

Phthalates removal from wastewater by different methods – a review

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ABSTRACT

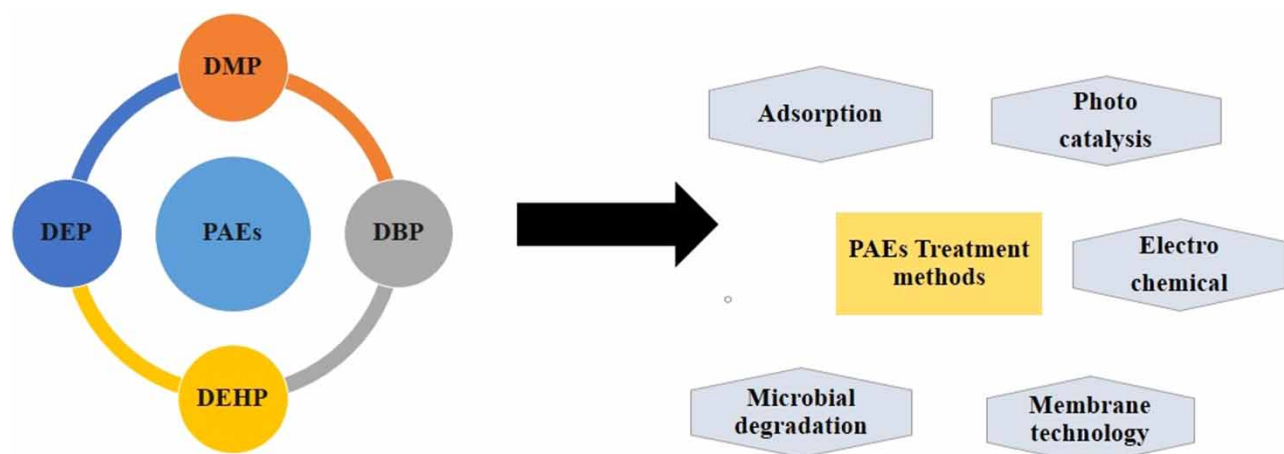
Phthalate esters are commonly used as plasticizers to improve the durability and workability of polymeric materials, locating and identifying them in various contexts has become a major challenge. Because of their ubiquitous use in plastic packaging and personal care items, as well as their tendency to leach out of these materials, phthalates have been detected in a variety of aquatic situations, including surface water, groundwater, drinking water, and wastewater. Phthalate esters have been shown to affect reproductive health and physical growth by disrupting the endocrine system. As a result, developing energy-efficient and effective technologies to eliminate these harmful substances from the atmosphere has become more important and urgent. This paper examines the existing techniques for treating phthalates and degradation mechanisms, as well as knowledge gaps and future research directions. These technologies include adsorption, electrochemical, photocatalysis, membrane filtration and microbial degradation. Adsorption and photo catalysis are the most widely used techniques for phthalate removal, according to the literature survey papers.

Key words: contamination, phthalates, pollution, removal technology, toxicity, wastewater

HIGHLIGHTS

- The existence of phthalates in wastewater are discussed.
- The aggressive effects due to the combined existence are summarized.
- Several technologies adopted for their simultaneous removal are reviewed.
- Different parameters used to study the removal efficiency are presented.
- The detection of pollutants by analytical techniques are defined.

GRAPHICAL ABSTRACT



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1. INTRODUCTION

Pollution in the ecosystem is a common problem with serious consequences for human health (Schell *et al.* 2006). Land pollution, air pollution, and water pollution are the three main forms of pollution. The aim of this research is to reduce water pollution (Owa 2013). Water quantity and efficiency concerns are at the root of many of humanity's large challenges in the twenty-first century (Schwarzenbach *et al.* 2010). Plastic pollution in the aquatic environment is becoming an increasing cause of concern (Wagner *et al.* 2014). Advances in materials science and engineering have caused the extensive and diverse use of plastics in recent decades to offer safer, cheaper, stronger, lighter and more durable flexible products and consumer goods that enhance our quality of life (Thompson *et al.* 2009). Plastics are used in almost every area of everyday life, including transportation, telecommunications, footwear, clothes, and also as packaging materials to help transport a wide variety of drink, food, and other products (Andrady & Neal 2009). Global plastic production reached 359 million tonnes in 2018, with up to 13 million tonnes of it ending up in aquatic systems, especially the oceans. A total of 250 million tonnes of plastic is expected to be discharged by 2025 (Shen *et al.* 2020). Micro plastics (MPs), or fragments with a diameter of less than 5 mm, are of special concern since they are more easily absorbed than larger particles in the food web (Wagner *et al.* 2014). MPs have become a global concern as an environmental pollutant, posing a risk to human health (Lu *et al.* 2019). In most plastic products, the basic polymer is coupled with various 'additives,' which are chemical compounds used to improve the polymer's performance, functionality, and ageing qualities (e.g., during shaping by injection moulding, extrusion, blow moulding, vacuum moulding, and other processes) (Hahladakis *et al.* 2018). A lot of these additives are used in a wide range of products (Meeker *et al.* 2009). The most widely used additives in different forms of polymeric packaging products are plasticizers, lubricants, acid scavengers, pigments, light and heat stabilisers, flame retardants, antistatic agents, antioxidants, slip substances, and thermal stabilisers (Hahladakis *et al.* 2018). Plasticizers are commonly used to improve polymeric film flexibility, durability, and stretchability (Suderman *et al.* 2018). Phthalates (Phthalic Acid Esters-PAEs) are among the most dangerous Endocrine-Disrupting Chemicals (EDCs) and well-known harmful plasticizers to human health (Julinová & Slavík 2012). PAEs are produced at a global scale of approximately 6 million tonnes per year (Wang *et al.* 2015). They are non-halogenated phthalic acid esters that have been commonly used for over 50 years in a number of industrial and consumer-oriented applications (Julinová & Slavík 2012). These PAEs are yellowish oil-like liquids or colourless with little odour. Their melting point is usually less than 25 °C, and their boiling points range from 230 to 486 °C (Roy 2012). By lowering shear during the polymer development mixing phases, it improves impact resistance in the final plastic film. They also give the material a limp and sticky appearance (Hahladakis *et al.* 2018). The highest levels of PAEs pollution in the atmosphere can typically be found near industrial estates (Fromme *et al.* 2002). Those pollutants are mostly lipophilic chemicals, they are easily absorbed into human blood or fluids and are quickly transformed into their respective primary and secondary metabolites, resulting in negative health effects (Benjamin *et al.* 2017). There are two kinds of phthalates: long-chain phthalates and short-chain phthalates. The long-chain phthalates used in PVC polymer include di(2-ethylhexyl) phthalate (DEHP), di(2-propylheptyl) phthalate (DPHP), di-iso-decyl phthalate (DiDP) and di-iso-nonyl phthalate (DiNP). Short-chain phthalates including dimethyl phthalate (DMP), butyl benzyl phthalate (BBzP), diethyl phthalate (DEP), di-iso-butyl phthalate (DnBP), and di-n-butyl phthalate (DnBP) are commonly used in non-PVC applications (Wittassek *et al.* 2011). The US EPA (Environmental Protection Agency) has designated several PAEs as priority toxic contaminants, including dimethyl phthalate (DMP), di-2-ethylhexyl phthalate (DEHP), dibutyl phthalate (DBP) and diethyl phthalate (DEP) (Wang *et al.* 2017). Different PAEs have different chemical and physical properties, which means they can be used for different purposes (Bornehag *et al.* 2005). DMP is one of the most commonly used PAEs compounds in industry for the production of a wide range of goods owing to its high saturation solubility (4860 mg L⁻¹) (Ahmadi *et al.* 2016) and it is used in insect repellents, solid rocket propellants, pesticides (ectoparasiticides), plastics, protective lenses, lacquers, rubber coating agents, insect repellents and moulding powders (Kaur *et al.* 2021). The USEPA, the Clean Water Act, and the World Health Organization have all listed DMP as a priority pollutant (Adhoum & Monser 2004). DBP is classed as an endocrine disruptor because of its capacity to harm the human endocrine, immunological, and brain systems even at very low concentrations (Wang *et al.* 2019a). As a result, DMP decomposition is crucial not only for scientific but also for industrial and medical reasons (Liao *et al.* 2010). DEP is the most often used plasticizer in a number of industrial items, including tools, automotive components, toothbrushes, food packaging, cosmetics, and pesticides, as well as in the perfume industries and as an alcohol denaturizing agent (Young 2003). The US EPA reported that total off-site DEP release was 1.26 tonnes per year based on data from the Toxics Release Inventory in 1994. The saturated solubility of DEP is extremely high and the value is 591 mg L⁻¹ (Özer *et al.* 2015). DEP has been

