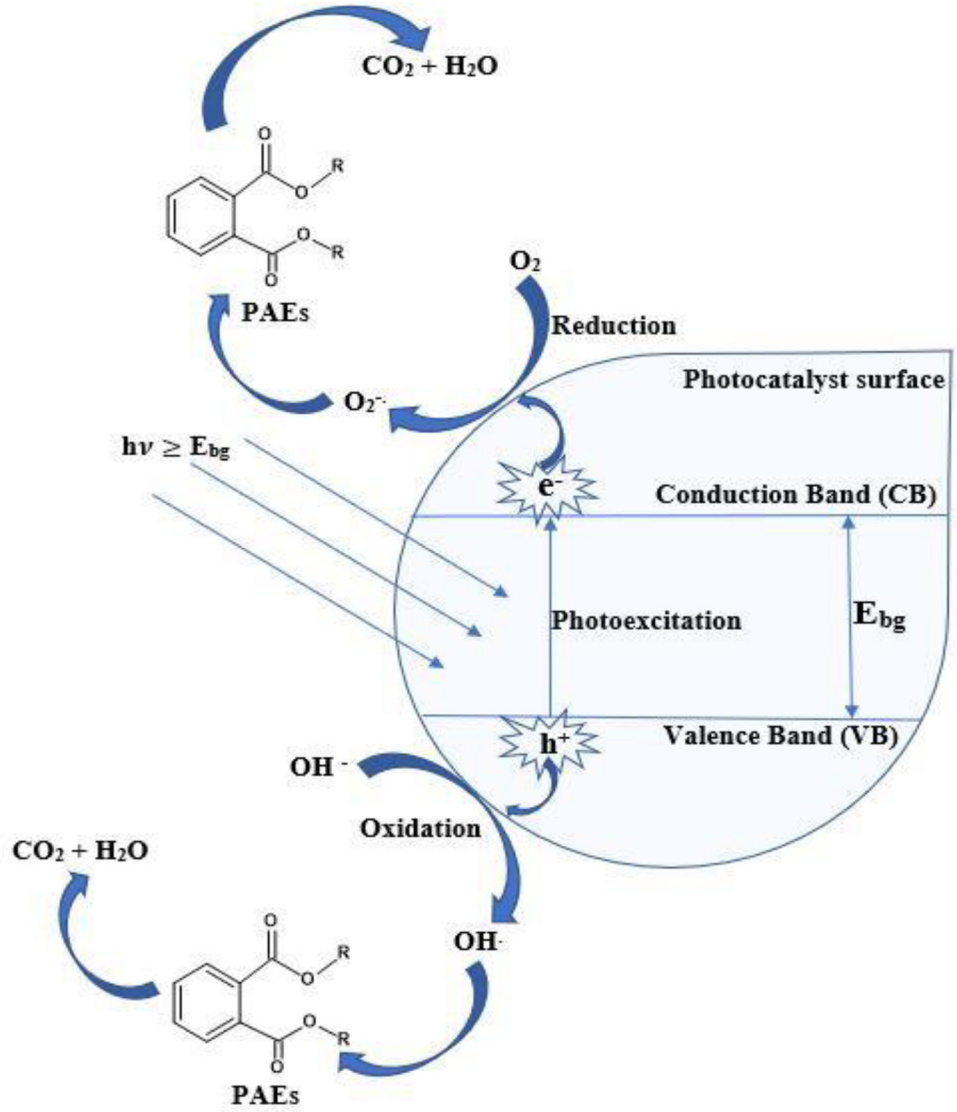

Fig. 4. Mechanisms of PAEs degradation by photocatalysis.

layered structure with stronger photo-oxidation abilities Motlagh et al., (2020). studied the fabrication of ZnFe-layered double hydroxides with sulfate-intercalated anion (ZnFe-SO_4^-LDH) modified with graphene oxide (GO) as an efficient catalyst for the visible light photodegradation of phenazopyridine hydrochloride (PhP). They concluded that under visible light irradiation, the photocatalytic efficiency for the degradation of PhP was 60.01% for the reaction time of 150 min. And the degradation efficiency was increased to 93.95% within 150 min by the addition of 1 mmol/l of potassium persulfate ($K_2S_2O_8$). It was also reported that this system can bring COD removal of 60% after 300 min of photocatalytic reactions .