described as an endocrine disruptor and has been linked to a variety of diseases, despite its widespread use. It has been discovered to affect the neuroendocrine and male reproductive systems, as well as alter childhood obesity, lipid metabolism and decrease fecundity. DEP must be removed from aquatic habitats as a result (Kabir *et al.* 2015). DBP is a common plasticizer, particularly in personal care products like perfume solvents and hair spray fixatives (Li *et al.* 2015a). Tolerable daily intakes (TDIs) of 0.01 mg were developed by the European Food Safety Authority (EFSA) for DBP (Fankhauser-Noti & Grob 2007). DBP has the ability to disrupt the endocrine system and cause significant changes in male reproductive organ growth and development, such as absent or deformed epididymides, hypospadias, cryptorchidism, Leydig cell adenomas and reduced fertility (Chen *et al.* 2011). Because of its toxicity and high bioaccumulation rate, DBP removal has received a lot of attention in recent years (Huang *et al.* 2015). In recent years, DEHP has accounted for roughly half of total PAEs production. Between the 1980s and the beginning of the twenty-first century, global output of PAEs, including DEHP, grew from 2 to 5.5 million tonnes (Liang *et al.* 2008). It is used in PVC formulations and accounts for roughly 80% of the plasticizer volume used in the material's production (Hahladakis *et al.* 2018). It normally accounts for 30% of the PVC by weight in PVC flooring (Bornehag *et al.* 2005). Solvents in adhesives, cosmetics, inks, perfumes, munitions, paints, insect repellents, hairspray additives and lubricating oil are non-polymeric products that contain DEHP (Zolfaghari *et al.* 2014). DEHP has been shown in several studies to have harmful environmental consequences, even at low concentrations (Shi *et al.* 2012). The optimal daily DEHP dose for adults has been determined to be 0.71 mg/kg/d (Benson 2009). Wastewater with a high concentration of DEHP must be subjected to a restrictive condition. Treatment at the source, for example, can also be used until effluent is discharged into sewage urban networks (Zolfaghari *et al.* 2014). DEHP has been shown in several studies to have endocrine disrupting properties and may cause cancer (Kamrin 2009).

Julinová & Slavík (2012) reported the concentrations of 1900–3120 µg/kg of DEHP and 720–800 µg/kg of DEP in freshwater. Due to the possible endocrine disrupting effects of PAEs, environmental quality standards (EQSs) based on yearly average concentrations in freshwater environments have been determined, ranging from 20 µg/L for DEHP to 800 µg/L for DMP. DEHP concentrations up to 470 µg/L have been found in groundwater in the United States. DEP (147 µg/L) and DBP (50 µg/L) concentrations in some areas were higher than those found in drinking water and surface water. DEP, DBP, and DEHP concentrations in surface waters ranged from 1.33 to 2300 ng/L, 1.69 to 4430 ng/L, and 2.26 to 5000 ng/L, respectively. DEHP concentrations ranged from 2.42 to 30.99 µg/L in China, 6.71–467 µg/L in France, 13–43.9 µg/L in Denmark, 3.1–34 µg/L in Austria, and 23.6 µg/L in the United States (US) in surface water. In Paris, DBP concentrations in industrial effluents ranged from 1.10 to 4.99 µg/L. The level of DEP and DBP concentrations in wastewater treatment plants in northern India was investigated and found to be 2.1–83.5 and 0.9–19.7 µg/L, respectively, which are comparable to those reported in China and France. The amount of phthalates in wastewater in a given country varies depending on the quantity of production and restrictions in that country (Gani *et al.* 2017). So these PAEs are now the environmental priority contaminants and one of the most important environmental issues, despite increasingly strict regulations. To safeguard humans and the environment, these dangerous substances should be eliminated from wastewater. Several methods for removing PAEs from water and wastewater have been established due to their widespread production and high toxicity. This present review article summarizes various methods for various types of PAEs removal.

1.1. Physical and chemical properties of PAEs

Phthalates are odourless liquids that are colourless or yellowish in appearance. Their melting point is typically below 25 °C, whereas their boiling point ranges from 230 to 486 °C. The most widely used phthalates are hydrophobic, which has a substantial impact on their environmental behaviour (Julinová & Slavík 2012). If the molecule comprises relatively lengthy alcohol moieties, solubility can be less than 1 mg L⁻¹. Table 1 shows physico-chemical data such as octanol-water partition

Table 1 | Physical and chemical properties of PAEs

Phthalates	Abbreviation	Chemical formula	Molar mass (g mol ⁻¹)	Melting point (°C)	Log K _{o/w}	Log C _{wsat}	Log K _{oc}
Di Ethyl Phthalate	DEP	C ₁₂ H ₁₄ O ₄	222.2	-40	2.72	2.364	4.2
Di Methyl Phthalate	DMP	C ₁₀ H ₁₀ O ₄	194.2	5.5	1.85	1.646	2.3
Di Butyl Phthalate	DBP	C ₁₆ H ₂₂ O ₄	278.4	-35	4.46	4.402	4.11
Di Ethyl hexyl Phthalate	DEHP	C ₂₄ H ₃₈ O ₄	390.6	-46	7.94	6.374	5.72

coefficients ($\text{Log } K_{o/w}$), solubility ($\text{Log } C_{\text{sat } w}$), and sorption ($\text{Log } K_{oc}$) for the most predominant phthalates (Cousins *et al.* 2003).

2. PHTHALATE REMOVAL METHODS

There are five major technologies used for the removal of PAEs, namely adsorption, photo catalysis, electrochemical, membrane technology and microbial degradation. Figure 1 represents these methods used to treat PAEs.

2.1. Adsorption

Adsorption is an advanced treatment method for small molecular contaminants in water that is commonly used as an alternative. As compared to other methods, adsorption has the advantages of ease of use, low cost, low energy consumption and high purification rate (Çeçen & Aktaş 2011). Adsorption is a surface-based exothermic process in which molecules of a gaseous or liquid chemical accumulate on an adsorbent surface. Adsorption takes place because the particle on the surface and the particle in the bulk of the adsorbent do not share the same environment. That is to say, the net force acting on them is different. Unbalanced forces, also known as residual attractive forces, act on the particle on the surface. Due to these forces, the adsorbent's surface particles attract the adsorbate particles. During adsorption, the surface's residual attractive forces constantly decrease (Julinová & Slavík 2012). Organic substances adsorption is highly influenced by their polarity, molecule size and chemical composition. The larger the molecule, the higher the adsorption (Fu & Wang 2011). Chemical structure is demonstrated by the presence of distinct functional groups that dissociate or do not dissociate. It may adsorb on different surfaces depending on the pH value. Organic molecules polarity has a significant impact on their experimental adsorption conditions (pH, initial adsorbate concentration, and temperature), adsorbate characteristics (molecular size, solubility, pKa, and electron distribution), and adsorbent properties (surface area, pore size distribution, and surface functionalization) (Tran *et al.* 2020). Different adsorbates adsorb on different adsorbents in different ways. Furthermore, adsorption can be reversed in some cases, and adsorbents can be regenerated with the right desorption process (Fu & Wang 2011). As a result, researching the removal of PAEs from wastewater via adsorption is useful (Yuan *et al.* 2020).

2.1.1. Low-cost adsorbents

The search for low-cost, easily accessible adsorbents to remove organic pollutants has moved into full force. Agricultural wastes, industrial by-products and wastes, and natural substances have all been studied as adsorbents for the treatment of PAEs wastewater. Many studies have looked into the usage of low-cost adsorbents to treat PAEs. Chen *et al.* (2019) studied the removal of DEP using smectite clay as an adsorbent and discovered that this phthalate was effectively degraded in the reaction system at pH 7.0. Adsorption of DBP using vanillin-modified chitosan beads was reported by Li *et al.* (2015a), and it could be considered as a potential adsorbent. Cao *et al.* (2014) explored the biofilm adsorption capacity on DEHP. One g biofilm had a DEHP adsorption capacity of 34.67 g. This study demonstrated a transient balance of DEHP concentrations between biofilms and wastewater. Qureshi *et al.* (2016) employed two adsorbents to remove DEHP from aqueous solutions: montmorillonite clay composites (MMT) and polyaniline functionalized montmorillonite clay composites

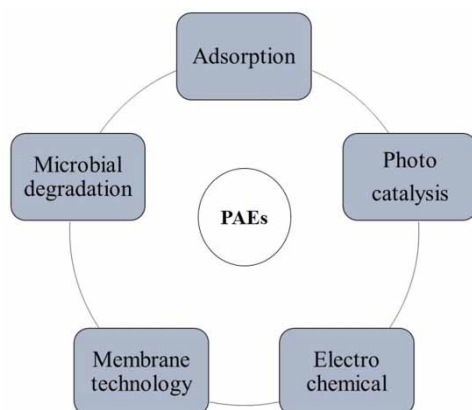


Figure 1 | Major techniques to remove PAEs.

(PANI/MMT). When compared to MMT, PANI/MMT demonstrated nearly complete adsorption for DEHP removal in this study. Xu & Li (2008) examined the use of DBP sorption in marine sediments. DBP has a high sorption capacity of 53–79 mg g⁻¹, which correlates with their organic content, and adsorption has been identified as a significant mechanism for DBP uptake.

2.1.2. Carbon and polymer based adsorbents

Several coating materials have been developed and widely used for PAEs removal due to their excellent qualities and uses, including ionic liquid/polymeric ionic liquids, carbon-based nanomaterials, metal/metal oxide nanoparticles, and molecularly imprinted polymers (e.g., graphene and carbon nanotubes). As a relatively novel adsorbent, carbon nano tubes have been proven to have a lot of potential for removing various forms of PAEs from waste water (Amanzadeh *et al.* 2016). According to the findings of the studies discussed, carbon nanotubes (CNTs) are promising candidates for PAEs adsorption. To eliminate DBP from tap water samples, Xu *et al.* (2017) employed surface molecular imprinted polymers based on carboxyl-modified silica nanoparticles. Tümay Özer *et al.* (2016) studied the adsorption capacity of DEP by using PHEMA nanobeads and the maximum capacity was determined as 265.1 mg/g at pH 4.0, 25 °C. The Sips isotherm model fits the experimental data in the wide range of DEP concentration tested (1–300 mg L⁻¹). To evaluate DEP in tap water, river water, and sea water samples, the recoveries of SPE (solid phase extraction) using multi-walled carbon nanotubes (MWCNTs) were compared to numerous commercial SPE adsorbents such as C8, C18, and PS-DVB. MWCNTs were found to be more effective than these adsorbents, with recovery rates ranging from 80.3 to 104.5% (Cai *et al.* 2003). Wang *et al.* (2016) examined the capacities of nonwoven polypropylene fabric (PP), nonwoven polypropylene fabric (PP) (PP-g-CaSiO₃) and CaSiO₃ grafted PP (PP-g-CaSiO₃SiO₂) for DBP removal. With an adsorption equilibrium period of 2 hours, DBP adsorption capacity by PP-g-CaSiO₃SiO₂ was 54.8 mg/g. PP-g-CaSiO₃SiO₂ showed more excellent DBP adsorption characteristics than PP-g-CaSiO₃ and PP. The non-woven PP-g-CaSiO₃SiO₂ processing method and recycling technique are simple, low-cost, and pollutant-free. Azari *et al.* (2019) studied the removal of DEP using magnetic iron oxide/graphene oxide (MGO) nanocomposites as adsorbent which was prepared by a simple and effective chemical co-precipitation method. The maximum adsorption factors and adsorption capacity were 100% and 116.933 mg/g respectively, while the relative standard deviations (RSDs) were <1.6% (N = 5). The DEP adsorption process was studied using magnetic iron oxide/graphene oxide (MGO) nanocomposites. The maximum adsorption capacity and adsorption factors were found to be 116.933 mg/g and 100%, respectively, under optimised conditions with relative standard deviations (RSDs) of 1.6% (N = 5). Lower concentrations resulted in greater clearance efficiency in this case. The DEP adsorption capacity on magnetic poly beads-ethylene glycol dimethacrylate-vinyl pyridine (mag-poly EGDMA-VP) was determined to be 98.9 mg/g at a temperature of 25 °C and a pH of 3.0, making it a promising adsorbent for potential applications (Tümay Özer *et al.* 2012). The adsorption of DEP on poly EGDMA-MATrp (ethylene glycol dimethacrylate-N-methacryloyl-L-tryptophan methyl ester) beads was investigated by Özer *et al.* (2015). DEP had an optimum adsorption capacity of 590.7 mg/g at 25 °C. Ahmadi *et al.* (2016) studied the use of magnetic zeolite nanocomposites (MZNC) to remove DMP. At pH 3, contact period of 20 minutes, zeolite: Fe₃O₄ ratio molar of 2:1, adsorbent dosage of 1 g/L, and temperature of 50 °C, this MZNC had the highest adsorption capacity. DMP was extracted using barium hexaferrite (BaFe₁₂O₁₉) beads with mag-poly (EGDMA-VP), with a capacity of 96.2 mg/g polymer. With minimal reduction in initial adsorption capability, these beads were easily regenerated by reducing the pH and reused for DMP adsorption (Osman *et al.* 2012). In the presence and absence of 50 mg L⁻¹ copper (II) (Cu²⁺) ion, DMP adsorption and desorption on five different types of carbon nanotubes (CNTs) were examined. This study used CNTs with outer diameters of 1–2 nm and four different varieties of multi-walled nanotubes (MWCNTs) with outer diameters of 10–20 nm. They are as follows: (MWCNT10), 20–40 nm (MWCNT20), 40–60 nm (MWCNT40), and 60–100 nm (MWCNT60). Without Cu²⁺ adsorption, the study goes as follows: SWCNT > MWCNT10 > MWCNT20 > MWCNT40 > MWCNT60. In the presence of 50 mg L⁻¹ Cu²⁺, the sorption isotherms shifted to SWCNT > MWCNT10 > MWCNT40 > MWCNT60 > MWCNT20 to SWCNT > MWCNT10 > MWCNT40 > MWCNT60 > MWCNT20. DMP adsorption on CNTs increases in the presence of Cu²⁺ ions. MWCNT60 > SWCNT > MWCNT40 > MWCNT20 > MWCNT10 when ordered by surface area (K/Asurf), and this finding showed that MWCNT60 may have more DMP and Cu²⁺ ion accessible surfaces (Wang *et al.* 2013). To remove DMP from aqueous solution, different organo-vermiculites (OVts) were utilised, with C14-4-C14im-Vt displaying the most promising adsorbability (274.4 mg g⁻¹) and almost 60% adsorbability after five cycles. (OVts) has the following adsorption order: C14-4-C14im-Vt > C12-4-C12imVt > C16-4-C16imVt (4.24, 3.70, and 2.66, respectively) (Xiang *et al.* 2019). In the adsorptive removal of DMP from synthetic and municipal wastewater, MWCNTs

and magnetic (Fe_3O_4) MWCNTs were utilised as adsorbents. MWCNTs had a maximum DMP adsorption capacity of 196.85 mg g^{-1} , compared to 136.99 mg g^{-1} for $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ (Zhuang *et al.* 2020). DEHP was removed using poly(phenyl(4-(6-thiophen-3-yloxy)-benzylidene)/ Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4\text{P}_3\text{TArH}$). The maximum adsorption capacity of $\text{Fe}_3\text{O}_4\text{P}_3\text{TArH}$ was determined to be 298.15 K at pH 7, and it was shown to be pH and temperature dependant (Baharin *et al.* 2016). The adsorption of DEHP from aqueous solution using C8-modified magnetic graphene oxide (C8-MGO) was investigated. The experimental results showed that sorption equilibrium was reached in 2.5 hours and the adsorption capacity was 2.5 mg/g (Wang *et al.* 2019b). For DEHP removal the used adsorbent was nano porous gold-polyethyleneimine, and the removal efficiency was approximately 90.9%, with enzymatic hydrolysis contributing approximately 81.9% (Zhang *et al.* 2014).

2.1.3. Biosorbents

Biosorption has long been touted as a promising method for the removal of various types of organic pollutants (Chan *et al.* 2004). Biosorption's main advantages are its great efficiency in decreasing PAEs levels and the utilisation of low-cost biosorbents. To eliminate DBP and DMP from polluted water, Yao *et al.* (2019) employed pepper straw as biochar. They discovered that turning pepper straw into biochar and using it as sorbents could be an environmentally friendly method to use vegetable waste. The adsorption of DBP, DMP, and DEHP on chitosan was investigated by researchers (Salim *et al.* 2010). DBP was adsorbed more than DEHP and DMP, with the order of adsorption capacity of PAEs being DBP (0.022 mg/g) > DEHP (0.01 mg/g) > DMP (0.009 mg/g). Beached seaweed and sargassum siliquastrum were utilised in the study by Chan *et al.* (2004) to remove DEHP, with mean removal capacities of 5.68 and 6.54 mg g^{-1} , respectively. DEHP adsorption by seaweed biomass is affected by temperature, with the best conditions being 25 mg biomass, pH 4, 25°C , and 40 mg L^{-1} DEHP. The summary and overview of adsorbents to be used for the degradation of PAEs are given in Table 2.