In addition to immobilizing photocatalyst, another feasible method was development of nanocomposites with magnetic nanoparticles, such as Zero Valent Iron (ZVI), so that it can be easily separated after treatment from aqueous medium using magnetic properties (Dong et al., 2013; Chang and Man, 2011). Another approach for the removal of TiO_2 nanoparticles from the aqueous solutions is by the process of electrocoagulation using iron electrodes. It was reported that more than 95% of TiO_2 nanoparticles was removed under neutral pH and applied current of 100 mA. Consecutively, the electrochemical sludge produced was considered as catalyst for peroxymonosulfate (PMS) activation to degrade emerging contaminants because of the presence of iron species (i.e., Fe_3O_4) (Ghanbari et al., 2020).

4.4. Degradation mechanisms of hydroxyl radicals

Hydroxyl radicals are highly electrophilic with strong oxidizing power (2.8 eV vs NHE). Therefore, they will seek electron pair from electron dense molecules like organic pollutants. Usually, in the aqueous solutions hydroxyl radicals oxidizes organic pollutants through three dominant reaction mechanisms, viz., dehydrogenation, hydroxylation and redox reactions. The addition of the radical to an aromatic ring or other unsaturated bond leads to the radical adduct formation (RAF) is known as hydroxylation; hydrogen atom transfer (HAT) by ·OH is called dehydrogenation, and single electron transfer with ·OH (SET) is called redox reactions. The reactions between the hydroxyl radicals and the organic pollutants are represented as follows:

$$\mathbf{RAF}: \mathbf{R} + \bullet\mathbf{OH} \rightarrow \mathbf{R} \bullet \mathbf{OH}$$
$$\mathbf{HAT}: \mathbf{R} + \bullet\mathbf{OH} \rightarrow \bullet\mathbf{R}(-\mathbf{H}) + \mathbf{H_2O}$$
$$\mathbf{SET}: \mathbf{R} + \bullet\mathbf{OOH} \rightarrow \bullet\mathbf{R}^+ + \mathbf{OH}^-$$

In the RAF mechanism, the ·OH reacts with aromatic compounds such as, benzene ring and forms OH-adducts by the electrophilic addition on unsaturated bonds. In the HAT mechanism, hydrogen atom abstraction takes place leading to release of water molecules. However, it is reported that in DMP degradation, SET is unimportant in the ·OH mediated degradation process and RAF and HAT are the dominant degrada-