2.1.4. Activated carbon

The most widely used and effective adsorbent for micro-contaminants is activated carbon. However, its high cost has prompted the development and exploration for novel non-conventional adsorbents to make the process more cost-effective and ecologically acceptable. Because phthalate removal treatment is directly linked to sorption to solids, improving solid separation would also improve phthalate removal. Wang (2015) investigated the adsorption of DBP from aqueous solution using activated carbon derived from phoenix leaves. DBP adsorption capacity was 48.68 mg/g at pH 13, with a maximum adsorption rate of 97.36%. The Langmuir isotherm was used to calculate the adsorbent's monolayer sorption capacity, which was found to be 133.33 mg/g .

For the various doses of DEP evaluated in the aqueous environment, the effectiveness of adsorption (120 min) varied, ranging from 82.6% (for 0.5 mg L^{-1}) to 53.2% (for 3 mg L^{-1}). The adsorption capacity of activated carbon was investigated by Venkata Mohan *et al.* (2007) at 30°C , 100 rpm stirring speed, pH 7, and a DEP concentration of 1 mg L^{-1} for 120 minutes. The amount of activated carbon used was between 0.2 and 0.4 mg L^{-1} . The adsorption of DBP onto nutshell-based activated carbon (BET area $1224 \text{ m}^2/\text{g}$) was investigated by Fang & Huang (2009). The researchers discovered that a low concentration of DBP resulted in a slow rate of DBP adsorption on nutshell activated carbon (NAC) and a low sorption capacity. This means that at low DBP concentrations, the interaction between DBP and NAC is minimal. At the same time, it was discovered that as the temperature (55°C) rises, the adsorption capacity of NAC rises from 40.1 to 104.7 mg/g , implying that this is an endothermic process influenced by intra-particle diffusion. This suggests that as the temperature rises, the rate of diffusion of DBP molecules increases while diffusion resistance lowers, increasing NAC's adsorption capability.

Some key factors of carbon materials involved in phthalate removal are contact time, initial concentration, carbon dose, and operational pH. Influence of pH has a main role in phthalate adsorption from aqueous solutions. Effect of pH restricts phthalate ionisation and the amount of charge density on activated carbon. The protonated effect of activated carbon surface functional groups such as amino, carboxyl, thiol, and others lend positive charge to the surface, which may add electrostatic attractions between PAEs and activated carbon to the usual hydrophobic interactions. At neutral pH, the neutral charge on the adsorbent and adsorbate prevents the production of any extra sorbed mechanisms other than hydrophobic contacts. However, at basic pH, an increase in hydroxyl ions causes the formation of aqua-complexes, which slow down adsorption. Adsorption inhibition at high pH can be caused by a variety of factors, the most important of which are the characteristics of the adsorbent and phthalate. The impact of contact time on the sorption kinetics has an

Table 2 | Adsorption of PAEs

Adsorbent used	PAEs	Adsorbent dosage	Initial concentration (mg L ⁻¹)	Temperature (°C)	pH	Contact time (hours)	Adsorption capacity (mg/g)	Inference
Biofilm	DEHP	60 mg	–	4	–	20	34.67	Cao <i>et al.</i> (2014)
Carboxyl-modified silica nanoparticles	DBP	–	4–18	25	–	24	64.3	Xu <i>et al.</i> (2017)
PHEMA poly (hydroxyethyl methacrylate) nanobeads	DEP	–	1–300	25	4	24	265.1	Tümay Özer <i>et al.</i> (2016)
PP-g-CaSiO ₃ SiO ₂	DBP	0.10 g	10–150	25	3	12	54.8	Wang <i>et al.</i> (2016)
Magnetic iron oxide/graphene oxide (MGO) nanocomposites	DEP	0.3 g	2–10	25	–	–	116.933	Azari <i>et al.</i> (2019)
Magnetic poly beads-ethylene glycol dimethacrylate-vinyl pyridine (mag-poly EGDMA-VP)	DEP	–	1–300	25	4	–	265.1	Tümay Özer <i>et al.</i> (2016)
Poly EGDMA-MATrp beads	DEP	0.02 g	1–500	25	3	3	590.7	Özer <i>et al.</i> (2015)
Barium hexaferrite (BaFe ₁₂ O ₁₉) beads containing mag-poly (EGDMA-VP)	DMP	–	1–500	25	3	3	98.9	Tümay Özer <i>et al.</i> (2012)
C14-4-C14im-Vt	DMP	0.05 g	–	35	9	12	274.4	Xiang <i>et al.</i> (2019)
MWCNTs	DMP	0.2 g	5–200	25	7	12	196.85	Zhuang <i>et al.</i> (2020)
Fe ₃ O ₄ /MWCNTs	DMP	0.2 g	5–200	25	7	24	136.99	Zhuang <i>et al.</i> (2020)
C8-modified magnetic graphene oxide (C8-MGO)	DEHP	20 mg	–	25	–	1	2.5	Wang <i>et al.</i> (2019b)
Nano porous gold-polyethyleneimine	DEHP	50 mg	5–100	25	7	24	32.12	Zhang <i>et al.</i> (2014)
Activated carbon from phoenix leaves	DBP	0.1 g	5–15	25	13	2	48.68	Wang (2015)
Chitosan beads	DBP	3 g	–	25	7	12	0.022	Salim <i>et al.</i> (2010)
	DEHP	3 g	–	25	7	12	0.01	Salim <i>et al.</i> (2010)
	DMP	3 g	–	25	7	12	0.009	Salim <i>et al.</i> (2010)
Seaweed	DEHP	25 mg	10–300	25	4	2	5.68	Chan <i>et al.</i> (2004)
Sargassum siliquastrum	DEHP	25 mg	10–300	25	4	2	6.54	Chan <i>et al.</i> (2004)

effect on the phthalate elimination efficiency of adsorption. Increased contact time increases adsorption capacity by binding phthalates to all active sites/pores. However, removal rates grow until an optimum contact duration has been reached, at which all specific adsorbent sites have been occupied. In the beginning, Venkata Mohan *et al.* (2007), found a high rate of DEP removal by activated carbon, but the rates steadily reduced after 120 minutes of contact time and became constant until reaching equilibrium. The adsorption of phthalates is also affected by temperature, and this impact is most noticeable when adsorption occurs by intra particle diffusion. The rate of diffusion of phthalate molecules into the pores of the adsorbent increases as the temperature rises, and the energy is derived from the ambient heat. In addition to an increase in surface diffusion rate with temperature, the authors also found a decrease in DEP surface tension at higher temperatures as a probable reason for increased adsorption. Adsorption removal increases as phthalate hydrophobicity is measured by the octanol-water partition coefficient (K_{ow}), which is directly proportional to phthalate molecular weight and side chain length. The removal rate also increases as the adsorbent concentration is increased (Gani & Kazmi 2016).

2.2. Photocatalytic degradation

Photocatalysis has developed as a hopeful method and plays an important role in the decomposition of PAEs due to its comprehensive advantages of simplicity, eco-friendliness, low cost, gentle operation, and it has the ability to remove multiple pollutants in complex water matrices simultaneously (Pang *et al.* 2021a). A photocatalytic reaction involves the use of ultra-violet (UV) or visible light, as well as a selective reagent, to facilitate a chemical reaction, the breaking of chemical bonds, and the formation of breakdown products from the targeted compounds. Although many compounds are resistant to direct photolysis, even direct absorption of light can result in photo degradation. As a result, another oxidant or catalyst is required, which usually leads in the creation of highly reactive and short-lived reactive oxygen species (ROS), such as hydroxyl radicals ($\cdot\text{OH}$) (Pang *et al.* 2021b). Photocatalysis is a low-cost, flexible green technique that is commonly utilised to degrade organic contaminants like EDCs. In photocatalytic processes, a semiconductor acts as a photocatalyst, absorbing light in a specified wavelength range and causing electron (e^-) excitation from the valence band (VB) to the conduction band (CB). As stated in Equation (1), this leap causes positive holes (h^+) in the photocatalyst's VB:



As seen in Equations (2) and (3), holes in the VB split H_2O molecules, resulting in the production of hydroxyl free radicals, whereas electrons in the CB are held by oxygen molecules, resulting in superoxide radicals:



Other reactions between the species can occur, resulting in more $\cdot\text{OH}$ radicals, as shown in Equations (4)–(6):



Organic pollutants, such as EDCs, can be degraded by the generated hydroxyl radicals, which are adsorbed/absorbed on the catalyst surfaces through a series of regulated stages to yield CO_2 and H_2O , as shown in Equation (7):



Photo generated holes may directly react with adsorbed organic targets, producing intermediates that can be oxidised to CO_2 and H_2O , in addition to ROS action (Imparato *et al.* 2022). However, in order to provide a more comprehensive review of materials employed, a broader range of catalysts is discussed here, which are classified into three categories: single metal oxide, doped, and composite photocatalysts.