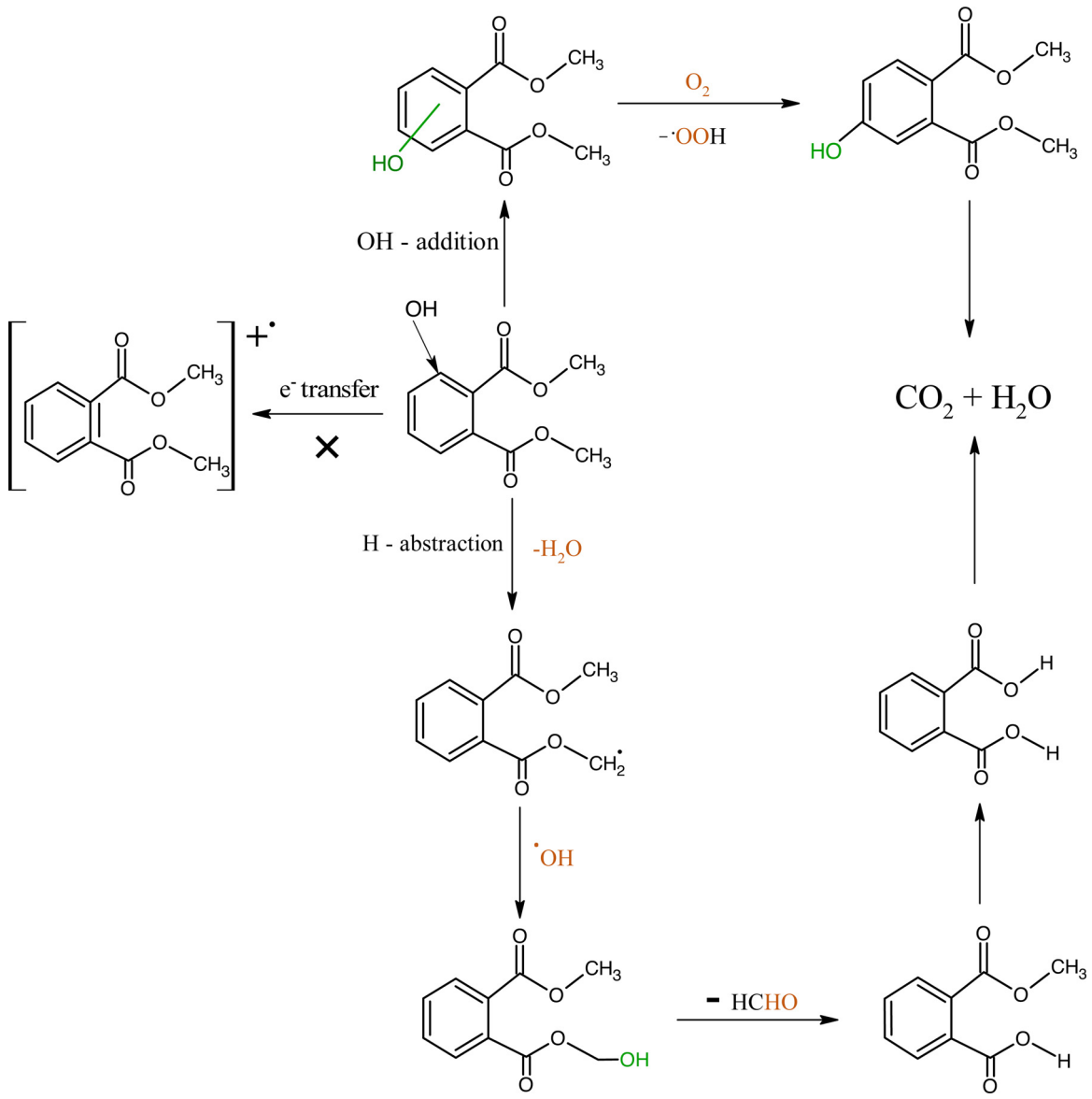

Fig. 5. Pathways of DMP degradation by hydroxyl radicals (An et al., 2014).

tion pathways (An et al., 2014). During the degradation process, four intermediate products, phthalic acid (PA), MMP, ortho-hydroxylated DMP and meta-hydroxylated DMP were reported and the possible reaction mechanism was represented in Fig. 5 (An et al., 2014). Finally, photocatalysis leads to the mineralization of products into CO_2 and H_2O, which would be expected if complete PAE removal was accomplished.

5. Scaling-up of technology

The demand for pure water brought new challenges to the scientific community. And, for the treatment of emerging contaminants (ECs), regulatory bodies are forcing industries to bring new and modified technologies to meet the specific standards set, by avoiding the use of traditional water treatment chemicals. For several years, traditional treatment processes like, biological treatment, physio-chemical treatment and chemical treatment (like, ozone, hydrogen peroxide, chlorine, potassium permanganate, etc.) have been used for the treatment of emerging contaminants. And the phase transfer technologies (e.g., air or steam stripping, adsorption, etc.) are non-destructive, as they only bring the physical separation of pollutants without transforming into non-toxic form, such that the final disposal of the transferred material creates problem. Recently, integrated processes (i.e., combination of phase transfer and oxidation processes) has been found to be effective for the mineralization of recalcitrant pollutants. However, the selection of operating process parameters is dependent on the type of pollutants present. Several by-products formed during the chemical treatment processes are more toxic than the parent compound so there is a chance of secondary pollution and because of low efficiency, the treatment cost increases if we want to achieve complete mineralization along with the destruction of intermediates. In this context, photocatalysis has several advantages over the conventional chemical oxidation methods such as, it does not require addition of oxidant compared with other methods, and has the potential to mineralize the pollutants into harmless form. Photocatalysis has been extensively studied in laboratory scale conditions for removal of various categories of toxic compounds in a simulated wastewater but it has not been scaled up yet.