Single metal oxide semiconductors such as ZnO , Fe_2O_3 , and TiO_2 have been widely documented in the literature for photocatalytic applications due to their commercial availability. TiO_2 is a photoactive material that comes in a range of shapes and sizes, including pellets, paints, and powders, each with its own crystal morphology. TiO_2 has been employed in much of the early work in photocatalytic applications because it is inexpensive, non-toxic, and chemically inert. Remarkably, one of the earliest reports on PAEs removal was from the late 1980s, despite the fact that much of the work on PAEs removal began in the early 2000s, in part due to growing concern about PAEs in water. Efforts to design materials that can eliminate PAE at high rates under visible light irradiation have continued to this day, with a number of studies published since 2005. During this time period, as well as in more recent years, papers investigating PAE removal at pilot scale and under solar irradiation were published (2017 onwards).

Photocatalytic research is frequently focused on materials synthesis and the development of novel photocatalysts, which is typically motivated by a desire to overcome the perceived limitations of single oxide materials like TiO_2 . TiO_2 has a significant energy band gap (3.2 eV for anatase and 3.0 eV for rutile), electron excitation from the VB to the CB must be driven by UV light. Second, for many photocatalytic degradation events, the electron-hole pair recombination rate is significant, resulting in

low photonic efficiency. As a result, early research focused on altering TiO_2 to produce a visible light absorption material with great photonic efficiency. This is frequently achieved by adding co-catalysts into the catalyst matrix or sprinkling small nanoparticles across the catalyst surface. Element doping with metals and non-metals has been proven to be a viable approach for reducing the energy band gap of photocatalysts and increasing visible light absorption because dopants can introduce intermediate energy levels (Hassan *et al.* 2016). Co-catalysts can also assist to minimise recombination by improving electron-hole charge separation, resulting in enhanced PAE degradation. Material development has focused on the production of composites by mixing semiconductors with a variety of materials and support structures that can improve light harvesting, charge separation, and downstream filtration capabilities, in addition to catalyst doping. The purpose of composite material manufacturing is typically to increase excitation across a larger wavelength range while also enhancing charge species. The purpose of composite material manufacturing is typically to increase excitation over a wider wavelength range while also enhancing charge species separation via efficient electron transfer (Zhang *et al.* 2010).

The degradation of dibutyl phthalate (DBP) in aqueous solution under visible LED irradiation was achieved by using a simple chemical co-precipitation approach to produce (Fe, Ag) co-doped ZnO nanostructure. A maximum reduction of 95% of DBP was achieved using a photocatalyst concentration of 150 mg L^{-1} , pH of 3, and a DBP initial concentration of 15 mg L^{-1} . Iron-loaded activated carbon was developed and used as a catalyst in the DBP heterogeneous catalytic ozonation. A catalyst dose of 10 mg L^{-1} resulted in a 25% improvement in DBP (initial concentration 2 mg L^{-1}) reduction in 60 minutes when compared to ozone alone, and a catalyst dose of 100 mg resulted in a 46% improvement in DBP removal (Huang *et al.* 2015). (Fe, Ag) co-doped ZnO nanorods degraded DBP in aqueous solution when exposed to visible LED light. A maximum DBP reduction of 95% was achieved at a pH of 3, a photocatalyst concentration of 150 mg L^{-1} , and an initial DBP concentration of 15 mg L^{-1} (Akbari-Adergani *et al.* 2018). The degradation of DBP photoinduced by Fe (III) in aqueous solution was examined under monochromatic and sunlight irradiation. This is the most common and effective method for removing DBP from water (Bajt *et al.* 2001). For the removal of DBP from waste water, Chalasani & Vasudevan (2013) developed a photocatalytic $\text{Fe}_3\text{O}_4/\text{TiO}_2$ core shell magnetic nanoparticles catalyst. The cyclodextrin-functionalized $\text{Fe}_3\text{O}_4/\text{TiO}_2$ nanoparticles in the dispersion can be removed and reused once the photo degradation is finished (Wang *et al.* 2020). Nearly 97% of DBP was removed from aqueous solution after 3 hours of visible light irradiation. The kinetic constants of DW-ATNTAs degradation are 50 and 7 times greater than those of TNTAs and A- TiO_2 (plate), respectively. Two sol gel procedures (citric acid gel and Pechini methods) were used to improve the properties of nano-sized undoped, Cu co-doped, Bi-doped, and Bi samples for photocatalytic degradation of DBP. For Bi, Cu co-doped SrTiO_3 samples, the citric acid gel method produced the best photocatalytic operation, and it is a successful photocatalyst material for environmental applications (Jamil *et al.* 2017). Salazar-Beltrán *et al.* (2019) proposed TiO_2 -based catalysts for photocatalytic degradation of DMP and DEP using sequential injection analysis (SIA) in combination with liquid chromatography (LC) with UV detection. Degradation percentages of two commercial TiO_2 products with mixed phases (anatase/rutile), Degussa P25 (82/18%) and Hombikat (76/24%), were close to 100% when exposed to UV-vis radiation. Using a laboratory-made pure anatase crystalline TiO_2 phase, 60% degradation was accomplished. DMP degradation efficiencies were least affected by pH and catalyst amount. Higher degradation efficiency was obtained with Degussa P25 at pH 10 and 1.5 g L^{-1} catalyst dosage. The UV/ H_2O_2 and direct UV degradation of DEHP were studied in Chen (2010). After 180 minutes of UV/ H_2O_2 treatment, DEHP was completely eliminated, and 73.5% after 180 minutes of direct UV photolysis. According to the findings, UV/ H_2O_2 can be used in the treatment of DEHP in wastewater. Huang & Chen (2010) found the photocatalysis of titanium dioxide (TiO_2) to decompose DEP in aqueous solution. After 50 minutes of irradiation, DEP was totally removed from the solution, and the TiO_2 photocatalyst was found to be inactive in the dark. The researchers discovered that the initial DEP concentration, pH, light intensity, and photocatalyst volume all influence the rate of DEP breakdown. Hung *et al.* (2017) demonstrated the degradation of DEP using a photocatalyst sequence of polyaniline-carbon nanotubes/ TiO_2 (PANi/CNT/ TiO_2) immobilised on a glass plate irradiated with visible light. Doping TiO_2 with polyaniline (PANi) and two functionalized carbon nanotubes (CNT-COCl and CNT-COOH), followed by a hydrothermal synthesis and a sol-gel hydrolysis, yielded this photocatalyst. The strongest DEP degradation was discovered in a simulated sunlight device that was exposed for 120 minutes for sol-gel hydrolysis. Ki *et al.* (2019) reduced the band gap energy of the initial photocatalyst titanium dioxide and increased DEP removal by utilising tungsten oxide as a photocatalyst. To make a modified photocatalyst, tungsten oxide was deposited over titanium dioxide using liquid phase plasma. By varying the tungsten oxide loading on the photocatalyst surface under various light sources, such as UV and blue light sources, the degradation of DEP was investigated. Under blue light, modified TiO_2 photocatalysts degraded at a pace 1.7–6.2 times quicker than bare TiO_2 photocatalysts, despite the fact that bare TiO_2

photocatalysts functioned better under UV light. Under xenon light irradiation, Sun *et al.* (2021) investigated wastewater treatment employing photocatalytic degradation of Nano-Fe₂O₃ embedded in montmorillonite particles (Fe-Mt) to break down DEP with citric acid (CA). The Fe-Mt/CA system outperformed the pure nFe₂O₃/CA system in terms of photocatalytic efficiency due to its porous structure, more oxygen vacancies and wide surface area. When exposed to sunlight, Fe-Mt/CA has been shown to efficiently degrade organic contaminants. Chen *et al.* (2009) used titanium dioxide-coated magnetic poly methyl methacrylate (TiO₂/mPMMA) microspheres and platinum-doped TiO₂/mPMMA (Pt-TiO₂/mPMMA) microspheres to demonstrate photocatalytic degradation of DMP. Furthermore, photocatalytic activity of Pt-TiO₂/mPMMA microspheres outperforms that of TiO₂/mPMMA microspheres, particularly in terms of mineralization efficiency. The ability of the two composites vanadium pentoxide (V₂O₅)/molybdenum trioxide (MoO₃) were used in Chuai *et al.* (2015) to photodegrade DMP under visible light irradiation to assess their photocatalytic activity. When compared to pure V₂O₅ and MoO₃, these composites showed higher visible light photocatalytic activity due to a V 3d impurity energy level and the development of heterostructures at the V₂O₅/MoO₃ interface. Ding *et al.* (2008) investigated the adsorption and photocatalytic degradation performance of DMP under UV irradiation using hydrophobic TiO₂ pillared montmorillonite photocatalyst. This photocatalyst was prepared using the sol-gel method and it was then modified with a surfactant cetyltrimethyl ammonium bromide (CTMAB). The photocatalytic activity of CTMAB-modified prepared photocatalysts was slightly lower than that of TiO₂ pillared montmorillonites. According to Gu *et al.* (2021), 001 TiO₂ can eliminate approximately 100% of DMP and DEP in simulated wastewater during 2 hours of illumination. The degradation rate constants (k) are 5.73 and 3.08 times higher than for pure TiO₂ (3.67 h⁻¹ for DMP and 2.19 h⁻¹ for DEP). In municipal wastewater, 001TiO₂ can remove almost 76% of DMP and 85% of DEP, which is nearly 36 times higher than pure TiO₂. By rebuilding mixed metal oxides, organic layered double hydroxides (LHDs)/TiO₂ composites with various mass ratios were formed. By modifying this with sodium dodecyl sulfate (SDS) surfactant, the adsorption capacity of (LHDs) composites can be significantly improved. SDS-LDHs/TiO₂ composites performed as an efficient adsorbent to remove DMP in aqueous solution because their photocatalytic reactivity was higher than that of bare TiO₂ nanoparticles (Huang *et al.* 2013). Using a cetyltrimethylammonium-assisted hydrothermal approach, Liao *et al.* (2010) used a highly active ZrOx/ZnO catalyst for microwave-assisted photocatalytic (MW/PC) destruction of the endocrine disruptor DMP. The removal effectiveness of DMP (100 mL of 50 mg L⁻¹) after 30 minutes of reaction and UV (9.79 mW/cm²) irradiation was 88%, which is nearly 15% higher than P₂₅ TiO₂. Chung & Chen (2009) investigated the photocatalytic degradation of DEHP in solution using TiO₂. They discovered that DEHP was completely eliminated from the solution after 150 minutes of irradiation, indicating that UV/TiO₂ radiation in wastewater treatment is a viable option for lowering DEHP concentrations. YuLiang *et al.* (2021) looked into the behaviour of DEHP photocatalytic reactions. They used catalysts made of titania platinized with oxidised Pt species (PtOx/TiO₂) and titania platinized with metallic Pt (Pt/TiO₂). The platinized titanias with the best catalytic efficiency are those with 1 weight percent PtOx/TiO₂. DEHP was eliminated in excess of 90% within 120 minutes with a dosage of 20 mg L⁻¹ Fe-AgZnO, according to Eslami *et al.* (2017). Fe-Ag doping on ZnO minimises the band gap and can be used in conjunction with LED-visible light to purify a contaminated area, according to this study. Adsorption onto the biomass of beached seaweed and sargassum siliquastrum successfully isolated DEHP from aqueous solution. Because biosorption cannot detoxify DEHP, photocatalytic oxidation (PCO) was used to degrade (and detoxify) desorbed DEHP from seaweed biomass. Under optimal conditions, DEHP full degradation of 20 mg L⁻¹ was achieved in 45 minutes (Chan *et al.* 2007b). Chen (2010) used UV/H₂O₂ and direct UV photolysis to explore the oxidation of DEHP in solution. In 180 minutes, he determined that UV/H₂O₂ treatment removed 100% of DEHP from the solution, but direct UV photolysis removed just 73.5%. Chan *et al.* (2007a) studied the photocatalytic performance of DEHP removal from aqueous solution. Under the following conditions: 0.65 mW/cm² UV-A with 100 mg L⁻¹ TiO₂ and 10 mM H₂O₂ at initial pH 12, 61% removal efficiency of 10 mg L⁻¹ DEHP was reached in 45 minutes. UV-A and TiO₂ are needed for DEHP degradation, according to the optimisation report. The degradation of PAEs by photocatalysts are summarized in Table 3.

2.3. Electrochemical method

Electrochemical methods have been identified as one of the most capable processes for PAEs removal due to their environmental friendliness, strong catalytic ability, lack of secondary pollution, low-volume application, mild operating conditions, and ease of operation. An effective method for quantifying DBP was presented that combines a molecularly imprinted conducting polymer, including sensitive electrochemical impedance sensing platform and polypyrrole. Furthermore, for six different electrodes that were made independently, the relative standard deviation (RSD) was determined to be 5.21%.

Table 3 | Photocatalytic degradation of PAEs

PAEs	Catalysts	Initial concentration (mg L ⁻¹)	Catalyst dosage	pH	Temperature (°C)	Light intensity	Light sources	References
DBP	(Fe, Ag) co-doped ZnO nanorods	150	–	3	25	7 W	Visible LED irradiation	Akbari-Adergani <i>et al.</i> (2018)
DMP/DEP	TiO ₂ -based catalysts	5	1.5 g	10	–	–	UV-vis radiation	Salazar-Beltrán <i>et al.</i> (2019)
DBP	Fe ₃ O ₄ /TiO ₂ core shell magnetic nanoparticles	20	15 mg	7	–	(400 Watt; 17 mW/cm ²)	UV	Chalasanani & Vasudevan (2013)
DEP	Polyaniline-carbon nanotubes/TiO ₂ (PANI/CNT/TiO ₂)	1	–	7	–	40 mW/cm ² (10 w)	Visible light	Hung <i>et al.</i> (2017)
DEP	Tungsten oxide	10	0.5 g	–	30	–	UV and blue light sources	Ki <i>et al.</i> (2019)
DEP	Nano-Fe ₂ O ₃ embedded in montmorillonite particles (Fe-Mt) with citric acid	20	0.1 g	5.5	–	500 W	Xenon light irradiation and sunlight	Sun <i>et al.</i> (2021)
DMP	Vanadium pentoxide (V ₂ O ₅)/molybdenum trioxide (MoO ₃)	10	–	6.5	25	–	UV	Chen <i>et al.</i> (2009)
DMP	ZrOx/ZnO	50	0.1 g	5	–	400 W 9.79 mW/cm ²	UV	Liao <i>et al.</i> (2010)
DEHP	TiO ₂	75	100 (ug/l)	4	25	3.00 × 10 ⁻⁶	UV	Chung & Chen (2009)