5.1. Photocatalytic reactor design

To design photocatalytic reactors various parameters like, mass transfer rate, reactant-catalyst interaction, reaction kinetics, flow pat-

terns, control of temperature, catalyst installation, and uniform distribution of light into the catalyst surfaces needs to be considered (Mills et al., 1993; Mukherjee & Ray, 1999). The water treatment capacity of the reactor was determined by the amount of catalyst getting activated by the irradiation of photons of appropriate energy content.

And the light sources determine the energy requirement and the feasibility for industrial deployment. However, utilisation of solar radiation is a viable option to drive visible light activated photocatalysis to reduce energy requirements in photocatalytic process. As mentioned earlier, a primary limitation of TiO_2 nanomaterials as photocatalyst for various processes is that, they are only activated under UV spectrum or lower than that (Gupta et al., 2013). It is desirable to have a photocatalyst materials on large scale that can be activated under sunlight. In a photocatalytic reactor, the solid catalyst particles are either dispersed within a liquid phase or remains stationary within the reactor. Now in case of suspension types, recovery and regeneration of the catalyst particles was needed from the treated effluent and it can be difficult and laborious. Similarly, the entry of photons is restricted due to strong absorption by both dissolved organic matters and catalyst particles. The mentioned problems may be resolve in stationary photoreactors also it will reduce the risks related to the release of nanoparticles into the environment. In stationary photoreactors, the photocatalyst particles are immobilized onto a fixed surface, such as the reactor wall or are supported on particles, such as glass or polymeric beads and carbon materials which are held in fixed positions within the photoreactor. The volume of a photoreactor can be calculated as

$$\mathrm{VR} = \frac{QC_{in}X}{kR}$$

Where, Q is the volumetric flow rate (m^3/s), C_{in} is the inlet pollutant concentration (mol/m^3), X is the desired fractional conversion, k is the illuminated catalyst surface area in contact with the reaction liquid inside the reactor volume (m^2/m^3), and R is the average mass degradation rate ($mol/m^2/s$). Hence, the smallest reactor volume will result when k and R are high for the specified values of Q, C_{in}, and X. R is a reaction-specific parameter as it represents the efficiency of the catalyst for the degradation of a model pollutant, but k is a reactor-specific parameter indicating the amount of catalyst inside a reactor that is sufficiently illuminated so that it is active. An increase in the value of R could be achieved by altering the physical properties of the catalyst like, shape and size, or by the addition of oxidants. While the parameter k represents the illuminated specific surface area, which helps to compare the design efficiency of different photocatalytic reactors (Mukherjee and Ray, 1999).

The packed bed and fluidized-bed photocatalytic reactors are the type of photocatalytic systems which keeps the photocatalyst within the reactor. Therefore, there is no need for a collection step. In this context, Fang et al., (2019) studied the adsorption and degradation of bisphenol A in a fluidized-bed reactor by using composite of TiO_2 nanotubes and graphene. They reported 86% and 50% pollutant removal for 0.05 mg/L and 0.5 mg/L bisphenol A solution with a flow rate of 1 mL/min. In another study, Sun et al., (2020) reported an interesting alternative based on a magnetic bed photocatalytic reactor. They reported 92% degradation of methyl orange in 60 min by using a magnetic photocatalyst particles of $CoFe_2O_4$-Ag_2O introduced at the bottom of the reactor and anchored by the magnet. The magnetization not only helped in holding the photocatalyst but also reduces the band gap to activate the composite by visible light. Despite several studies, there are lot of issues associated with scaling up of reactors with immobilized photocatalyst like, providing high surface areas for the catalyst per unit of reactor volume (Mukherjee and Ray, 1999). Moreover, studies on reactor configurations focus on the degradation of model pollutant without providing information on the reaction intermediates and by-products, which are still toxic may be more toxic than parent compounds and poorly biodegradable.