The suggested polypyrrole film-based sensor, according to the findings of Bolat *et al.* (2019), is a viable medium for label-free PAEs monitoring in environmental investigations. Wang & Liu (2017) proposed a DBP removal technique based on electrocoagulation. Under similar conditions, the experimental data showed that iron was preferable to aluminium in terms of treatment efficiency and power consumption. With an initial pH of 8–9, 2.5 kWh m⁻³ of energy was required for 75% DBP removal using iron as the anode type. To make a DBP electrochemical sensor, Li *et al.* (2015b) used magnetic graphene oxide gold nanoparticles-molecular imprinted polymers (MGOAuNPs-MIPs) as a molecular recognition element. DBP may be detected and determined with this modified electrode throughout a linear range of 2.5×10^{-9} to 5.0×10^{-6} mol/L. The innovative DBP electrochemical sensor also demonstrated excellent consistency, with a relative standard deviation (RSD) of nearly 2.50%. According to de Souza *et al.* (2014), DMP can be successfully removed utilising electrolysis with conductive-diamond anodes. According to the research, this method can eliminate this pollutant in a wide range of initial concentrations. Souza *et al.* (2013) investigated DMP removal via electrolyses and sono electrolyses using conductive diamond anodes. With increasing current density, the rate of the removal processes increases. In the experimental circumstances, photo-assisted electrochemical reduction of the DMP compound was successfully performed using a DSA anode (Souza *et al.* 2014b). Souza *et al.* (2014a) used a one-compartment filter press flow cell and a commercial dimensionally stable anode (DSA[®]) to examine DMP degradation. At a current density of 20 mA cm⁻², the ideal parameters for the relationship between maximal pollutant elimination and energy savings can be found. Because the electrochemical system was used in mass transit, low current density values were the best operational option for saving electric energy. Kabdaşlı *et al.* (2009) investigated the use of stainless steel electrodes to electro coagulate aqueous DMP (50–100 mg L⁻¹) under various working circumstances (initial pH values, electrolyte concentrations and current densities). At a high initial concentration of 100 mg L⁻¹, DMP was completely degraded in 30 minutes. Deng *et al.* (2020) used a Ce-doped Ti/PbO₂ electrode to test the simultaneous degradation of three PAEs, such as DMP, DEP, and DBP, in synthetic wastewaters. This electrode was made by electrodeposition in a solution containing Ce³⁺ and Pb²⁺ ions. The electrode displayed excellent

electrocatalytic activity, as well as good reusability and stability, according to the data, with removal efficiencies of 5 mg L^{-1} . After 10 hours of degradation in $0.05 \text{ M Na}_2\text{SO}_4$ (pH 7) at a current density of 25 mA cm^{-2} , DBP, DMP, and DEP had removal efficiencies of 98.2, 95.8, and 81.1%, respectively. To enhance the formation of hydrogen peroxide during the breakdown of DMP, a modified graphite felt cathode doped with nitrogen and boron was designed and employed in a peroxi-coagulation system (H_2O_2). With a slight modification, the H_2O_2 yield on the cathode increased from 9.39 to 152.8 mg L^{-1} , and the current efficiency increased from 1.61 to 70.3%. Under ideal conditions of pH 5, cathodic potential of 0.69 V (versus. SCE), oxygen aeration, and electrode gap of 1 cm, Ding *et al.* (2020) studied the entire breakdown of DMP and 80% elimination of TOC, with the maximum removal achieved in 2 hours. DEP degradation was compared to the electro-peroxone (E-peroxone) approach employing three different carbon-based cathodes: carbon polytetrafluorethylene (carbon-PTFE), carbon felt, and reticulated vitreous carbon (RVC). The three carbon-based cathodes produced good DEP removal and total organic carbon removal yields (76.4–91%) after 60 minutes of E-peroxone treatment. The carbon-PTFE cathode exhibited the best removal efficiency because to its strong activity for H_2O_2 generation (Hou *et al.* 2016). Wang *et al.* (2010) used a self-made Pd/C gas-diffusion electrode as the cathode and a Ti/IrO₂/RuO₂ anode in an undivided electrolysis system to evaluate the degradation of DEP by electrochemical oxidation processes. Meanwhile, after 9 hours of electrolysis, the percentage of DEP removed was 80.9%, showing that the Pd/C gas-diffusion electrode oxidised the bulk of DEP to intermediates. Under galvanostatic conditions, the electrochemical oxidation (EO) of DEP in aqueous solution was examined using Pb/PbO₂ and Ti/SnO₂ anode materials. The EC for DEP reduction using PbO₂ lowers from 770.8 to $398.22 \text{ kWh kg}^{-1}$ when the current density is increased from 20 to 40 mA cm^{-2} . The EC increases from 740.5 to $1353.7 \text{ kWh kg}^{-1}$ when SnO₂ is used, and the current density rises from 20 to 40 mA cm^{-2} . The energy loss in the undesired reaction is responsible for this shift. Based on these findings, the best results were obtained using a PbO₂ anode material and a 40 mA cm^{-2} applied current density. This anode is crucial for establishing the mechanisms and by-products generated throughout the oxidation process (Vazquez-Gomez *et al.* 2012). Espinoza *et al.* (2016) examined the dependability of DEHP removal via electro-oxidation. Three types of anode materials (Ti/IrO₂-RuO₂, Ti/IrO₂, and Nb/BDD) were discovered, with the Nb/BDD anode with Na₂SO₄ as a supporting electrolyte at 0.5 A showing the best DEHP removal effectiveness of 87.2% after 120 minutes of treatment.

2.4. Membrane technology

A basic membrane technology mechanism is illustrated in Figure 2. The red colour circle shows the solute particle and the yellow one shows the solvent in this figure. While this feed solution passes through the membrane, solute particles will retain on the membrane surface. The pure solvent will come out from the membrane.

Due to their high efficiency, ability to reduce space and ease of operation, membrane filtration methods using various types of membranes show tremendous potential for PAEs removal (Bodzek *et al.* 2004). Membranes are made from a variety of materials, each with its own set of filtering characteristics (pore size, surface charge, and hydrophobicity) that determine the type of pollutant that can be retained. The pore size, hydrophobicity, functional groups, and pKa of membrane materials and pollutants, as well as the quality of the water treated, are some of the complicated parameters that influence the removal. Despite the enormous pore sizes of the microfiltration membrane, the combined system was able to remove around 98% of the endocrine disruptor from the effluent. Membrane procedures are another sort of phase shifting technique that can be used to remove ECs (Rodriguez-Narvaez *et al.* 2017). The retention of PAEs increased as the molecular weight increased, which might be explained by the influence of steric hindrance. Organic compounds with a higher molecular weight usually have a larger molecular size. At the same time, the structure of organic molecules influences the size of the molecules (Wei *et al.* 2016). The most prevalent membrane techniques for removing PAEs from wastewater are ultrafiltration, electrodialysis, nanofiltration and reverse osmosis. Bodzek *et al.* (2004) investigated the degradation of DEP and DEHP using three membranes: reverse osmosis membrane RO-DS3SE, nanofiltration membrane NF-DS5DK, and ultrafiltration membrane UF-DSGM. Under regulated conditions (RO, NF 2.0 MPa, UF 0.3 MPa), all membranes removed a substantial percentage of PAEs from water, ranging from 97.6% to nearly 99.9%. The researchers devised a new hollow fibre liquid-phase micro extraction (HF-LPME) method for extracting a group of nine PAEs of interest from a variety of water samples, including mineral, pond, tap, and waste water samples. Sample pH, removal time, ionic strength, stirring rate, back removal conditions and removal temperature were all studied for their impact on HF-LPME. The established technique provided satisfactory recovery (74–120%) and relative standard deviation values for the selected PAEs (20%). For identifying 11 PAEs, a method combining graphene oxide coated hollow fibre membrane extraction (GO-HFME) and supercritical fluid chromatography (SFC) was proposed as an environmentally friendly, fast, and sensitive method (González-Sálamo *et al.* 2018). This technology is a

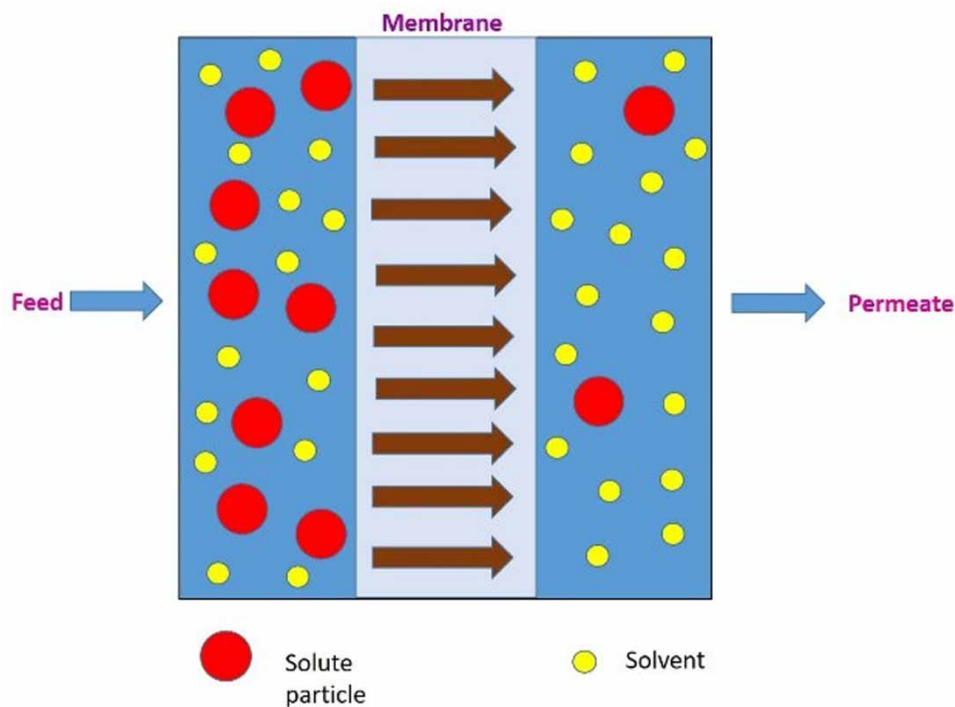


Figure 2 | Schematic diagram of membrane technology.

low-cost way to reduce the time and effort required to regulate PAEs in real products, and it could have a future in other samples like environmental and biological samples. *Lou et al. (2018)* have used Polytetrafluoroethylene (PTFE) hollow fiber membrane with a pore size of 0.2 mm, outer diameter of 0.978 mm and inner diameter of 0.800 mm. The removal efficiency of DMP, DEP and DBP were found to be 92.6–97.5, 92.1–99.3 and 93.4–99.1% respectively. *Wei et al. (2016)* used lab-fabricated hollow fibre nanofiltration (NF) membranes to study the rejection behaviour of a few types of PAEs from water sources, including DMP, DBP, DEP and DEHP. After adsorption equilibrium, the rejection rates of these PAEs were found to be 82.3, 91.5, 86.7 and 95.4%, respectively. Temperature, operation pressure, ionic strength and pH were the parameters that had an effect. To eliminate DEHP from a model solution, *Yang et al. (2016)* used a lab-prepared graphene-containing ceramic composite tubular membrane (TGCCM) in conjunction with a simultaneous electrocoagulation and electro filtration approach (EC/EF) in crossflow filtration mode. According to the findings, DEHP elimination efficiency was about 99% in this investigation.

According to the findings, adsorption fouling could be a contributing factor to the high retention coefficients. It is thought to be the result of negatively charged organic foulants being attracted to positively charged membrane surfaces. These chemicals begin to build up in the polymer structure during the filtration of such foulants by polyamide membranes via hydrogen bonds that are likely to form. This type of adsorption can cause membrane blockage, either completely or partially. According to the work induced by the adsorption of the compounds under retention, and the creation of hydrogen bonds with membrane polymer, the result of the removal was probably impacted by the membrane blocking total for RO and NF, and UF. Modeling permeate and retention based on a single parameter is insufficient. The characterization of membrane separation at the molecular level (particle removed – membrane polymer) based on chemical-physical properties of the components, as well as the identification of process parameters, appears to be proper and correct (*Rodriguez-narvaez et al. 2017*).

2.5. Microbial degradation

The breakdown of PAEs by microorganisms is considered to be one of the major routes of environmental degradation for these widespread pollutants. Abiotic (non-biological) degradation of PAEs is very slow, e.g., DMP has an aqueous photolysis half-life of about three years, and for DEHP 2000 years. Compared to non-biological destruction, microbial degradation is rather fast and a promising, cost-effective and environmentally-friendly method for removal of phthalates from contaminated

sites. Several studies have shown that bacteria in wastewater can degrade a variety of PAEs in aerobic, anaerobic, and facultative conditions.

Microbial breakdown of individual PAEs in pure culture under aerobic conditions has been extensively investigated and is assumed to be the primary mechanism for eliminating PAEs from the environment. To enhance PAE biodegradation, several researchers changed environmental variables as temperature, pH, co-substrate, surfactant, and others. Liao *et al.* (2010) studied the effects of different surfactants on the degradation of DBP, including Brij-35, Tergitol, and Triton X-100, and found that adding Brij-35 and Tergitol did not improve DBP degradation by *Pseudomonas stutzeri* and *Deinococcus radiodurans*. The biodegradation of DEP by *Bacillus subtilis* 3C3 was greatly enhanced when a yeast extract was used as a co-metabolic substrate.

In the presence of Tween-80, *Bacillus subtilis* 3C3 degraded a variety of DEP effectively at 1000 mg L⁻¹. The impact of heavy metals (Cr⁶⁺ and Cu²⁺) on DBP biodegradation was studied using *Diaphorobacter* sp. QH-6.55. According to their observations, heavy metals in the 5–30 mg L⁻¹ concentration range decreased DBP biodegradation (Decai *et al.* 2011). However, when compared to aerobic conditions, anaerobic conditions have a much reduced rate of PAEs biodegradation. In addition to bacteria, a few fungal and algal species have been linked to PAEs biodegradation. *Phanerochaete chrysosporium*, *Trametes versicolor*, and *Daldinia concentrica* have all been found to degrade 28 mg L⁻¹ of DBP in just 6 days. In 18 days, the white rot fungus *Polyporus brumalis* decomposes 448 mg L⁻¹ of DBP. Gao & Chi (2015) investigated the biodegradation of DEP and DBP by three marine microalgae: *Dunaliella salina* and *Chaetoceros muelleri*, both planktonic, and *Cylindrotheca closterium*, a benthic microalgae. Microalgae can also breakdown PAEs, according to the findings.

On the other hand, DBP biodegradation requires both external and intracellular enzymes. In natural environments, a collaboration of bacteria is usually responsible for the complete breakdown of complex organics like PAEs. The most critical stage in the biodegradation of PAEs is the sequential hydrolysis of ester linkage to produce phthalate monoesters and then phthalic acid. Alcohols are made from alkyl or aryl chains through de-esterification. As a result, microbial digestion of PAEs necessitates the use of many metabolic genes and enzymes, implying that a single organism may not be capable of complete mineralization of PAEs. When DMP was biodegraded by *Rhodococcus ruber* Sa, for example, monomethyl phthalate accumulated and did not degrade further (Gani *et al.* 2017).

According to Wang *et al.* (2004), DMP was mineralized fully by two consortia of bacteria: one including *Pseudomonas uorescens*, *Pseudomonas aureofaciens*, and *Sphingomonas paucimobilis*, and the other having *Xanthomonas maltophilia* and *Sphingomonas paucimobilis*. DMP was not used as the sole source of carbon for the isolation of the bacterial species mentioned above. After 48 hours of incubation, a bacterial consortia mineralized 1200 mg L⁻¹ DBP (He *et al.* 2015). A binary combination of *Variovorax* sp. BS1 and *Achromobacter denitricans* was recently found to degrade DMP. This binary mixture degraded >90% of 300 mg L⁻¹ DMP within 24 hours of incubation, and the rate of degradation followed the following pattern: *A. denitricans* > *Variovorax* sp. BS1 > binary mixture (Prasad 2021). Complete mineralization of PAEs requires a mix of metabolic capabilities from several bacteria capable of degrading side chain alcohols as well as phthalate residues (Boll *et al.* 2020).

3. CONCLUSION

Water pollution from hazardous PAEs is one of the world's most serious environmental issues. A variety of treatment technologies for PAEs removal from wastewater have been developed to meet progressive severe environmental regulations, including adsorption, photocatalytic degradation, electrochemical method, membrane technology and microbial degradation. Even though many treatment techniques can be used to remove PAEs, each has its own set of advantages and disadvantages. Adsorption is a well-known method for removing PAEs from low-concentration wastewater. A variety of low-cost adsorbents have been designed and evaluated. The type of adsorbents utilised, however, has an impact on adsorption efficiency. Due to its expensive cost, activated carbon is not frequently utilised in adsorption. Adsorption by nano composites is a common process that has shown great promise for the removal of PAEs from wastewater. Immobilising the photocatalysts on multiple supports limits the effective surface for photocatalytic reaction, lowering the photocatalytic system's overall effectiveness. Electrochemical methods for PAEs wastewater treatment are thought to be well-controlled, fast, producing less sludge, requiring fewer chemicals and producing good reduction yields. However, the high initial capital investment required for electrochemical technologies, as well as the high cost of electricity supply, limit their development. The membrane filtration technique offers a high efficiency for removing PAEs, but it has been limited in usage due to process complexity, low permeate

flux, membrane fouling, and high operating costs. Furthermore, degradation by microorganisms is considered as the most effective means of PAEs elimination from the environment.

This paper gives a comprehensive review on the removal of various PAEs using the above mentioned techniques. Although these techniques can be used to treat PAEs effluent, the most appropriate treatment technology is decided by a variety of parameters, including the initial metal concentration, capital investment, component of the wastewater, plant flexibility, plant performance, operational cost and environmental effect (Kurniawan *et al.* 2006).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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