5.2. Key considerations for advancing the technology

While designing a reactor many factors influences, but major challenge arises with the water matrix. Majority of photocatalytic experiments were conducted in laboratory conditions with a simulated wastewater focusing on a particular pollutant at a quantifiable concentration while, actual scenario differs from controlled conditions. The industrial effluent always contains a variety of substances, which include numerous electrolytes, heavy metals, oil, grease and other additional pollutants which tend to reduce the photocatalytic efficiency. Actually, in a reaction system, where variety of co-contaminants are present, the efficiency of PAE removal will get reduced as competition for both the active sites and ROS at the catalyst surfaces increases. These occurs due to blocking of active sites of the catalyst and radical scavenging by co-contaminants present within the system (Pang et al., 2021). In addition, a change in pH influences the interaction between PAEs and catalyst, because pH of the medium determines the chemical structure of PAEs (Julinová & Slavík, 2012; Pang et al., 2021). Also, turbidity reduces the photo-excitation of the catalyst by hampering the light penetration and distribution within the suspension (Drosos et al., 2015). Natural organic matters (NOMs) with high aromatic content are hydrophobic in nature, and hence it is easily adsorbed at the catalyst surface (Gora & Andrews, 2019). And ultimately, aromatic NOMs traps the holes from the valence band of the photocatalyst, which not only reduces the degradation caused by the holes but also inhibits the production of hydroxyl radicals (Drosos et al., 2015). Finally, natural organic matters and its transformation products further scavenge the generated ROS from the reaction system, preventing the degradation of the model pollutants.

5.3. Economic analysis

The economic analysis of photocatalytic wastewater treatment on an industrial scale is usually expressed in terms of operational cost which includes chemical cost as well as energy cost. And, the energy cost is calculated as electrical energy per order (E_{EO}) value which is electrical energy (in kWh) required to remove a pollutant by one order of magnitude in 1 m^3 of polluted water (Miklos et al., 2018). Mathematically, it is calculated by the equation,

$$\mathrm{EEO} = \frac{P\Delta t}{V\ log\frac{C_o}{C_t}}$$

Where, P is the power in KW, Δt is the reaction time in hours, V is the reactor volume in m^3, C_0 is the initial concentration of the pollutant and C_t is the concentration of pollutant at any time (Pang et al., 2021). Now, the ideal technology should be efficient, cost friendly and easy to implement, to reduce the operational cost of the industrial plant. Various advanced oxidation technologies, including ozonation, UV/chlorine, UV/persulfate, and UV/H_2O_2 present median E_{EO} values < 1 kWh/m^3 while, the E_{EO} values for photocatalysis with UV activation are generally >10–100 kWh/m^3 (Miklos et al., 2018; Fernandes et al., 2019). Thus, to transform photocatalytic water treatment into a bigger scale, electrical energy per order (E_{EO}) value needs to be reduced. Although it is encouraged to use electrical energy per order (E_{EO}) value for evaluating energy efficiency, but comparing on this single parameter with different technologies can be misleading. Therefore, an estimated operational cost of water treatment by various technologies has been compared in Table 8 showing the cost variation of the processes based on different parameters. In summary, the criteria for assessing the performance on a large scale must consider the photocatalyst cost, recovery and reusability of the photocatalyst, and scavenging of radicals in the real wastewater system under typical operating conditions (Pang et al., 2021). Each of these issues need to be addressed to make the photocatalytic process technologically and economically viable.

Table 8
Estimated Process Costs for Different Water Purification Systems to treat 1 m^3.

Processes	k (1/min)	Treatment time (min)	Oxidant amount (kg)	Catalyst amount (kg)	Energy demand (kJ)	Chemical cost			Energy cost			Operation alcost ($/m3)
						Cost ofO_3($)	Cost of H_2O_2($)	Cost of TiO_2($)	Cost of O_3 ($)	Cost of H_2O_2($)	Cost of UV($)	
H_2O_2/UV	9.0E-04	770	33	-	3049.8	-	16	-	-	23	71	110
TiO_2/O_3/UV	1.4E-03	495	20	0.5	4158.9	-	-	1.5	82	-	45	129
TiO_2/O_3/UV	1.0E-03	693	22	0.5	5822.4	-	-	1.5	114	-	64	179
O_3/UV	9.0E-04	770	32	-	6469.4	-	-	-	127	-	71	198
TiO_2/O_3/H_2O_2/UV	9.0E-04	770	O_3: 19 H_2O_2:6	0.1	7208.7	-	3	0.3	127	23	71	223
TiO_2/O_3/H_2O_2/UV	1.6E-03	433	O_3:14 H_2O_2:4	0.5	4054.9	-	2	1.5	71	13	40	127
O_3/H_2O_2	1.0E-03	693	O_3:22 H_2O_2:7	-	4408.4	-	3	-	114	20	-	138
O_3/H_2O_2/UV	1.2E-03	578	O_3:19 H_2O_2:6	-	5406.5	-	3	-	95	17	53	168

Source: https://doi.org/10.1016/j.cej.2019.123488 (Fernandes et al., 2019, Chemical Engineering Journal, 123488).

6. Conclusions and future prospects

This review has highlighted the fate and distribution of PAEs in different parts of the environment due to its high leaching capacity as it is not chemically bonded to the polymeric materials and the health risk associated it. PAEs follows different transformation pathways depending on various physiochemical factors. And, also have a number of exposure pathways from the contaminated air, water and soil. PAEs requires special attention due to their toxicity to all forms of life and can even sustain after primary and secondary treatments of wastewater. Due to these detrimental effects of PAEs, there is an increased focus on achieving removal as well as mineralization of these pollutants. There are various treatment processes available for the removal of PAEs like, coagulation-flocculation, adsorption, biodegradation, and advanced oxidation technologies. But conventional treatments are not effective for the treatment due to inherent physicochemical properties of PAEs and limitations of the processes. However, advanced oxidation processes have the capability to degrade the pollutant in a short span of time by the generation of various oxidants like, ·OH. Among various oxidation processes, semiconductor photocatalysis seems to be one of the most efficient process for mineralization of phthalate compounds as it brings complete mineralization of organic pollutants into non-toxic form. And for large scale PAEs removal using photocatalytic technology, several factors need to be taken into consideration such as, improve reactor design, sources as well as uniform light irradiation inside the reactor, providing high surface areas for the catalyst per unit of reactor volume, scavenging of hydroxyl radicals (·OH) by organic matter and other interfering species present in wastewaters, competitive adsorption of co-contaminants into the active sites, recovery and regeneration capacity of photocatalyst and pH dependency of the process. All these parameters may affect cost as well as process efficiency for industrial deployment. Therefore, techno-economic analysis coupled with field studies under actual treatment conditions are prescribed, so that the data generated could be applied to tackle the real-world problems. In last few years, significant developments have taken place towards detection, environmental fate and health effects of PAEs. However, in terms of process development for the removal of PAEs many issues remain unresolved and requires further investigations which are as follows:

a) Despite significant advancement in catalytic performance for the AOPs, the agglomeration tendency of the catalyst was not studied in the real wastewater matrix in a suspension system. It is important to study the agglomeration potential of the catalyst as it helps to recognize the interaction between catalyst surface and the pollutant as well as the efficiency of the catalyst.
b) From the perspective of adsorbents and modified adsorbents, the potential modifications to promote different adsorption mechanisms helps in improving adsorption capacity. Therefore, for the adsorption from the real wastewater having various types of PAEs, different interactions for different types of PAEs and the synergistic interactions should be explored. It will help in design of modifications of the adsorbents for the removal of PAEs. Similarly, in terms of scaling up, the regeneration and reusability potential of adsorbents are one of the critical factors. Hence, regeneration study was needed to restore the modifications of the adsorbents for the removal of PAEs.
c) In terms of scaling up, another important aspect would be the material synthesis strategies. It is essential to develop low cost synthesis processes which has the potential to produce large amount of catalyst for supporting the industrial demand. In this regard, raw materials such as, various agricultural waste, chitosan, alginate, etc. can reduce the overall cost of the process and helps to produce low cost materials having higher adsorption efficiency.
d) In terms of energy efficiency, future research is also needed to shift the absorption spectrum of photocatalyst from shorter wavelengths to longer wavelengths so that the energy requirement will get reduce. In this context, it is important to study the efficacy of natural

sensitizing materials which can improve the visible light activity of the photocatalyst.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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